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# New Advances into Nanostructured Oxides, 2nd Edition

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Edited by  
Silvia Mostoni and Roberto Nisticò

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# **New Advances into Nanostructured Oxides, 2nd Edition**



# **New Advances into Nanostructured Oxides, 2nd Edition**

Guest Editors

**Silvia Mostoni**

**Roberto Nisticò**



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# Contents

|                             |     |
|-----------------------------|-----|
| About the Editors . . . . . | vii |
|-----------------------------|-----|

**Silvia Mostoni and Roberto Nisticò**

New Advances into Nanostructured Oxides, 2nd Edition

|                                                                                                                                                                       |   |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| Reprinted from: <i>Inorganics</i> <b>2025</b> , 13, 60, <a href="https://doi.org/10.3390/inorganics13020060">https://doi.org/10.3390/inorganics13020060</a> . . . . . | 1 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|

**Mariyem Abouri, Abdellah Benzaouak, Fatima Zaaboul, Aicha Sifou, Mohammed Dahhou and Mohammed Alaoui El Belghiti et al.**

Efficient Catalytic Reduction of Organic Pollutants Using Nanostructured CuO/TiO<sub>2</sub> Catalysts: Synthesis, Characterization, and Reusability

|                                                                                                                                                                        |   |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| Reprinted from: <i>Inorganics</i> <b>2024</b> , 12, 297, <a href="https://doi.org/10.3390/inorganics12110297">https://doi.org/10.3390/inorganics12110297</a> . . . . . | 7 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|

**Mahboubeh Dolatyari, Mehdi Tahmasebi, Sudabeh Dolatyari, Ali Rostami, Armin Zarghami and Ashish Yadav et al.**

Core/Shell ZnO/TiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> Nanoparticles for the Photodecomposition of Brilliant Blue E-4BA

|                                                                                                                                                                        |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Reprinted from: <i>Inorganics</i> <b>2024</b> , 12, 281, <a href="https://doi.org/10.3390/inorganics12110281">https://doi.org/10.3390/inorganics12110281</a> . . . . . | 23 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

**Tiangui Zhao, Tihao Cao, Qifu Bao, Weixia Dong, Ping Li and Xingyong Gu et al.**

Significantly Enhanced Self-Cleaning Capability in Anatase TiO<sub>2</sub> for the Bleaching of Organic Dyes and Glazes

|                                                                                                                                                                        |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Reprinted from: <i>Inorganics</i> <b>2023</b> , 11, 341, <a href="https://doi.org/10.3390/inorganics11080341">https://doi.org/10.3390/inorganics11080341</a> . . . . . | 37 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

**Tan Mao, Junyan Zha, Ying Hu, Qian Chen, Jiaming Zhang and Xueke Luo**

Research Progress of TiO<sub>2</sub> Modification and Photodegradation of Organic Pollutants

|                                                                                                                                                                        |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Reprinted from: <i>Inorganics</i> <b>2024</b> , 12, 178, <a href="https://doi.org/10.3390/inorganics12070178">https://doi.org/10.3390/inorganics12070178</a> . . . . . | 52 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

**Ahmed H. Naggar, Abdelaal S. A. Ahmed, Tarek A. Seaf El-Nasr, N. F. Alotaibi, Kwok Feng Chong and Gomaa A. M. Ali**

Morphological Dependence of Metal Oxide Photocatalysts for Dye Degradation

|                                                                                                                                                                        |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Reprinted from: <i>Inorganics</i> <b>2023</b> , 11, 484, <a href="https://doi.org/10.3390/inorganics11120484">https://doi.org/10.3390/inorganics11120484</a> . . . . . | 75 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

**Adil Alshoaibi**

The Influence of Annealing Temperature on the Microstructure and Electrical Properties of Sputtered ZnO Thin Films

|                                                                                                                                                                        |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Reprinted from: <i>Inorganics</i> <b>2024</b> , 12, 236, <a href="https://doi.org/10.3390/inorganics12090236">https://doi.org/10.3390/inorganics12090236</a> . . . . . | 110 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

**Dmitrii Filimonov, Marina Rozova, Sergey Maksimov and Denis Pankratov**

Synthesis and Redox Properties of Iron and Iron Oxide Nanoparticles Obtained by Exsolution from Perovskite Ferrites Promoted by Auxiliary Reactions

|                                                                                                                                                                        |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Reprinted from: <i>Inorganics</i> <b>2024</b> , 12, 223, <a href="https://doi.org/10.3390/inorganics12080223">https://doi.org/10.3390/inorganics12080223</a> . . . . . | 123 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

**Anil Abduraman, Ana-Maria Brezoiu, Rodica Tatia, Andreea-Iulia Iorgu, Mihaela Deaconu and Raul-Augustin Mitran et al.**

Mesoporous Titania Nanoparticles for a High-End Valorization of *Vitis vinifera* Grape Marc Extracts

|                                                                                                                                                                        |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Reprinted from: <i>Inorganics</i> <b>2024</b> , 12, 263, <a href="https://doi.org/10.3390/inorganics12100263">https://doi.org/10.3390/inorganics12100263</a> . . . . . | 147 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

**Reo Kimura, Kota Shiba, Kanata Fujiwara, Yanni Zhou, Iori Yamada and Motohiro Tagaya**

Precipitative Coating of Calcium Phosphate on Microporous Silica–Titania Hybrid Particles in Simulated Body Fluid

|                                                                                                                                                                        |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Reprinted from: <i>Inorganics</i> <b>2023</b> , 11, 235, <a href="https://doi.org/10.3390/inorganics11060235">https://doi.org/10.3390/inorganics11060235</a> . . . . . | 165 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|

**Dilshat U. Tulyaganov, Simeon Agathopoulos, Konstantinos Dimitriadis, Hugo R. Fernandes, Roberta Gabrieli and Francesco Baino**

The Story, Properties and Applications of Bioactive Glass “1d”: From Concept to Early Clinical Trials

Reprinted from: *Inorganics* **2024**, *12*, 224, <https://doi.org/10.3390/inorganics12080224> . . . . . **178**

# About the Editors

## **Silvia Mostoni**

Silvia Mostoni earned a MSc degree in Chemistry at the University of Milano in 2015 and received her PhD in Materials Science and Nanotechnology at the University of Milano–Bicocca in 2019. Her research interests focus on the synthesis, characterization and surface functionalization of inorganic nanomaterials mainly based on metal oxide nanoparticles for applications in the catalytic field, automotive sector, and materials with luminescent properties. Since 2023, she has been a Researcher with a fixed-term contract in General and Inorganic Chemistry at the University of Milano–Bicocca.

## **Roberto Nisticò**

Roberto Nistico (RN) is Associate Professor in General and Inorganic Chemistry at the University of Milano-Bicocca (Department of Materials Science, Italy). Up until today, RN has published more than 90 papers in renowned international journals and 2 book chapters. Additionally, RN is a member of the Editorial Board of the journal *Inorganics* (“Inorganic Materials” Section). RN’s research mainly focuses on several aspects at the interface between inorganic chemistry and materials science, always looking for novel and appealing solutions for a sustainable future. RN’s principal field of interest is the development of magnet-responsive nanomaterials (i.e., iron oxides, ferrites) and other inorganic systems for the environmental remediation of contaminated (waste)water, (photo)catalysis, and energetic applications.



# New Advances into Nanostructured Oxides, 2nd Edition

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## 1. Introduction

The interest in inorganic nanostructured oxides is growing extensively, thanks to their remarkable features and their wide range of applications, which include (photo)catalysis [1–4], controlled drug-delivery and chemical release [5–7], environmental remediation [8–10], energy and batteries [11], smart materials [12], and so on. One interesting aspect of inorganic nanostructured oxides is the high level of control that can be achieved over particle morphology, size, shape, and porosity [13], as well as their surface properties [14,15], which further broaden the possible application of these materials in a wide variety of fields. In fact, the use of suitable synthetic pathways and ad hoc surface functionalization procedures provides a powerful tool to obtain pure inorganic or hybrid inorganic–organic composite materials that represent strategic materials in the most recent research literature [16,17].

In this context, after the success of the first edition published in *Inorganics* in 2022, the second edition of the Special Issue, entitled “New Advances into Nanostructured Oxides, 2nd Edition” was launched to bring together the most recent developments on the class of inorganic materials. This Special Issue is inserted in the “Inorganic Materials” section that, since its birth, has rapidly grown thanks to its attention to advanced inorganic materials, as well as their high technological demand. The aim was to collect research papers and reviews focused on the synthesis and characterization of inorganic oxide nanomaterials through soft chemistry approaches, favoring a high control on the particle morphology, size, porosity and surface functionalities. In addition, in view of their application, the materials’ performances are described with the ambitious goal of identifying the structure–property relations to connect the surface, morphological and structural features to the material activity. This represents a shared interest in the development of innovative materials, as the modulation of the key structural parameters may be used to tune and improve the materials’ resulting performances.

Prior to proceeding with the overview of the contributions, the Guest Editors would like to thank all of the reviewers who spent their valuable time thoroughly reviewing and improving the articles published in this volume. We also sincerely thank all the authors for choosing *Inorganics*, and, in particular, the “Inorganic Materials” section, as the recipient of their excellent science.

## 2. An Overview of the Published Articles

Overall, this Special Issue collected 10 original papers (i.e., seven research articles and three reviews) and received more than 16,000 views, which paved the way for the further proposal of a third edition of the same Special Issue. The published papers can be categorized into three main subsections as reported in Table 1, including: (i) environmental



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remediation, (ii) development and optimization of new synthetic routes for metal oxides, and (iii) drug-delivery and biomedicine. This classification was made considering both the materials applications and the applied synthetic routes for the preparation of the materials.

**Table 1.** Correlation between subsections and contributions collected in the present Special Issue.

| Subsections                                                           | Title                                                                                                                                                                                                                                                                 | References |
|-----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Environmental remediation                                             | “Efficient catalytic reduction of organic pollutants using nanostructured CuO/TiO <sub>2</sub> catalysts: synthesis, characterization, and reusability”                                                                                                               | [18]       |
|                                                                       | “Core/shell ZnO/TiO <sub>2</sub> , SiO <sub>2</sub> /TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> , and Al <sub>1.9</sub> Co <sub>0.1</sub> O <sub>3</sub> /TiO <sub>2</sub> nanoparticles for the photodecomposition of Brilliant Blue E-4BA” | [19]       |
|                                                                       | “Significantly enhanced self-cleaning capability in anatase TiO <sub>2</sub> for the bleaching of organic dyes and glazes”                                                                                                                                            | [20]       |
|                                                                       | “Research progress of TiO <sub>2</sub> modification and photodegradation of organic pollutants”                                                                                                                                                                       | [21]       |
|                                                                       | “Morphological dependence of metal oxide photocatalysts for dye degradation”                                                                                                                                                                                          | [22]       |
| Development and optimization of new synthetic routes for metal oxides | “The influence of annealing temperature on the microstructure and electrical properties of sputtered ZnO thin films”                                                                                                                                                  | [23]       |
|                                                                       | “Synthesis and redox properties of iron and iron oxide nanoparticles obtained by exsolution from perovskite ferrites promoted by auxiliary reactions”                                                                                                                 | [24]       |
|                                                                       | “Mesoporous titania nanoparticles for a high-end valorization of <i>Vitis vinifera</i> grape marc extracts”                                                                                                                                                           | [25]       |
| Drug-delivery and biomedicine                                         | “Precipitative coating of calcium phosphate on microporous silica–titania hybrid particles in simulated body fluid”                                                                                                                                                   | [26]       |
|                                                                       | “The story, properties and applications of bioactive glass “1d”: from concept to early clinical trials”                                                                                                                                                               | [27]       |

### 2.1. Environmental Remediation

A large portion of the contributions reported in this Special Issue is focused on the exploitation of inorganic nanomaterials (mainly TiO<sub>2</sub>) for environmental remediation. In fact, the urgency of solving environmental pollution caused by the anthropogenic activities both in gaseous and liquid phases has driven research interest from more than a decade [28–30]. In this field, the use of photocatalysis is one of the most studied techniques to reduce the concentration of organic pollutants in wastewater, by using inorganic nanomaterials as efficient photo-catalysts. At the same time, organic pollutants can be degraded by using other catalytic reactions, such as catalytic reduction reactions in the presence of suitable nanostructured catalysts. In this first section, three research papers and two reviews were published [18–22].

Abouri et al. [18] reported the synthesis of nanostructured CuO/TiO<sub>2</sub> catalysts via a combustion technique, followed by calcination at 700 °C to achieve a rutile-phase TiO<sub>2</sub> structure with varying copper loadings (in the 5–40 wt.% range). Tests were performed aiming to reduce 4-Nitrophenol and Methyl Orange as target molecules with sodium borohydride (NaBH<sub>4</sub>) in the presence of the CuO/TiO<sub>2</sub> catalysts. Results indicated a 98% reduction of 4-Nitrophenol in 480 s and 98% reduction of Methyl Orange in 420 s. The catalysts exhibited high stability over 10 reuse cycles, maintaining over 96% efficiency for Methyl Orange and 94% efficiency for 4-Nitrophenol.

Dolatyari et al. [19] reported the synthesis of core/shell ZnO/TiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanoparticles using ethylene glycol for governing the nanoparticle size, fol-

lowed by calcination at 400 °C to decompose the organic residues at the nanoparticles' surface. Furthermore, Cobalt ( $\text{Co}^{3+}$ ) was added during the  $\text{Al}_2\text{O}_3$  nanoparticle synthesis to form Co-doped nanoparticles with formula  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ . All of the synthesized nanoparticles were tested for the photocatalytic degradation of Brilliant Blue E-4BA under UV and visible light irradiation. Photocatalytic tests revealed that both  $\text{Al}_2\text{O}_3/\text{TiO}_2$  and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  showed superior degradation under UV and visible light compared to  $\text{ZnO}/\text{TiO}_2$  and  $\text{SiO}_2/\text{TiO}_2$  with complete photodecomposition of the target dye (20 ppm) in only 20 min using a 10 mg of photocatalyst. Furthermore, the "Co-doped"  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  nanoparticles showed the best performance under visible light irradiation, due to the increased absorption in the visible range as Co-doping introduces additional energy levels into  $\text{Al}_2\text{O}_3$ , resulting in improved electron–hole pair generation.

Zhao et al. [20] reported the hydro/solvothermal synthesis of Mg-doped  $\text{TiO}_2$  anatase samples in water/ethanol environment at 180 °C for 36 h without using any surfactants or templates. Subsequently, glaze samples were prepared by sintering the raw powders (95% Kaolin clay, 5% Mg-doped  $\text{TiO}_2$ ) at ca. 1200 °C. Photocatalytic experiments revealed that Mg-doped  $\text{TiO}_2$  samples have higher photocatalytic activities (99.5% in 80 min under visible light) against Rhodamine B compared with undoped ones, due to pure anatase phase formation. Moreover, ceramic glaze materials present self-cleaning properties, achieving a water contact angle of ca. 6° at room temperature.

Mao et al. [21] analyzed the scientific literature describing the latest advances in the synthesis procedures and strategies to produce and/or properly modify  $\text{TiO}_2$ -based nanomaterials, aiming at maximizing/improving the photocatalytic performances in environmental remediation processes for the abatement of organic pollutants.

Lastly, Naggar et al. [22] reviewed the latest scientific literature describing the recent progress regarding the use of metal oxides in photocatalysis, with a particular focus on the critical role played by their morphology in the overall degradation process. The state-of-the-art analysis revealed that non-spherical morphologies exhibit enhanced photocatalytic performance due to their unique crystal facets and surface areas, which can promote charge transfer and improve catalytic efficiency. Furthermore, porous design and substantial specific surface area are responsible for an increased photocatalytic activity, whereas flake-like structures exhibit comparatively lower performance.

## 2.2. Development and Optimization of New Synthetic Routes for Metal Oxides

Careful consideration has been dedicated in this Special Issue to the development of new synthetic routes for metal oxides, and to the optimization of the synthetic approaches for the preparation of metal oxide nanostructures. In fact, the use of specific experimental conditions can drive the structural and morphological properties of the materials, and the fine control of these parameters play a key role in the determination of the material performances. Moreover, the use of innovative and more recent methodologies is reported, as well as the preparation of hybrid materials [23–25].

Alshoaibi [23] reported a study involving the deposition of a hetero-structured ( $\text{ZnO}/\text{Zn}/\text{ZnO}$ ) thin film on a glass substrate using the DC magnetron sputtering technique. Subsequently, samples were annealed at different temperatures in the 100–500 °C range. Characterization results indicated the formation of both metallic zinc and the hexagonal  $\text{ZnO}$  crystal structure for samples annealed below 200 °C, whereas pure hexagonal  $\text{ZnO}$  formed for samples annealed at 300 and 500 °C, with a slight crystallinity decrease for the sample annealed at the highest temperature. Since both roughness and particle size are inversely proportional to the annealing temperature (with the exception of the sample annealed at 500 °C), the optimal annealing temperature was determined to be 400 °C.

Filimonov et al. [24] reported an original approach to synthesize hollow and layered oxide magnetic nanoparticles (either  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , or  $\text{Fe}_3\text{O}_4/\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\gamma}$ ), by a solid-state exsolution process carried out in a reducing environment at elevated temperatures from Ca- and La-based unsubstituted (and substituted) perovskite-related ferrites, and using h-BN as a reducing agent.

Lastly, Abduraman et al. [25] reported a synthetic sol-gel protocol assisted by solvothermal treatment (100 °C, 24 h) using either a triblock copolymer (Pluronic P123) or a nonionic surfactant (Pluronic F127) as soft-templating agents, followed by purification through either Soxhlet extraction or calcination at 400 °C for the production of mesoporous titania nanoparticles. The results indicated that samples prepared using Pluronic F127 presented a higher surface area and less agglomeration than the sample synthesized with Pluronic P123. Furthermore, an extract from *Vitis vinifera* grape marc (*Feteasca neagra* cultivar) with high radical scavenging activity was encapsulated in mesoporous titania and compared with reference SBA-15 silica support. Both resulting materials showed biocompatibility and even better radical scavenging potential than the free extract. Furthermore, the titania encapsulated sample showed better cytocompatibility than the silica one, thus making it suitable for skin-care products.

### 2.3. Drug Delivery and Biomedicine

In this last part, inorganic nanomaterials for drug delivery systems and for biomedicine purposes are discussed [26,27].

Kimura et al. [26] reported the development of a calcium phosphate-coating method to homogeneously cover silica–titania porous nanoparticles (with a well-defined spherical shape, uniform size, and tunable nanoporous structure) in simulated body fluids. The results indicated that the pore size distribution is a fundamental parameter significantly affecting the coating formation, with surfaces with bimodal pore sizes becoming rough after the calcium phosphate precipitation, whereas those with a unimodal pore size remaining smooth, thus indicating that pore sizes serve as different nucleation sites leading to different surface morphologies.

Lastly, Tulyaganov et al. [27] reviewed and critically discussed the genesis, development, properties, and applications of the bioactive glass “1d” (i.e., from the primary crystallization field of pseudo-wollastonite in the  $\text{CaO-MgO-SiO}_2$  ternary system, after addition of  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$  and  $\text{CaF}_2$ ) and its relevant glass-ceramic derivative products (i.e., diopside, fluorapatite, and wollastonite crystalline phases, formed by performing a thermal treatment), which are extremely appealing inorganic biomaterials alternatives to the reference 45S5 Bioglass<sup>®</sup> exploitable in a variety of bone-regenerative clinical applications, such as the repair of periodontal defects, ridge preservation and sinus augmentation.

## 3. Conclusions

With this Special Issue “New Advances into Nanostructured Oxides, 2nd Edition” published in the “Inorganics Materials” section, and also published as a book, the Editors hope that the high quality of the contributions collected here will receive the visibility and attention they deserve. These would help readers to increase their knowledge in the field of inorganic materials, and be a new source of inspiration for novel, focused investigations.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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## Article

# Efficient Catalytic Reduction of Organic Pollutants Using Nanostructured CuO/TiO<sub>2</sub> Catalysts: Synthesis, Characterization, and Reusability

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**Abstract:** The catalytic reduction of organic pollutants in water is a critical environmental challenge due to the persistent and hazardous nature of compounds like azo dyes and nitrophenols. In this study, we synthesized nanostructured CuO/TiO<sub>2</sub> catalysts via a combustion technique, followed by calcination at 700 °C to achieve a rutile-phase TiO<sub>2</sub> structure with varying copper loadings (5–40 wt.%). The catalysts were characterized using X-ray diffraction (XRD), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, thermogravimetric analysis-differential thermal analysis (TGA-DTA), UV-visible diffuse reflectance spectroscopy (DRS), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). The XRD results confirmed the presence of the crystalline rutile phase in the CuO/TiO<sub>2</sub> catalysts, with additional peaks indicating successful copper oxide loading onto TiO<sub>2</sub>. The FTIR spectra confirmed the presence of all the functional groups in the prepared samples. SEM images revealed irregularly shaped copper oxide and agglomerated TiO<sub>2</sub> particles. The DRS results revealed improved optical properties and a decreased bandgap with increased Cu content, and 4-Nitrophenol (4-NP) and methyl orange (MO), which were chosen for their carcinogenic, mutagenic, and nonbiodegradable properties, were used as model organic pollutants. Catalytic activities were tested by reducing 4-NP and MO with sodium borohydride (NaBH<sub>4</sub>) in the presence of a CuO/TiO<sub>2</sub> catalyst. Following the in situ reduction of CuO/TiO<sub>2</sub>, Cu (NPs)/TiO<sub>2</sub> was formed, achieving 98% reduction of 4-NP in 480 s and 98% reduction of MO in 420 s. The effects of the NaBH<sub>4</sub> concentration and catalyst mass were investigated. The catalysts exhibited high stability over 10 reuse cycles, maintaining over 96% efficiency for MO and 94% efficiency for 4-NP. These findings demonstrate the potential of nanostructured CuO/TiO<sub>2</sub> catalysts for environmental remediation through efficient catalytic reduction of organic pollutants.

**Keywords:** titanium dioxide; catalysts; catalytic reduction; 4-nitrophenol; methyl orange; copper oxide

## 1. Introduction

Across the world, water and energy shortages represent urgent and increasingly severe global challenges. On a global level, over one billion people face the critical issue of not having access to clean drinking water, which is a necessity for human existence. Furthermore, more than two billion individuals lack proper sanitation facilities, resulting in almost two million annual fatalities due to diseases transmitted through impure water sources or insufficient sewage systems [1]. Water pollution occurs when the concentration of harmful chemicals or biological substances in a water body surpasses established standards, leading to adverse impacts on both human health and the natural environment [2].

Azo dyes and nitroaromatic compounds exhibit high stability and are known for their carcinogenic, mutagenic, and nonbiodegradable properties, posing a significant threat to human life, water quality, and the environment. These substances, such as Congo red, rhodamine B (RhB), and methyl orange (MO), are extensively used in numerous chemical sectors, including paper, textiles, paint, and plastics. These industrial processes produce significant quantities of dyes, leading to the emergence of dye-laden particles that are introduced directly into the environment [3,4]. MO, for example, is a highly toxic and nonbiodegradable azo. The adverse effects of this toxic dye may disrupt the balance of water within ecosystems and pose health risks, including symptoms such as vomiting, diarrhea, breathing difficulties, and nausea [5]. In particular, 4-Nitrophenol (4-NP) is a highly toxic compound that is challenging to degrade and treat effectively [6].

Compared with alternative methods, nitrophenol and dye reduction in the presence of a suitable catalyst and sodium borohydride ( $\text{NaBH}_4$ ) is a recommended protocol, since it is relatively more affordable, secure, and environmentally friendly [7–9]. Therefore, the exploration of techniques such as chemical reduction to efficiently degrade diverse chemical pollutants is of considerable interest. However, this method commonly faces a challenge in achieving a fast degradation rate at lower concentrations of reducing agents, such as sodium borohydride. Consequently, to minimize the quantity of reducing agent required and increase the reaction rate, the development of an efficient catalyst for this chemical reduction becomes crucial [10,11]. Owing to their exceptional physicochemical properties, there has been significant interest in the field of catalysis regarding transition and noble metal nanoparticles in recent years [12–16]. Among these materials, copper nanoparticles (CuNPs) have gained recognition as excellent materials that exhibit novel physiochemical characteristics. This has prompted their investigation in various applications, including catalysis, sensors, photocatalysis, diverse biological activities, energy storage, and organic synthesis applications [17–21]. The catalytic activity is closely related to the degree of dispersion of the Cu(NPs), and a superior performance has been noted with smaller-sized nanoparticles [22,23].

One significant challenge in employing nanoparticles as catalysts involves their agglomeration and accumulation, resulting in a decrease in their catalytic efficiency. A viable solution to address this concern is the utilization of solid supports to stabilize the nanoparticles [24]. For this purpose, a series of solid supports, such as polymers, metal oxides, and carbon materials [25–28], have been adopted to avoid sintering, enhance stability, and facilitate the optimal mobilization/dispersion of nanoparticles, aiming to maximize catalytic activities across a wide variety of applications. Among these supports, the immobilization of CuNPs on  $\text{TiO}_2$ , which is a representative n-type semiconductor material, has been extensively used as a photocatalyst, catalyst support, and cocatalyst because of its high oxidation ability, environmental friendliness, physicochemical stability, and cost effectiveness [29,30]. Research on the use of Cu/ $\text{TiO}_2$  for catalytic reduction has gained significant attention because of its promising applications in environmental remediation. One study focused on synthesizing Cu- $\text{TiO}_2$  nanoparticles from the extract of Phoenix

dactylifera. These catalysts effectively degraded dyes, such as RhB, in 11 min and MO in 25 min, achieving reductions of 89.8 and 95.3%, respectively, with 21.3 mg/mL of the catalyst [31]. Other investigations explored various shapes and sizes of Cu nanostructures and revealed that smaller particles and specific morphologies enhanced the catalytic activity for nitroaromatic reduction [32]. Additionally, Cu/TiO<sub>2</sub> catalyst synthesized from *Chimonanthus praecox* extract exhibited superior performance in degrading pollutants, such as 4-nitrophenol and other organic dyes, with 10 mg of catalyst [33]. CuO/TiO<sub>2</sub> composite created using *Tilia platyphyllos* extract also demonstrated high catalytic activity, reducing MO in 10 min and methyl blue in 9 min with 3 mg of the catalyst [34]. Recent studies of CuO/TiO<sub>2</sub> nanocomposite have further highlighted their exceptional catalytic performance, particularly under direct sunlight, where these photocatalysts effectively drive the selective hydrogenation of 4-NP to 4-AP in the presence of NaBH<sub>4</sub> [35]. Moreover, binary CuO/TiO<sub>2</sub> composites have demonstrated excellent reactivity in tandem hydrogenation processes for nitro compounds [36].

In the present study, different wt.% CuO/TiO<sub>2</sub> (rutile) were synthesized through the combustion technique followed by calcination at 700 °C to ensure a complete transition from anatase to rutile. The prepared catalysts were characterized via X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy, attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy, thermogravimetric analysis–differential thermal analysis (TGA–DTA), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS). The catalytic performance of CuO/TiO<sub>2</sub> was evaluated afterwards via the reduction of MO and 4-nitrophenol as models of organic contaminants in the presence of NaBH<sub>4</sub>. The influence of parameters, including NaBH<sub>4</sub> concentration, catalyst mass and reusability of the catalyst, were examined.

## 2. Results and Discussion

### 2.1. X-Ray Diffraction

The XRD patterns of the CuO/TiO<sub>2</sub> catalyst series are presented in Figure 1. The results obtained reveal that the materials are primarily composed of the rutile phase of TiO<sub>2</sub> in accordance with ICDD 21-1276. The presence of CuO in its monoclinic form was also verified in accordance with the ICDD 48-1548 reference pattern, confirming the effective loading of copper oxide in TiO<sub>2</sub>. Figure 1 also reveals a correlation between the deposited quantity of Cu(II) ions and the intensities of the characteristic CuO peaks. These findings collectively indicate the successful preparation of the CuO/TiO<sub>2</sub> catalysts with varying percentages of CuO deposition. The average crystallite size of CuO was determined to be 26, 27, 32, 35, 36 nm for 40, 30, 20, 10 and 5 wt.% CuO/TiO<sub>2</sub> catalysts, respectively. The crystallite size was determined using the Scherrer equation [37]:

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

where  $\lambda$  is the X-ray wavelength (0.1540 nm),  $\beta$  is the full width at half maximum (FWHM),  $\theta$  is Bragg's angle, and  $L$  represents the average crystallite size.

On the other hand, the absence of the anatase phase of TiO<sub>2</sub> is due to its transformation to rutile upon heating at 700 °C, as observed in Figure 2, which shows the XRD curves for the 40 wt.% CuO/TiO<sub>2</sub> catalysts subjected to various calcination temperatures. The primary difference observed was the phase transition of TiO<sub>2</sub> from anatase (ICDD 21-1272) to rutile (ICDD 21-1276), with complete transformation occurring at 700 °C. The same results were observed in many previous studies [38].

Following the reduction experiment using NaBH<sub>4</sub>, the rutile structure of TiO<sub>2</sub> remained unchanged, indicating its stability under the reaction conditions. However, the monoclinic structure of CuO significantly decreased, leading to the formation of Cu(NPs), as depicted in Figure 3. Notably, two additional peaks emerged at 43.28° and 50.37°, corresponding to the (111) and (200) planes, respectively. These peaks are characteris-

tic of the face-centered cubic (FCC) crystal structure of metallic copper nanoparticles (ICDD No. 04-0836). The average Cu(NP) size is about 15 nm.

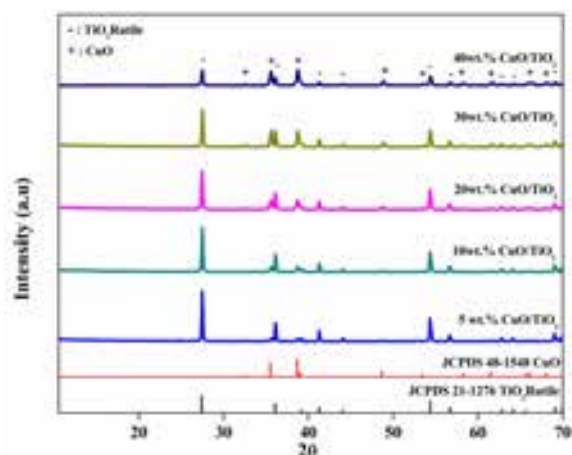


**Figure 1.** XRD patterns of different wt.% CuO/TiO<sub>2</sub> samples.

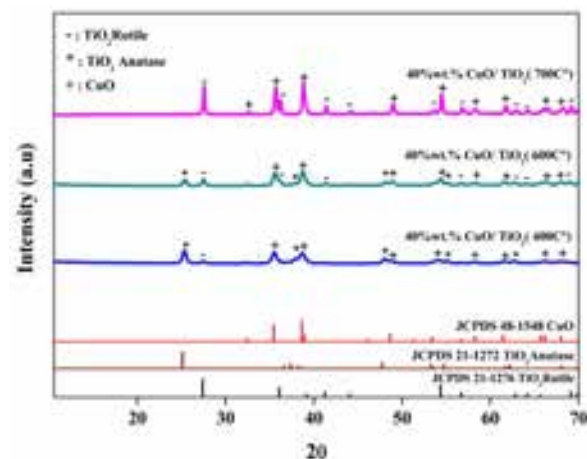


**Figure 2.** XRD patterns of 40 wt.% CuO/TiO<sub>2</sub> samples calcined at different temperatures.

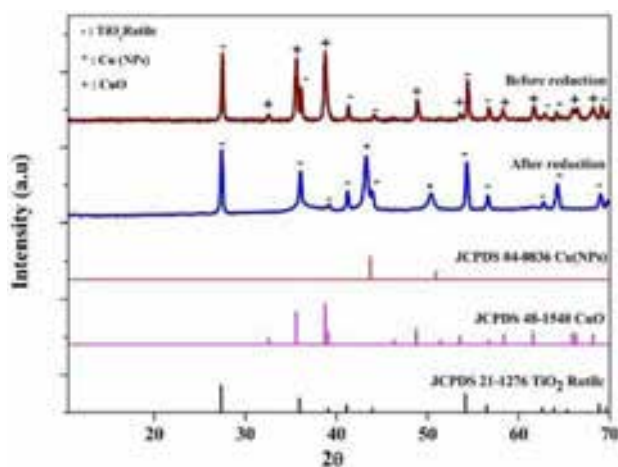


**Figure 3.** XRD patterns of 40 wt.% CuO/TiO<sub>2</sub> before and after the reduction experiment.

## 2.2. Thermal Analysis Measurement

To examine the thermal behavior of CuO/TiO<sub>2</sub>, thermal experiments involving thermogravimetric and differential measurements were performed. The results are shown in Figure 4. The initial step, characterized by a weight loss of 3% within the temperature range

of 30 to 150 °C, can be attributed to the vaporization of water [39]. The notable weight reduction occurring between 200 and 350 °C, as evaluated at 30%, appears to be associated with the decomposition and combustion of the organic constituents. The latter was confirmed by an intense exothermic peak observed in the DTA curve and two intense peaks in the DTG curve [40]. On the other hand, no weight loss was observed at temperatures above 450 °C, and the anatase to rutile phase transition that should occur above 600 °C [38] was not observed in the DTA curve because of its reduced sensitivity compared with that of differential scanning calorimetry (DSC).

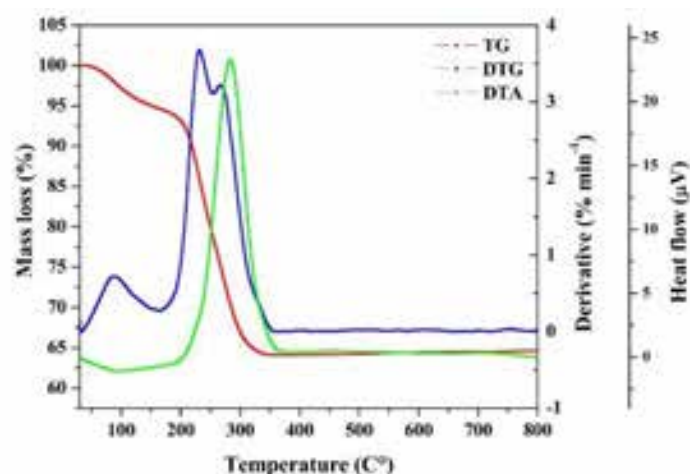


**Figure 4.** Thermal curves of the as-prepared 40 wt.% CuO/TiO<sub>2</sub> without calcination under air flow at 10 °C min<sup>−1</sup>.

### 2.3. ATR-FTIR Spectroscopy

ATR-FTIR spectroscopy was performed on the catalysts calcined at 700 °C. The measurements were conducted across the spectrum ranging from 400 to 4000 cm<sup>−1</sup>, and the results are shown in Figure 5. The analysis revealed similar results for the different catalysts with different percentages of CuO. The absence of water molecules and other contaminants in the catalyst was confirmed by the observation of strong bands in the infrared spectrum just below 1000 cm<sup>−1</sup>. These bands typically correspond to lattice vibrations within metal oxides. The peak observed at approximately 650 cm<sup>−1</sup> is associated with the presence of the Ti-O-O stretching vibration bond. Additionally, the spectra revealed two other distinct bonds below 500 cm<sup>−1</sup> that were attributed to metal-oxygen (M-O) bond vibrations. All the observed bands suggest the existence of both Ti-O vibrational stretching and Cu-O stretching vibration bonds [41], which confirms the successful incorporation of CuO into TiO<sub>2</sub>.

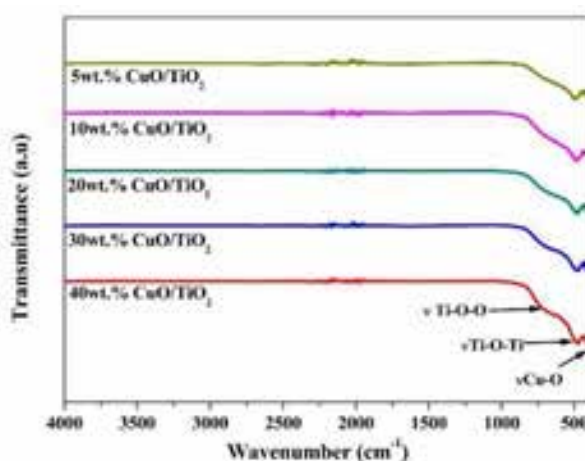


**Figure 5.** Infrared spectra of the wt.% CuO/TiO<sub>2</sub> samples.

#### 2.4. UV–Vis Diffuse Reflectance Spectroscopy

Figure 6a presents the diffuse reflectance spectroscopy (DRS) results for TiO<sub>2</sub> and the various wt.% CuO/TiO<sub>2</sub> catalysts, revealing their optical properties in the 200–800 nm range. TiO<sub>2</sub> exhibits a pronounced absorption peak below 400 nm, which is attributed to its intrinsic interband absorption [42]. In contrast, the spectrum of the wt.% CuO/TiO<sub>2</sub> catalysts displays additional absorption bands in the 400–800 nm range. The absorption band between 400 and 600 nm is attributed to charge transfer from the valence band (VB) of TiO<sub>2</sub> to CuO. Additionally, the lower absorption band within the 500–800 nm range is associated with the intrinsic exciton band of CuO and the d–d transition of Cu<sup>2+</sup> species [43]. The band gap energies (E<sub>g</sub>) of TiO<sub>2</sub>, CuO, and the different wt.% CuO/TiO<sub>2</sub> catalysts were determined by identifying the intersection of the linear portion of the  $(\alpha h\nu)^2$  vs. energy (eV) curves, as detailed in Figure 6b. The E<sub>g</sub> values for TiO<sub>2</sub> and wt.% CuO/TiO<sub>2</sub> are summarized in Table 1. These results indicate that increasing the CuO content leads to a progressive narrowing of the band gap. This trend can be attributed to the incorporation of Cu, which introduces additional energy states within the band structure, thereby lowering the bandgap. The reduced bandgap in the CuO/TiO<sub>2</sub> catalysts enhances their visible light absorption, which is beneficial for photocatalytic applications [44].

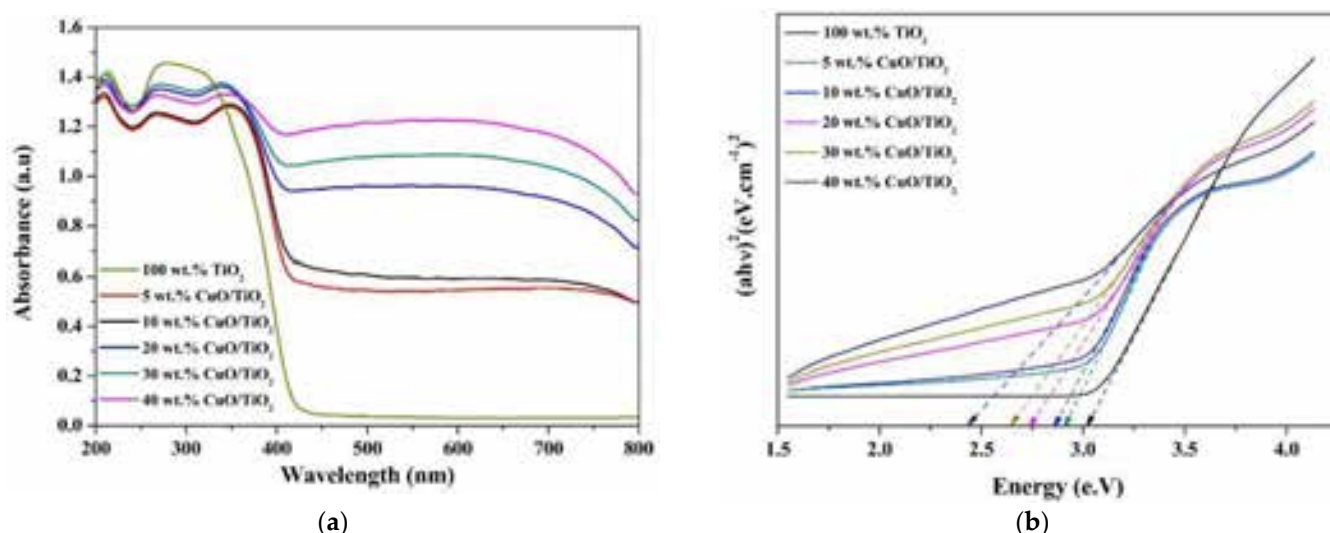


**Figure 6.** (a) UV–Vis diffuse reflectance spectra of TiO<sub>2</sub> and wt.% CuO/TiO<sub>2</sub> and (b) Tauc plot.

**Table 1.** Bandgaps of different catalysts.

| Catalyst      | TiO <sub>2</sub> | 5 wt.% CuO | 10 wt.% CuO | 20 wt.% CuO | 30 wt.% CuO | 40 wt.% CuO |
|---------------|------------------|------------|-------------|-------------|-------------|-------------|
| Band gap (eV) | 3.02             | 2.91       | 2.86        | 2.73        | 2.65        | 2.43        |

#### 2.5. SEM–EDS Analysis

Morphological studies via SEM–EDS were carried out on the CuO/TiO<sub>2</sub> catalyst. Figure 7 shows representative SEM images of synthesized CuO/TiO<sub>2</sub>, which reveal a homogeneous spherical morphology with varying diameters and numerous micrometer-sized particles. Additionally, the catalyst has a porous structure and some aggregation of spheres. The analysis of the CuO/TiO<sub>2</sub> catalyst via energy dispersive X-ray (EDX) spectroscopy aimed to examine the presence and distribution of copper, titanium, and oxygen within the material. The EDX spectrum of CuO/TiO<sub>2</sub> is shown in Figure 8, and the results indicate the successful incorporation of copper into the TiO<sub>2</sub> sample. Additionally, the elemental mapping analysis revealed a uniform distribution of copper (depicted in yellow), titanium (represented in pink), and oxygen (shown in blue) in the samples, as illustrated in Figure 9.

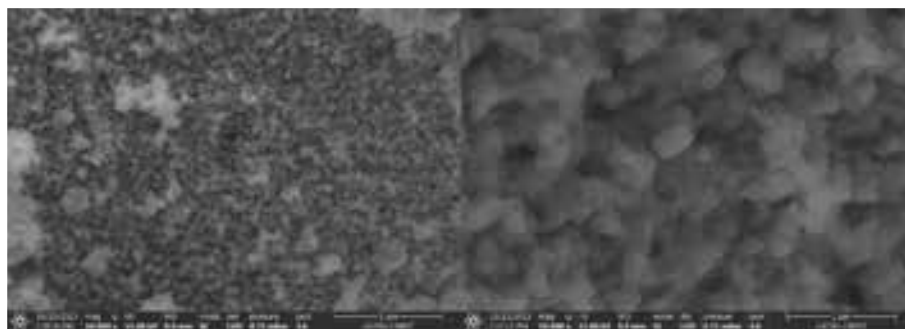


Figure 7. SEM micrographs of 40 wt.% CuO/TiO<sub>2</sub>.

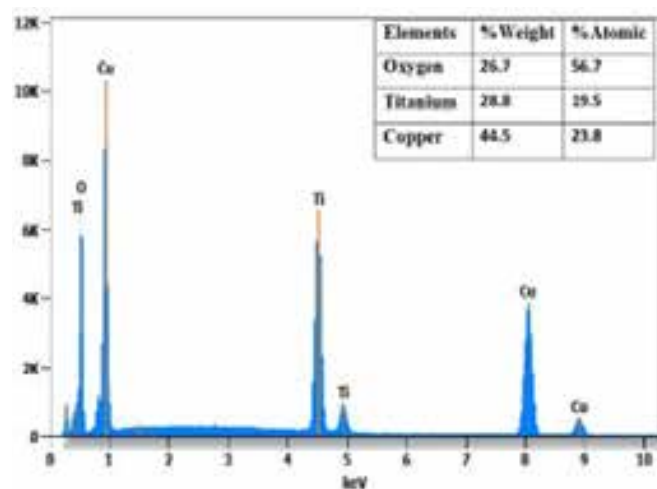


Figure 8. EDS Spectrum of 40 wt.% CuO/TiO<sub>2</sub>.

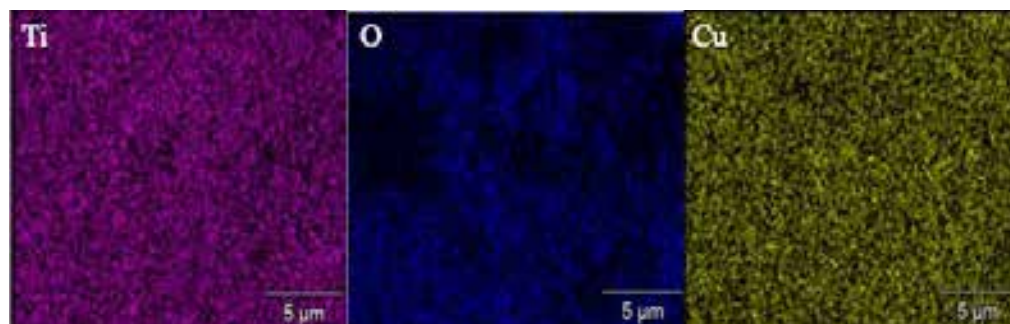


Figure 9. EDX mapping of the 40 wt.% CuO/TiO<sub>2</sub> catalyst.

#### 2.6. Catalytic Reduction of 4-NP and MO by a CuO/TiO<sub>2</sub> Catalyst

The catalytic performance of the CuO/TiO<sub>2</sub> samples with different CuO loadings (5 to 40 wt.%) was evaluated for the reduction of organic pollutants via NaBH<sub>4</sub>, as shown in Figure 10a,b. As shown in Figure 10a, which represents the reduction of 4-nitrophenol (4-NP), the 40 wt.% CuO/TiO<sub>2</sub> catalyst exhibited the fastest catalytic activity, reaching nearly 100% removal within a shorter reaction time than the other catalysts and pure CuO. Similarly, in Figure 10b, which shows the reduction of MO, 40 wt.% CuO/TiO<sub>2</sub> again demonstrates the fastest catalytic performance. The pure CuO sample exhibited lower catalytic activity than the 40 wt.% CuO/TiO<sub>2</sub> sample did, likely due to the agglomeration of copper oxide nanoparticles, which reduced the number of accessible active sites. On the other hand, at lower CuO loadings (e.g., 5 wt.%), the catalytic activity is the slowest, which can be attributed to the lower number of active CuO/TiO<sub>2</sub> sites available for the reduction process.

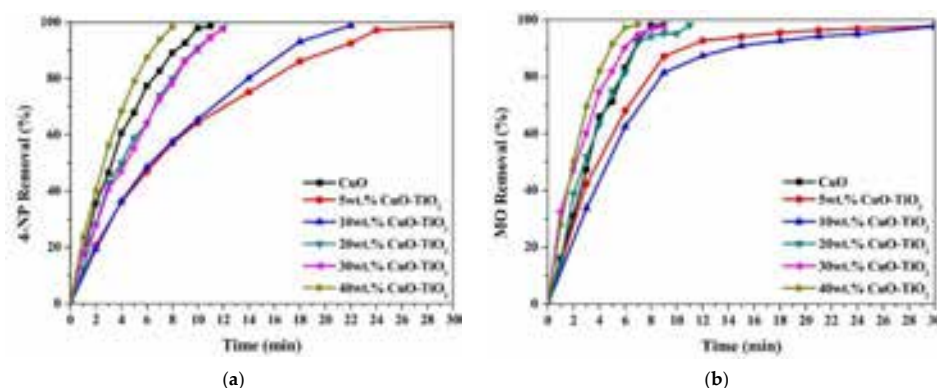


**Figure 10.** Reduction performance of the wt.% CuO/TiO<sub>2</sub> catalysts for 4-NP (a) and MO (b).

Figure 11a,b display the absorption spectra of 4-NP and MO in the presence of NaBH<sub>4</sub> but without the use of a catalyst. Under these conditions, the peak intensities show little change even after 180 min, indicating a negligible reduction rate, as no significant degradation occurred during this time. However, when CuO/TiO<sub>2</sub> is introduced alongside NaBH<sub>4</sub> (Figure 11c,d) and forming Cu(NPs)/TiO<sub>2</sub>, a rapid and noticeable reduction in the characteristic absorption peaks of both 4-NP and MO is observed. For 4-NP, the peak at ~400 nm diminished progressively, vanishing completely within 480 s (Figure 11c). Similarly, the absorption peak of MO at approximately 464 nm disappears within 420 s (Figure 11d). This demonstrates a much faster and more efficient reduction process in the presence of the CuO/TiO<sub>2</sub> catalyst than in the presence of NaBH<sub>4</sub> alone. Simultaneously, a pair of new peaks emerged at 297 nm and 231 nm for the reduction of 4-NP and at 242 nm during the reduction of MO. These new peaks can be attributed to the characteristic absorption bands of the colorless 4-aminophenol (4-AP) from 4-NP and sulfanilic acid along with dimethyl-4-phenylenediamine from OM [45,46].

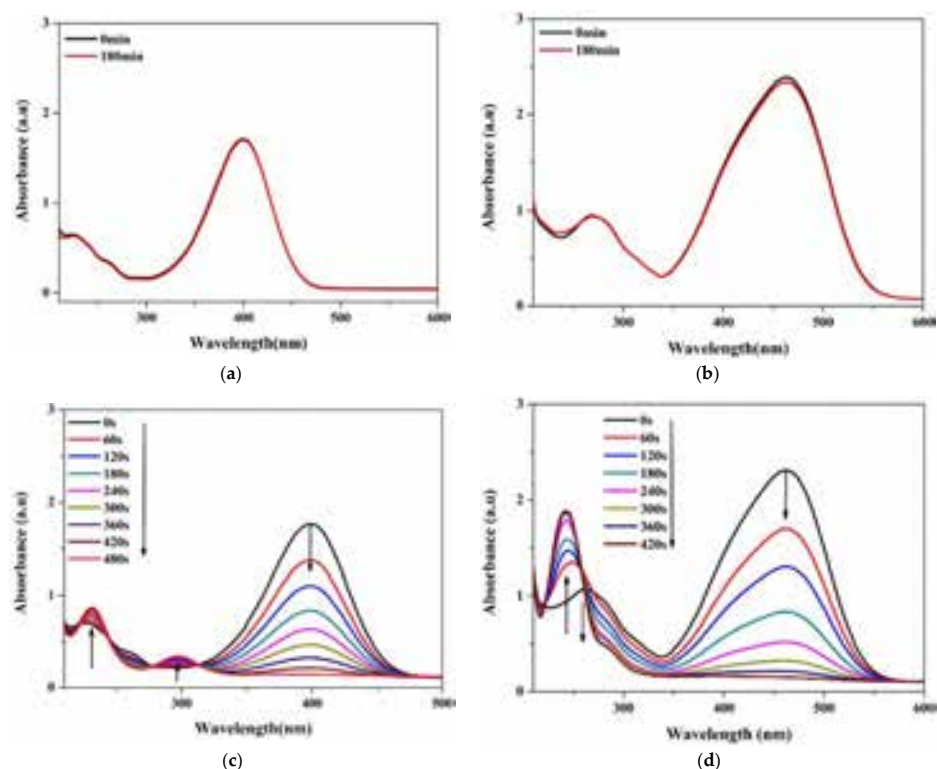


**Figure 11.** UV-vis spectra of the reduction of (a) 4-NP and (b) MO by NaBH<sub>4</sub> without the catalyst and absorbance spectra of (c) 4-NP and (d) MO in the presence of NaBH<sub>4</sub> and CuO/TiO<sub>2</sub>.

### 2.6.1. Kinetic Study

The pseudo-first-order kinetic model of Langmuir–Hinshelwood was employed to analyze the kinetics data due to the substantial excess of  $\text{NaBH}_4$  compared with the organic dyes, denoted as  $([\text{NaBH}_4]/[\text{Pollutant}]) = 40$ . The rate constants ( $k_{\text{app}}$ ) governing the conversion reactions for both 4-NP and MO were determined via the following equation:

$$\ln \frac{C_t}{C_0} = \ln \frac{A_t}{A_0} = -k_{\text{app}} t \quad (1)$$

As depicted in Figure 12a,b, the  $\ln(A_t/A_0)$  vs. time of reaction was determined by analyzing the absorption peak intensities at 400 nm (4-NP) and 464 nm (MO). Remarkably, the reduction process was initiated promptly, devoid of any induction time requirement. The graphical representation of  $\ln(A_t/A_0)$  against time exhibited a robust linear correlation, aligning well with the expectations of pseudo-first-order kinetics. Consequently, the calculated rate constants were determined to be  $0.00517 \text{ s}^{-1}$  for 4-NP and  $0.00727 \text{ s}^{-1}$  for MO. To enable a comparative assessment of  $\text{CuO}/\text{TiO}_2$  performance, an activity factor denoted as  $k'$  was computed via the following equation:

$$k' = \frac{k_{\text{app}}}{m} \quad (2)$$

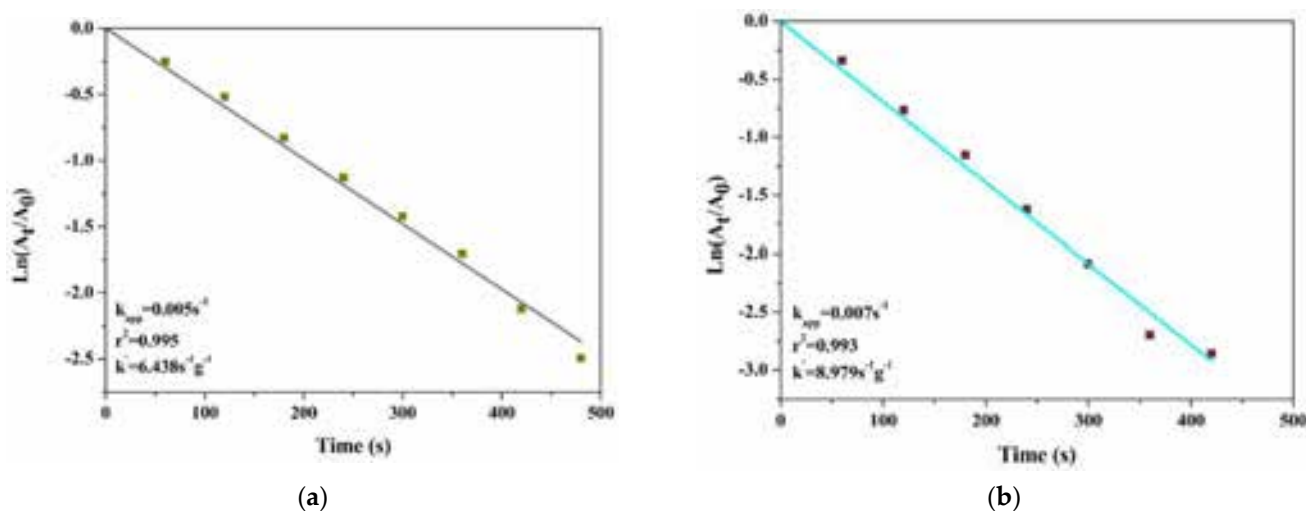


**Figure 12.** First-order plot for the catalytic reduction of (a) 4-NP and (b) MO. Experimental conditions: 40 wt.%  $\text{CuO}/\text{TiO}_2$  dose = 0.04 g/L,  $[\text{NaBH}_4] = 14 \text{ mM}$ , and  $[4\text{-NP or MO}] = 0.35 \text{ mM}$ .

In this equation,  $m(\text{g})$  represents the mass of the copper in the catalyst involved in the reaction.

In this context, the derived  $k'$  values were  $6.46 \text{ s}^{-1} \text{ g}^{-1}$  for 4-NP and  $8.98 \text{ s}^{-1} \text{ g}^{-1}$  for MO. For a comprehensive comparison, Table 2 illustrates the varying efficacies of  $\text{Cu}(\text{NPs})$  catalysts documented in the literature.

Tables 3 and 4 show an increase in the observed rate constants ( $k_{\text{app}}$ ) with increasing  $\text{CuO}$  percentage in the catalyst. The 40 wt.%  $\text{CuO}/\text{TiO}_2$  catalyst exhibits the highest rate constant ( $0.005 \text{ s}^{-1}$ ), indicating that a higher copper loading favors faster reduction kinetics for 4-NP and MO. However, when considering the mass of active copper in the catalyst, the normalized values ( $k'$ ) indicate that the 5 wt.%  $\text{CuO}/\text{TiO}_2$  catalyst exhibits the highest activity ( $17.5 \text{ s}^{-1} \text{ g}^{-1}$ ). This suggests that, although increasing the  $\text{CuO}$  loading accelerates the overall reaction, the efficiency per unit mass of copper is maximized at lower loadings.

After the in situ reductive reaction of  $\text{CuO}/\text{TiO}_2$  to  $\text{Cu}(\text{NPs})/\text{TiO}_2$  with  $\text{NaBH}_4$ , an underlying mechanism enables the catalytic reduction of 4-NP and MO using  $\text{Cu}(\text{NPs})/\text{TiO}_2$  in the presence of  $\text{NaBH}_4$  (Figure 13). In this process, the  $\text{BH}_4^-$  ions adhere to the surface of the catalyst, thereby initiating the creation of  $\text{BO}_2^{2-}$  through the self-hydrolysis

of  $\text{NaBH}_4$ . Moreover,  $\text{BH}_4^-$  interacts with the catalyst, facilitating the transfer of active hydrogen species, leading to the formation of an energetically charged hydrogen layer on the catalyst surface [47]. The organic pollutants subsequently attach themselves to the catalyst surface, undergoing reduction into 4-AP for 4-NP and sulfanilic acid along with dimethyl-4-phenylenediamine for MO during the step that governs the reaction rate. The produced compounds are then desorbed from the surface of the  $\text{Cu}(\text{NPs})/\text{TiO}_2$  catalyst. As a result,  $\text{Cu}(\text{NPs})/\text{TiO}_2$  exhibits highly efficient catalytic reduction due to the supply of electrons to the catalyst by  $\text{BH}_4^-$  ions, a mechanism that enables 4-NP and MO to bond with the catalyst surface, consequently yielding enhanced catalytic activity [48].

**Table 2.** Comparison of the catalytic properties of catalysts with those of  $\text{Cu}(\text{NPs})$  reported in the literature and this work.

| Pollutant            | Catalyst                                  | $k'$<br>( $\text{s}^{-1} \text{g}^{-1}$ ) | Time (min) | Conditions          |               |                    | Reference |
|----------------------|-------------------------------------------|-------------------------------------------|------------|---------------------|---------------|--------------------|-----------|
|                      |                                           |                                           |            | $\text{NaBH}_4$ (M) | Pollutant (M) | Catalyst Mass (mg) |           |
| 4-Nitrophenol (4-NP) | Cu10/MZ                                   | 5.00                                      | 10         | 0.0045              | 0.0000675     | 1                  | [22]      |
|                      | Cu10/ZSM-5                                | 1.17                                      | 50         | 0.0045              | 0.0000675     | 1                  | [22]      |
|                      | CuO/TiO <sub>2</sub>                      | 6.46                                      | 8          | 0.014               | 0.00035       | 2                  | This work |
|                      | Cu NPs@Fe <sub>3</sub> O <sub>4</sub> -LS | 1.87                                      | 3          | 0.125               | 0.00125       | 7                  | [4]       |
|                      | MnO@Cu/C                                  | 17.33                                     | 1.5        | 0.0193              | 0.0008        | 4                  | [16]      |
|                      | C@Cu                                      | 59.00                                     | 1          | 0.033               | 0.00014       | 1                  | [49]      |
|                      | Cu-Ag/GP                                  | 0.40                                      | 10         | 0.0714              | 0.000857      | 10                 | [50]      |
|                      | Cu-Ni/GP                                  | 0.60                                      | 7          | 0.0714              | 0.000857      | 10                 | [50]      |
|                      | CuVOS@SiO <sub>2</sub> -3                 | 1.57                                      | 2          | 0.00528             | 0.00014377    | 5                  | [51]      |
|                      | CuVOS-3                                   | 8.20                                      | 2          | 0.00582             | 0.000138      | 5                  | [52]      |
| Methyl orange (MO)   | C@Cu                                      | 62.00                                     | 1          | 0.033               | 0.000061      | 1                  | [49]      |
|                      | CuO/TiO <sub>2</sub>                      | 8.98                                      | 7          | 0.014               | 0.00035       | 2                  | This work |
|                      | Cu-Ag/GP                                  | 0.77                                      | 4          | 0.0714              | 0.00004286    | 10                 | [50]      |
|                      | Cu-Ni/GP                                  | 0.38                                      | 5          | 0.0714              | 0.00004286    | 10                 | [50]      |
|                      | CuVOS@SiO <sub>2</sub> -3                 | 1.37                                      | 4          | 0.00528             | 0.0003055     | 5                  | [51]      |
|                      | CuVOS-3                                   | 6.47                                      | 2          | 0.00582             | 0.00029       | 5                  | [52]      |

**Table 3.** Rate constants obtained for 4-NP reduction by wt.% CuO/TiO<sub>2</sub>.

| Catalyst                     | $k_{\text{app}}$ ( $\text{s}^{-1}$ ) | $k'$ ( $\text{s}^{-1} \text{g}^{-1}$ ) |
|------------------------------|--------------------------------------|----------------------------------------|
| 5 wt.% CuO/TiO <sub>2</sub>  | 0.00175                              | 17.5                                   |
| 10 wt.% CuO/TiO <sub>2</sub> | 0.00175                              | 8.7                                    |
| 20 wt.% CuO/TiO <sub>2</sub> | 0.00328                              | 8.2                                    |
| 30 wt.% CuO/TiO <sub>2</sub> | 0.00308                              | 5.1                                    |
| 40 wt.% CuO/TiO <sub>2</sub> | 0.00512                              | 6.4                                    |

**Table 4.** Rate constants obtained for MO reduction by wt.% CuO/TiO<sub>2</sub>.

| Catalyst                     | $k_{\text{app}}$ ( $\text{s}^{-1}$ ) | $k'$ ( $\text{s}^{-1} \text{g}^{-1}$ ) |
|------------------------------|--------------------------------------|----------------------------------------|
| 5 wt.% CuO/TiO <sub>2</sub>  | 0.00150                              | 15.0                                   |
| 10 wt.% CuO/TiO <sub>2</sub> | 0.00126                              | 6.3                                    |
| 20 wt.% CuO/TiO <sub>2</sub> | 0.00479                              | 12.0                                   |
| 30 wt.% CuO/TiO <sub>2</sub> | 0.00546                              | 9.1                                    |
| 40 wt.% CuO/TiO <sub>2</sub> | 0.00727                              | 8.9                                    |

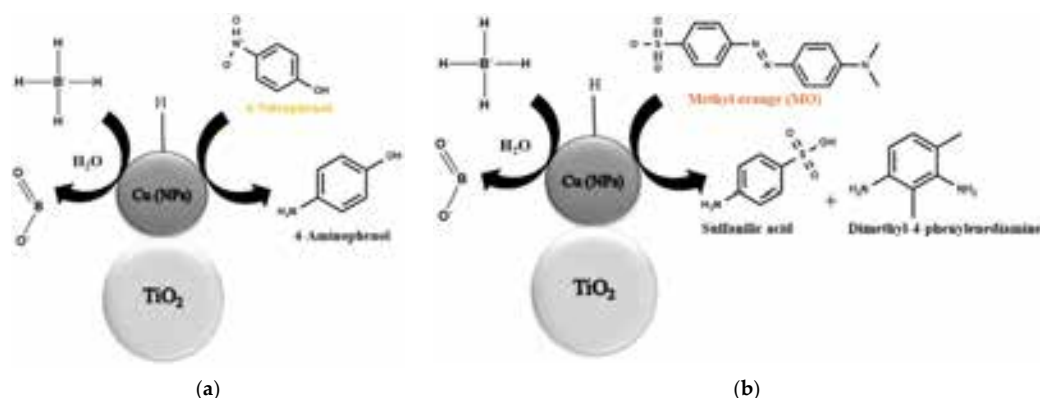


**Figure 13.** Schematic reactions of (a) 4-NP and (b) MO, by  $\text{NaBH}_4$  in the presence of  $\text{Cu(NPs)/TiO}_2$ .

### 2.6.2. Effects of Parameters and Reusability

Multiple factors were investigated to understand their influence on the catalyzed reduction of 4-NP and MO using 40 wt.%  $\text{CuO/TiO}_2$  catalysts. The parameters examined included the catalyst dosage and concentration of  $\text{NaBH}_4$ . Figure 14a,b show the impact of varying catalyst amounts on the rate of pollutant reduction. By making more active sites accessible for the reaction, the large amount of catalyst led to improved efficiency. The performance constantly increased as the catalyst amount increased from 0.02 g/L to 0.06 g/L, which confirms the principle of Sabatier [53]. The variation in  $\text{NaBH}_4$  concentration had a pronounced influence on the catalytic reduction of 4-NP and MO (Figure 14c,d). Because of the limited quantity of hydrogen emitted, the catalytic reduction rate decreased as the  $\text{NaBH}_4$  concentration decreased [54].

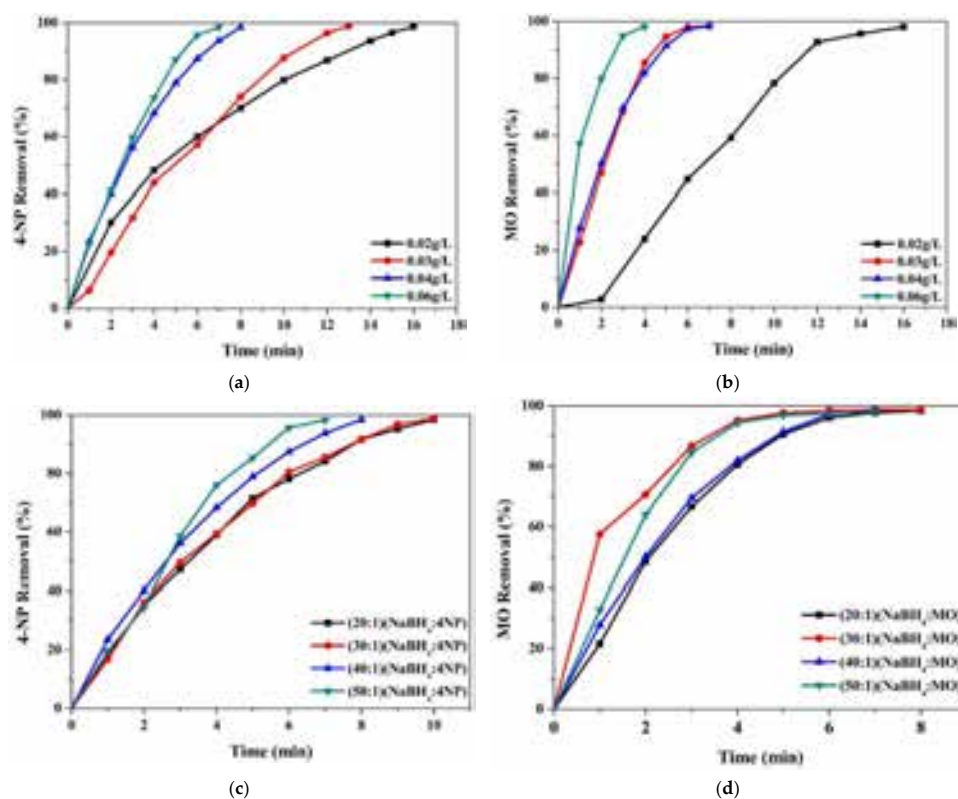


**Figure 14.** Pollutant removal versus time plots for catalytic reduction using 40 wt.%  $\text{CuO/TiO}_2$ , showing the effect of catalyst dose on the reduction of (a) 4-NP and (b) MO, and the effect of  $\text{NaBH}_4$  concentration on the reduction of (c) 4-NP and (d) MO.

An essential characteristic of catalysts is their stability and reusability. To assess this, a fresh solution containing pollutants was introduced after each catalytic reduction cycle. The initial concentration remained constant at 0.35 mM throughout. As depicted in Figure 15a,b, the catalyst consistently maintained over 96% MO capacity and 94% 4-NP capacity for reduction of the dyes across 10 successive reaction cycles. This outcome highlights the exceptional reusability of the CuO/TiO<sub>2</sub> catalyst. This excellent reusability can be attributed to the even distribution and robust stability of Cu on the TiO<sub>2</sub> surface, which in turn provides a greater number of active sites for catalytic processes.

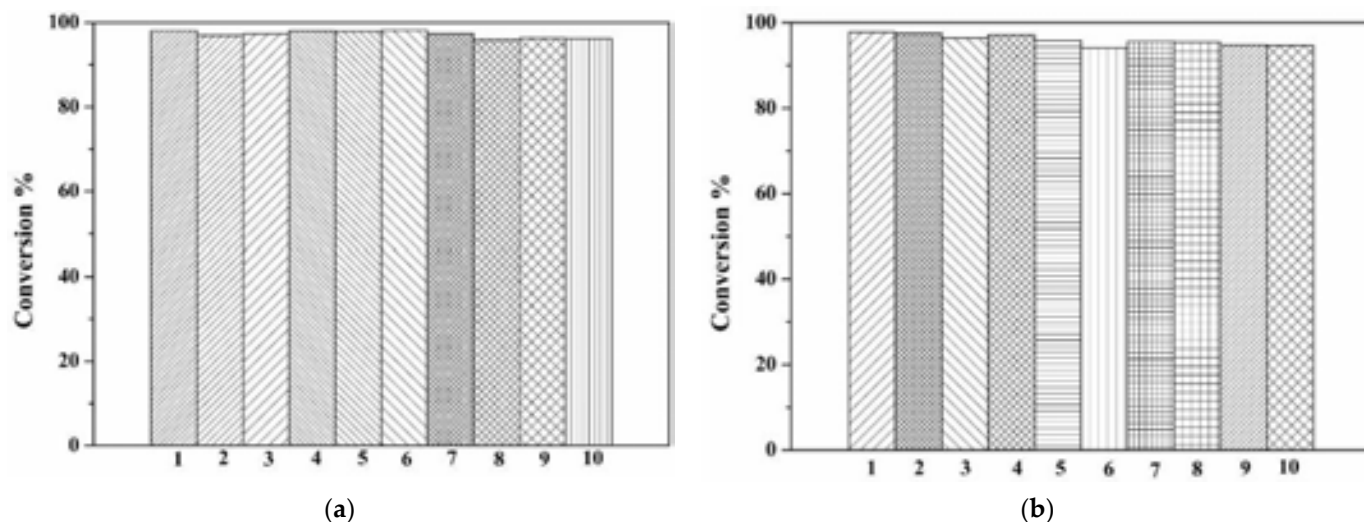


**Figure 15.** Recycling of CuO/TiO<sub>2</sub> in the hydrogenation of (a) 4-NP and (b) MO.

### 3. Materials and Methods

#### 3.1. Synthesis of the CuO/TiO<sub>2</sub> Catalysts

The combustion technique was used to prepare different percentages of wt.% CuO/TiO<sub>2</sub> (wt = 5, 10, 20, 30, and 40%). Analytical grade Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma Aldrich, ≥99.9%), along with TiO<sub>2</sub>-P25 (Degussa Aeroxide P25) and citric acid as a fuel (Sigma Aldrich, ≥99.5%), served as the starting materials. Initially, these materials were added to deionized water with a fixed weight percentage of metal on TiO<sub>2</sub> and an excess amount of citric acid. The resulting mixtures were then stirred to achieve a well-dispersed suspension. The suspension subsequently underwent evaporation from 80 to 130 °C to yield a thick gel. This gel was subsequently converted into a dry form. Finally, the dry gel was calcined in an air atmosphere at 700 °C for 4 h with a ramp rate of 10 °C/min. Figure 16 represents the synthesis method for the catalysts.

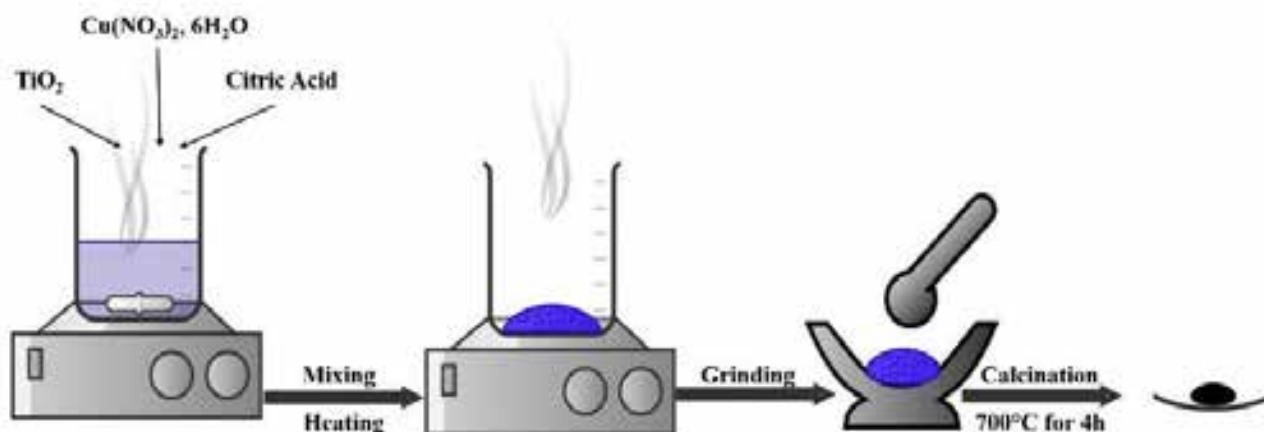


**Figure 16.** Synthesis procedure for the catalysts.

### 3.2. Catalytic Reduction of Organic Pollutants

The catalytic activity of CuO/TiO<sub>2</sub> was evaluated by studying the reduction of MO (Sigma Aldrich, ≥98.0%) and 4-nitrophenylphenol (Sigma Aldrich, ≥99.0%) as the target pollutants for the experiments. The experimental setup involved a beaker (50 mL) placed at room temperature. The catalytic reaction proceeded as follows: 2 mg of CuO/TiO<sub>2</sub> was uniformly dispersed in 35 mL of deionized water, followed by the addition of 10 mL of freshly prepared aqueous NaBH<sub>4</sub> (Sigma Aldrich, ≥99.0%) (70 mM). The solution was sonicated for 10 min, resulting in a color change from a black CuO/TiO<sub>2</sub> suspension to a gray color, indicating the formation of Cu(NPs)/TiO<sub>2</sub>. Next, 5 mL of MO (3.5 mM) or 4-NP (3.5 mM) was added to the mixture. The overall concentrations of the organic dyes and NaBH<sub>4</sub> were 0.35 mM and 14 mM, respectively. The progress of the reaction was monitored by recording the time-dependent UV–vis absorption spectra of the reaction mixture in the wavelength range between 210 and 600 nm via a spectrophotometer (Techcomp UV 2300). The catalytic reduction experiment is shown in Figure 17.

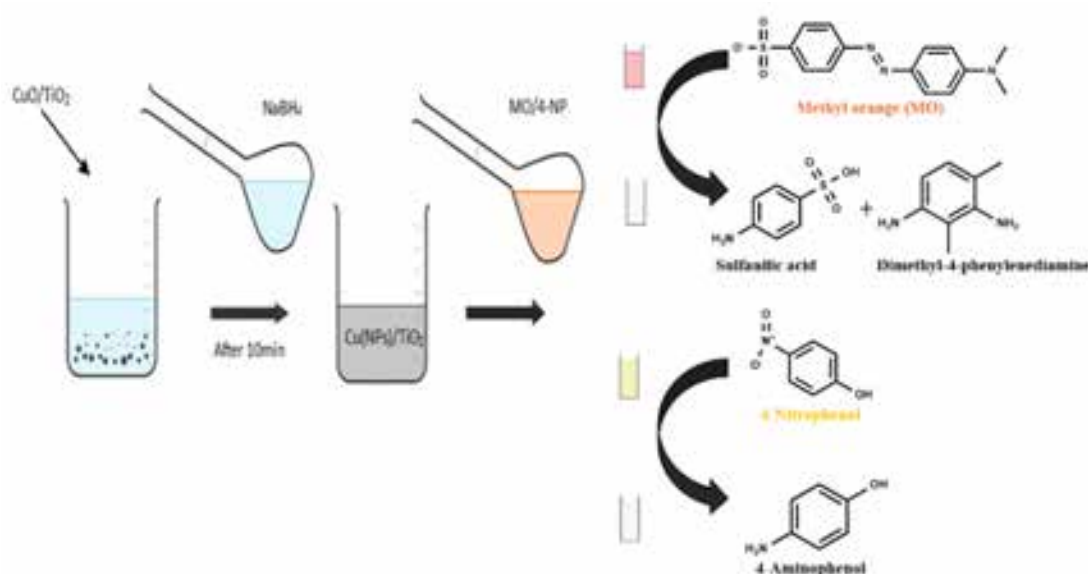


**Figure 17.** Catalytic reduction experiments of organic pollutants.

### 3.3. Characterization Techniques

The identification of the mineral crystalline phase of the catalysts was carried out via X-ray diffraction, via a Shimadzu 6100 powder diffractometer with a monochromatic beam ( $\lambda_{\text{CuK}\alpha} = 1.541838^\circ$ ). These measurements were taken at room temperature over a  $2\theta$  range of  $10^\circ$  to  $70^\circ$ , with a scanning rate of  $2^\circ/\text{min}$ . A UV–vis spectrophotometer, namely, a PerkinElmer Lambda 900 UV/Vis/NIR spectrometer, was used to obtain diffuse reflectance spectra of the catalysts in the wavelength range of 200–800 nm. To identify the main functional groups of the catalyst, ATR–FTIR spectroscopy was used with a Nicolet iS50 instrument with a resolution of  $4\text{ cm}^{-1}$  in the spectral range of  $400\text{--}4000\text{ cm}^{-1}$ . The thermal stability and degradation behavior of the catalysts were verified via simultaneous TGA and DTA under an air flow rate of  $30\text{ mL/min}$  via a Labsys<sup>TM</sup> (1F) Setaram instrument. An 8 mg sample was placed in an alumina crucible and heated from  $30^\circ\text{C}$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C/min}$ . The surface morphology and chemical analysis of the samples were performed by SEM–EDX on a Quattro S-FEG-ThermoFisher scientific instrument.

## 4. Conclusions

In this study, CuO/TiO<sub>2</sub> catalysts were prepared through a combustion technique. The catalysts were characterized via XRD, ATR–FTIR spectroscopy, TGA–DTA, UV–vis DRS, and SEM–EDX techniques. Compared with TiO<sub>2</sub> and CuO, the presence of Cu in the CuO/TiO<sub>2</sub> catalysts significantly enhanced the reduction of 4-NP and MO. The

fastest dye reduction was obtained with 40 wt.% CuO, followed by 40 > 30 > 20 > 10 > 5 wt.% CuO/TiO<sub>2</sub> in the presence of NaBH<sub>4</sub> and 2 mg of catalyst. The kinetic data were successfully modeled via the pseudo-first-order Langmuir–Hinshelwood mechanism, yielding rate constants of 0.000517 s<sup>−1</sup> for 4-NP and 0.00727 s<sup>−1</sup> for MO. The efficiency of 4-NP and MO reduction with the CuO/TiO<sub>2</sub> catalyst improved as the catalyst dosage increased from 0.02 g/L to 0.06 g/L, offering more active sites. However, a decrease in NaBH<sub>4</sub> concentration led to a decrease in the catalytic reduction rate due to reduced hydrogen production. The presence of TiO<sub>2</sub> rutile functions as a protective agent to slow catalyst damage and agglomeration of particles. This material can be reused for several cycles without significant loss of catalytic activity.

**Author Contributions:** Conceptualization, M.A.; methodology, M.A.; software, M.A. and B.H.; validation, A.B. and A.E.H.; formal analysis, M.A. and A.B.; investigation, M.A.; resources, A.E.H. and A.B.; data curation, M.A.; writing—original draft preparation, M.A.; writing—review and editing, A.B., F.Z., A.E.H., A.S., M.D., K.A., R.S. and L.R.; visualization F.Z., M.D. and L.R.; supervision, A.E.H., A.B., M.A.E.B. and M.M.A. All authors have read and agreed to the published version of the manuscript.

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## Article

# Core/Shell ZnO/TiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> Nanoparticles for the Photodecomposition of Brilliant Blue E-4BA

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**Abstract:** The synthesis and characterization of ZnO/TiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> core/shell nanoparticles (NPs) is reported. The NPs were used for photocatalytic degradation of brilliant blue E-4BA under UV and visible light irradiation, monitored by high-performance liquid chromatography and UV-vis absorption spectroscopy. The size of the NPs ranged from 10 to 30 nm for the core and an additional 3 nm for the TiO<sub>2</sub> shell. Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> showed superior degradation under UV and visible light compared to ZnO/TiO<sub>2</sub> and SiO<sub>2</sub>/TiO<sub>2</sub> with complete photodecomposition of 20 ppm dye in 20 min using a 10 mg/100 mL photocatalyst. The “Co-doped” Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> NPs show the best performance under visible light irradiation, which is due to increased absorption in the visible range. DFT-calculated band structure calculations confirm the generation of additional electronic levels in the band gap of γ-Al<sub>2</sub>O<sub>3</sub> through Co<sup>3+</sup> ions. This indicates that Co-doping enhances the generation of electron–hole pairs after visible light irradiation.

**Keywords:** photocatalyst; nanomaterials; heterojunction; dye degradation; DFT calculations



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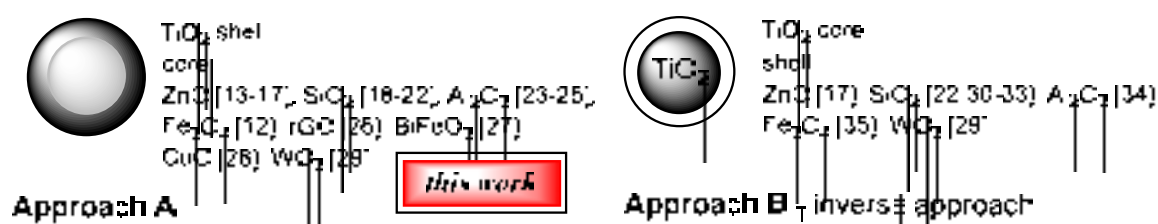
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## 1. Introduction

Organic dyes represent an important class of environmental pollutants, and their decomposition and removal are of technical and social importance [1–4]. Photocatalytic advanced oxidation processes (AOPs) based on TiO<sub>2</sub> are technically available [1–4], but are established almost exclusively in developed countries [5]. Photoconducting anatase (β-TiO<sub>2</sub>, tetragonal) is the base of the photocatalytic process [3–7] and is technically preferred due to its robust oxidizing capability, good photostability, and the non-toxic nature of TiO<sub>2</sub> materials [1–4]. However, conventional TiO<sub>2</sub> photocatalysis faces limitations such as rapid electron–hole recombination, low solar light absorption, and low activity on conventional crystal facets [3–8]. To overcome these obstacles and enhance photocatalytic efficiency, the creation of heterojunctions with other photoconductors has been explored [1,6,8–11]. Amongst such TiO<sub>2</sub>-based heterojunction materials, core/shell nanoparticles (NPs) combine the large surface with an intimate contact of the two photoconductors [1]. Basically, two different approaches are possible. The first is to cover various functional oxides (core) with TiO<sub>2</sub> as the shell (Approach A, Scheme 1) [7,8,11–29]. Alternatively, a TiO<sub>2</sub> core can be supported by an oxide shell (Approach B) [7,8,17,22,30–35].



**Scheme 1.** Two different approaches for the use of  $\text{TiO}_2$  in core/shell NPs.

Recent work on core/shell NPs for the photodecomposition of dyes, following approach A (Scheme 1), included magnetically separable  $\text{Fe}_3\text{O}_4$  (core)/ $\text{TiO}_2$  (shell) [12], NPs  $\text{ZnO}/\text{TiO}_2$  core/shell nanorods [16],  $\text{SiO}_2/\text{TiO}_2$  NPs [18], or rGO/ $\text{TiO}_2$  NPs (rGO = reduced graphene oxide) [26] for the photodegradation of methylene blue (MB).  $\text{ZnO}@\text{TiO}_2$  core/shell NPs were reported for the photodecomposition of rhodamine B (RhB) along with antimicrobial activity [13].  $\text{Al}_2\text{O}_3/\text{TiO}_2$  NPs were used for the photodecomposition of RhB and methyl orange [23],  $\text{SiO}_2/\text{TiO}_2$  NPs were applied in the photodecomposition of crystal violet [19,20], and  $\text{BiFeO}_3/\text{TiO}_2$  NPs, including the ferroelectric  $\text{BiFeO}_3$ , were used for methyl violet degradation [27]. These examples have in common that the  $\text{TiO}_2$  shell was chemically built-up around the core, and characterization of the materials showed that the  $\text{TiO}_2$  shell fully covers the core and thus very likely forms an intimate heterojunction between the core and shell (Scheme 1, Approach A). This is not necessarily the case in examples such as the reported  $\text{CuO}/\text{TiO}_2$  heterojunction NPs that were synthesized by ball-milling  $\text{Cu}_2\text{O}$  and  $\text{TiO}_2$  [28] or the  $\text{Al}_2\text{O}_3/\text{TiO}_2$  (or  $\text{TiO}_2/\text{Al}_2\text{O}_3$ ) NPs that were obtained through oxidation of bimetallic Ti/Al NPs [34].

The above examples differ also from the inverse approach (Approach B, Scheme 1) of using  $\text{TiO}_2$  as the core, as in the  $\text{TiO}_2/\text{SiO}_2$  NP photocatalysts used for singlet oxygen generation or the decomposition of MB [30,32] or RhB [33], the  $\text{TiO}_2/\text{Al}_2\text{O}_3$  NPs for photodecomposition of the typical textile dye reactive brilliant red, the dye X-3B [24], the  $\text{TiO}_2/\text{WO}_3$  photocatalyst reported for photocatalytic ozonation of organic contaminants [29], or the  $\text{TiO}_2/\text{Fe}_3\text{O}_4$  NPs used for photodecomposition of X-3B [35]. The approach of modifying the  $\text{TiO}_2$  surface with  $\text{SiO}_2$ ,  $\text{WO}_3$ , or  $\text{Fe}_3\text{O}_4$  (Scheme 1, Approach A) was driven by the idea to optimize the Fenton process, which is the production of the reactive superoxide  $\text{O}_2^{\bullet-}$  and hydroxy  $\bullet\text{OH}$  radicals [1,3,4,7,24,29–35] in addition to the electronic effect of a heterojunction. The approach of using  $\text{TiO}_2$  as the reactive shell (Scheme 1, Approach B) relies on the  $\text{TiO}_2$  photochemistry in combination with the electronic modification of the surface  $\text{TiO}_2$  through the formation of the heterojunction and faster charge transport, leading to decreased recombination rates [1,3,12,13,18–20,23,26–28].

Starting from the idea that cheaper and environmentally benign oxides like ZnO,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  as core materials would allow for producing metal oxide/ $\text{TiO}_2$  core/shell NPs also for large-scale applications, we embarked on synthesizing core/shell  $\text{ZnO}/\text{TiO}_2$ ,  $\text{SiO}_2/\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3/\text{TiO}_2$  NPs and studying their behavior as photocatalysts for photodegradation of the dye brilliant blue E-4BA, thus following the approach of modifying the electronic inventory of  $\text{TiO}_2$  for high photoreactivity (Scheme 1). Similar materials with ZnO,  $\text{SiO}_2$ , or  $\text{Al}_2\text{O}_3$  cores and  $\text{TiO}_2$  shells have been reported as photocatalysts for such applications [13–25]. Cobalt ( $\text{Co}^{3+}$ ) was added during the  $\text{Al}_2\text{O}_3$  NP synthesis to generate  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ , what we will further call “Co-doped” [36]. From the fractional replacement of  $\text{Al}^{3+}$  through  $\text{Co}^{3+}$ , we expected extension of the absorption into the visible range and thus substantial improvements in the photocatalytic properties. A similar idea of Co doping for visible photocatalytic applications has been reported for materials such as  $\text{LuFeO}_3$  [37], ZnO [38–40], and  $\text{Eu}(\text{OH})_3$  [41].

## 2. Results and Discussion

### 2.1. Synthesis and Characterization of the NPs

In the synthesis of the NPs, ethylene glycol serves as the key agent for governing the nanoparticle size. Upon heating the glycol-covered as-prepared NPs to 400 °C, ethylene glycol on the NP surface decomposed and led to an increased surface-to-volume ratio. The decomposition of ethylene glycol begins at 110 °C, resulting in a color change in the sample from white to gray. After one hour at 400 °C, the obtained powder turns yellowish, indicating that the degradation of ethylene glycol is complete.

Transmission electron micrographs (TEMs) show NPs of spherical shape for SiO<sub>2</sub> and ZnO, while the TiO<sub>2</sub> particles display a cubic morphology, and Al<sub>2</sub>O<sub>3</sub> appears flake-like (Figure S1, Supplementary Materials). Their approximate diameters are 12, 10, 10, and 30 nm for Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, and ZnO, respectively. After covering the NPs with TiO<sub>2</sub>, the TEM shows sizes that are about 3 nm larger than those of the pure core materials (Figure S2). Previously, it was suggested that NPs for efficient photocatalysis should have sizes below 30 nm with a preferred range from 10 to 20 nm [42,43].

Brunauer–Emmett–Teller (BET) analysis shows a surface area of 583 m<sup>2</sup>/g for Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, 160 m<sup>2</sup>/g for ZnO/TiO<sub>2</sub>, and 87 m<sup>2</sup>/g for SiO<sub>2</sub>/TiO<sub>2</sub>. The surface area for Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> is 618 m<sup>2</sup>/g (Figure S3). The high surface areas for Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> are very promising for the adsorption of the dye on the surface for photodegradation.

Powder XRD (PXRD) patterns of the synthesized Al<sub>2</sub>O<sub>3</sub> NPs (Figure S4A) confirm the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (cubic, spinel, *Fd-3m*) structure with observed peaks at 31.92°, 37.60°, 45.86°, and 67.03° corresponding to the (220), (311), (222), (400), and (440) planes, respectively. The crystallinity is low, as can be seen from the broad reflections. The Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub> NPs have retained the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure (Figure S4B). However, the reflections exhibit a shift to lower angles in line with increased lattice parameters caused by the larger Co<sup>3+</sup> (*r* = 75 pm) [44] ion partially replacing the smaller Al<sup>3+</sup> ions (*r* = 67 pm) [44], assuming that large parts of the Al<sup>3+</sup> ions residing in octahedral positions [45] were replaced by high-spin Co<sup>3+</sup>. The ZnO particles show higher crystallinity, with peaks located at 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, 68.13°, and 69.18° corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes (Figure S4C) of hexagonal ZnO crystallizing in the space group *P63mc* (wurtzite type). The SiO<sub>2</sub> NPs show only a broad peak at 23.36° (Figure S4D), which is probably due to the largely amorphous character of the material.

The PXRD of the TiO<sub>2</sub>-coated particles show the peaks corresponding to the core materials together with additional signals agreeing with the anatase ( $\beta$ -TiO<sub>2</sub>, tetragonal, *I4<sub>1</sub>/amd*) structure with peaks at 25.39°, 37.89°, 48.1°, and 55.18° corresponding to the (101), (004), (200), and (211) planes, respectively (Figure 1, compare Figure S4E).

The sharp signals of the core materials in the core/shell NPs are in line with the small but highly crystalline TiO<sub>2</sub> shell of only a few nm concluded from the TEM. This is supported by previously reported Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> core/shell NPs for which the PXRD exclusively showed the signals for TiO<sub>2</sub> at an estimated thickness of the TiO<sub>2</sub> shell of 17 nm [23]. Furthermore, for SiO<sub>2</sub>/TiO<sub>2</sub> core/shell NPs of 20 to 30 nm core and about 3 nm shell size, broad signals for the TiO<sub>2</sub> shell were found along with one broad reflection for SiO<sub>2</sub> [19]. The crystallinity of the TiO<sub>2</sub> shell is thus strongly dependent on the preparation method, and our method seems very suitable to produce high crystallinity.

Energy-dispersive X-ray spectroscopy (EDX) of the core/shell Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, ZnO/TiO<sub>2</sub>, and SiO<sub>2</sub>/TiO<sub>2</sub> NPs shows the core elements Al, Si, Zn, and O together with smaller amounts of Ti from the shell (Figure 2) in line with a thin TiO<sub>2</sub> shell. For Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>, cobalt was found with an Al/Co ratio in keeping with 5 to 10% Co in the structure.

The UV-vis absorption spectrum of the pristine Al<sub>2</sub>O<sub>3</sub> NPs (Figure 3A) shows the typical absorption band at around 200 nm [46]. For ZnO, a characteristic maximum at 378 nm was recorded in keeping with previous reports [47,48], and for SiO<sub>2</sub> and TiO<sub>2</sub> absorption, the UV-vis range shows only tails down from 170 to 1000 nm (Figure S5). The Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub> NPs show an additional broad absorption band in the visible range at 520 nm (2.38 eV) (Figure 3B,C). A very similar absorption band at 2.58 eV was reported for ZnO

NPs containing 3, 5, and 7 mol% Co [38] and for  $\text{LaAl}_{0.98}\text{Co}_{0.02}\text{O}_3$  containing 2% Co(III) and corresponds to the  $^5\text{T}_2 \rightarrow ^5\text{E}$  transition [49]. Thus, the spectrum of  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$  is in line with high-spin  $\text{Co}^{3+}$  ions replacing  $\text{Al}^{3+}$  at the octahedral sites, supporting our assumption from PXRD.

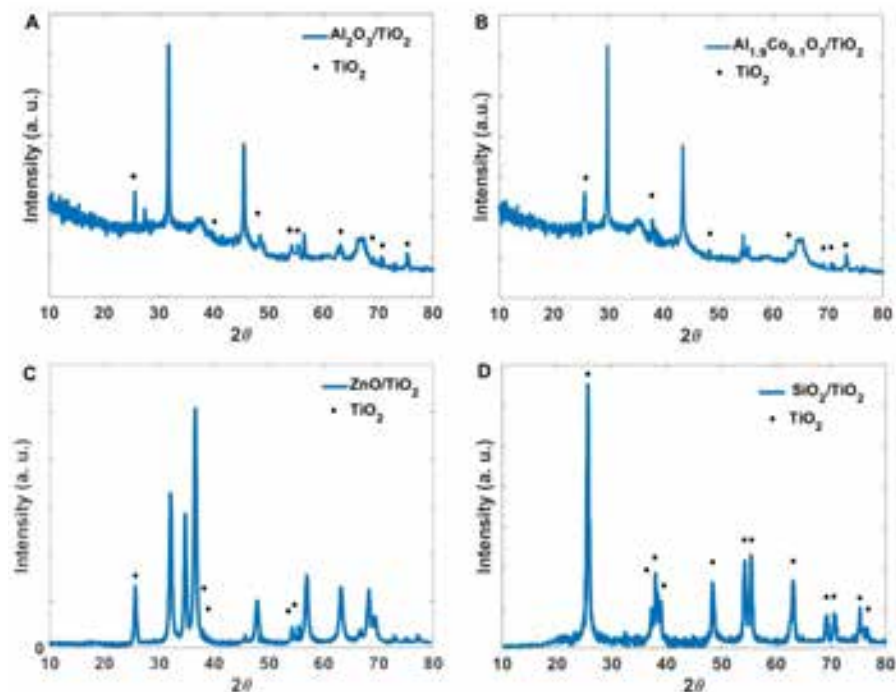


**Figure 1.** XRD patterns of the core/shell nanoparticles (A)  $\text{Al}_2\text{O}_3/\text{TiO}_2$ , (B)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ , (C)  $\text{ZnO}/\text{TiO}_2$ , and (D)  $\text{SiO}_2/\text{TiO}_2$ . The signals corresponding to  $\text{TiO}_2$  are marked with black dots.

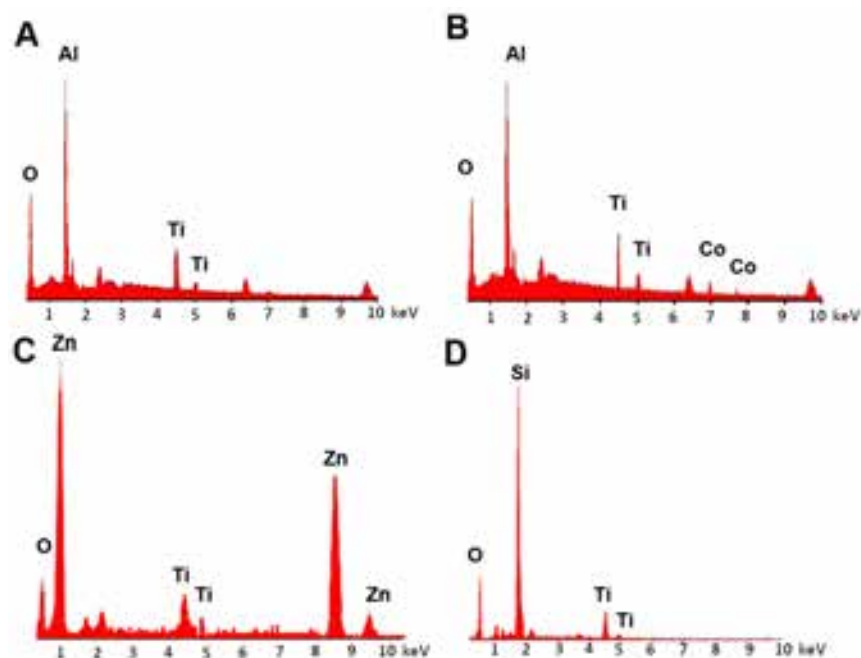


**Figure 2.** EDX images of (A)  $\text{Al}_2\text{O}_3/\text{TiO}_2$ , (B)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ , (C)  $\text{ZnO}/\text{TiO}_2$ , and (D)  $\text{SiO}_2/\text{TiO}_2$  NPs.

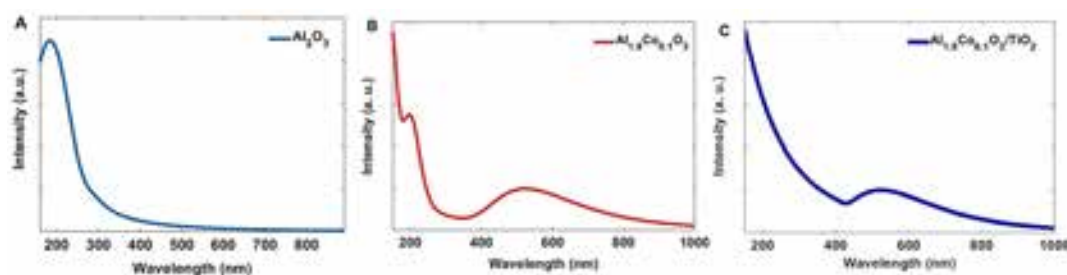


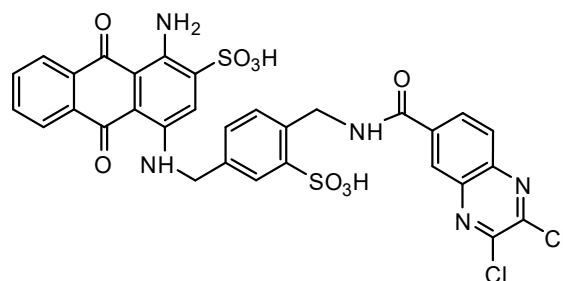
**Figure 3.** UV-vis absorption spectra for the NPs (A)  $\text{Al}_2\text{O}_3$ , (B)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$ , and (C)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  NPs.

The tiny red shift in the peak observed at around 200 nm for  $\text{Co}^{3+}$ -doped nanoparticles compared to undoped  $\text{Al}_2\text{O}_3$  can be attributed to oxygen defects in the structure of alumina, known as F centers [50]. Two types of F centers can be created in the structure of alumina. F and  $\text{F}_2$  centers can be reversibly interconverted by irradiating them with different wavelengths of light. For example, irradiating with 300 nm light can convert  $\text{F}_2$  and  $\text{F}_2^+$  centers, and irradiating with about 200 nm light can convert F centers [51,52]. Previous studies [53,54] report that the impact of electronic defects on optical properties is more significant than that of the electronic levels introduced by the doped ions.

The UV-Vis spectra of similarly reported  $\text{Al}_2\text{O}_3/\text{TiO}_2$  [23],  $\text{ZnO}/\text{TiO}_2$  [15], and  $\text{SiO}_2/\text{TiO}_2$  [16] NPs show a broad UV absorption tailing down till 400 nm (3.1 eV) originating from the  $\text{TiO}_2$  shells. This is fully in line with our results (Figure 3C).

## 2.2. Photocatalysis

The photocatalytic degradation of brilliant blue E-4BA (Scheme 2) under both UV and visible light irradiation was studied for pure  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3/\text{TiO}_2$ ,  $\text{ZnO}/\text{TiO}_2$ ,  $\text{SiO}_2/\text{TiO}_2$ , and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  NPs.



**Scheme 2.** The chemical structure of brilliant blue E-4BA.

The photodegradation was first monitored using UV-vis absorption spectroscopy with the visible and UV bands of the dye with progressing reactions (Figures 4 and 5). In the first experiments, the optimum amount of catalyst was found at around 10 mg/100 mL, and the time for complete photodecomposition ranged from 15 to 200 min. Without any catalyst, no photodecomposition was observed, neither under UV nor under visible light irradiation.

When comparing identical amounts of catalyst (10 mg) under the same UV irradiation conditions, the reactivity increased within the series—no catalyst (no reaction) < pure  $\text{TiO}_2$  <  $\text{SiO}_2/\text{TiO}_2$  <  $\text{ZnO}/\text{TiO}_2$  <  $\text{Al}_2\text{O}_3/\text{TiO}_2$  <  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ —(Figure 4). The time for complete conversion under UV irradiation was 70 min for pure  $\text{TiO}_2$ , 60 min for  $\text{SiO}_2/\text{TiO}_2$ , 30 min for  $\text{ZnO}/\text{TiO}_2$ , 15 to 20 min for  $\text{Al}_2\text{O}_3/\text{TiO}_2$ , and 15 to 20 min for  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ .

No significant degradation of the dye under visible light irradiation was found for  $\text{Al}_2\text{O}_3/\text{TiO}_2$ ,  $\text{ZnO}/\text{TiO}_2$ , and  $\text{SiO}_2/\text{TiO}_2$  NPs within 90 min. The catalysts seem to absorb a small amount of dye after adding it, but the solution retains the blue color of the dye. In contrast to this, more than 95% of the dye can be degraded in the solution containing  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  NPs under visible light irradiation within 90 min (Figure 5).

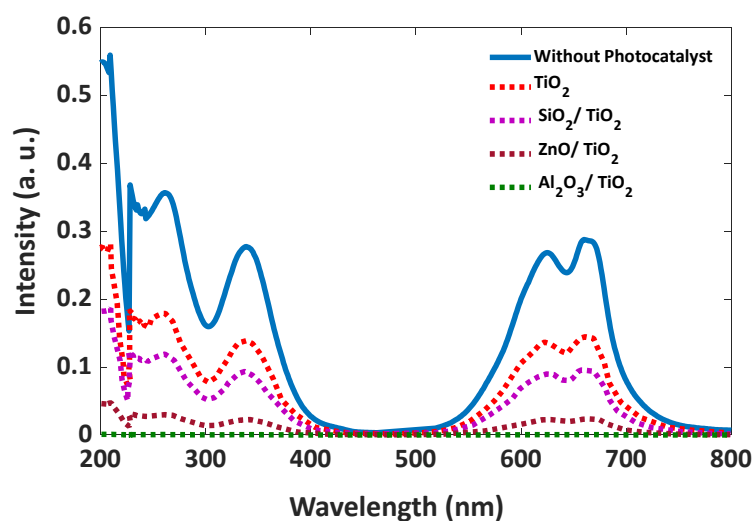


**Figure 4.** Absorption spectra of brilliant blue E-4BA in H<sub>2</sub>O after addition of 10 mg catalyst (or none) to a 20 ppm dye solution and UV light irradiation for 15 min.

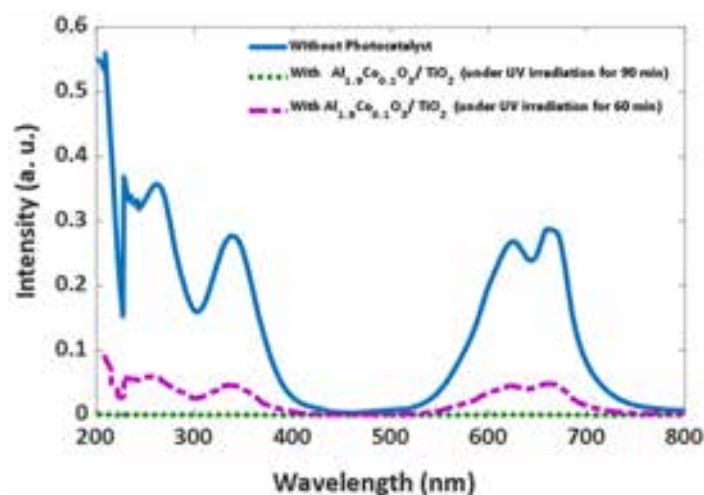


**Figure 5.** Absorption spectra of brilliant blue E-4BA in H<sub>2</sub>O after addition of 10 mg Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub> (or none) to a 20 ppm dye solution and visible light irradiation for 90 min.

HPLC analysis of the reaction mixtures (Figure 6 and Figure S6) gave the same sequence for the reactivity – no catalyst < pure TiO<sub>2</sub> < SiO<sub>2</sub>/TiO<sub>2</sub> < ZnO/TiO<sub>2</sub> < Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> < Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub>.

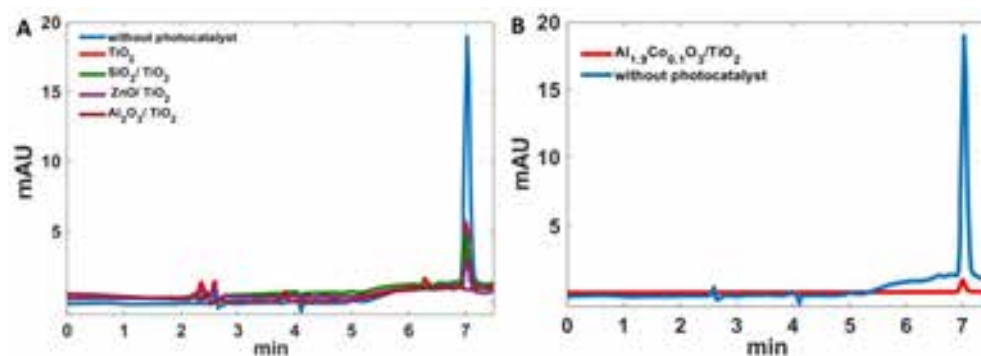


**Figure 6.** (A): HPLC plots of reaction solutions containing 20 ppm brilliant blue E-4BA in H<sub>2</sub>O after addition of 10 mg catalyst (or none) and UV irradiation for 15 min. (B): HPLC plots of products of a 20 ppm dye solution after visible irradiation for 90 min in the absence and presence of Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub>/TiO<sub>2</sub>.

Thus, all NP catalysts were active, and the core/shell NPs were more active than the pure  $\text{TiO}_2$  particles. For the core/shell NPs, reactivity increased along the series  $\text{SiO}_2/\text{TiO}_2 < \text{ZnO}/\text{TiO}_2 < \text{Al}_2\text{O}_3/\text{TiO}_2$ . The increase from  $\text{SiO}_2$  to  $\text{ZnO}$  is roughly in line with the decreasing band gap, with reported values around 4 eV for  $\text{SiO}_2$  [54] and around 3 eV for  $\text{ZnO}$  [55] NPs. The high activity of the  $\text{Al}_2\text{O}_3/\text{TiO}_2$  NPs does not agree with this idea, as  $\gamma\text{-Al}_2\text{O}_3$  has the highest band gap in the series, with reported values ranging from 5 to 8 eV [56,57]. The 195 nm absorption found in the UV-vis absorption spectrum of  $\text{Al}_2\text{O}_3$  (Figure 3) recalculates to 6.36 eV, in agreement with these reports. The superior properties of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  over the other two materials can be explained in terms of the heterojunction effect.

On the other hand, the activities correlate quite well with the BET analysis showing far larger surface areas for  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ( $583 \text{ m}^2/\text{g}$ ) and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  ( $618 \text{ m}^2/\text{g}$ ) than for  $\text{ZnO}/\text{TiO}_2$  ( $160 \text{ m}^2/\text{g}$ ) and  $\text{SiO}_2/\text{TiO}_2$  ( $87 \text{ m}^2/\text{g}$ ). This underlines that adsorption of the dye onto the surface is crucial for the photodegradation, which is supported by other reports [2,7,13,18–20,23,26]. The reactivity of the  $\text{SiO}_2/\text{TiO}_2$  NPs in our study compares well to a recent report on the photodecomposition of methylene blue (MB) [18]. The therein reported rather amorphous core/shell  $\text{SiO}_2/\text{TiO}_2$  NPs with sizes around 330 nm (shell about 35 nm) and BET surfaces ranging from 300 to  $400 \text{ m}^2/\text{g}$  allowed for complete photodecomposition using UV light within 30 min. Crystal violet was photodecomposed using  $\text{SiO}_2/\text{TiO}_2$  NPs within 60 min, while the BET surface for these particles was smaller ( $50$  to  $100 \text{ m}^2/\text{g}$ ) [20]. Another study using  $\text{Al}_2\text{O}_3/\text{TiO}_2$  NPs for the photodecomposition of methyl orange and rhodamine B reported more than 120 min till completeness under similar conditions [23].

The higher activity found for the  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  compared with the non-doped  $\text{Al}_2\text{O}_3/\text{TiO}_2$  NPs can additionally be rationalized with the introduction of Co(III)-based traps into the  $\text{Al}_2\text{O}_3$  electronic structure. To shed more light on this, a theoretical study based on density functional theory (DFT) was started, comparing  $\text{Al}_2\text{O}_3$  and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$ . While the band structure of  $\gamma\text{-Al}_2\text{O}_3$  has previously been calculated on a high level of sophistication [57,58], a comparison of  $\text{Al}_2\text{O}_3$  and Al-doped  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$  has not been reported.

### 2.3. DFT-Calculated Electronic Structures of $\text{Al}_2\text{O}_3$ and $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$

The DFT-calculated band structure for  $\text{Al}_2\text{O}_3$  (Figure 7A) shows a direct band gap of 6.106 eV, in good agreement with reported values [57,58], and the experimental value of 6.36 eV we derived from UV-vis absorption measurements.

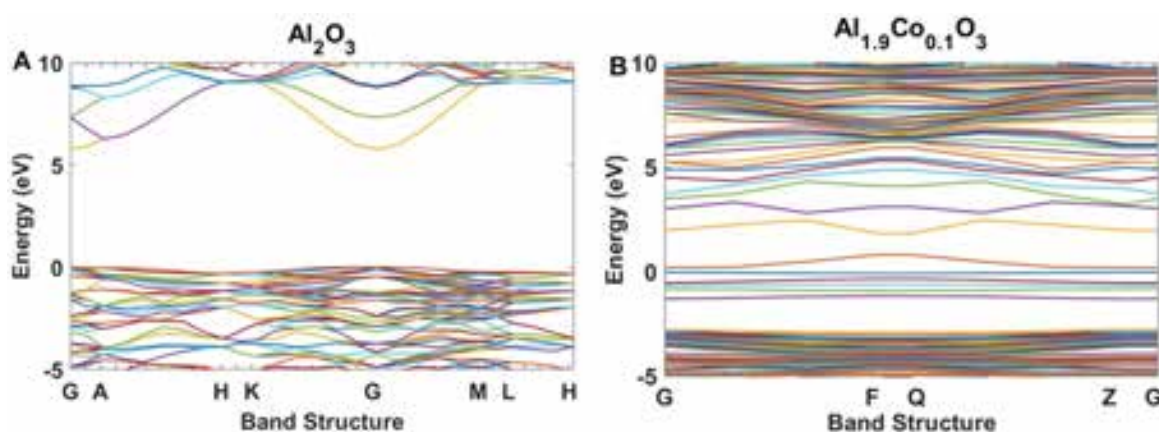


**Figure 7.** Calculated band structure for (A)  $\text{Al}_2\text{O}_3$  and (B)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$  NPs with the highest valence band = Fermi level set to  $E = 0$  eV.

The band structure of  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$  contains a number of additional donor (below 0 eV) and acceptor (above 0 eV) levels (Figure 7B). When converting the DFT-calculated band structure into a calculated UV-vis absorption spectrum (Figure 8), the experimentally observed long-wavelength absorption at 520 nm was well reproduced by the calculations. The calculated minimum band gap energy of 1.35 eV agrees reasonably well with the end

of the broad absorption from 400 to 900 nm, which recalculates to 3.10 to 1.38 eV. The calculations predict also a band at 280 nm and strong absorptions in the UV range around 200 nm. While the 200 nm band was found in the experimental structure and is attributed to the  $\text{Al}_2\text{O}_3$  host material, the 280 nm band was not experimentally found and might lie below the very intense band centered at 200 nm.

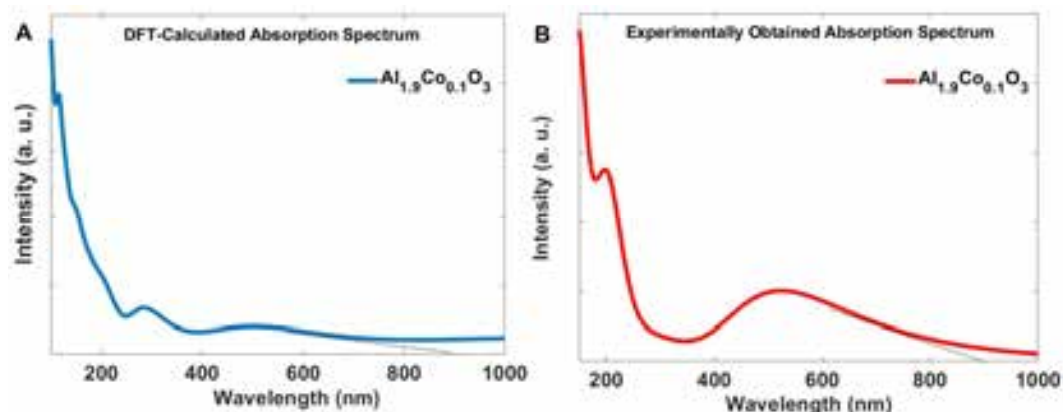


**Figure 8.** (A) DFT-calculated and (B) experimentally obtained UV-vis absorption spectra for  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$ .

Thus, while the generation of electrons and holes in nano- $\text{Al}_2\text{O}_3/\text{TiO}_2$  requires UV irradiation (Figure 9), the incorporation of  $\text{Co}^{3+}$  ions in the  $\text{Al}_2\text{O}_3$  lattice generates additional donor and acceptor levels and shifts the energy into the visible range.

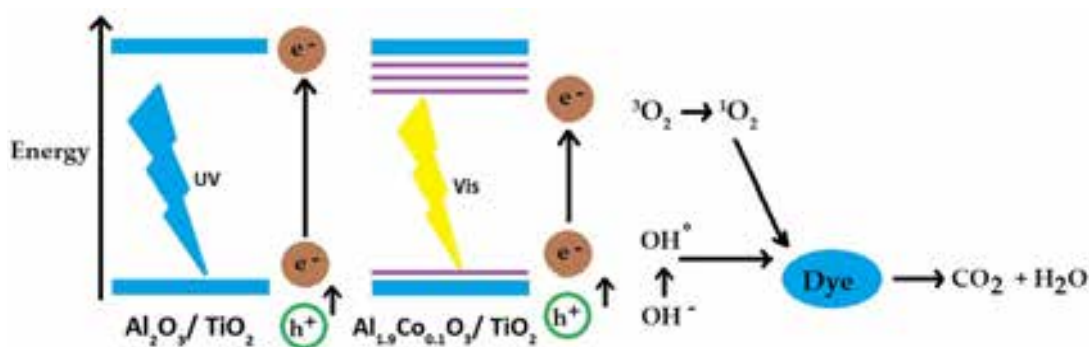


**Figure 9.** Proposed mechanism for dye photodegradation by  $\text{Al}_2\text{O}_3$  and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$  NPs under UV and visible light.  $^3\text{O}_2$  and  $^1\text{O}_2$  represent triplet and singlet oxygen,  $\text{OH}^\bullet$  the OH radical.

#### 2.4. FT-IR Stability Tests on $\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$

Previous reports indicated that gamma alumina exhibits limited stability in aqueous environments, eventually becoming hydrated over time. To assess the stability of the synthesized  $\text{Al}_2\text{O}_3/\text{TiO}_2$  nanoparticles, we used FT-IR spectroscopy. Within one week of storage in water, the synthesized  $\text{Al}_2\text{O}_3/\text{TiO}_2$  nanoparticles are seemingly stable (Figure S7). After two weeks, peaks at 3551, 3460, and 3400  $\text{cm}^{-1}$  indicate hydrolysis (formation of OH-functions). The results for the  $\text{Co}^{3+}$ -doped particles are essentially the same (Figure S8).

### 3. Materials and Methods

#### 3.1. Materials

The starting materials, tetraethyl orthosilicate  $\text{Si}(\text{OEt})_4$ , titanium tetraisopropoxide  $\text{Ti}(\text{OiPr})_4$ ,  $\text{AlCl}_3$ , ethylene glycol, ethylene diamine, EtOH, cobalt nitrate hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , zinc nitrate dihydrate  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ , and ethylamine ( $\text{EtNH}_2$ ) were all provided from Merck (Darmstadt, Germany) and used without further purification.

### 3.2. Preparation of $\gamma$ - $\text{Al}_2\text{O}_3$ NPs

A total of 1 g of  $\text{AlCl}_3$  and 3 g of ethylene glycol were dissolved in 100 mL of deionized water. Subsequently, 10 mL of ethylene diamine diluted with 50 mL of water were added dropwise to the reactor, and the reaction mixture was stirred for 4 h. The resulting NPs were separated and washed with deionized water and EtOH using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.3. Preparation of $\text{Al}_2\text{O}_3/\text{TiO}_2$ NPs

The  $\text{Al}_2\text{O}_3$  particles were dispersed in 100 mL of deionized water. In a separate beaker, 1 mL of  $\text{Ti}(\text{OiPr})_4$  and 5 mL of ethylene glycol were mixed and added dropwise to the first beaker. The mixture was stirred for 5 h, and the resulting precipitated NPs were separated and washed with deionized water and EtOH using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.4. Preparation of $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ NPs

A total of 0.95 g of  $\text{AlCl}_3$ , 0.09 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and 3 g of ethylene glycol were dissolved in 100 mL of deionized water. Subsequently, 10 mL of ethylene diamine, diluted with 50 mL of water, was added dropwise to the reaction mixture. The resulting  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$  NPs were isolated and washed several times with deionized water and EtOH using centrifugation. The NPs were then dispersed in 100 mL of deionized water. In a separate beaker, 1 mL of  $\text{Ti}(\text{OiPr})_4$  and 5 mL of ethylene glycol were mixed and added dropwise to the first beaker. The mixture was stirred for 5 h, and the resulting precipitated NPs were separated and washed with deionized water and EtOH using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.5. Preparation of ZnO NPs

A total of 1 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and 3 g of ethylene glycol were dissolved in a beaker. Subsequently, 1 g of dissolved  $\text{Na}_2\text{CO}_3$  was added dropwise to the first beaker. The precipitated NPs were separated and washed with deionized water and EtOH using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.6. Preparation of ZnO/ $\text{TiO}_2$ NPs

The ZnO particles were dispersed in 100 mL of deionized water. In another beaker, 1 mL of  $\text{Ti}(\text{OiPr})_4$  and 5 mL of ethylene glycol were mixed and added dropwise to the first beaker. The resulting mixture was stirred for 5 h, and the precipitated NPs were separated and washed with deionized water and EtOH using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.7. Preparation of $\text{SiO}_2$ NPs

A total of 10 mL of  $\text{Si}(\text{OEt})_4$  and 50 mL of EtOH were mixed in a beaker and stirred for 15 min. Then, 50 mL of deionized water and  $\text{EtNH}_2$  were added immediately under stirring. After 12 h, the  $\text{SiO}_2$  NPs were separated and washed with deionized water and EtOH using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.8. Preparation of $\text{SiO}_2/\text{TiO}_2$ NPs

The  $\text{SiO}_2$  particles were dispersed in 100 mL of deionized water. In another beaker, 1 mL of  $\text{Ti}(\text{OiPr})_4$  and 5 mL of ethylene glycol were mixed and added dropwise to the first beaker. The resulting mixture was stirred for 5 h, and the precipitated NPs were separated and washed with deionized water and EtOH, using centrifugation. The final material was calcinated at 400 °C for 1 h.

### 3.9. Photocatalysis

A solution was prepared by dissolving 0.2 g of brilliant blue E-4BA ( $\text{C}_{31}\text{H}_{19}\text{O}_9\text{N}_5\text{S}_2\text{Cl}_2\text{Na}_2$ ) in 100 mL deionized water (20 ppm). Subsequently, 10 mg of the NPs was added to 100 mL of

the prepared solution. The solution was irradiated at 475 nm using an Osram, 3.8 mW/cm<sup>2</sup> UV light-emitting diode (LED)(ams-OSRAM International, Regensburg, Germany) or at 525 nm using an Osram, 4 mW/cm<sup>2</sup> visible light LED. The light sources were kept at a distance of 10 cm from the samples. During irradiation, samples were taken in time intervals of 5 to 200 min, and UV-vis absorption spectra were recorded. After the complete irradiation time, the solutions were filtered and analyzed using HPLC.

### 3.10. Chromatography

The mobile phase consisted of Solution A: 0.1 M ammonium acetate adjusted to pH = 6.7, and Solution B: MeCN. Gradient elution was set as summarized in Table 1.

**Table 1.** Details for the gradient elution <sup>a</sup>.

| Time | A  | B  | Flow |
|------|----|----|------|
| 0    | 97 | 3  | 1    |
| 18   | 40 | 60 | 1    |
| 20   | 40 | 60 | 1    |

<sup>a</sup> Flow: 1 mL/min, wavelength: 261 nm, injection volume: 20 µL. Calibration curves were generated from five different concentrations between 25 and 75 ppm of brilliant blue E-4BA with three replicates, and the correlation coefficient was assessed.

### 3.11. Instrumentation

Transmission electron micrographs (TEMs) were recorded using a TEM Philips EM 208S (Philips, Beaverton, OR, USA). Powder XRD (PXRD) was carried out using a PW 1730 (Philips, Eindhoven, The Netherlands) diffractometer in the range of  $2\theta = 4$  to  $100^\circ$  and using Cu-K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. Energy-dispersive X-ray spectroscopy (EDX) was measured on a FE-SEM TESCAN MIRA2 (Tescan, Kohoutovice, Czech Republic). UV-vis absorption spectra of the NPs were measured on powder samples in transmission mode using a T70 UV-vis photospectrophotometer (PG Instruments, Wiltshire, UK). HPLC was carried out on an Agilent instrument AGI1200-120013780 (Agilent, Santa Clara, CA, USA). Brunauer–Emmett–Teller (BET) analysis was measured using a BET BELSORP Mini II instrument (Microtrac Retsch, Haan/Duesseldorf, Germany). FT-IR measurements were recorded using an FT-IR spectrometer MB3000 (ABB, Zürich, Switzerland).

### 3.12. DFT Calculations

Electronic band structures and optical properties of Al<sub>2</sub>O<sub>3</sub> and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub> nanoparticles were computed using density functional theory (DFT) calculations. The CASTEP code was employed for the calculations, and optimization was achieved through the BFGS (Broyden–Fletcher–Goldfarb–Shanno) geometry optimization method (CASTEP version 16.11) [59]. The calculations utilized the generalized gradient approximation (GGA) and the non-local gradient-corrected exchange–correlation functional, parameterized using the Perdew–Burke–Ernzerhof (PBE) approach [60]. The plane-wave cutoff energy was set to 550 eV. The optical characteristics of Al<sub>2</sub>O<sub>3</sub> and Al<sub>1.9</sub>Co<sub>0.1</sub>O<sub>3</sub> were investigated using the CASTEP frequency computation results at the gamma point (GP). Brillouin zone summation employed *k*-point sampling with a Monkhorst–Pack grid at a  $2 \times 2 \times 2$  parameter set. The “ $2 \times 2 \times 2$  parameter” refers to the grid used for *k*-point sampling within the Brillouin zone when performing calculations on a material’s electronic band structure. In this case, the Monkhorst–Pack grid with a  $2 \times 2 \times 2$  parameter indicates that the Brillouin zone is divided into a grid of *k*-points in each direction (*x*, *y*, *z*) with two points in the *x*-direction, two points in the *y*-direction, and two points in the *z*-direction. This grid defines the discretization of the Brillouin zone for numerical calculation. Additionally, geometry optimization under applied hydrostatic pressure was utilized to determine the material modulus (*B*) and its pressure derivative,  $B' = dB/dP$  [59,61].

#### 4. Conclusions

Metal oxide core/shell nanoparticles (NPs),  $\text{Al}_2\text{O}_3/\text{TiO}_2$ ,  $\text{ZnO}/\text{TiO}_2$ ,  $\text{SiO}_2/\text{TiO}_2$ , and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ , were synthesized, characterized, and investigated for their photocatalytic activity in the degradation of the dye brilliant blue E-4BA. The size of the cores ranged from 10 to 30 nm, while the  $\text{TiO}_2$  shells were about 3 nm thick. This thin shell was confirmed by powder X-ray diffraction (PXRD) showing reflections for both the core and the shell material and makes sure that both the core and shell can absorb photons. Furthermore, both parts are highly crystalline, except for the  $\text{SiO}_2$  core. The optimal catalyst dosage for the photodegradation was identified at 10 mg per 100 mL of a 20 ppm dye solution using UV-vis absorption spectroscopy and HPLC for reaction monitoring. No reactivity was found without a catalyst, while for the studied NPs, the reactivity increased along the series—pure  $\text{TiO}_2 < \text{SiO}_2/\text{TiO}_2 < \text{ZnO}/\text{TiO}_2 < \text{Al}_2\text{O}_3/\text{TiO}_2 < \text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ —under UV irradiation, which translates into times for complete conversion of 70 min for pure  $\text{TiO}_2$  and 15 min for  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ . This aligns well with the increasing BET surfaces  $\text{SiO}_2/\text{TiO}_2$  ( $87 \text{ m}^2/\text{g}$ )  $< \text{ZnO}/\text{TiO}_2$  ( $160 \text{ m}^2/\text{g}$ )  $< \text{Al}_2\text{O}_3/\text{TiO}_2$  ( $583 \text{ m}^2/\text{g}$ ) and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  ( $618 \text{ m}^2/\text{g}$ ), underpinning that the adsorption capacity of a material is crucial for photodegradation. Under visible light irradiation, only  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  was found to be active in photodecomposition of the dye, decomposing the dye within 90 min. DFT-based band structure calculations showed that Co-doping introduces additional energy levels into  $\text{Al}_2\text{O}_3$ , resulting in improved electron–hole pair generation. The DFT-calculated absorption spectra of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  agree very well with the experimental spectra, thus supporting the band structure calculations.

On the other hand, from this preliminary study, it is not possible to identify the “best material” from our series or the “most important parameter” for determining this. Size, layer thickness, specific surface area, band gap, and photon absorptions are strongly interconnected. Especially, we were not able to quantitatively assess the heterojunction effect of combining ZnO,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  with  $\text{TiO}_2$ . The experimentally observed increasing reactivity along the series  $\text{SiO}_2/\text{TiO}_2 < \text{ZnO}/\text{TiO}_2 < \text{Al}_2\text{O}_3/\text{TiO}_2$  correlates with the BET surfaces, but additionally,  $\text{Al}_2\text{O}_3$  might show a pronounced heterojunction effect decreasing the band gap of pure  $\text{Al}_2\text{O}_3$  around 6 eV, thus reaching those of ZnO (around 3 eV) and  $\text{SiO}_2$  (around 4 eV). Thus, manufacturing of core/shell NPs with thin  $\text{TiO}_2$  shells using these basically cheap and highly abundant metal oxides allows for generating potent photocatalysts for UV photocatalysis. The introduction of transition metals such as Co turns out to be suitable to shift the irradiation wavelength into the visible range.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12110281/s1>, Figure S1: TEM images of synthesized (A)  $\text{Al}_2\text{O}_3$ , (B)  $\text{TiO}_2$ , (C)  $\text{SiO}_2$ , and (D) ZnO nanoparticles; Figure S2: TEM images of the synthesized (A)  $\text{Al}_2\text{O}_3/\text{TiO}_2$ , (B)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$ , (C)  $\text{ZnO}/\text{TiO}_2$ , and (D)  $\text{SiO}_2/\text{TiO}_2$  nanoparticles; Figure S3: BET plots of the  $\text{ZnO}/\text{TiO}_2$  (top left),  $\text{SiO}_2/\text{TiO}_2$  (top right),  $\text{Al}_2\text{O}_3/\text{TiO}_2$  (bottom, left), and  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  (bottom right) nanoparticles; Figure S4: XRD patterns of the synthesized NPs (A)  $\text{Al}_2\text{O}_3$ , (B) ZnO, (C)  $\text{TiO}_2$ , (D)  $\text{SiO}_2$ , and (E)  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3$ ; Figure S5: UV-vis absorption spectra for the synthesized NPs (A)  $\text{SiO}_2$ , (B)  $\text{TiO}_2$ , and (C) ZnO; Figure S6: HPLC from reaction mixtures containing 20 ppm brilliant blue E-4BA in  $\text{H}_2\text{O}$  after addition of 10 mg bare  $\text{SiO}_2$  or  $\text{TiO}_2$  NPs as catalyst (or none) and UV irradiation for 15 min; Figure S7: FT-IR spectra of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  nanoparticles stored in water and after synthesis; Figure S8: FT-IR spectra of  $\text{Al}_{1.9}\text{Co}_{0.1}\text{O}_3/\text{TiO}_2$  nanoparticles stored in water and after synthesis.

**Author Contributions:** M.D. synthesized and characterized the nanoparticles and evaluated the photocatalytic reactions. The synthesized nanoparticles were characterized by A.R. A.Z. set up the UV and visible reaction box for the photocatalytic reaction. The UV-vis absorption and chromatographic analysis of reaction mixtures were carried out by S.D. and M.T. A.Y. edited the manuscript and evaluated the photocatalytic reactions. A.R. and A.K. supervised the project. A.K. wrote and edited the manuscript. All authors contributed to revising the manuscript and have agreed with the last version. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** Authors Mahboubeh Dolatyari and Ali Rostami were employed by the ASEPE company. Authors Mehdi Tahmasebi and Sudabeh Dolatyari are employees of the company Alborz Farmad. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Article

# Significantly Enhanced Self-Cleaning Capability in Anatase TiO<sub>2</sub> for the Bleaching of Organic Dyes and Glazes

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**Abstract:** In this study, the Mg<sup>2+</sup>-doped anatase TiO<sub>2</sub> phase was synthesized via the solvothermal method by changing the ratio of deionized water and absolute ethanol ( $V_{\text{water}}/V_{\text{ethanol}}$ ). This enhances the bleaching efficiency under visible light. The crystal structure, morphology, and photocatalytic properties of Mg-doped TiO<sub>2</sub> were characterized by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, N<sub>2</sub> adsorption-desorption, UV-Vis spectroscopy analysis, etc. Results showed that the photocatalytic activity of the Mg<sup>2+</sup>-doped TiO<sub>2</sub> sample was effectively improved, and the morphology, specific surface area, and porosity of TiO<sub>2</sub> could be controlled by  $V_{\text{water}}/V_{\text{ethanol}}$ . Compared with the Mg-undoped TiO<sub>2</sub> sample, Mg-doped TiO<sub>2</sub> samples have higher photocatalytic properties due to pure anatase phase formation. The Mg-doped TiO<sub>2</sub> sample was synthesized at  $V_{\text{water}}/V_{\text{ethanol}}$  of 12.5:2.5, which has the highest bleaching rate of 99.5% for the rhodamine B dye during 80 min under visible light. Adding Mg<sup>2+</sup>-doped TiO<sub>2</sub> into the phase-separated glaze is an essential factor for enhancing the self-cleaning capability. The glaze samples fired at 1180 °C achieved a water contact angle of 5.623° at room temperature and had high stain resistance (the blot floats as a whole after meeting the water).

**Keywords:** solvothermal method; Mg-doped TiO<sub>2</sub>;  $V_{\text{water}}/V_{\text{ethanol}}$ ; self-cleaning properties; visible light



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## 1. Introduction

With the deterioration of environmental pollution, low-consumption and high-efficiency pollution technologies have received more attention [1,2]. As the durative utilizes clean energy, solar energy has vast potential for exploitation and application. Titanium dioxide is an important photocatalyst that has been widely studied because of its high activity, non-toxic characteristics, environmental friendliness, and good chemical stability [3–6]. As the energy barrier of the metastable phase was less than that of the stability phase, it was more likely to excite electrons and holes for the metastable phase [7,8]. Hence, anatase TiO<sub>2</sub> is considered to be the best photocatalyst of all of the structures of TiO<sub>2</sub> [9,10]. It can fully effectively utilize UV light from sunlight [11–13]. Several factors affect anatase TiO<sub>2</sub> photoactivity, such as crystal size, specific surface area, and crystallinity [14–16]. The performance of the TiO<sub>2</sub> was optimized by doping [17–20], loading [21,22], and thin-film preparation [23,24]. Available studies indicated that some ions could enter the lattice as substitutional or interstitial; the titanium ions are substituted by metal ions in the crystal lattices. Some studies illustrate that rare-metal-ion-doped titania nanoparticles were prepared by the hydrothermal method, and their photocatalytic performance was greatly improved under UV irradiation [25,26]. At present, there exist a few studies concerning magnesium-ion-doped TiO<sub>2</sub> obtained by the sol-gel reaction synthesis route and the solvothermal method [27,28], but its processing is complex and needs HF as a capping agent to form the anatase phase. It would therefore be interesting to investigate how a simple method can be used for preparing a glaze containing Mg(II)-doped anatase that is stable in a medium-/high-temperature (>1000 °C) ceramic glaze [29] and has self-cleaning properties, as anatase TiO<sub>2</sub> has a nanometer size.

This study presents the simple synthetic procedure of producing Mg-doped  $\text{TiO}_2$  anatase samples without surfactants or templates and evaluates the influence of the structure and  $V_{\text{water}}/V_{\text{ethanol}}$  on their photocatalytic activity in decomposing rhodamine B (RhB). The self-cleaning activities of Mg-doped and undoped  $\text{TiO}_2$  anatase glaze samples are evaluated by comparing their anti-pollution ability.

## 2. Experimental Section

### 2.1. Preparation of the Samples

The samples, with various deionized water and absolute ethanol contents, were prepared from tetrabutyl titanate (TBOT),  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and NaOH using the hydrothermal method. In a typical synthesis, firstly, solution A was made, which included  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , deionized water, and absolute ethanol. Subsequently, solution B was made, which included TBOT and ethanol. Finally, suspension C was prepared by dripping solution B into system A. The molar ratio of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ :TBOT:ethanol: water was 0.03:1:10:50. After 15 min, after adding suspension C into the reactor, it was heated at  $180^\circ\text{C}$  for 36 h and then naturally cooled to room temperature. The final sample obtained was centrifuged and washed with deionized water and absolute ethanol. The photocatalytic properties of the samples were investigated by changing the molar ratio of water/ethanol ( $V_{\text{water}}:V_{\text{ethanol}}$ ), keeping other experimental parameters unchanged. Figure 1 is the schematic diagram of Mg-doped  $\text{TiO}_2$  sample preparation.



**Figure 1.** Schematic diagram of Mg-doped  $\text{TiO}_2$  sample preparation.

The Mg-doped  $\text{TiO}_2$  in the glaze sample was fabricated by sintering at  $1180\sim1200^\circ\text{C}$  using raw powders, i.e., 95% of the as-prepared Kaolin clay was subjected to phase separation melting at  $1500^\circ\text{C}$  for 4 h and 5% by adding 5% Mg-doped  $\text{TiO}_2$  ( $V_{\text{water}}/V_{\text{ethanol}}$  of 12.5:2.5) photocatalysts, and the self-cleaning and hyper-hydrophilic properties of the fired glaze samples were characterized and tested, respectively. Figure 2 is the schematic diagram of the glaze firing processes.



**Figure 2.** Schematic diagram of the glaze firing processes.

### 2.2. Characterization of the Samples

The crystalline phase was identified by X-ray diffractometer (XRD, D8 Advance Bruker AXS, Germany) using Cu K $\alpha$  radiation. Compared with the standard pattern in the XRD standard database, including JCPDS (i.e., PDF cards), the phase composition of the sample was analyzed using Jade 6.0 software. Photocatalyst morphology was investigated by scanning electron microscopy (SEM, JSM-6700F, Japan) using a device equipped with an EDS system operating at an accelerating voltage of 5.0 kV or 15 kV (15 kV for EDS). The crystal surface of nanocrystals was evaluated by high-resolution microscopy. The microstructures of the samples were studied by transmission electron microscopy (TEM, FEI Tecnai G2 F-30, Holland) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F-30, Holland) at accelerating voltages of 160 kV and 200 kV, respectively. The valence states of the samples were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, United States) using Al K $\alpha$  radiation. The specific surface areas were determined by the Brunauer–Emmett–Teller method, and the pore size was determined by the Barrett–Joyner–Hallenda method. Nitrogen adsorption-desorption isotherms were collected on a Micromeritics TriStar ii 3020 analyzer at 77 K. The analysis of samples by UV-Vis diffuse reflectance spectroscopy was carried out. The hydrophilicity of the samples was tested by a contact angle meter (JGW-360D, China).

### 2.3. Photocatalytic Activity of the Samples

The photocatalytic activity of the TiO<sub>2</sub> was evaluated by bleaching the RhB with a concentration of 10<sup>−4</sup> mol/L. The total volume of RhB was 50 mL, irradiated with 0.05 g of the photocatalyst and a 500 W Xeon light with a cut-off filter of 420 nm. This was to prove that the RhB was exhibiting bleaching rather than adsorption after the dark experiment was carried out. Samples were taken out at 20 min intervals and analyzed with a spectrophotometer. The photocatalytic activity was characterized by the apparent first-order rate constant  $k$ , as in equation  $k = \ln(A_0/A)$ , where  $A$  was the absorbance of RhB at 553 nm after bleaching and  $A_0$  was the absorbance of the initial RhB solution at 553 nm.

## 3. Results and Discussion

### 3.1. Structural and Morphology

The crystal phase of the samples was studied as shown in Figure 3. The obtained diffraction peak of the doped TiO<sub>2</sub> matched very well with the standard values (PDF-#21-1272) and the diffraction peaks at  $2\theta = 25.281(101)$ ,  $37.800(004)$ ,  $48.049(200)$ ,  $53.890(105)$ , and  $62.688(204)$ , illustrating that the samples were in the anatase phase. However, the obtained undoped TiO<sub>2</sub> was in a mixed phase of anatase and brookite. The cell volume was calculated by Fourier synthesis with the program SHELXS-97 [30]. When the solvent was water, the sample consisted of nanoparticles 10–20 nm in mean size, as determined by Nano Measurer 1.2 software using 10 nanoparticles. The average crystallite size of TiO<sub>2</sub> samples with different Mg-doped ions was calculated by XRD–Scherrer formula:

$d = 0.91 \lambda / \beta \cos \theta$ , where  $d$  is the mean crystallite size,  $k$  is 0.9,  $\lambda$  is the wavelength of Cu K $\alpha$  (i.e.,  $\lambda = 0.15420$  nm),  $\beta$  is the full width at half maximum intensity of the peak (FWHM) in radian, and  $\theta$  is Bragg's diffraction angle [31]. The crystallite size and cell volume were calculated as shown Table 1. When increasing  $V_{\text{water}}/V_{\text{ethanol}}$ , there are differences in the diffraction peak intensity and minor shifts in the peak occur, which indicates a reduction in crystalline size and an increase in the volume of unit cells (Table 1). Since the ionic radius of  $\text{Mg}^{2+}$  (0.072 nm) is close to that of  $\text{Ti}^{4+}$  (0.061 nm),  $\text{Mg}^{2+}$  easily enters the  $\text{TiO}_2$  lattice [32] and the lattice volume increases (Table 1), indicating that the formation of a crystal defect. Based on the experimental results, the formation of the crystal defect promotes the formation of the anatase phase, which is accordance with the reported literature [27,29]. Hence, after the addition of the magnesium source, a pure-anatase  $\text{TiO}_2$  phase appears. The intensity of the (004) direction is significantly enhanced compared to undoped  $\text{TiO}_2$ . In addition, the FWHM of the (101) peak was calculated by using Lorentz fitting. According to the Scherrer formula,  $d = 0.91 \lambda / \beta \cos \theta$ , the crystallite size was calculated; it is shown in Table 1.

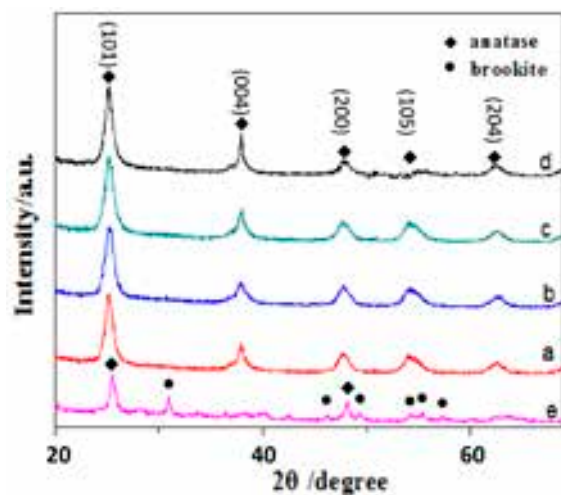


**Figure 3.** XRD patterns of the samples with different volume ratios of water: ethanol: (a) 15: 0, (b) 12.5:2.5, (c) 10:5, (d) 7.5:7.5, (e) undoped  $\text{TiO}_2$  (12.5:2.5).

**Table 1.** Effect of different ratios of water: ethanol in the solvent on the crystal size, BET surface area, pore size, pore volume, and cell volume of Mg-doped  $\text{TiO}_2$ .

| $V_{\text{water}}/V_{\text{ethanol}}$ | Crystal Size (nm) | BET (m <sup>2</sup> /g) | Pore Size (nm) | Pore Volume (cm <sup>3</sup> /g) | Cell Volume Å <sup>3</sup> |         |
|---------------------------------------|-------------------|-------------------------|----------------|----------------------------------|----------------------------|---------|
| Mg-doped TiO <sub>2</sub>             | 15:0              | 13.6                    | 152            | 13.8                             | 0.415                      | 136.458 |
|                                       | 12.5:2.5          | 13.2                    | 148            | 12.5                             | 0.402                      | 136.315 |
|                                       | 10:5              | 10.3                    | 105            | 12.4                             | 0.378                      | 136.452 |
|                                       | 7.5:7.5           | 8.1                     | 101            | 12.0                             | 0.350                      | 136.689 |
| Pure TiO <sub>2</sub>                 | 12.5:2.5          | 14.0                    | 98             | 11.2                             | 0.340                      | 136.089 |

Figure 4 shows SEM images of the as-synthesized samples. When the solvent was water, the sample consisted of nanoparticles 5–10 nm in size. When the  $V_{\text{water}}/V_{\text{ethanol}}$  ratio was 12.5:2.5, agglomerated nanoparticles had a grape-like morphology (Figure 4b). With the increase in ethanol dosage, nanoparticles increased (Figure 4c,d). The experimental results show that the morphology of the samples was greatly affected by  $V_{\text{water}}/V_{\text{ethanol}}$ . Their morphology is determined by the relationship between crystal formation and growth. Moreover, crystal growth is influenced by the adsorption of certain crystalline facets into  $\text{OH}^-$ . This adsorption hinders the growth of these facets, resulting in different rates of crystalline growth. Ethanol is a typical polar solvent and amphiphilic molecule. It

was vertically adsorbed on the hydrophilic surface of the  $\text{TiO}_2$  particles, forming a two-amphiphilic bilayer, which limited the immersion of the water molecule in the hydrophilic side surface and the  $\text{TiO}_2$  particles [33]. The rapid hydrolysis of TBOT promoted the rapid generation of  $\text{TiO}_2$ , which led to  $\text{TiO}_2$  particle agglomeration with an increase in  $V_{\text{water}}/V_{\text{ethanol}}$ . Figure 5a,b show TEM and the corresponding SAED pattern (inset) and HRTEM images of the sample prepared at  $V_{\text{water}}/V_{\text{ethanol}} = 12.5:2.5$ . From Figure 5a, it is observed that the aggregated particles in Figure 4b consist of nanoparticles. The major diffraction rings for the crystal surface at (101), (004), and (105) match well with XRD analysis. The d spacing is 0.325 nm (Figure 5b), and it matches well with the lattice spacing of anatase  $\text{TiO}_2$  (101). Furthermore, the corresponding EDX spectrum shown in Figures 5c and S1 verifies the existence of Mg, Ti, and O ions. Other impurities were not detected in the EDX spectra.

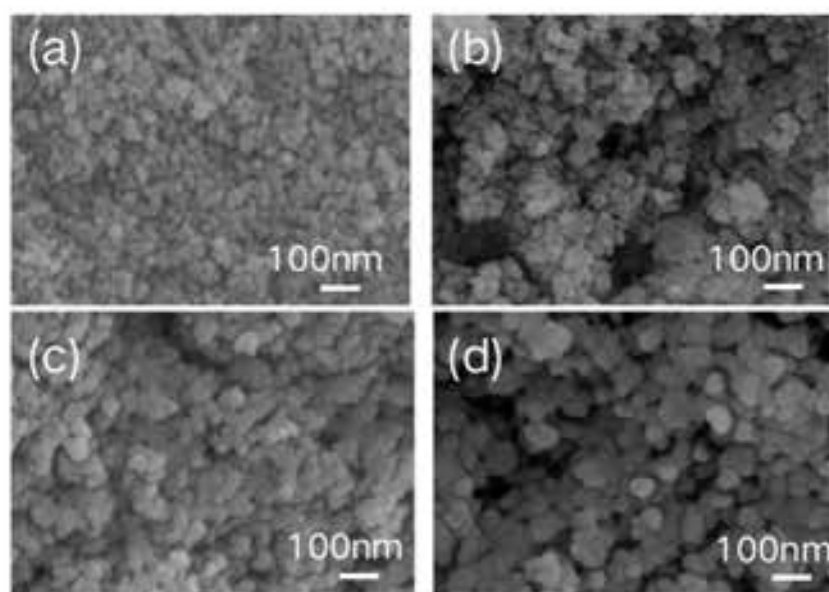


**Figure 4.** SEM images of  $\text{TiO}_2$  with different volume ratios of water: ethanol (a) 15:0, (b) 12.5:2.5, (c) 10:5, (d) 7.5:7.5.

As can be seen from Table 1 and Figure 3, the morphologies of the samples strongly depend on Mg-doped ions and  $V_{\text{water}}/V_{\text{ethanol}}$ . Because the current system contains ethanol, water, Mg-doped ions, and TBOT, we can reasonably assume that the formation of anatase  $\text{TiO}_2$  is due to the dehydrating condensation between  $\text{Ti}(\text{OH})_6^{2-}$  and Mg-doped ions under solvothermal conditions [34]. Thus, due to the formation of a lower number of active  $\text{OH}^-$  ions and a lower number of soluble species,  $\text{Ti}(\text{OH})_6^{2-}$  and  $\text{TiO}_6$  octahedrons in one cluster may construct a chain via the corner-sharing of  $\text{Ti}(\text{OH})_6^{2-}$  growth units. Due to doped Mg ions entering the  $\text{TiO}_2$  lattice, resulting in  $\text{TiO}_6$  octahedron lattice distortion (Table 1) and an increase in the charge density of Ti and reduction in the electron density of oxygen, the preferred  $\text{TiO}_6$  octahedron chain-shaped clusters further adsorb  $\text{OH}^-$  soluble species into the (101) plane (Figure 5b) and anatase  $\text{TiO}_2$  monomers form through a dehydrating condensation process. Therefore, these planes could be freely bonded by interactions between  $\text{OH}^-$  and nuclei to obtain aggregated nanoparticles (Figure 4). The solubility of salt increases with the dielectric constant of the solvent [35], and the dielectric constant of water is bigger than that of ethanol. When  $V_{\text{water}}/V_{\text{ethanol}}$  decreases, that is, ethanol content increases, this could decrease the solubility of the precursor and increase the viscosity of the solution, thereby decreasing the diffusion ability of  $\text{Ti}(\text{OH})_6^{2-}$  ions and causing the crystal size of the  $\text{TiO}_2$  sample to decrease (Table 1).

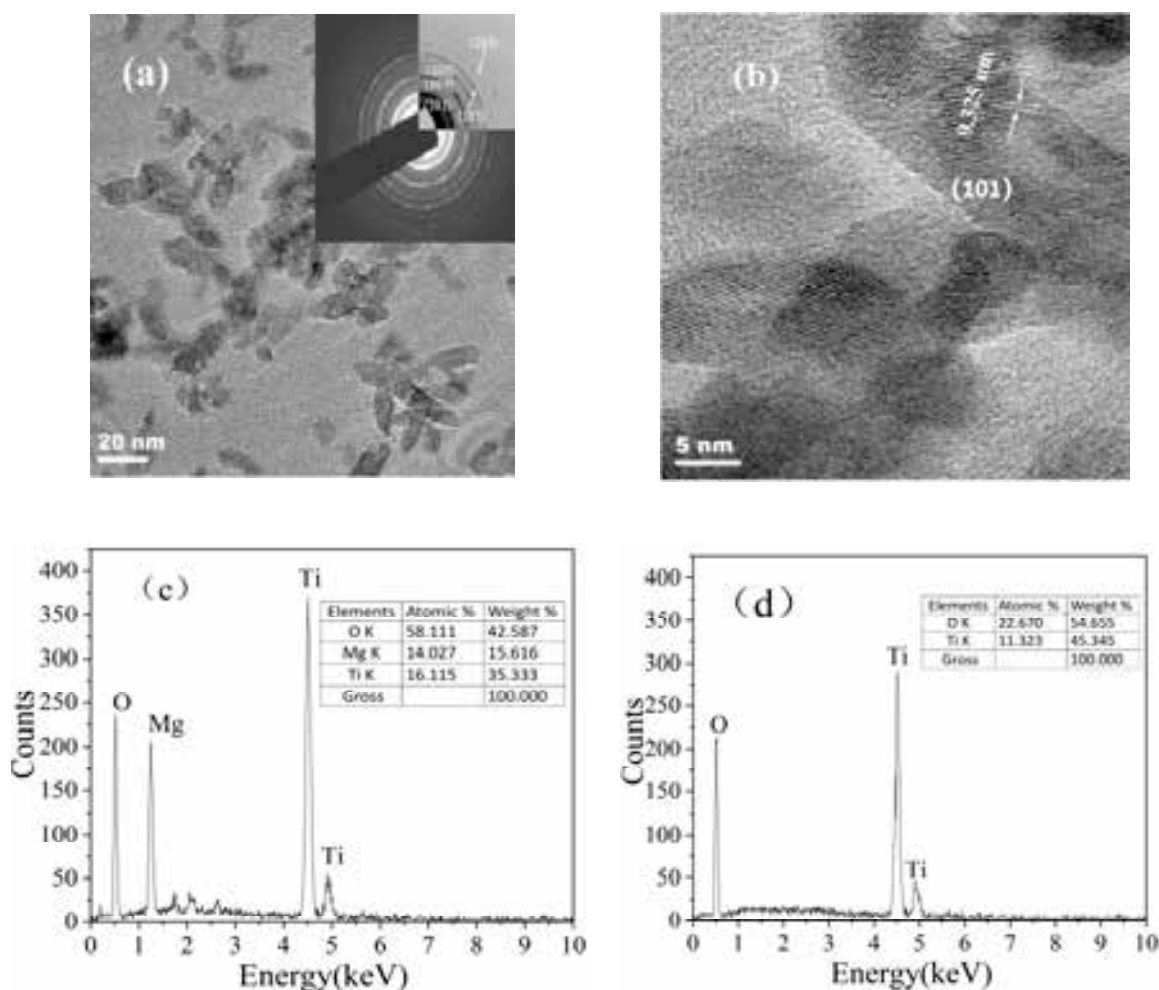


**Figure 5.** (a) TEM images and SAED pattern, (b) HRTEM images, (c,d) EDX spectra. (a–c) Mg-doped sample prepared using  $V_{\text{water}}/V_{\text{ethanol}} = 12.5:2.5$ , (d) pure TiO<sub>2</sub> sample prepared using  $V_{\text{water}}/V_{\text{ethanol}} = 12.5:2.5$ .

Figure 6 shows XPS spectra of pure and Mg-doped TiO<sub>2</sub> samples. Peaks located around 457 eV and 464 eV resulted from Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, respectively, corresponding to the oxidation state of Ti<sup>4+</sup>. Meanwhile, due to the partial substitution of Ti<sup>4+</sup> ions by Mg<sup>2+</sup>, the binding energy of Ti decreases, thus increasing the charge density of Ti. The binding energy of O 1s in the pure TiO<sub>2</sub> sample is 529.8 eV, owing to the intrinsic binding energy of oxygen in TiO<sub>2</sub>. The Mg-doped TiO<sub>2</sub> sample shows a shoulder peak near 532.3 eV in addition to the intrinsic binding energy of O 1s (shown in Figure 6b). This may be due to the addition of small amounts of Mg atoms, causing new oxygen vacancies [36]. Oxygen vacancies in TiO<sub>2</sub> are usually created in doped TiO<sub>2</sub> to maintain charge neutrality and improve the service life of the photocatalyst [37]. When oxygen vacancies are generated, a higher energy peak can be seen due to the decrease in the electron density of oxygen [37]. A peak at 49.93 eV was associated with Mg 2p, which is further verified by the incorporation of Mg<sup>2+</sup> into the titanium dioxide lattice.

Figure 7 shows the typical FT-IR spectrum of undoped TiO<sub>2</sub> and Mg-doped TiO<sub>2</sub> samples with different  $V_{\text{water}}/V_{\text{ethanol}}$  ratios. All samples have absorption peaks at 3380 cm<sup>−1</sup> and 1640 cm<sup>−1</sup>, corresponding to O–H stretching vibration and bending vibration, respectively [38]. For the undoped TiO<sub>2</sub> sample, the bands at 1450 cm<sup>−1</sup> and 1538 cm<sup>−1</sup> are attributed to the H–O–H bending of the lattice water [39]. The band centered at 510 cm<sup>−1</sup> is due to isolated tetrahedral TiO<sub>4</sub> stretching vibrations and only occurs in the pure TiO<sub>2</sub> sample [40]. As a result of Mg-doping, the bands at 1065 cm<sup>−1</sup> and 458 cm<sup>−1</sup> show the

vibration of Ti-O-Mg [41]. With the increase in ethanol content, the intensities of the absorption peaks at  $3380\text{ cm}^{-1}$  and  $458\text{ cm}^{-1}$  increase, respectively. This indicates that Mg ions are doped into the lattice of  $\text{TiO}_2$ , and the HRTEM, TEM, and XRD results further confirmed this point.

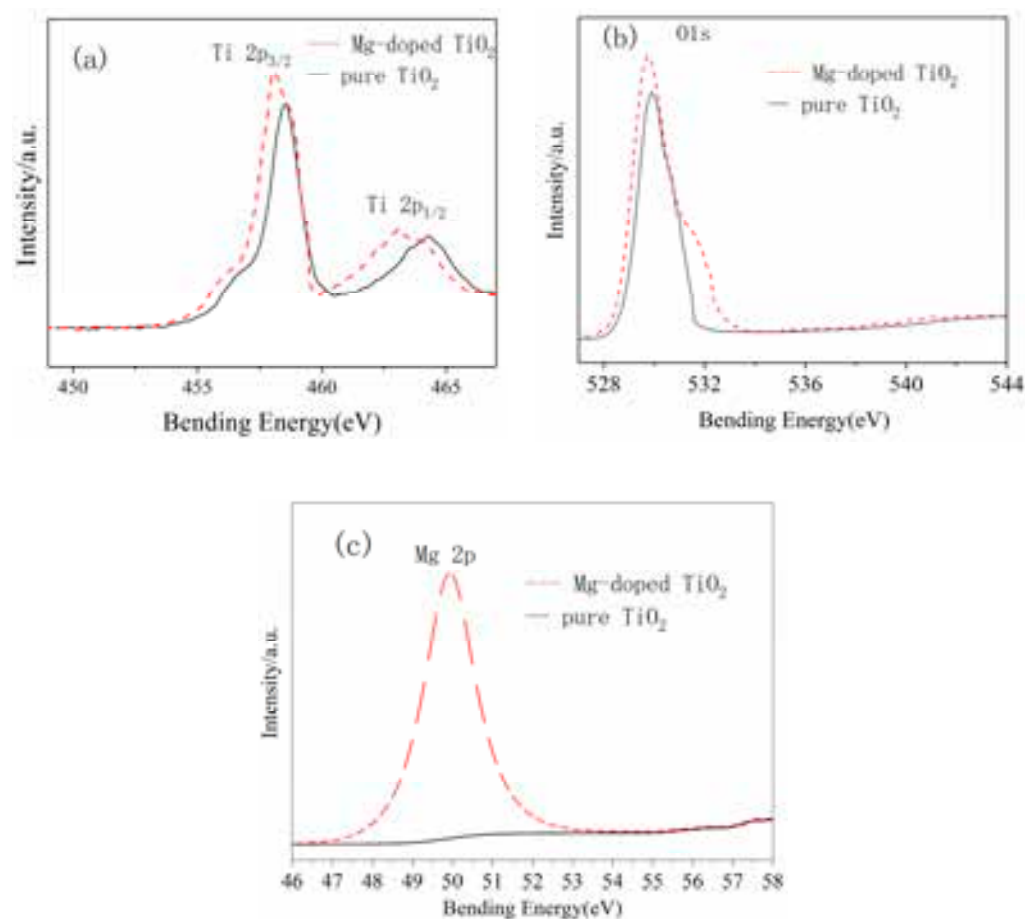


**Figure 6.** XPS spectra of the undoped  $\text{TiO}_2$  and Mg-doped  $\text{TiO}_2$  samples prepared using  $V_{\text{water}}/V_{\text{ethanol}}$  ratio of 15:0 (a) Ti, (b) O, (c) Mg.

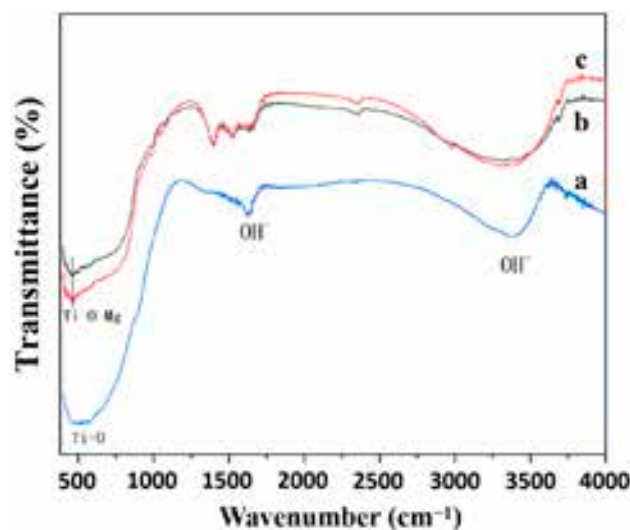


**Figure 7.** FT-IR spectrum of the typical samples: (a) undoped  $\text{TiO}_2$ , (b) Mg-doped  $\text{TiO}_2$  samples prepared using  $V_{\text{water}}/V_{\text{ethanol}}$  ratio of 15:0, (c) Mg-doped  $\text{TiO}_2$  samples prepared using  $V_{\text{water}}/V_{\text{ethanol}}$  ratio of 12.5:2.5.

### 3.2. BET Analysis

Figure 8 shows the BET analysis of the samples using nitrogen adsorption-desorption. For all samples, the isotherms are type IV, and clear hysteresis loops can be identified. With the increase in  $V_{\text{water}}/V_{\text{ethanol}}$ , the BET surface area of the Mg-doped  $\text{TiO}_2$  samples decreases. However, the pore volume and porosity of the samples exhibit a prominent enhancement compared with the undoped  $\text{TiO}_2$  sample, as shown in Table 1 and Figure 8. The BJH average pore diameters, calculated from the adsorption branch of the isotherms, are 11.205 nm, 12.560 nm, 12.365 nm, and 12.807 nm for pure  $\text{TiO}_2$  and Mg-doped  $\text{TiO}_2$  samples prepared with different  $V_{\text{water}}/V_{\text{ethanol}}$  ratios of 12.5:2.5, 10:5, and 7.5:7.5, respectively. The mesoporous structure is mainly due to the porous accumulation of nanoparticles [42]. The porosity increase is due to the crystal size reducing with the decrease in  $V_{\text{water}}/V_{\text{ethanol}}$ .

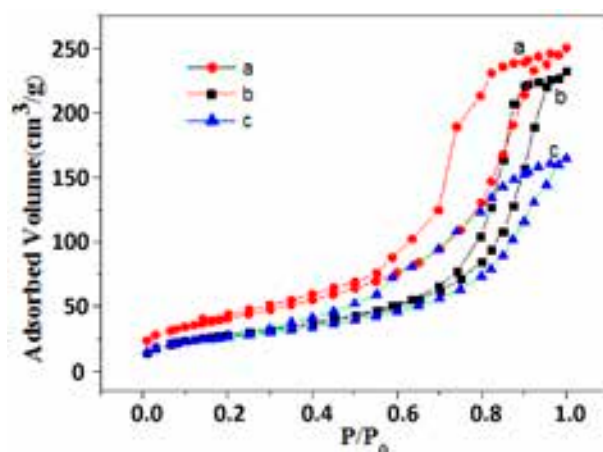


**Figure 8.**  $\text{N}_2$  adsorption-desorption isotherm samples with different ratio of water: ethanol (a) doped  $\text{TiO}_2$  12.5:2.5, (b) doped  $\text{TiO}_2$  10:5, (c) undoped  $\text{TiO}_2$  12.5:2.5.

### 3.3. Optical Properties

Figure 9 shows the UV-Visible diffuse reflectance spectra of  $\text{TiO}_2$ . The absorption edge of doped  $\text{TiO}_2$  had more of a blue shift than the undoped  $\text{TiO}_2$ . The Kubelka–Munk formula,  $(E(\text{eV}) = hc/\lambda, h = 6.626 \times 10^{-34} \text{ Js}, C = 3.0 \times 10^8 \text{ ms}^{-1})$ , was used to acquire the exact band gap of  $\text{TiO}_2$  from 3.26 eV to 3.13 eV, which can be attributed to the  $\text{Mg}^{2+}$ -doped  $\text{TiO}_2$  in the framework. Since  $\text{Mg}^{2+}$  ions generated from oxygen vacancies are known to cause the photoexcitation of long-wavelength light, the UV-Vis absorption spectrum was inferred to verify the presence of  $\text{Mg}^{2+}$  in the  $\text{TiO}_2$ -doped sample.

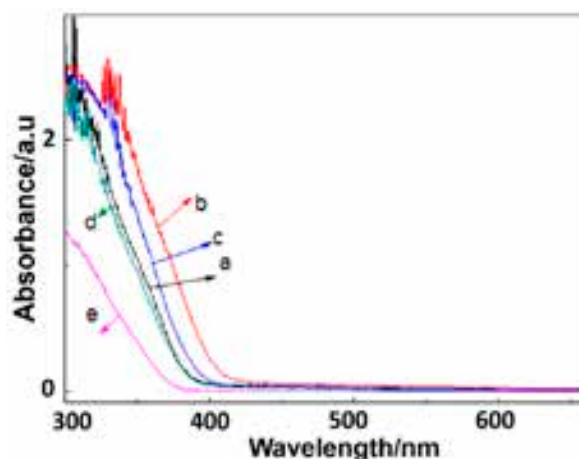


**Figure 9.** UV-Vis spectra of  $\text{TiO}_2$  with different rate of water: ethanol (a) 15:0, (b) 12.5:2.5, (c) 10:5, (d) 7.5:7.5, (e) undoped  $\text{TiO}_2$  12.5:2.5.

Moreover, from the spectrum, the energy gap of the semiconductor nanoparticles is related to the particle size. The band gap increases as the particle size decreases, resulting in a phenomenon known as a “blue shift” in light absorption at a specific wavelength due to the quantum size effect [43]. With the increase in ethanol content, the absorption edge of the doped TiO<sub>2</sub> is blue-shifted, illustrating the particle size reduction. The results obtained are well-matched with the sizes of the crystals that were measured. The band gap energies of the prepared TiO<sub>2</sub> doped by adding 0 to 7.5 mL ethanol were found to be 3.17 eV, 3.03 eV, 3.13 eV, and 3.25 eV, respectively. From Figure 4, it is clear that the size of anatase nanoparticles increases with the increase in ethanol content. Optical absorption is highly dependent on the internal structure of the material [44]. Compared with pure TiO<sub>2</sub>, the longer-wavelength region of Mg-doped TiO<sub>2</sub> samples implies that the only possible transition is from the oxygen vacancies causing a red shift of the absorption edge (Figure 6), which also implies that Mg<sup>2+</sup> has been incorporated into the lattice of TiO<sub>2</sub> (Table 1). From Figure 6, it can be observed that compared with the pure TiO<sub>2</sub> sample, the Ti and O binding energy in Mg-doped TiO<sub>2</sub> samples has been shifted to a lower energy and a higher energy peak, because some Ti<sup>4+</sup> ions are replaced by Mg<sup>2+</sup> ions in order to increase the charge density of Ti and reduce the electron density of oxygen [45]. The new oxygen vacancies are created through the doping of small amounts of Mg atoms [46]. For the Mg-doped TiO<sub>2</sub> sample, the peak of 49.9 eV is ascribed to Mg 2p (Figure 6c), which is consistent with the value of Mg<sup>2+</sup> [27,41]. These observations further verify the existence of Mg<sup>2+</sup> in the Mg-doped TiO<sub>2</sub> sample, which is consistent with XRD (Figure 3), increased cell volume (Table 1), and FT-IR spectrum (Figure 7).

### 3.4. Photocatalytic Activity

Figure 10 shows the photocatalytic bleaching of RhB through the as-prepared sample under visible light. As shown in Figure 10, RhB concentration is unchanged, illustrating that RhB adsorbed on the TiO<sub>2</sub> surface had reached equilibrium in 30 min. Figure 10b shows kinetic curves of  $\ln(C_0/C)$  versus irradiation time during RhB bleaching under visible light irradiation. It has been found that the apparent rate constants [47] for the reaction of RhB with Mg-doped TiO<sub>2</sub> samples ( $V_{\text{water}}/V_{\text{ethanol}} = 15:0, 12.5:2.5, 10:5, 7.5:7.5$ ) and Mg-undoped TiO<sub>2</sub> ( $V_{\text{water}}/V_{\text{ethanol}} = 12.5:2.5$ ) were 0.01704, 0.06335, 0.04153, 0.01668, and 0.00203 min<sup>−1</sup>, respectively, which illustrates that the photocatalytic activity of the samples was effectively improved by Mg<sup>2+</sup>-doping (due to pure anatase phase formation (Figure 3)). Moreover, the photocatalytic properties of Mg-doped TiO<sub>2</sub> can be further improved by changing the ratio of water to ethanol. The photocatalytic properties of the samples increased first and then decreased gradually with the increase in  $V_{\text{water}}/V_{\text{ethanol}}$ . When the  $V_{\text{water}}/V_{\text{ethanol}}$  ratio was 12.5:2.5, Mg-doped TiO<sub>2</sub> had the maximum photocatalytic activity. In addition, by combining Table 1 with Figures 4 and 9, we can observe that the aggregated nanoparticles increase in size and thus  $E_g$  increases, which leads to the easy recombination of the electron and hole in the migration process, and therefore, the photocatalytic activity of the samples decreases with the increase in ethanol volume (i.e.,  $V_{\text{water}}/V_{\text{ethanol}}$  decreases). Although TiO<sub>2</sub> ( $V_{\text{water}}/V_{\text{ethanol}} = 15:0$ ) has a larger specific surface area and smaller crystal size (Table 1) compared with the Mg-doped samples, the sample had lower porosity and pore size, which caused the decrease in the sample of RhB adsorption. This clearly indicates that the adsorption of samples was determined by the surface area and characteristics of the pore. Obviously, Mg-doped TiO<sub>2</sub> samples exhibited better photocatalytic activities than pure TiO<sub>2</sub> samples. The narrowing of the band gap is a result of Mg doping into the TiO<sub>2</sub> lattice, which enables the trapping of the photo-induced electron and facilitates the separation of electron-hole pairs (Figure 11a).

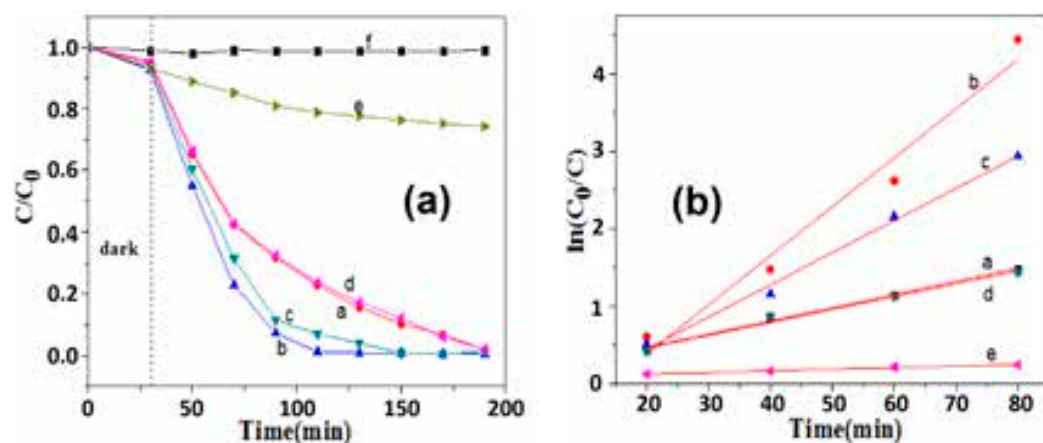


**Figure 10.** (a) Photocatalytic performance, (b) Kinetic curves of  $\ln(C_0/C)$  as a function of irradiation time for RhB bleaching under visible light irradiation: (a) 15:0, (b) 12.5:2.5, (c) 10:5, (d) 7.5:7.5 of the Mg-doped samples, (e) Mg-undoped  $\text{TiO}_2$  sample, (f) without photocatalyst.

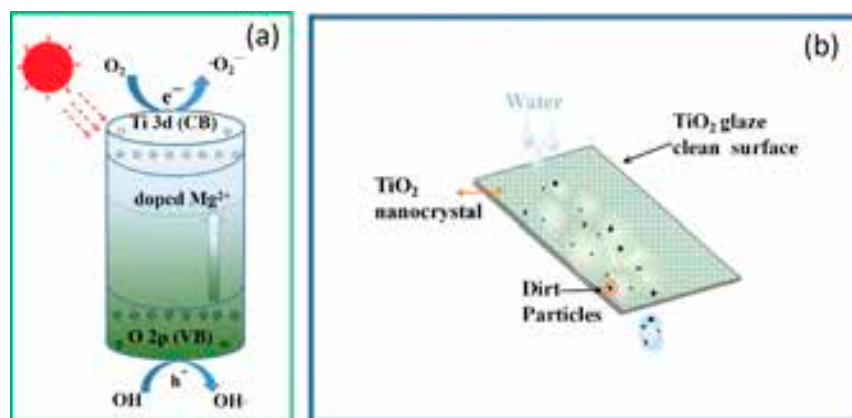


**Figure 11.** Schematic representation of photo processes using Mg-doped  $\text{TiO}_2$  photocatalysts (a) and the self-cleaning process using Mg-doped  $\text{TiO}_2$  in glaze sample (b), respectively.

### 3.5. Self-Cleaning Properties of Mg-Doped $\text{TiO}_2$ in Glaze Sample

It can be seen the wet angle of pure  $\text{TiO}_2$  glaze samples is obviously higher than those of Mg-doped  $\text{TiO}_2$  glaze samples (Figure 12). The super-hydrophilicity of Mg-doped  $\text{TiO}_2$  glaze samples is attributed to several comprehensive factors. Based on the experimental results, Mg ions are helpful for the growth of the  $\text{TiO}_2$  crystal grain, and thus separates the phase size in Mg-doped  $\text{TiO}_2$  glaze more than pure  $\text{TiO}_2$ . This makes the Mg-doped  $\text{TiO}_2$  glaze surface rougher than that of the pure  $\text{TiO}_2$  glaze (Figure 12). A large surface roughness could improve the hydrophilicity, according to the Wenzel equation (1):  $\cos \theta_r = r \cos \theta$ , where  $r$  denotes the surface roughness of the glaze,  $\cos \theta$  is the classical contact angle depicted by the Young equation, and  $\theta_r$  is the measured real contact angle. Moreover, the partial substitution of  $\text{Mg}^{2+}$  ions for Ti sites increases the slight  $\text{TiO}_2$  lattice distortion, which is available for a low initial contact angle and hydrophilicity [48]. From Figure 12, it can be seen that the contact angles of Mg-doped  $\text{TiO}_2$  samples are smaller than that of the pure  $\text{TiO}_2$  glaze sample in the dark condition, indicating that the greater roughness and lattice distortion are helpful for decreasing the contact angle. This could be because the incorporation of Mg makes the band gap of  $\text{TiO}_2$  narrow, thus the visible light can excite pairs of electrons and holes (Figure 11a), just as in the case of ultraviolet irradiation for the pure  $\text{TiO}_2$  glaze.  $\text{Ti}^{4+}$  ions could be united with the photo-induced electron and thus  $\text{Ti}^{3+}$  ions could be obtained.  $\text{Ti}^{3+}$  sites can be substituted by  $\text{Mg}^{2+}$  ions, which produces one excess positive charge. Those excess positive charges could capture the photo-induced electrons quickly, and thus photo-generated holes are available for

combining more H<sub>2</sub>O adsorbed on the glaze surface and react with water, producing hydroxyl radicals that are also available for maintaining the hydrophilicity of Mg-doped TiO<sub>2</sub> glaze samples [29]. Therefore, the super-hydrophilicity of Mg-doped TiO<sub>2</sub> glaze samples could be attributed to the visible-light-exciting photo-induced pairs of electrons and holes. For the sample with a  $V_{\text{water}}/V_{\text{ethanol}}$  ratio of 10:5 and 7.5:7.5, the contact angles of water droplets on Mg-doped TiO<sub>2</sub> glaze samples increase slightly, which could be attributed to the decrease in the  $V_{\text{water}}/V_{\text{ethanol}}$  ratio. However, when  $V_{\text{water}}/V_{\text{ethanol}}$  is 10:5 and 7.5:7.5, the hydrophilicity of Mg-doped TiO<sub>2</sub> glaze samples decreases slightly, though it still has super-hydrophilicity. The hydroxy groups anchoring on the Mg-doped TiO<sub>2</sub> glaze surface have a significant impact on the hydrophilicity. The formation of hydroxy groups results in the dissociative adsorption of water molecules at oxygen vacancy sites on the Mg-doped TiO<sub>2</sub> glaze surface. The extra hydroxy groups and oxygen vacancies on the surface are produced by electron-hole pairs, which lead to the hydrophilicity of the Mg-doped TiO<sub>2</sub> glaze surface [39]. Because oxygen vacancy is produced by the doping of Mg in the TiO<sub>2</sub> crystal and the separation of electron-hole pairs is facilitated (Figure 11a), the Mg-doped TiO<sub>2</sub> glaze surface has more photo-induced wettability than the pure TiO<sub>2</sub> glaze surface.

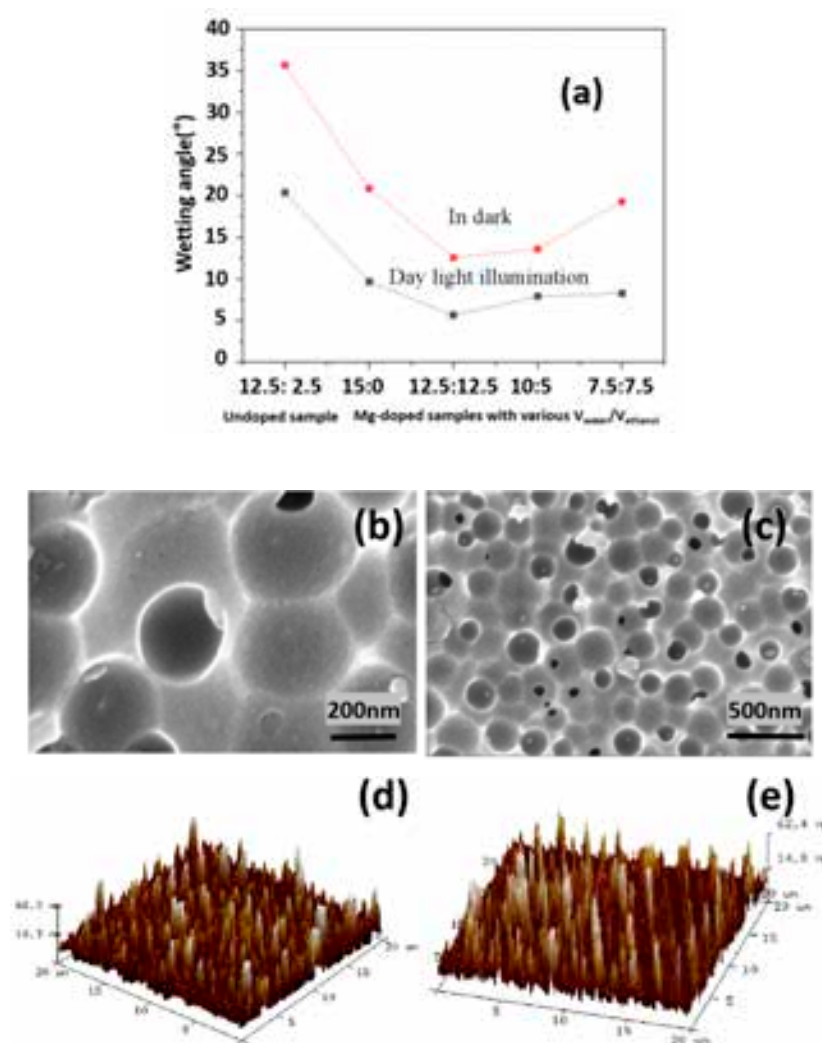


**Figure 12.** Wetting angle of Mg-undoped TiO<sub>2</sub> glaze sample prepared at  $V_{\text{water}}/V_{\text{ethanol}}$  of 12.5:2.5, and Mg-doped TiO<sub>2</sub> glaze samples with various  $V_{\text{water}}/V_{\text{ethanol}}$  ratios in dark and daylight illumination (a), respectively; SEM images of the Mg-doped TiO<sub>2</sub> glazes prepared using  $V_{\text{water}}/V_{\text{ethanol}}$  of 12.5:2.5 (b) and pure TiO<sub>2</sub> glaze prepared using  $V_{\text{water}}/V_{\text{ethanol}}$  of 12.5:2.5 (c); AFM surfaces of the Mg-doped TiO<sub>2</sub> glaze (d) and pure TiO<sub>2</sub> glaze sample (e) with  $V_{\text{water}}/V_{\text{ethanol}}$  of 12.5:2.5, respectively.

The self-cleaning performance was tested using a Japan Marker pen. The glaze surface was drawn on after drying for 1 h. After that, after placing a few drops of water on the glaze, we could observe whether the ink blots were floating. Table 2 shows that after firing at 1180~1200 °C, the water contact angle (5.623° vs. 15.23°) and stain resistance (the blot floats as a whole vs. not floating, as shown in Figure 13) of the sample fabricated were improved compared to commercial self-cleaning ceramic glazes [49]. The above results indicate the great potential application for enhancing the self-cleaning properties of glazes by introducing Mg-doped TiO<sub>2</sub>.

**Table 2.** Performances of Mg-doped TiO<sub>2</sub> in the ceramic samples obtained in this study and from other literature studies.

| Type                                                                                    | Firing Temperature (°C) | Water Contact Angle (°) |                       | Stain Resistance                                                            | Ref.      |
|-----------------------------------------------------------------------------------------|-------------------------|-------------------------|-----------------------|-----------------------------------------------------------------------------|-----------|
|                                                                                         |                         | Before Use              | Irradiation after Use |                                                                             |           |
| Mg-doped TiO <sub>2</sub> in glaze sample                                               | 1180~1200               | 5.623                   | 5.124                 | After dripping water droplets, the blot floats as a whole                   | This work |
| TiO <sub>2</sub> doped in glaze sample                                                  | 1180~1200               | 12.26                   | 13.56                 | Not floating                                                                | This work |
| The commercial self-cleaning ceramic products                                           | 1180~1200               | 21.23                   | 28.96                 | Not floating                                                                | This work |
| C-PEG/TiO <sub>2</sub> coating                                                          | -                       | 26                      | 11                    | Blot cannot be completely removed                                           | [50]      |
| Commercial ceramic tiles with groove-like microstructure surfaces                       | -                       | 164.75                  | -                     | Blot cannot be completely removed                                           | [51]      |
| Hybrid sol-gel coating and industrial application on polished porcelain stoneware tiles | -                       | -                       | -                     | With the help of cleaning agent, the stains can be removed from the surface | [52]      |

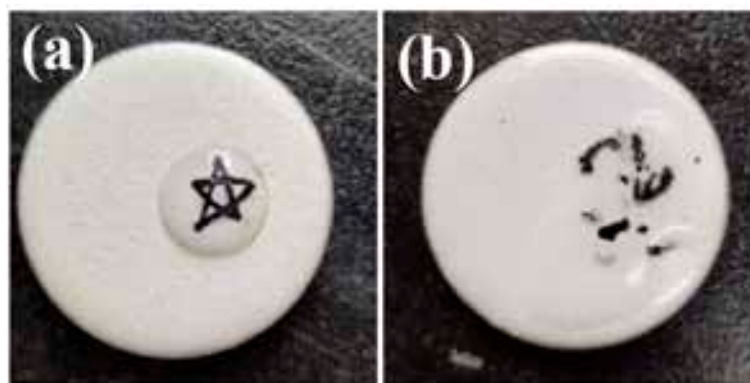


**Figure 13.** Photos of the as-prepared samples immediately meeting the water in this study (a) Mg-undoped TiO<sub>2</sub> in glaze sample, (b) Mg-doped TiO<sub>2</sub> in glaze sample.

#### 4. Conclusions

In this paper, Mg-doped TiO<sub>2</sub> samples with various  $V_{\text{water}}/V_{\text{ethanol}}$  ratios were successfully prepared through the solvothermal method at 180 °C for 36 h. The Mg-doped ( $V_{\text{water}}/V_{\text{ethanol}} = 12.5:2.5$ ) sample had higher surface area, porosity, optical performance, and photocatalytic activity than other samples. Undoped and Mg-doped TiO<sub>2</sub> glaze ceramic samples were prepared using a medium-/high-temperature solid-firing process. Mg-doped TiO<sub>2</sub> samples ( $V_{\text{water}}/V_{\text{ethanol}} = 12.5:2.5$ ) illustrated superior hydrophilicity properties, photocatalytic activity in terms of bleaching organic dye, and self-cleaning capability in ceramic glaze samples than other samples after visible light exposure. This study provides a preparation approach for the synthesis of TiO<sub>2</sub> while controlling crystal size and morphology, which can be utilized with solar energy for bleaching the contaminants in water and enhancing the self-cleaning properties of medium-/high-temperature glazes.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11080341/s1>, Figure S1: EDX spectroscopy mapping performed in the TEM microscope.

**Author Contributions:** Conceptualization, T.Z., Q.B. and W.D.; methodology, T.C. and Q.B.; software, P.L. and Y.L.; validation, X.G. and Q.B.; formal analysis, T.Z. and J.Z.; investigation, T.C. and Y.L.; resources, Q.B. and J.Z.; data curation, T.Z. and W.D.; writing—original draft preparation, T.Z. and W.D.; writing—review and editing, T.Z. and W.D.; visualization, P.L. and X.G.; supervision, X.G. and J.Z.; project administration, T.Z. and T.C.; funding acquisition, W.D. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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## Review

# Research Progress of TiO<sub>2</sub> Modification and Photodegradation of Organic Pollutants

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**Abstract:** Titanium dioxide (TiO<sub>2</sub>) photocatalysts, characterized by exceptional photocatalytic activity, high photoelectric conversion efficiency, and economic viability, have found widespread application in recent years for azo dye degradation. However, inherent constraints, such as the material's limited visible light absorption stemming from its bandgap and the swift recombination of charge carriers, have impeded its broader application potential. Encouragingly, these barriers can be mitigated through the modification of TiO<sub>2</sub>. In this review, the common synthesis methods of TiO<sub>2</sub> are reviewed, and the research progress of TiO<sub>2</sub> modification technology at home and abroad is discussed in detail, including precious metal deposition, transition metal doping, rare earth metal doping, composite semiconductors, and composite polymers. These modification techniques effectively enhance the absorption capacity of TiO<sub>2</sub> in the visible region and reduce the recombination rate of carriers and electrons, thus significantly improving its photocatalytic performance. Finally, this paper looks forward to the future development direction of TiO<sub>2</sub> photocatalytic materials, including the exploration of new modified materials, in-depth mechanism research, and performance optimization in practical applications, to provide useful references for further research and application of TiO<sub>2</sub> photocatalytic materials.



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**Keywords:** titanium dioxide; modification; photocatalysis; organic pollutants

## 1. Introduction

In recent years, acid rain, eutrophication of water bodies, black and smelly water bodies, PM<sub>2.5</sub> exceeding standards, and other environmental issues have occurred frequently, warning us that environmental protection cannot be delayed. Among them, the content of organic pollutants and pigments is high, which seriously affects the regional water quality [1,2]. Due to their highly stable structure and difficulty in handling, most of them are toxic to organisms, including direct lethality and carcinogenicity [3–5]. This highlights the urgent need for effective treatment of pollutants in water, and the current treatment methods for organic pollutants are mainly the combination of physical, biochemical, and chemical treatment methods [6].

Physical treatment methods include adsorption, extraction, radiation-based techniques, and membrane separation [7–9]. Biochemical treatment methods include aerobic treatment, anaerobic treatment [10,11], and so on. Chemical treatment methods include chemical oxidation, photocatalytic oxidation, electrochemical methods, chemical coagulation, and others [12–14]. Although the traditional physical and chemical treatment methods can remove azo dyes to a certain extent, there are often problems such as high energy consumption, long treatment cycles, and secondary pollution. Therefore, the development of efficient and environmentally friendly treatment of water pollutants has become the focus of current research.

As a new type of wastewater treatment technology being gradually developed based on photochemical oxidation [15], photocatalytic technology has garnered widespread favor among scholars due to its numerous advantages including good stability, high activity, non-toxicity, a wide range of applicability, and the absence of secondary pollution. Its ability to effectively degrade dye pollutants in water bodies is particularly noteworthy [16,17]. Photocatalysts are primarily composed of n-type semiconductor materials, including TiO<sub>2</sub>, ZnO, CdS, and others. TiO<sub>2</sub> stands out as the most extensively studied and utilized n-type semiconductor material due to its exceptional chemical stability, non-toxicity, low cost, and strong photosensitivity [18,19]. Its application areas span water treatment, air purification, solar cell photosensitizers, self-cleaning materials, and medical applications [20]. In the degradation of organic pollutants in water, TiO<sub>2</sub> photocatalysis technology has shown unique advantages. TiO<sub>2</sub> photocatalyst can generate photogenerated electrons and holes under ultraviolet irradiation and then trigger a series of REDOX reactions. These reactions can break the chemical bonds of organic pollutant molecules and degrade them into small molecular compounds, ultimately achieving the purpose of removing the pollutants [21].

Although TiO<sub>2</sub> photocatalysis technology has many advantages in the degradation of pollutants in water, pure TiO<sub>2</sub>, with a band gap of 3.0~3.2 eV [22], can only be excited by ultraviolet light with a wavelength less than 387 nm and photogenerated electron-hole pairs are easy to recombine, resulting in low photo quantum efficiency and limited photocatalytic activity [23]. To further improve the photocatalytic performance of TiO<sub>2</sub>, researchers modified TiO<sub>2</sub> through doping [24], composite, surface modification [25], and other means to optimize the structure of TiO<sub>2</sub>, thereby expanding its photoresponse range and reducing the carrier recombination rate [26,27]. Thus, its application effect in the photodegradation of organic pollutants was enhanced. These modification methods can significantly improve the efficiency and performance of TiO<sub>2</sub> photocatalysts in degrading pollutants and provide better technical support for practical applications. In addition, the study of TiO<sub>2</sub>-modified photocatalysis technology has far-reaching significance [28]. It not only helps to solve the environmental problems of organic pollutants such as azo dyes but also promotes the application and development of photocatalysis technology in other fields [29]. Through in-depth research on the mechanism and methods of TiO<sub>2</sub> modification, theoretical guidance, and practical experience can be provided for the development of more efficient and environmentally friendly photocatalytic materials and contribute to environmental protection and sustainable development [30].

## 2. Mechanism and Kinetics of Photodegradation of Organic Pollutants by TiO<sub>2</sub> Photocatalyst

### 2.1. Mechanism of Photodegradation of Organic Pollutants by TiO<sub>2</sub> Photocatalyst

TiO<sub>2</sub> is a semiconductor, and its band structure is composed of a low-level valence band and a high-level conduction band [31]. The valence band is mainly composed of 2p orbitals of oxygen atoms, and the conduction band is mainly composed of 3d, 4s, and 4p orbitals of titanium atoms [32]. The band discontinuity of the semiconductor is bandgap between the valence band and the conduction band, and the energy difference between the conduction band and the valence band is called bandgap width [33].

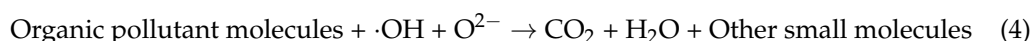
TiO<sub>2</sub> mainly has three crystal structures, namely Anatase type, Rutile type, and Brookite type, of which rutile TiO<sub>2</sub> is the most stable crystal type, even at high temperatures will not be transformed and decomposed. The photocatalytic activity of anatase TiO<sub>2</sub> is higher than that of rutile TiO<sub>2</sub> because anatase TiO<sub>2</sub> has a lighter effective mass, smaller particle size, and longer life of photoexcited electrons and holes [34]. As a metastable phase, titanite is rarely found in nature, is difficult to synthesize, and has low practical application value, so anatase-type TiO<sub>2</sub> is often used to photocatalyze the degradation of organic pollutants in water. For anatase phase TiO<sub>2</sub>, when it is irradiated by photons with energy greater than 3.2 eV (wavelength < 387.5 nm), the photoexcitation reaction will produce free electrons and holes:



Excited electrons react with oxygen in the air to produce superoxide radical anions, which combine with water molecules to form hydroxyl radicals:



Hydroxyl radicals and superoxide radicals with strong oxidation react with organic pollutants, destroying their molecular structure; they are easily broken by oxidation. After a series of reactions, organic pollutant molecules are decomposed into harmless small molecules or low-toxicity compounds, such as water and carbon dioxide. The process is as follows:



The photocatalytic mechanism of  $TiO_2$  is depicted in Figure 1.

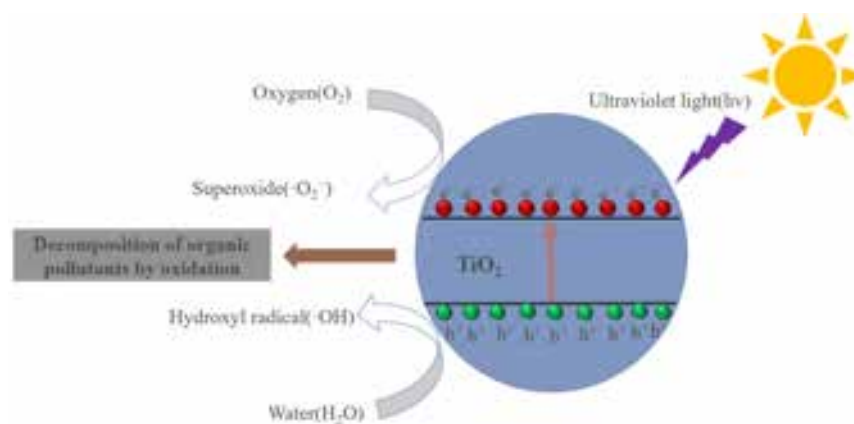


**Figure 1.** Photocatalytic mechanism of  $TiO_2$ .

## 2.2. Kinetics of Photodegradation of Organic Pollutants by $TiO_2$ Photocatalyst

The photocatalytic degradation of organic pollutants by  $TiO_2$  is analyzed by the Langmuir–Hinshelwood model [35]; Arikal [36] et al. used chitosan as a carrier to immobilize  $TiO_2$ /MgO nanocomposites on chitosan beads. MO and azo red S (ARS) were used as model dye compounds. The experimental results showed that the degradation of the pollutants followed first-order kinetics, and the Langmuir–Hinshelwood model was suitable for describing the kinetics of the photocatalytic degradation of wastewater. This is simplified as the first-order kinetics formula:  $\ln(C_0/C) = kt$ , ( $C_0$ ) the initial concentration of organic pollutants, ( $C$ ) the concentration of organic pollutants after degradation, ( $k$ ) the apparent reaction rate constant, and ( $t$ ) the photodegradation time. The model takes into account the adsorption and reaction processes on the catalyst surface and can describe the kinetic behavior of photocatalytic degradation well. The kinetics of photocatalytic degradation can be described by the degradation rate constant. The degradation rate constant reflects the relationship between degradation rate and pollutant concentration.

The influencing factors of reaction kinetics are as follows:

- Solution pH value has an important effect on photocatalytic degradation. The photocatalytic activity of  $TiO_2$  may vary under acidic and alkaline conditions.
- The amount of catalyst dosing will also affect the degradation rate. Less than or more than the optimal dosage will lead to a decrease in the degradation rate.
- Factors such as organic pollutant's initial concentration and light intensity also affect the kinetic process of photocatalytic degradation.

In summary, the process of photodegradation of organic pollutants using  $\text{TiO}_2$  photocatalyst involves complex chemical reactions and kinetic behaviors. Through an in-depth understanding of its mechanism and kinetics, the photocatalytic degradation process can be optimized, and the degradation efficiency and environmental protection effect can be improved.

### 3. Synthesis Method of $\text{TiO}_2$ Photocatalyst

As a functional material,  $\text{TiO}_2$  has high photocatalytic activity and, therefore, has an excellent advantage in the field of photocatalytic degradation. At present, the methods commonly used to synthesize  $\text{TiO}_2$  include the sol-gel method, hydrothermal method, atomic layer deposition method, and microemulsion method. In terms of structure and morphology, a variety of morphologically controllable  $\text{TiO}_2$  micro-nano meters, such as nanorods, nanotubes, nano-flowers, nano-hollow spheres, and mesoporous structures, were prepared through various experiments. As shown in Figure 2, these micro-nano  $\text{TiO}_2$  materials with large specific surface areas usually have more excellent photocatalytic properties.

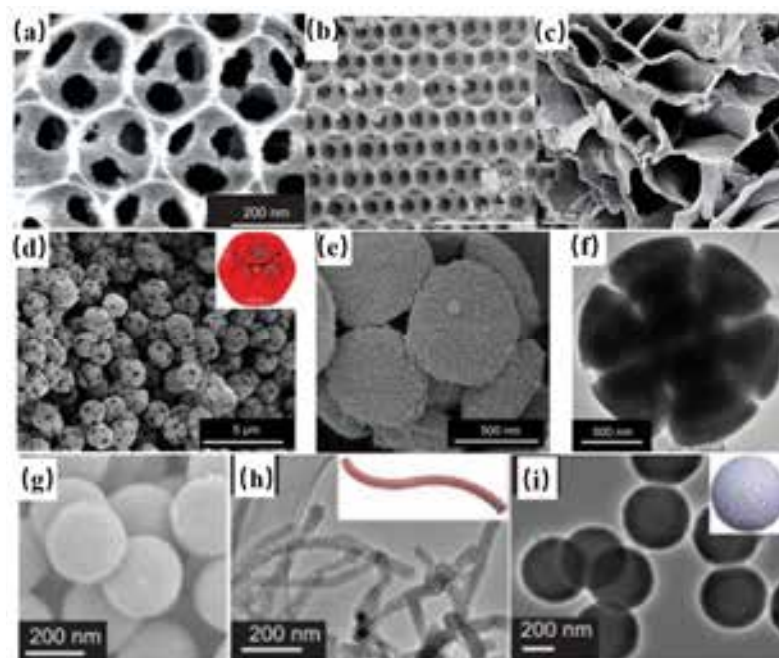


**Figure 2.** Different  $\text{TiO}_2$  micro-nano structure diagram: (a) SEM image of ordered macroporous  $\text{TiO}_2$ ; (b) Porous  $\text{TiO}_2$  TEM image; (c) TEM image;  $\text{TiO}_2$  flower-like superstructure self-assembled by limiting microemulsions. FESEM (d,e) and TEM (f) images of primary mesoporous  $\text{TiO}_2$ ; (g)  $\text{SiO}_2$  monolayer mesoporous  $\text{TiO}_2$  core-shell structure; (h) Carbon nanotube-coated  $\text{TiO}_2$  TEM and FESEM images; (i) carbon cluster  $\text{TiO}_2$  TEM image [37].

#### 3.1. Sol-Gel Method

Sol-gel is the most commonly used process method for preparing  $\text{TiO}_2$  photocatalytic materials [38]. Inorganic salts and Alkoxides (including tetraethyl titanate, butyl titanate, isopropanol titanium, etc.) are placed in distilled water, mixed evenly at room temperature under liquid phase conditions, and a stable, transparent sol system is formed in solution through chemical reaction steps such as hydrolysis and condensation, as shown in Figure 3. After aging for some time, the colloidal gel slowly polymerizes to form a wet gel with a three-dimensional network structure, and the gel network is filled with solvent that loses fluidity. The wet gel is prepared by vacuum drying, high-temperature roasting, and curing to produce molecular and even nanostructured materials. Nanomaterials prepared by the sol-gel method have the advantages of high purity, uniformity, and controllable morphology and have been widely used in the preparation of  $\text{TiO}_2$ .

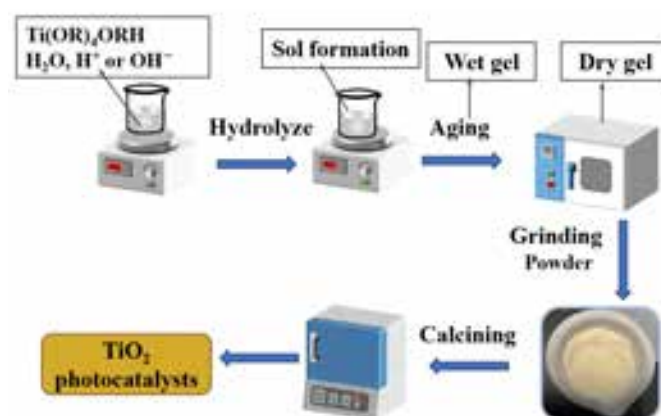


**Figure 3.** Schematic diagram of TiO<sub>2</sub> preparation process by sol-gel method.

Jamil [39], Huo [40], Fermeli [41], et al. prepared a composite photocatalyst by sol-gel method. The results show that the prepared TiO<sub>2</sub> composite photocatalyst has good dispersibility, a large specific surface area, and good photocatalytic activity. Dinkar Parashar [42] prepared photocatalysts by sol-gel method at different calcination temperatures (400–800 °C) and hydroalcohol ratios. The activity of TiO<sub>2</sub> prepared by the sol-gel method was higher than that of commercially available pure anatase TiO<sub>2</sub> nanoparticles due to the smaller average particle size. It was found that the ratio of water to alcohol in the preparation of TiO<sub>2</sub> catalysts had a significant effect on antibiotic removal. Namely, the removal-rate constants of metronidazole (MNZ), ciprofloxacin (CIP), and tetracycline (TET) were improved by a factor of 2.7, 3.3, and 1.6, which further indicates that the sol-gel prepared TiO<sub>2</sub> can effectively remove the harmful substance. Lalitha [43] et al. synthesized TiO<sub>2</sub>/ZnO with quadrilateral and hexagonal structures by sol-gel method; the catalyst displayed 90% degradation within 40 min under UV light conditions.

### 3.2. Hydrothermal Synthesis

The hydrothermal synthesis method is a reaction occurring at high temperature and high pressure [44], which uses water or organic solvent as a medium through heating so that insoluble or insoluble substances are dissolved or recrystallized after washing and centrifugation to obtain the required nanoparticle. Rawat [45], Matakane [46], et al. prepared composite photocatalysts by hydrothermal method. The results of photocatalytic performance show that it has good absorption ability to ultraviolet light and good transmittability to visible light. Yang [47] et al. synthesized a novel 3D sea urchin-type titanium dioxide by the EDTA-Na<sub>2</sub>-assisted hydrothermal method (Figure 4). Benefiting from the conical structure prepared by the hydrothermal method and the rapid separation of photogenerated electron holes in the mixed crystal phase, the sub-micron-sized 3D sea urchin-type titanium dioxide can efficiently degrade 94.1% of the methicillin in the aqueous solution in 90 min, which is superior to that of the commercially available 25 nm-sized rutile titanium dioxide. Zhang [48] et al. modified TiO<sub>2</sub> with a carboxyl group and amino group by hydrothermal method, making the adsorption performance of functionalized TiO<sub>2</sub> better than P25 (unmodified commercial TiO<sub>2</sub>). Moreover, the functionalized TiO<sub>2</sub> has good reusability for the removal of azo dye acid red G even after 5 adsorption–desorption cycles.

With the progress of scientific research, the hydrothermal method has attracted more and more attention from researchers, especially hydrothermal crystal growth, which has become the focus of research and will become the development object of the scientific research community. Hydrothermal preparation of nanomaterials equipment and conditions still need to be further explored and studied.



**Figure 4.** Preparation process of sea urchin-type titanium dioxide [47].

### 3.3. Atomic Layer Deposition Method

Atomic layer deposition (ALD) technology, also known as Atomic layer epitaxy (ALE) technology, is a chemical vapor deposition technology based on ordered surface autosaturation reactions. Generally speaking, it is a method of coating the material layer by layer on the substrate surface in the form of a single atomic film. Jialin [49], Abidi [50], et al. used the atomic deposition method to prepare  $\text{TiO}_2$  and found that the prepared  $\text{TiO}_2$  nanoparticles were still anatase-type at high temperatures, had particularly good dispersion, and had high photocatalytic activity after degrading dyes. Cao [51] et al. modified the ultra-thin  $\text{Fe}_2\text{O}_3$  layer of industrial anatase  $\text{TiO}_2$  powder by atomic layer deposition (ALD). The ultra-thin  $\text{Fe}_2\text{O}_3$  coating with a small band gap of 2.20 eV can increase the visible light absorption of the  $\text{TiO}_2$  carrier, and the degradation efficiency of  $\text{TiO}_2$  powder coated with ALD  $\text{Fe}_2\text{O}_3$  is the highest within 90 min, reaching 97.4%. Feng [52] et al. used atomic layer deposition (ALD) to deposit  $\text{TiO}_2$  nanoparticles on carbon nanotube membranes to prepare hydrophilic electrodes, as shown in Figure 5. After 20 ALD cycles, the modified carbon nanotube membranes showed better electrosorption performance and reusability in the CDI process. The total Cr and Cr(VI) removal significantly increased to 92.1% and 93.3%, respectively. This work demonstrates that ALD is a highly controllable and simple method for the preparation of advanced CDI electrodes, broadening the application of metal oxide/carbon composites in electrochemical processes, especially in the field of photocatalytic degradation of organic pollutants.

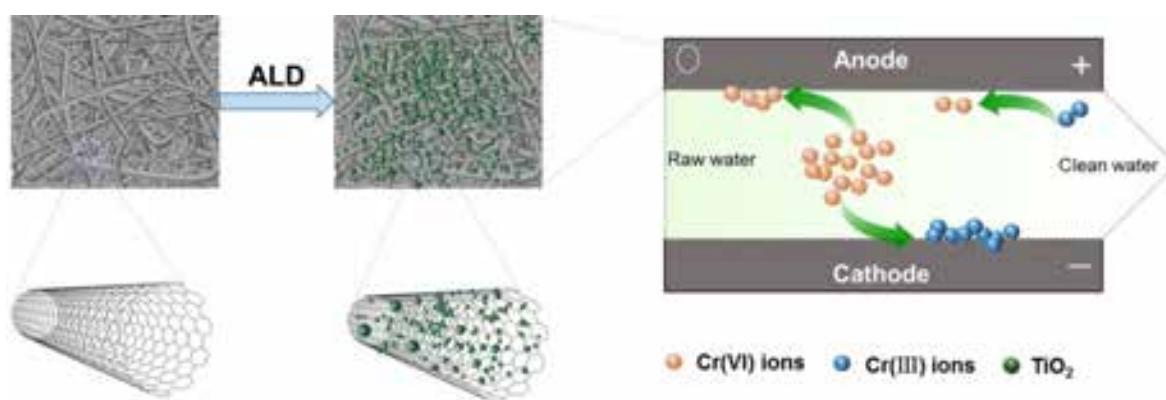


**Figure 5.** Atomic layer deposition (ALD) deposition of  $\text{TiO}_2$  nanoparticles on carbon nanotube film [52].

Furthermore, Ostyn et al. [53] prepared  $\text{TiO}_2$  film on graphene with ALD and oxidized the surface of graphite. The film has a high UV transmittance of 95%, which simplifies the experimental design. No chemical reagents are used to reduce the risk of contamination.  $\text{TiO}_2$  films prepared by ALD react rapidly in graphite photooxidation, which is superior to traditional powder photocatalysts. Ke et al. [54] grew  $\text{TiO}_2$  films by depositing atomic layers on silica support (SBA-15) and depositing precious metal Au on them and found

that titanium dioxide films can successfully grow on mesoporous materials, increasing the specific surface area of the catalyst. Lys et al. [55] successfully combined laser-induced Si nano-fringes (SiNR), MXene, and  $\text{TiO}_2$  to produce efficient ternary photocatalytic materials through ALD technology. Experiments show that the material has strong absorption capacity in the spectrum range, high stability, repeatability, and photocatalytic efficiency, which provides a new way for the photodegradation of azo dyes in wastewater treatment and shows broad application prospects.

### 3.4. Microemulsion Method

The microemulsion method is used for the preparation of nano or polymeric materials by adding surfactants and co-solvents and mixing the immiscible solution into a homogeneous phase [56]. Its advantage is that it can prepare nano-sized and highly dispersible materials with mild conditions and high-quality performance. Because of the large interfacial area and high surface activity of microemulsion, it can improve the reaction efficiency and yield, which is widely used in the preparation of nanomaterials, polymer materials, and catalysts.

Sun [57] et al. prepared  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  composite photocatalyst by microemulsion-solvothermal method. It was found that  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  could reduce the band gap, and the degradation rates of  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  and  $\text{TiO}_2$  for acid red 73 were 93.56% and 74.47%, respectively. Yang [58] et al. successfully prepared  $\text{TiO}_2$  nanofibers with porous and mixed-crystal structures by the microemulsion method, which can directly regulate the structure of titanium dioxide nanofibers by changing the microemulsion system. The titanium dioxide obtained by the microemulsion method shows a porous and mixed-crystal structure and excellent photocatalytic properties. It is simple to prepare and is of great importance for the application of the preparation and enhancement of the performance of the special-shape photocatalytic materials. The degradation rate of methylene blue solution was as high as 98% after 90 min, which was effective in the treatment of printing and dyeing wastewater.

However, the microemulsion method also has limitations that include the following: the product purity is not high, the reagent is difficult to completely remove, the precursor must be water-soluble or oil-soluble, and the preparation and control of the microemulsion is complicated, which requires experimental experience and technical skill.

### 3.5. Other Synthesis Methods

In addition to the above four most common methods for synthesizing  $\text{TiO}_2$ , there is also the Suzuki coupling reaction method [59], the electrostatic spinning method [60], the one-pot method [61], etc. Suzuki coupling reaction is a palladium-catalyzed cross-coupling reaction of aryl or alkenyl boronic acids or boronic esters with chlorine, bromine, iodine-substituted aromatic hydrocarbons or olefins. The one-pot method is a method in which the reactants are made to undergo successive multi-step reactions in a single reactor to improve the reaction efficiency.  $\text{TiO}_2$  preparation by electrostatic spinning is a method of stretching titanium-containing solution into fibers using a high-voltage electric field, followed by heat treatment to obtain  $\text{TiO}_2$  nanofibers. Djeda [62] et al. prepared layered double hydroxide (LDH)/ $\text{TiO}_2$  nanocomposites with photocatalytic properties by immersion and direct coprecipitation methods and compared them with pure  $\text{TiO}_2$  colloidal solutions. The degradation experiments showed that MgAl LDH/ $\text{TiO}_2$  prepared by the coprecipitation method had the highest photodegradation efficiency for Orange II, which emphasized the importance of the preparation method of nanocomposites. Suitable synthesis methods can be selected according to different application requirements.

In summary, the most commonly used synthesis methods of  $\text{TiO}_2$  photocatalysts, their reaction principles, and their advantages and disadvantages are shown in Table 1.

**Table 1.** Reaction Principle of TiO<sub>2</sub> Photocatalyst Common Preparation Methods and Their Advantages and Disadvantages.

| Preparation Methods     | Reaction Principle                                                                                                                                                          | Advantages                                                                                                              | Disadvantages                                                                    |
|-------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| sol-gel method          | Inorganic salts and alcohol salts are hydrolyzed in distilled water, polymerized into a gel after hydrolysis, dried in a vacuum, and cured by high-temperature calcination. | Good dispersion; easy to control the reaction; simple process; low cost and cost-effective.                             | Long preparation time; many operating steps.                                     |
| hydrothermal synthesis  | In a closed system, using water as a solvent, the mixture reacts under certain temperature conditions.                                                                      | Mild reaction conditions; high purity, good dispersion, crystalline form, controllable shape; environmentally friendly. | High equipment requirements; technically difficult and costly.                   |
| atomic layer deposition | A chemical vapor phase thin film deposition technique in which a substance is deposited on the surface of a substrate layer by layer in a single-atom-film format.          | High accuracy; high atom utilization.                                                                                   | Expensive equipment; cumbersome process; difficult to promote industrialization. |
| microemulsion method    | Mutually incompatible liquids form microreactors in the presence of surfactants for the preparation of nanomaterials.                                                       | Good dispersion of prepared samples; mild conditions; improved precursor reaction rate.                                 | Poor purity; precursors may not be soluble; complex preparation.                 |

Combined with the advantages and disadvantages of the four preparation methods—the sol-gel method, hydrothermal method, microemulsion method, and atomic deposition method—the improvement measures of TiO<sub>2</sub> preparation in the future can be focused on improving the preparation efficiency, reducing the cost, optimizing the performance, and meeting specific application needs. Through the above different preparation methods, two or more preparation methods can be combined according to the need to prepare the new, more stable, and higher photocatalytic efficiency of terpolymer or multi-component modified TiO<sub>2</sub> photocatalytic materials.

#### 4. Modification Method of TiO<sub>2</sub> Photocatalyst

The direct preparation of TiO<sub>2</sub> sols can effectively solve the application challenges of TiO<sub>2</sub> particles, such as easy agglomeration and difficult loading [63]. However, TiO<sub>2</sub> nanocrystals in sol still face the problems of limited photoresponse range and high carrier complexation rate. To further enhance its photocatalytic performance, it is necessary to broaden the light absorption range of TiO<sub>2</sub> nanocrystalline sols and improve the separation efficiency of their photogenerated carriers by various modification methods.

##### 4.1. Precious Metal-Doped Titanium Dioxide

Precious metals and TiO<sub>2</sub> have different Fermi energy levels, and the work function of the metal is higher than that of the semiconductor TiO<sub>2</sub>; electrons usually tend to flow from the semiconductor to the metal when the two are in contact [64]. This cross-interface migration of electrons contributes to the efficient separation of electrons and holes in the semiconductor, as shown in Figure 6. Therefore, noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) can significantly enhance the photocatalytic activity of TiO<sub>2</sub> materials [65]. In these applications, noble metal nanoparticles play a key role in trapping or transferring photogenerated electrons [66].

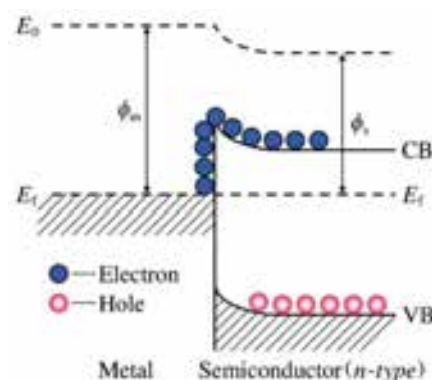


**Figure 6.** Schematic diagram of electron transfer in the noble metal deposition system [67].

The precious metal silver is relatively cheap and readily available [68]. Several studies, such as Chacon-Argaez [69], Borrego Pérez [70], etc., have found that the photocatalytic activity of composites is indeed significantly improved. Mohammed, W [71] et al. found that Schottky promoted electron transfer at Ag-TiO<sub>2</sub>, transferred the absorption to the visible region, reduced the band gap of TiO<sub>2</sub>, and inhibited electron-hole recombination, thus enhancing the photocatalytic activity and stability.

Other precious metal deposits, such as Wang et al. [72] promoted the interaction between Pt and TiO<sub>2</sub> by introducing oxygen vacancies through the carrier material, which facilitated the charge transfer from the carrier to Pt and exhibited excellent redox properties. Liu et al. [73] successfully prepared Au-TiO<sub>2</sub> nanoparticles by the hydrothermal synthesis method and found that the optical band gap value of the composites decreased due to the doping of Au or the formation of oxygen vacancies, etc., which induced a narrowing of the Au-TiO<sub>2</sub> band gap and increased visible light absorption, thus effectively degrading the MB.

The noble metal nanoparticles have a high specific surface area, good surface activity, and small particle size, which are characteristic of multiphase catalysis [74,75]. However, the catalytic activity may be limited by the limited ability of noble metals to absorb light at specific wavelengths [76,77]. In addition, the precious metal deposited TiO<sub>2</sub> is less efficient in utilizing visible light and requires higher energy of UV light for better catalytic effect. However, precious metals are expensive resources, and doping them into TiO<sub>2</sub> also increases the processing cost, which may be less economical in large-scale applications.

#### 4.2. Transition Metal-Doped Titanium Dioxide

Interestingly, doping a moderate amount of transition metal ions in TiO<sub>2</sub>, the electrons in the d- and f-orbitals can undergo a transition and enter into the TiO<sub>2</sub> structure, which reduces the bandgap and shifts the absorption edge to the visible region and reduces the rate of carrier complexation, thus improving the photocatalytic efficiency of TiO<sub>2</sub> [78]. At present, the transition metal doped ions are applied more: iron (Fe<sup>3+</sup>), copper (Cu<sup>2+</sup>), manganese (Mn<sup>2+</sup>), vanadium (V<sup>4+</sup>), zinc (Zn<sup>2+</sup>), etc [79].

##### 4.2.1. Doping with a Single Transition Metal Elements

When TiO<sub>2</sub> is doped with a single transition metal ion, the addition of the transition metal elements will change the lattice structure of TiO<sub>2</sub> and thus its crystal crystallinity since they have multiple valences. This change affects the compounding process of photogenerated electrons and holes, thus improving the photocatalytic activity. Meshram et al. [80] microwave synthesized TiO<sub>2</sub>-Al composite photocatalysts and found that the surface area and porosity of the composites were significantly reduced compared to their pristine components and were successfully used for the degradation of mixed azodyes such as methylene blue and rhodamine B. Zhu et al. [81] prepared iron-doped TiO<sub>2</sub> thin films, and concluded that the right amount of iron ions effectively inhibited the composite to enhance the photogeneration of the rate of electron holes and that the enhanced photoactivity of

Fe-doped TiO<sub>2</sub> samples was due to the generation of new elements to generate electronic states within the TiO<sub>2</sub> band gap. Mingmongkol et al. [82] prepared TiO<sub>2</sub>-doped composite photocatalysts with transition metal Cu and found that Cu doping did not cause any difference in the particle size or specific surface area, and on the other hand, the surface of the TiO<sub>2</sub> material doped with high concentration of Cu charge transfer had a negative effect. Cu-doped TiO<sub>2</sub> showed much greater photocatalytic degradation of methylene blue compared to undoped TiO<sub>2</sub>.

#### 4.2.2. Co-Doping of Transition Metal Elements

In contrast, co-doping transition metals may produce more complex effects. Co-doping implies the simultaneous introduction of two or more different transition metal ions into TiO<sub>2</sub>. Co-doping may further enhance the efficiency of photogenerated electron-hole separation through synergistic effects or broaden the light absorption range of TiO<sub>2</sub> by introducing new energy levels. Rao et al. [83] prepared Cu and Zn co-doped TiO<sub>2</sub> nano-photocatalysts and found that the addition of Cu and Zn to TiO<sub>2</sub> hindered the growth of nanoparticles, and there existed a more efficient electron-hole generation. Sukhadeve et al. [84] prepared Zn and Fe co-doped TiO<sub>2</sub> nanoparticles using a simple sol-gel process, and the absorption spectra of the prepared nanoparticles showed strong absorption in visible light. The synergistic effect produced by Zn and Fe blocked the photoinduced charge carriers and delayed the complexation probability, which greatly improved the RhB, MG, and MB mixture pollution degradation efficiency.

Transition metal elements have multiple valence, which can promote the chemical reaction in the electronic conduction of TiO<sub>2</sub>, but it is worth noting that the doping amount should be controlled. Otherwise, it is not conducive to the improvement of the catalytic performance, and dopants are prone to agglomeration [85], such as the surface of the enriched or even the formation of new phases, so that the effective surface area of the semiconductor material is reduced, resulting in a decrease in the activity [86].

#### 4.3. Rare Earth Metal-Doped Titanium Dioxide

Due to their unique electronic orbital structure [87], the doping of rare earth metal ions can adjust the energy level structure of TiO<sub>2</sub>, enabling it to absorb more light within the visible light range and thus enhancing photocatalytic activity [88]. Additionally, rare earth metal doping can introduce additional energy levels, promoting the separation of photogenerated electrons and holes [89]. It can also improve the photostability of titanium dioxide, enhancing its long-term stability and extending the lifespan of photocatalytic materials [90]. This opens up new possibilities for its application in environmental purification, water treatment, energy conversion, and other fields [91]. Common rare earth metals used for doping include ytterbium, erbium, holmium, lan, cerium, yttrium, and europium [92].

##### 4.3.1. Doping with a Single Rare Earth Metal Element

Single rare earth element doped TiO<sub>2</sub> is relatively easy to synthesize and can be more easily achieved in the TiO<sub>2</sub> lattice for control and regulation [93]. Ćurković et al. [94] prepared Ce doped TiO<sub>2</sub> nanocomposites by sol-gel method and found that the absorption of the composites in the visible light band was higher than that of pure TiO<sub>2</sub> nanomaterials, and three cycles could be reused. Ikram Benammar et al. [95] used a hydrothermal-assisted sol-gel method to prepare rare earth ytterbium and erbium-doped TiO<sub>2</sub>, respectively, and the optical properties were improved after heat treatment of the powders and down-conversion of erbium-doped nanoparticles was observed.

##### 4.3.2. Co-Doping with Rare Earth Metal Elements

Single transition metal element doping may not be able to fully optimize the energy band structure of TiO<sub>2</sub> [96], while rare earth element co-doping can extend the light absorption range of TiO<sub>2</sub>, enabling it to absorb wider wavelength bands of light [97],

enhancing the light absorption capacity and photoelectric conversion efficiency of  $\text{TiO}_2$ , and improving the stability of the catalyst surface [98].

Pascariu [99] et al. used electrospinning calcination of normal  $\text{TiO}_2$  doped with  $\text{Sm}^{3+}$  and  $\text{Er}^{3+}$  to demonstrate the stability and reusability of the catalyst in five repeated cycles of photodegradation of MB. Guetni et al. [100] designed a new co-doped  $\text{TiO}_2$  with Nd-Sm and La/Y apatite nanoparticles, which showed the highest degradation rate of 96.49% for azo dye Orange Yellow G within 105 min. Ren et al. [101] used the classical sol-gel method to prepare  $\text{TiO}_2$  nanoparticles co-doped with rare earth elements Ce and Er, as shown in Figure 7. The composite photocatalyst is a spherical particle with an uneven radius. It can be seen in Figure 7c that the polyhedral structure is mainly composed of hexagons and rhomboids, with an average size of 30 nm. The results show that Ce doping can reduce the band gap width of the composite and give it the ability to respond to visible light. At the same time, the upconversion luminescence characteristics of Er can convert near-infrared light in the solar spectrum into short-wave light that is more easily absorbed by  $\text{TiO}_2$ , thus enhancing the utilization rate of sunlight by the material. In addition, the doping of these two rare earth elements can effectively promote the separation and migration of photogenerated electrons and holes and optimize carrier utilization efficiency. Therefore, doped  $\text{TiO}_2$  nanoparticles show better photocatalytic performance.

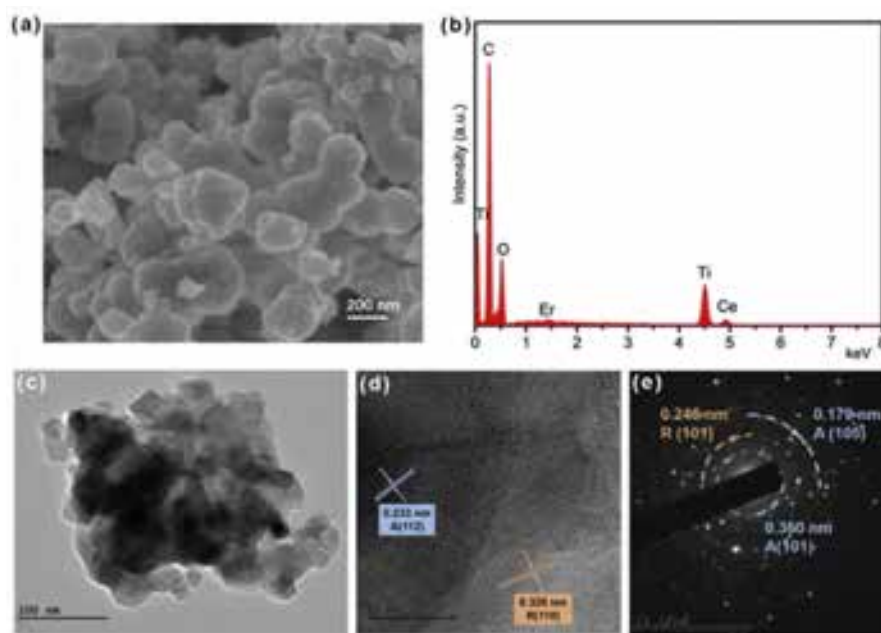


**Figure 7.** Characterizations of the  $\text{Er}_{0.5}\text{Ce}_{0.2}\text{Ti-O}$ : (a) SEM image; (b) EDS spectrum; (c) TEM image; (d) High-resolution TEM image; (e) selected area electron diffraction (SAED) pattern [101].

#### 4.3.3. Co-Doping of Rare Earth Elements with Other Elements

Co-doping of rare earth elements with other elements has also attracted extensive research [102,103]. Li Jia et al. [104] synthesized lanthanum, graphene oxide (GO), and  $\text{TiO}_2$  by sol-gel method to prepare an efficient photocatalytic material with visible light response. Lattice distortion occurred in the samples added with the rare earth element lanthanum, which increased the surface area of the photocatalyst and significantly improved the photocatalytic activity of  $\text{TiO}_2$ . The degradation efficiency of acid red B reached 95.6% after 5 h of simulated sunlight irradiation.

Co-doping of rare earth elements with other elements increases the separation efficiency of photogenerated electron-hole pairs and the number of surface active sites and improves the utilization efficiency of visible and infrared light. However, the co-doping of rare earth elements with other elements involves the synthesis and control of multi-element systems, so the preparation process and conditions are more complicated [105,106].

#### 4.4. Compound Semiconductors Based on Titanium Dioxide

Semiconductor compounding is a method used to enhance photocatalytic efficiency by combining different types of semiconductor materials to form heterojunctions, as exemplified in Figure 8, which depicts a p-n heterojunction formed by  $\text{TiO}_2$  and  $\text{ZnO}$ . The semiconductor composite effectively improves photocatalytic efficiency due to the following advantages:

1. By manipulating the size of the modified particles, the spectral absorption range and bandgap of the semiconductor material can be effectively tuned utilizing the quantum size effect [107,108].
2. Surface modification of  $\text{TiO}_2$  plays a role in improving the photostability of the semiconductor materials [109].
3. Given that light absorption in semiconductors mainly occurs at the band-edge, the semiconductor composite facilitates more efficient harvesting of sunlight [110].

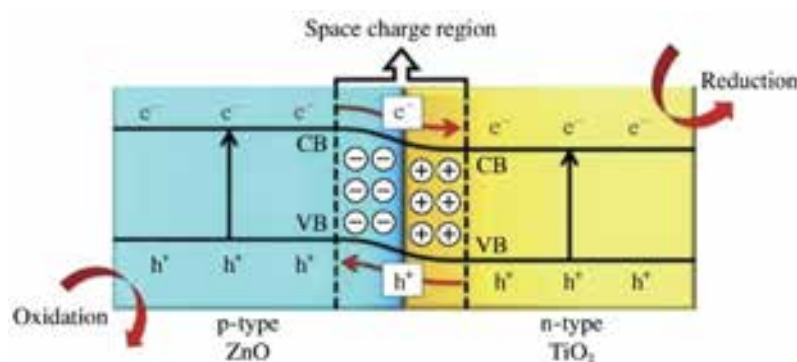


**Figure 8.** Schematic diagram of p-n junction formation between  $\text{TiO}_2$  and  $\text{ZnO}$  [110].

##### 4.4.1. Titanium Dioxide Composites with Common Semiconductors

Wongburapachart [111] et al. prepared  $\text{TiO}_2/\text{NiO-TiO}_2$  bilayer film photocatalyst (BLF) for photocatalytic degradation measurement using acid orange 7 (AO7) solution under light and dark conditions. It was found that compared with ordinary  $\text{TiO}_2$ , the photocatalytic activity of the prepared sample was increased by about 8 times after 48 h of AO7 degradation. Bai [112] et al. synthesized  $\text{TiO}_2/\text{ZnO}$  composites by the sol-gel method and the hydrothermal method and found that they have obvious heterostructures, which can reduce the band gap width and improve the light absorption intensity. The photocatalytic mechanism is shown in Figure 9. Ratanathavorn Wittawat et al. [113] prepared  $\text{TiO}_2/\text{ZnO}$  composite spherical particles.  $\text{TiO}_2/\text{ZnO}$  composite also showed much higher catalytic activity compared to a single component. In addition, Wang et al. [114] also prepared  $\text{ZnO-TiO}_2$  materials with different composite ratios and found that the specific surface area, pore volume, and pore diameter of  $\text{ZnO-TiO}_2$  composites were significantly larger than those of  $\text{TiO}_2$  and the  $\text{ZnO-TiO}_2$  composites were more surface acidic. The energy band structure facilitates the efficient separation of electrons and holes, and the catalytic reduction activity and selectivity are stronger. It is further shown that  $\text{TiO}_2$  composite with  $\text{ZnO}$  can inhibit  $\text{TiO}_2$  crystal transition and particle growth, and the UV absorption ability is enhanced [115]. Abumousa [116] et al. prepared ternary  $\text{TiO}_2/\text{Y}_2\text{O}_3@g\text{-C}_3\text{N}_4$  nanocomposites by a simple sonochemical method, which showed excellent photocatalytic properties in the degradation of Congo red dye, Malachite green, and other dyes in aqueous solutions in a short time. These binary semiconductor composites and ternary composites are based on  $\text{TiO}_2$  to form heterostructures, and the interface effect and energy band migration in the heterostructures can promote the transfer of photogenerated electrons and holes, thereby improving the rate and efficiency of the photocatalytic reaction.

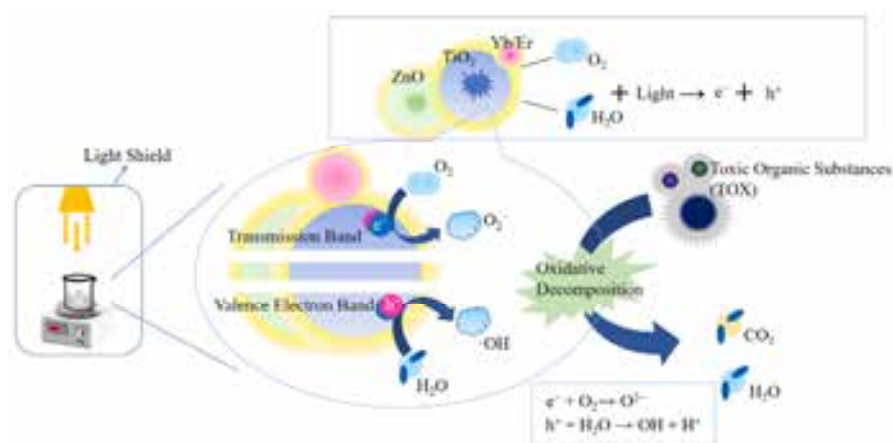


**Figure 9.** Proposed schematic diagram of the  $\text{TiO}_2/\text{ZnO}$  photocatalyst.

$\text{TiO}_2$  is composited with other semiconductors to form a composite semiconductor material. This new composite material broadens the excitation wavelengths available to the catalyst, effectively regulates the performance of individual materials, and generates numerous novel photochemical and photophysical properties. In recent years, numerous studies have been conducted on binary semiconductor composites, such as  $\text{TiO}_2/\text{ZnO}$ ,  $\text{TiO}_2/\text{CdS}$ ,  $\text{TiO}_2/\text{WO}_3$ , and  $\text{ZnO}/\text{ZnS}$ , among others. The photocatalytic performance of these compound semiconductors surpasses that of a single semiconductor.

#### 4.4.2. Titanium Dioxide Hybrid Materials with Graphene

In recent years, the modification of graphene composite  $\text{TiO}_2$  has become the focus of many researchers. Graphene with a two-dimensional structure has a large number of two-dimensional conjugated structures, so people combine graphene with  $\text{TiO}_2$  to enhance the photocatalytic performance of  $\text{TiO}_2$ , which has been extensively studied in this area. Heltina [117], Wang [118], and others prepared  $\text{TiO}_2$  with different graphene (GO) composite ratios compared to the pure  $\text{TiO}_2$  and the composite  $\text{TiO}_2/\text{GO}$  catalysts. The smaller grain size and higher adsorbed oxygen/lattice oxygen ratio exhibited superior photocatalytic performance. In addition, GO acts as a capture center for photogenerated electrons and transfers electrons to the target reactants, thus inhibiting the recombination rate of photogenerated electron-hole pairs and increasing the photocatalytic rate of  $\text{TiO}_2$ .

However, graphene tends to aggregate in solution to form clusters, which can lead to difficulties in controlling the homogeneity and dispersion of graphene in the composites [119], and the preparation of composites of titanium dioxide and graphene usually requires special synthesis techniques and equipment, which may lead to high preparation costs. This makes these composites difficult to commercialize on a large scale for some applications.

#### 4.5. $\text{TiO}_2$ Composite Polymers

Combining modified  $\text{TiO}_2$  with polymers can endow nanocomposite materials with new properties. Additionally, polymers can enhance the adsorption and photocatalytic performance of nano- $\text{TiO}_2$ , facilitating its separation and recovery [120].

Maeda et al. [121] first employed a phosphorus coupling agent to modify the surface of the modified  $\text{TiO}_2$  particles, aiming to enhance their compatibility with specific organic monomers (Figure 10).  $\text{TiO}_2/\text{PMMA}$  hybrids were successfully obtained through in situ polymerization. It can be observed that as the in situ polymerization time elongates, the PMMA polymer chains growing on the surface of  $\text{TiO}_2$  particles lead to an increase in the distance between the nanoparticles, thereby enhancing the transparency of the PMMA composites. This method maintains the flexibility, film forming, and electrical conductivity of the polymer. In addition, the composite may also exhibit better photocatalytic activity and antimicrobial properties.

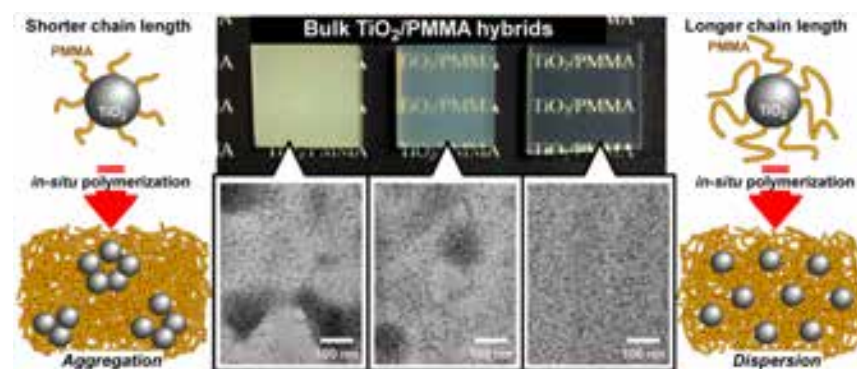


**Figure 10.** Appearance and TEM image of  $\text{TiO}_2$ /PMMA hybrid plate at different polymerization times [121].

Interestingly, Shi et al. [122] first coated stearic acid on the surface of  $\text{TiO}_2$  particles by impregnation method and then further modified it with paraffin wax to prepare  $\text{TiO}_2$  with Janus structure, which enhances the surface charge separation efficiency and adsorption capacity of organic matter (Figure 11). In addition, the modified Janus-like  $\text{TiO}_2$  can be used as an additive to stabilize Pickering emulsion, which in turn enhances its efficiency in degrading oil-phase pollutants in high-concentration kerosene and nitrobenzene wastewater.

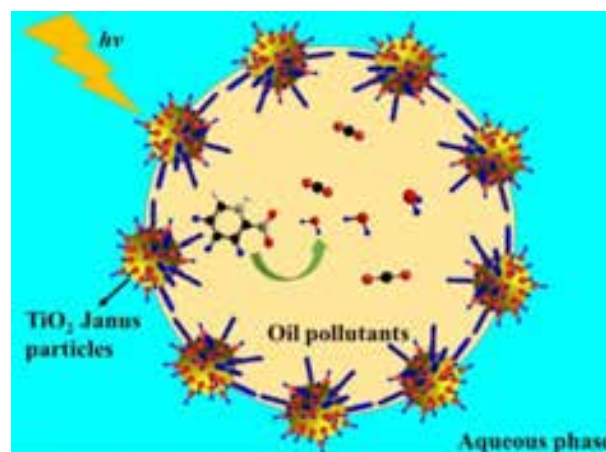


**Figure 11.** Photocatalytic mechanism diagram of modified  $\text{TiO}_2$ /polymer composites [122].

Nair [123] et al. fixed PANI- $\text{TiO}_2$  nanocomposites in polystyrene cubes to form PANI- $\text{TiO}_2$ @polystyrene cubes for photocatalytic degradation of acid yellow 17 (AY 17) dyes under visible light. And the photocatalytic activity was significantly improved. It provides a way to prepare more excellent new photocatalysts. Tran et al. [124] formulated different concentrations of acrylic acid (AA) mixed with isopropanol to modify the nano- $\text{TiO}_2$  and then uniformly coated it on the surface of polyvinylidene fluoride (PVDF) film. At high temperatures, AA reacts with PVDF, and nano- $\text{TiO}_2$  is fixed on the surface of the film to maintain its flexibility and film formation, which can improve the photocatalytic activity of the composite. Neves et al. [125] used polydimethylsiloxane-modified  $\text{TiO}_2$  nanoparticles to increase the surface roughness, enhance their hydrophobic strength and photocatalytic activity, and provide ideas for achieving complete degradation of polymers.

## 5. Summary and Outlook

In recent years, significant progress has been made in the field of  $\text{TiO}_2$  modified photodegradation of organic pollutants. Through a series of modification methods, the photocatalytic performance of  $\text{TiO}_2$  has been significantly improved, providing a more efficient and reliable solution for the photodegradation process of organic pollutants. The

following is a summary of the research progress in this field in recent years, including prospects of future research development.

### 5.1. Summary of Research Progress

- By doping precious metals, transition metals, rare earth metals, or non-metallic elements,  $\text{TiO}_2$  can change the band structure, broaden its light absorption range, and improve the separation efficiency of photoelectron-hole pairs, which can significantly improve the photocatalytic activity of  $\text{TiO}_2$ .
- $\text{TiO}_2$  was mixed with other semiconductor materials to form a composite photocatalytic material with a heterogeneous structure. This modification method can make use of the synergistic effect between different materials to improve the utilization efficiency of photogenerated electron-hole pairs and enhance photocatalytic performance. For example, the composite of  $\text{TiO}_2$  with  $\text{SiO}_2$ ,  $\text{ZnO}$ , and other materials can form heterogeneous structures and improve photocatalytic efficiency.
- By introducing functional material polymer on the surface of  $\text{TiO}_2$ , the surface properties of  $\text{TiO}_2$  are improved, and the photocatalytic performance is improved. Surface modification can increase the active sites on the surface of  $\text{TiO}_2$  and promote the separation and migration of photogenerated electrons and holes.

The five modification methods mentioned in this paper, the dopants commonly used, the specific surface area, the band gap energy, and degradation effects of the modified  $\text{TiO}_2$  photocatalyst are shown in Table 2.

**Table 2.** Characterization and degradation effect of modified  $\text{TiO}_2$  photocatalyst.

| Modification Methods of $\text{TiO}_2$               | Doping Agents   | The Surface Area (Before~After/ $\text{m}^2 \text{ g}^{-1}$ ) | Bandgap Energy (Before~After/eV) | Catalytic Effect                                                                                                | Reference |
|------------------------------------------------------|-----------------|---------------------------------------------------------------|----------------------------------|-----------------------------------------------------------------------------------------------------------------|-----------|
| Precious Metal-Doped $\text{TiO}_2$                  | Ag              | — —                                                           | 3.15~2.31                        | The degradation rate of methylene blue under visible light was 93%.                                             | [126]     |
|                                                      | Au              | 17.8~28.7                                                     | 3.15~2.9                         | Methyl orange is completely dissolved within 90 min.                                                            | [127]     |
|                                                      | Pt              | 42~68                                                         | 3.24~2.92                        | The degradation rate of Dichlo-Rophenoxyacid (2,4-D) was 99%.                                                   | [128]     |
| Transition Metal-Doped $\text{TiO}_2$                | Fe              | — —                                                           | 3.22~3.20                        | The removal rate of pollutants reached 97% within 240 min.                                                      | [129]     |
|                                                      | Mn              | 50~93.35                                                      | 3.20~2.21                        | The degradation rate of pollutants increased from 48.17% to 60.12%.                                             | [130]     |
|                                                      | Cu              | 43~46                                                         | 3.08~2.78                        | The reduction rate of organic carbon within 6 h is 75%.                                                         | [131]     |
| Rare Earth Metal-Doped $\text{TiO}_2$                | La              | — —                                                           | 3.16~3.12                        | The degradation rate of p-azo dye orange-yellow G was 96.49% in 105 min under UV-VIS spectral radiation.        | [100]     |
|                                                      | Er              | — —                                                           | 3.15~2.69                        | The degradation rate of methylene blue was 80% under visible light.                                             | [132]     |
|                                                      | Eu              | — —                                                           | 3.43~3.40                        | The degradation rate of Congo red reached 97%.                                                                  | [133]     |
| $\text{TiO}_2$ Composites with Common Semiconductors | ZnO             | 50.05~107.98                                                  | 3.26~2.76                        | Under sunlight irradiation, when pH is 5.8, the degradation efficiency of the dye is the highest, which is 92%. | [134]     |
|                                                      | $\text{SiO}_2$  | 217~256                                                       | 3.22~3.22                        | At 300 W Xenon lamp irradiation for 60 min, the degradation efficiency of TC is 96%.                            | [135]     |
|                                                      | $\text{BiVO}_4$ | 60.6~95.3                                                     | 3.2~3.03                         | The degradation rate of formaldehyde reached 97.1%.                                                             | [136]     |
|                                                      | $\text{WO}_3$   | 95~117                                                        | 3.0~2.6                          | Under no light conditions, the degradation rate of pollutants reached 22%.                                      | [137]     |

Table 2. Cont.

| Modification Methods of TiO <sub>2</sub> | Doping Agents                                        | The Surface Area (Before~After/m <sup>2</sup> g <sup>−1</sup> ) | Bandgap Energy (Before~After/eV) | Catalytic Effect                                                                                                                                                  | Reference |
|------------------------------------------|------------------------------------------------------|-----------------------------------------------------------------|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| TiO <sub>2</sub> composite polymers      | Triformyl chlorine-melamine polymer (TMP)            | 13~17                                                           | 3.78~2.82                        | It can degrade 96.1% RhB.                                                                                                                                         | [138]     |
|                                          | Polyaniline titanium Dioxide quantum Dots (PAN-TiQD) | — —                                                             | 2.95~2.82                        | The degradation rate of Dianix blue dye reached 91%.                                                                                                              | [139]     |
|                                          | Polydopamine (PDA)                                   | — —                                                             | 3.22~3.15                        | The photocatalytic CO <sub>2</sub> reduction yield of CH <sub>4</sub> by the composite was up to 1.50 μmol/g·h, which was 5 times that of pure TiO <sub>2</sub> . | [140]     |

In summary, the modified TiO<sub>2</sub> photocatalyst significantly improves its photocatalytic performance in UV and visible light by increasing the specific surface area and reducing the band gap energy. The larger specific surface area increases the catalyst’s active site and improves the contact efficiency with pollutant molecules, while the reduced band gap energy enables the catalyst to absorb a wider spectrum, including visible light, thereby broadening the photoresponse range and enhancing the utilization of sunlight. In addition, the specific modification method can further promote the separation and migration of photogenerated electrons and holes and further improve photocatalytic efficiency. These improvements make the modified TiO<sub>2</sub> photocatalyst show a broader application potential in the field of environmental governance and new energy development.

The photocatalytic performance of TiO<sub>2</sub> was improved to varying degrees. However, due to problems such as low efficiency, insufficient stability, and secondary pollution, TiO<sub>2</sub> modification methods cannot be widely used. The advantages and disadvantages of TiO<sub>2</sub> modification methods are shown in Table 3.

Table 3. Advantages and disadvantages of TiO<sub>2</sub> modification methods.

| Modification Methods                      | Advantages                                                                                                                                                                                                         | Disadvantages                                                |
|-------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|
| TiO <sub>2</sub> -doped noble metals      | High specific surface area; good surface activity; good stability; characteristics of multiphase catalysis.                                                                                                        | Inefficient use of visible light; Expensive precious metals. |
| TiO <sub>2</sub> -doped transition metal  | The presence of polyvalent transition metals promotes chemical reactions, modulates the electronic structure of TiO <sub>2</sub> to improve its photocatalytic properties, and extends the light absorption range. | Prone to focusing; not environmentally friendly.             |
| TiO <sub>2</sub> -doped rare earth metals | Good stability; high catalytic activity; expanding the range of TiO <sub>2</sub> light absorption and promoting photocatalytic reactions.                                                                          | Complicated operating procedures; not easy to recycle.       |
| TiO <sub>2</sub> compound semiconductors  | Formation of heterojunctions to expand the light absorption range of the material and improve photocatalytic efficiency. Reduction in electron-hole complex reaction.                                              | The complexity of design and preparation.                    |
| TiO <sub>2</sub> composite polymers       | More environmentally friendly; Mechanical properties will be improved; Can be repeated many times.                                                                                                                 | The dispersion is not good; May degrade the polymer matrix.  |

5.2. Future Research Direction and Development Trend

Although TiO<sub>2</sub> modified photodegradation of organic pollutants has made remarkable progress, there are still some key problems and shortcomings. First, the stability of the modification effect is still a challenge, which can lead to performance fluctuations in practical applications. Secondly, the high preparation cost limits the possibility of large-scale

applications. Therefore, future research needs to further explore and optimize modification methods to improve their stability and reduce costs.

In addition, the importance of mechanism research cannot be ignored. Strengthening the mechanism study can not only provide solid theoretical support for the optimization of modification methods but also help us to understand more deeply the reaction mechanism of TiO<sub>2</sub> photocatalytic degradation of organic pollutants. This will lay the foundation for the design of more efficient and stable TiO<sub>2</sub> photocatalytic materials.

In practical applications, the effect of TiO<sub>2</sub> photocatalytic degradation of organic pollutants may be affected by a variety of factors, including water quality, light conditions, dye type, and concentration. Therefore, future research also needs to focus on how to optimize the performance of TiO<sub>2</sub> photocatalytic degradation of organic pollutants in various real-world environments.

In conclusion, optimizing the preparation method and process of TiO<sub>2</sub> composite photocatalytic materials has become an important direction of future research on the photodegradation of organic pollutants. By introducing visible light absorbing inorganic substances or modifying TiO<sub>2</sub>, we can prepare multi-functional composite materials that can expand the range of light absorption and, at the same time, play the role of photocatalysis, adsorption, and catalysis, thus significantly improving the degradation efficiency of organic matter. With continuous research and exploration, we look forward to developing more efficient, stable, and environmentally friendly TiO<sub>2</sub> photocatalytic materials, making important contributions to environmental protection and sustainable development.

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**Data Availability Statement:** No new data were created or analyzed in this study. Data sharing is not applicable to this article.

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## Review

# Morphological Dependence of Metal Oxide Photocatalysts for Dye Degradation

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**Abstract:** There is no doubt that organic dyes currently play an indispensable role in our daily life; they are used in products such as furniture, textiles, and leather accessories. However, the main problems related to the widespread use of these dyes are their toxicity and non-biodegradable nature, which mainly are responsible for various environmental risks and threaten human life. Therefore, the elimination of these toxic materials from aqueous media is highly recommended to save freshwater resources, as well as our health and environment. Heterogeneous photocatalysis is a potential technique for dye degradation, in which a photocatalyst is used to absorb light (UV or visible) and produce electron–hole pairs that enable the reaction participants to undergo chemical changes. In the past, various metal oxides have been successfully applied as promising photocatalysts for the degradation of dyes and various organic pollutants due to their wide bandgap, optical, and electronic properties, in addition to their low cost, high abundance, and chemical stability in aqueous solutions. Various parameters play critical roles in the total performance of the photocatalyst during the photocatalytic degradation of dyes, including morphology, which is a critical factor in the overall degradation process. In our article, the recent progress on the morphological dependence of photocatalysts will be reviewed.

**Keywords:** organic dyes; wastewater treatment; photocatalyst; photocatalytic degradation; metal oxides; morphology



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## 1. Introduction

Due to the growth of societies and the speeding up of industry over the last few decades, environmental pollution is considered the biggest challenge facing our societies [1]. Almost all activities of humans to produce commodities and services lead to the creation of environmental contaminants. These pollutants cause harm to the health of people, plants, animals, and microbes when they are discharged into the air, water, and soil [2]. Since humans depend on the creation and enhancement of commodities and services to survive on earth, these practices cannot be completely abandoned [2]. Major contributors toward aquatic pollution include industrial dyes, which are the greatest class of organic pollutants [3,4]. Due to their intricate chemical compositions, the majority of synthetic dyes are poisonous and extremely durable. Currently, synthetic dyes as organic compounds or mixtures are widely utilized in the leather, pharmaceutical, food, cosmetic, color photography, paper printing, textile dyeing, and textile dyeing industries [5–8].

The last two decades have seen a dramatic rise in public understanding of the toxic and cancer-causing effects of many pollutants that were previously not thought to be dangerous [2]. Some man-made chemicals can linger in the environment for a very long time without degrading, in contrast to naturally occurring compounds that break down immediately. These substances, which include pesticides, organochlorines, polychlorinated biphenyls, synthetic polymers, and synthetic dyes, are regarded as the main environmental contaminants [9]. Most dyes are organic, multidimensional compounds with the property of adhering to various surfaces, including fabrics, leathers, and others. The paper, textile, dyestuff, and distilling industries release highly colored wastewaters [10]. By increasing the demand for dyes, a larger amount of water is polluted [11,12]. As reported by Couto et al., in traditional dyeing processes, each 1 kg of textile materials required about 100 L of water to obtain the final product [5]. As per O'Neill et al., not every type of dye adheres to fabric, and their discharge in wastewater varies. Basic dyes may lose up to 2% while reactive dyes can lose up to 50%, resulting in the contamination of surface and ground waters in the dyeing industries [13].

It has been reported that each year about 280,000 tons of textile dyes are released into industrial wastewater by the textile industry [14]. In general, it is thought that throughout the industrial processes, roughly 12% of the total generated synthetic dyes, including methyl orange (MO), methyl red (MR), methylene blue (MB), rhodamine B (RhB), remazol brilliant blue (RB), congo red (CR), and many others, are lost [3,15]. Additionally, 15–20% of global dye production is wasted during the dyeing process and released into water without additional treatment, resulting in significant environmental damage [16]. The presence of color in dye effluents serves as a clear indicator that water is contaminated since it is easier to see, and the discharge of these strongly colored effluents can directly impact the receiving waterways [17]. Even a very small concentration ( $1 \text{ mg L}^{-1}$ ) of synthetic dyes in water can generate color and create an unfavorable concentration for ingestion, and also can significantly harm the environment and pose substantial health risks [18]. When utilizing the untreated dyeing effluents in agriculture purposes, both the environment and human health are badly affected [19]. In light of the harmful and cancer-causing properties associated with dyes, and considering that numerous dyes are known carcinogens, significant recent endeavors have been directed towards regulating the release of dyes into the environment [20,21]. The remediation of dye wastewaters can be accomplished using various techniques. A variety of procedures are involved, comprising biological and microbiological methods, along with physicochemical techniques such as adsorption, chemical oxidation, precipitation, coagulation, filtration, electrolysis, and photodegradation [22]. Based on its suitability, each strategy can be used to target a certain class of toxins and offers advantages of its own. Despite their usefulness, physicochemical techniques often suffer from several limitations, including high costs, low efficiency, limited flexibility, susceptibility to interference from other wastewater constituents, and the challenge of managing the waste generated [18].

Therefore, it is crucial to develop affordable, effective, and environmentally friendly methods to reduce the amount of dye in wastewater [5]. Advanced oxidation processes (AOPs) can be used for treating most industrial effluents. Among the numerous AOPs that are recognized, photocatalytic degradation has emerged as a promising method for destroying organic substances [23,24]. The photodegradation process of dyes involves oxidizing large dye molecules into smaller ones such as water, carbon dioxide, and other byproducts. Compared to other AOPs, photocatalytic degradation is more successful since semiconductors are less expensive and can easily mineralize a variety of organic molecules. The materials used as effective photocatalysts should have an appropriate energy band gap, appropriate morphology, high surface area, long term stability, and considerable recycling ability [25,26]. Due to the high surface-to-volume ratio of nanomaterials, more surface area is available for redox reactions. In recent years, metal oxides have garnered significant interest in environmental remediation due to their ability to generate charge carriers upon activation by sufficient energy [27]. Numerous metal oxide nanoparticles

have been employed as photocatalysts in the past, including zinc oxide (ZnO), titanium dioxide (TiO<sub>2</sub>), copper oxide (CuO), nickel oxide (NiO), and tungsten oxide (WO<sub>3</sub>). This is a result of their potential optical, chemical, and physical capabilities, including their distinct electronic structures, abilities to absorb light, and capacities for charge transport [28]. The composition, size, doping, and shape of metal oxides are only a few of the variables that might influence their photocatalytic activity. These factors are all crucial for photocatalytic activity [29–32]. This study mainly reviews the recent progress on the morphologically dependent photocatalytic activity of the metal oxides toward degradation of organic dyes from aqueous solutions. From the metal oxides, TiO<sub>2</sub>, ZnO, CuO, NiO, and WO<sub>3</sub>, with various morphologies, will be presented. To provide a big picture, our article starts with an introduction that outlines the dye classifications and their environmental problems. Additionally, this article outlines the principle of the photocatalytic process and the different photocatalytic reaction mechanisms.

In addition, this review presents a comprehensive study of the recent progress made in the field of the morphological dependence of photocatalysts for the photocatalytic degradation of organic dyes. It discusses the latest developments in the synthesis and characterization of metal oxide photocatalysts with tailored morphologies. Furthermore, it analyzes the underlying mechanisms governing morphology-induced effects and provides insights into the prospects and challenges in this research area.

According to publication records during the last decade, there were about 77,214 publications on photocatalysis. The research output on photocatalysis has continued growing with time, with 4155 and 10,550 publications in 2013 and 2023, respectively, as shown in Figure 1. Among the metal oxides, most publications investigated TiO<sub>2</sub>, ZnO, CuO, NiO, and WO<sub>3</sub> materials.

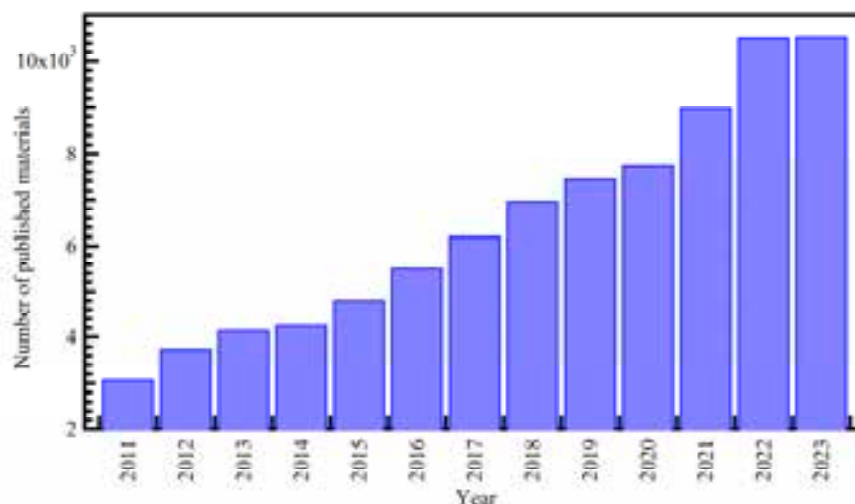


**Figure 1.** Distribution of the cumulative number of publications on photocatalysis per year from the Scopus database (November 2023).

## 2. Principles of Photocatalysis

In the last decades, the use of photocatalysis technology as a quick, affordable, and efficient way to get rid of the majority of poisonous dyes has received a lot of interest [33–35]. Photocatalysis is a field that utilizes catalysts to enhance the speed of some chemical reactions. A photocatalyst is a material capable of absorbing light, generating electron–hole pairs that enable the participants in a reaction to undergo chemical transformations [36]. The primary factor behind photocatalytic activity (PCA) is the catalyst’s capability to produce electron–hole pairs, which leads to the creation of free radicals such as hydroxyl radicals (•OH). These radicals can then undergo secondary reactions. There are two primary categories of photocatalytic reactions: homogeneous photocatalysis and heterogeneous

photocatalysis. The ability of any specific photocatalytic technique to work properly depends on several characteristics, including bandgap, shape, and high surface area [37].

Since dyes are colored, it is simple to track how they change color throughout the experiment. The dye sample is exposed to UV light for a predetermined amount of time in the photocatalytic process. The variations in solution color are then measured in terms of decreasing absorbance using a spectrophotometer. The degree of discoloration ( $\tau$ ) is determined from the dye absorption before and after irradiation by the following relation (Equation (1)) [38].

$$\tau = 1 - \frac{A_i}{A_o} * 100 \quad (1)$$

The equation includes  $A_o$ , which denotes the absorbance of the dye solution before irradiation, and  $A_i$ , which represents the absorbance of the dye solution after irradiation.

Heterogeneous photocatalysis is an environmentally friendly, low-cost method of decontaminating organic materials. Organic contaminants can be effectively reduced through heterogeneous photocatalysis in both the atmosphere and water. The mechanism of the photocatalytic degradation of organic pollutants has been previously discussed by several groups [39,40]. Usually, sunlight in the presence of a semiconductor photocatalyst is utilized to speed up the removal of environmental contaminants and the obliteration of extremely harmful compounds [41]. The process of heterogeneous photocatalysis comprises five sequential steps: (i) transferring the reactants from the liquid phase to the catalyst surface; (ii) adsorbing the reactants onto the catalyst surface; (iii) enabling the reaction to occur in the adsorbed phase; (iv) desorbing the final product; and (v) removing the final products from the liquid phase [42].

The following steps are stated as the mechanism of dye and other organic compound degradation via photocatalysis: When the catalyst is exposed to UV light, electrons move from the valence band (VB) to the conduction band (CB), resulting in the formation of an electron-hole pair (Equation (2)) [43,44].

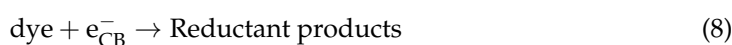


Here,  $e_{CB}^-$  and  $h_{VB}^+$ , respectively, represent the electrons in the CB and the holes in the VB.

The produced excited substances (excitons) may travel to the catalyst surface and engage in a redox reaction with other species already there. Usually,  $h_{VB}^+$  may readily form  $\bullet\text{OH}$  radicals through the reaction with surface-bound  $\text{H}_2\text{O}$  molecules (Equation (3)), whereas  $e_{CB}^-$  can produce superoxide radical anions of oxygen through the reaction with  $\text{O}_2$  (Equation (4)) [42].



The combination of the electron and the hole created in the first step is prevented by this reaction. The  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$  that are created in the following equations react with the dye to create additional species, which results in the dye discoloration.



Due to the presence of dissolved oxygen and water molecules, all above reactions are possible in photocatalysis. In Figure 2, the pathways of oxidative species formation in photocatalytic research are presented schematically.

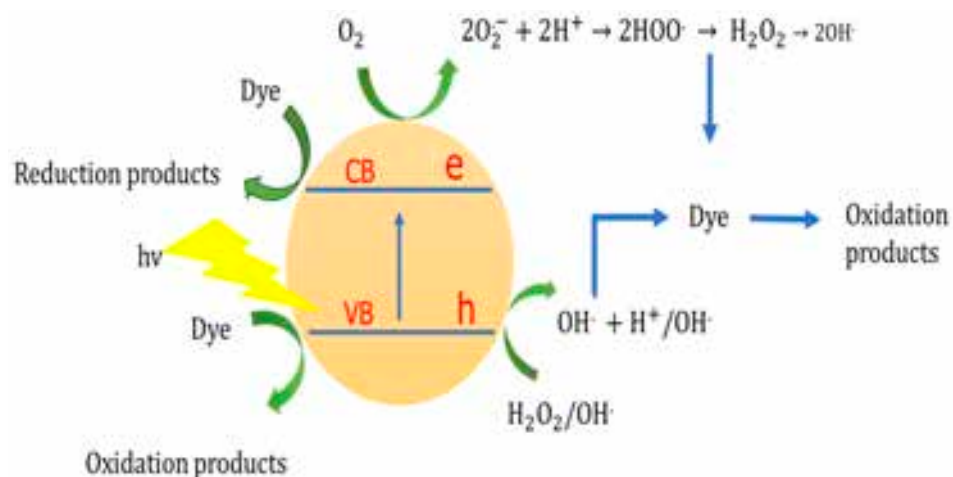


**Figure 2.** The mechanism of the oxidative species in heterogeneous photocatalysis. Adopted with permission from Ref. [42] Copyright 2017, Royal Society of Chemistry.

### 3. Mechanisms of Photocatalyzed Dye Degradation

There are two main pathways for photocatalytic reactions, as described below.

#### 3.1. Direct Photocatalytic Pathway

There are two proposed mechanisms describing heterogeneous photocatalysis.

##### 3.1.1. The Langmuir–Hinshelwood Model

This model is used to describe the mechanism of solid catalytic reactions [45]. As reported in the published review by Uyen N. P. Tran et al. [46], typically, the L–H mechanism model consists of four sequential steps: (1) molecules are absorbed on a catalytic surface, (2) adsorbed molecules dissociate, (3) products are produced by reactions between dissociated molecules, and (4) products are liberated to the medium. Usually, this model is used to study the heterogeneous catalytic degradation of organic pollutants in wastewater [47,48].

Based on step (1), the adsorption and desorption rate can be expressed as Equations (9) and (10).

$$r_a = k_a(1 - \theta)C_p \quad (9)$$

$$r_d = k_d\theta \quad (10)$$

Here,  $k_a$  and  $k_d$  are the adsorption and desorption rate constants,  $\theta$  is a fraction of the coverage site, and  $C_p$  is the concentration of pollutant “p”.

At equilibrium,  $r_a = r_d$ , which results in Equation (11) [49].

$$\theta = \frac{kC_p}{1 + kC_p} \quad (11)$$

$k$  = the equilibrium constant,  $k = \frac{k_a}{k_d}$

Usually, the photocatalytic degradation of an organic pollutant (P) occurs after adsorption; thus, the degradation rate is proportional to  $\theta$ , as shown in Equation (12) [45].

$$r_{deg} = k_{deg}\theta = \frac{k_{deg}kC_p}{1 + kC_p} \quad (12)$$

Here,  $k_{deg}$  is the degradation rate constant.

Based on the rate law of chemical reaction, the rate of the degradation can also be expressed by the following relation:

$$r_{deg} = -\frac{dC_p}{dt} \quad (13)$$

By combining Equations (12) and (13), L–H kinetic model can be obtained.

$$-\frac{dC_P}{dt} = \frac{k_{deg}kC_P}{1 + kC_P} \quad (14)$$

By integrating Equation (14) from  $C_P = C_{P,0}$  at  $t = 0$  to  $C_P$  at the interval time,  $t$ :

$$\frac{1}{k_{deg}k} \ln \frac{C_P}{C_{P,0}} + \frac{1}{k_{deg}}(C_P - C_{P,0}) = -t \quad (15)$$

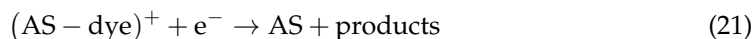
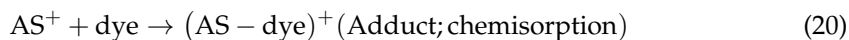
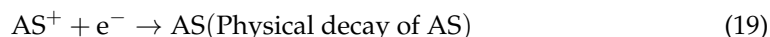
$$\frac{-t}{C_P - C_{P,0}} = \frac{1}{k_{deg}} + \frac{1}{k_{deg}k} \ln \left( \frac{C_P}{C_{P,0}} \right) / (C_P - C_{P,0}) \quad (16)$$

By linearly plotting the above equation, the obtained intercept and slope are  $\frac{1}{k_{deg}}$  and  $\frac{1}{k_{deg}k}$ , respectively.

According to previous studies, the kinetic of the photocatalytic degradation is fitted well with the L–H model. For instance, Cao et al. showed that the kinetics of the photodegradation of gaseous benzene by nitrogen-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) under visible light irradiation agreed with the L–H model [50]. Another study by M. Klumpp et al. [51] confirmed that the experimental data of the degradation of rhodamine B (RhB) by TiO<sub>2</sub> thin film also agreed with L–H model. Furthermore, Yang et al. [52] reported that the catalytic photodegradation of norfloxacin and enrofloxacin under visible light irradiation with bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) synthesized by combining ultrasonic solvothermal treatment and high-temperature calcination adopted the L–H kinetic model with a high correlation coefficient ( $R^2 > 0.95$ ).

### 3.1.2. The Eley–Rideal Model

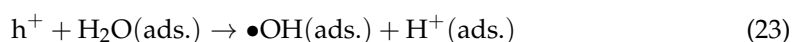
In this method, the holes are first photo-created, then the free charged carriers are trapped by surface flaws. The dye is then chemically altered by the active centers (AS) to produce an adduct species such as (S-dye)<sup>+</sup>, which can then degrade further to produce products or recombine with electrons. The subsequent reactions depict the reaction structure [34,53]:

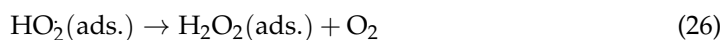
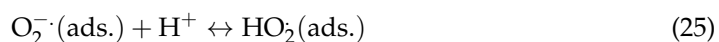


### 3.2. Indirect Photocatalytic Pathway

On the surface of the catalyst, electron–hole pairs are photogenerated during this process. After that, water molecules trap the holes and create H<sup>+</sup> and •OH radicals. The •OH radicals can attack the dye to produce intermediates and finished products, or they can interact with one another to form H<sub>2</sub>O<sub>2</sub>. The superoxide radical, which can start a chain reaction that produces HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, can also trap the electron by binding to molecules of oxygen.

The organic molecule is oxidized as a result of all these radicals being produced, creating intermediates and finished products [54]. The following equations serve as examples of the mechanism [54]:





The photodegradation efficiency and oxidation rates of a photocatalytic system are heavily dependent on various operational parameters. These parameters play a crucial role in regulating the degradation of organic molecules and include the effects of the dye concentration, catalyst dose, solution pH, light intensity, and exposure period. A comprehensive discussion of all these factors can be found in the literature [47,54].

#### 4. Morphological Dependence of Metal Oxide Photocatalysts

Due to their capacity to produce charge carriers when stimulated with effective energy, metal oxides are generally of great interest in both environmental remediation and electronics. Numerous metal oxide nanoparticles have been utilized as photocatalysts and adhere to the fundamental principles of photocatalytic activity [28,55,56]. The first step in the photocatalytic reaction is the absorption of light, which separates charges and creates ( $\text{h}^+$ ) positive holes that can oxidize substrates [57]. The metal oxide is activated by exposure to UV light, visible light, or a combination of both. Consequently, photoexcited electrons are raised from the valence band to the conduction band, forming an electron–hole pair ( $\text{e}^-/\text{h}^+$ ). This generated pair ( $\text{e}^-/\text{h}^+$ ) has the capability to either reduce or oxidize a compound adsorbed on the photocatalyst's surface. These excitons initiate the oxidation or reduction of substrates and reactants on the surface of photocatalysts. The photocatalytic efficacy of the metal oxide originates from two distinct mechanisms: (i) the generation of  $\bullet\text{OH}$  radicals through the oxidation of  $\text{OH}^-$  anions and (ii) the production of  $\text{O}_2^{\cdot-}$  radicals through the reduction of  $\text{O}_2$ . Both these radicals and anions can subsequently interact with pollutants, resulting in their degradation or conversion into less harmful byproducts. These produced radicals and anions cause contaminants to degrade and change into byproducts with low risks [58]. In the following sections, the recent progress on the morphological dependence of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CuO}$ ,  $\text{NiO}$ , and  $\text{WO}_3$  in the degradation of organic dyes in aqueous media will be presented.

##### 4.1. Titanium Dioxide Photocatalysts

Since Fujishima and Honda's great discovery of water splitting in 1972 [59], great attention has been paid to utilizing the photocatalytic properties of some materials to convert solar energy into chemical energy for the oxidation or reduction of materials to produce useful materials such as hydrogen [60] and hydrocarbons [61], as well as to remove pollutants and bacteria from air, water, wall surfaces, and other environments [62,63].

$\text{TiO}_2$  has four polymorphs in nature, namely, tetragonal anatase, orthorhombic brookite, tetragonal rutile, and monoclinic. Two extra high-pressure forms were also produced using the rutile,  $\text{TiO}_2$ , and hollandite structures. Rutile, which is the most stable form of  $\text{TiO}_2$ , is the primary source of this compound. Conversely, anatase and brookite are metastable and transform into rutile during calcination [64].  $\text{TiO}_2$  is categorized as an n-type semiconductor and has varying energy bandgaps depending on its crystalline form. The energy bandgap is approximately 3.2 eV for anatase, 3.0 eV for rutile, and 3.2 eV for brookite [42]. Among the many different photocatalysts,  $\text{TiO}_2$  has received the most attention and has been utilized in the most applications. This is due to its potent oxidizing properties [65–68], its ability to degrade organic pollutants [69], its superhydrophilicity [70], its chemical stability, long durability, nontoxicity, low cost, and transparency to visible light [62,71], as well as its good anti-corrosion performance, high mechanical strength, low density, and a competitive price.

TiO<sub>2</sub> exhibits photocatalytic properties by producing photogenerated charge carriers upon absorption of UV light which correspond to the energy band gap of TiO<sub>2</sub>. These photogenerated holes in the valence band (VB) move to the TiO<sub>2</sub> surface and interact with adsorbed water molecules, resulting in the formation of hydroxyl radicals (•OH). Nearby organic molecules on the catalyst's surface are oxidized by the photogenerated holes and the •OH radicals. Meanwhile, superoxide radical anions (O<sub>2</sub><sup>•−</sup>) are typically produced when molecular oxygen in the air reacts with electrons in reduction processes in the CB.

It has been reported that using pristine TiO<sub>2</sub> is not recommended because of its low electron transfer rate, light absorption, and electron–hole pair recombination. Thus, TiO<sub>2</sub> is produced in various nanostructures to improve electron transport and reduce electron–hole recombination in order to weaken these restrictions [72]. Several factors can significantly impact the effectiveness of photocatalytic systems, such as the size, specific surface area, pore volume, pore shape, crystalline phase, and exposed surface facets of the photocatalyst. Morphological factors can also affect photocatalytic performance as well as the properties of TiO<sub>2</sub> materials. Therefore, recently, there has been a lot of interest in the preparation of TiO<sub>2</sub> nano- or micro-structures with various morphologies [73,74], and a variety of TiO<sub>2</sub> nanostructural materials have been created, including spheres [74,75], nanorods [76], fibers [77], tubes [78], sheets [79], and interconnected architectures [80]. Due to their interconnected structure, three-dimensional (3D) monoliths may have high carrier mobility and be used in environmental decontamination as opposed to two-dimensional (2D) nanosheets, which have flat surfaces and good stickiness [69,81,82]. In the following section, the photocatalytic properties of TiO<sub>2</sub> with various morphologies are used for the breakdown of organic pigments.

In the last decade, Zhen et al. [83], simply treated amorphous anodic TiO<sub>2</sub> nanotubes (TiO<sub>2</sub> NTs) in situ hydrothermally at 70 °C to prepare anatase porous TiO<sub>2</sub> nanowires (TiO<sub>2</sub> NWs) (Figure 3a–f). The estimated BET surface area of the prepared TiO<sub>2</sub> NWs was 267.56 m<sup>2</sup> g<sup>−1</sup>, nearly four times that of the utilized amorphous anodic TiO<sub>2</sub> NTs. The photocatalytic capability of porous TiO<sub>2</sub> NWs towards MB and Rhodamine 6G (Rh6G) were studied. Compared to TiO<sub>2</sub> NTs or Degussa P25, the porous TiO<sub>2</sub> NWs had superior photocatalytic activity (Figure 3g,h). The porous design and the substantial specific surface area are responsible for the increased photocatalytic activity.

Furthermore, anatase TiO<sub>2</sub> NWs were prepared by Lou et al. [84] using a facile one-pot solvothermal approach (Figure 4). Due to the high productivity and yield of the solvothermal reaction, a significant amount of what appears to be white mud is produced afterward. The choice of the DMF/HAc volumetric ratio in the solvent system used for synthesis determines whether the TiO<sub>2</sub> NWs assemble into hierarchical architectures or remain in freestanding form. The 1D nanostructure with outstanding photocatalytic activity for RhB degradation was perfectly preserved in both the synthesized and the annealed TiO<sub>2</sub> NWs.

Recent studies on the morphology of TiO<sub>2</sub> nanostructures in the photocatalytic degradation of several organic dyes (MB, MV, MO) have been published by Zhang et al. [85]. The balanced angle deposition technique (GLAD) was used to create nanorod, nanohelic, and nanozigzag TiO<sub>2</sub> nanofilms (Figure 5a). It can be observed that the morphology displayed significantly influences the performance of the photocatalytic degradation under UV-Vis light irradiation (Figure 5b,c). This is mostly explained by the variation in the produced nanostructures' specific surface area and pore volume. TiO<sub>2</sub> nanozigzag films demonstrate superior degradation capabilities compared to nanohelics and nanorods due to their extensive surface area, increased porosity, distribution of active sites at varying pore lengths, and the existence of oxygen vacancies.

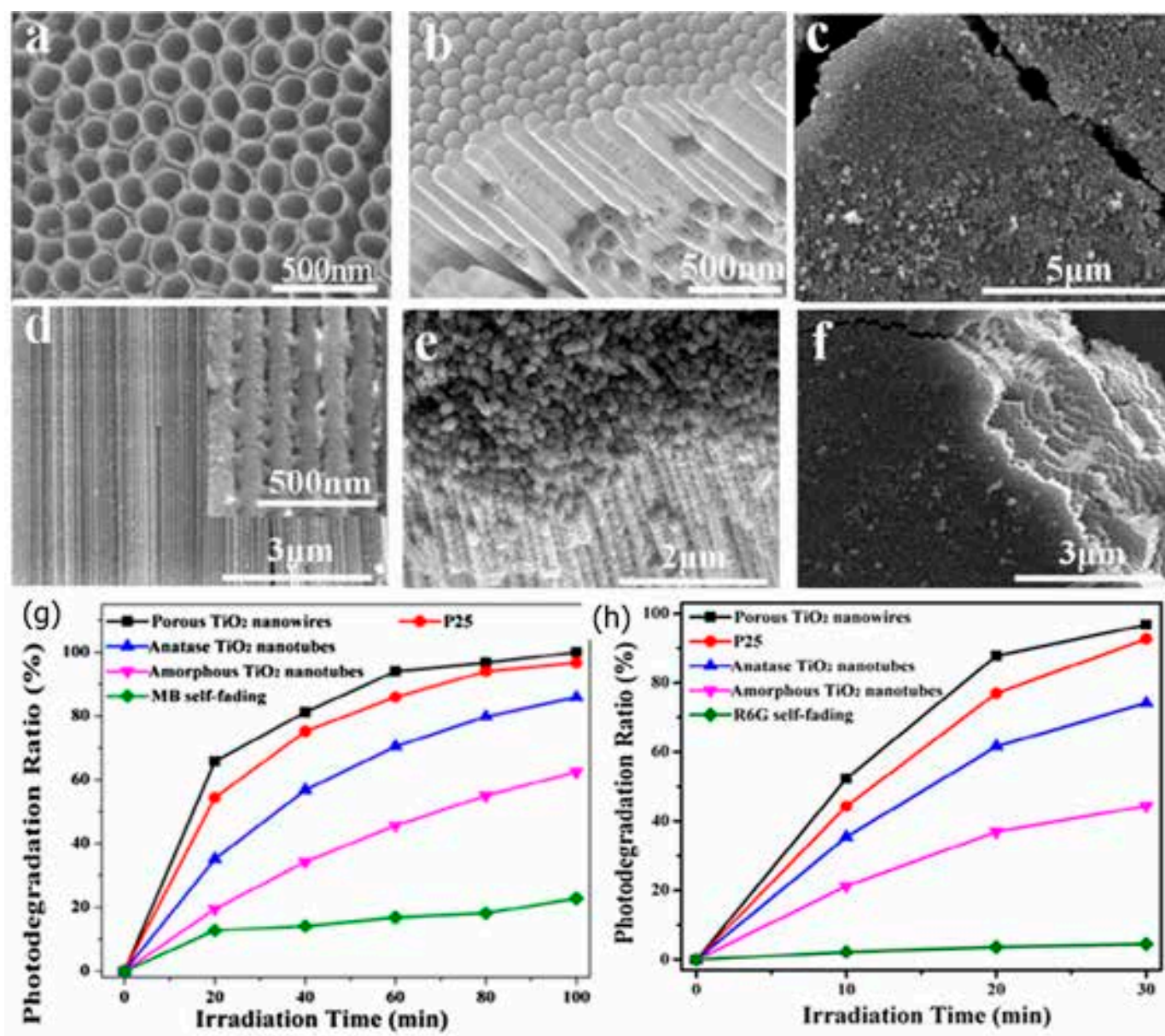


**Figure 3.** (a) SEM image of the anodic TiO<sub>2</sub> NTs, (b) cross-section and surface view image of the bottom side of the anodic TiO<sub>2</sub> NTs, (c) the porous TiO<sub>2</sub> NWs, (d) cross-section image of the porous TiO<sub>2</sub> NWs, (e) high and (f) low magnification cross-sections and surface views of the porous TiO<sub>2</sub> NWs. The photocatalytic degradation performance of (g) MB and (h) R6G with time of irradiation. Adopted with permission from Ref. [83] Copyright 2013, Elsevier.

By carefully hydrolyzing titanium tetrachloride (TiCl<sub>4</sub>) with a homemade glass apparatus, Zidki et al. [86] prepared TiO<sub>2</sub> nanoparticles. The photoactive anatase and brookite phases make up the TiO<sub>2</sub> nanoparticles, as indicated by XRD and TEM/HRTEM image studies (Figure 6a,b). The photodegradation of MB and CR under UV–Vis light was used to illustrate the photocatalytic activity of TiO<sub>2</sub> nanoparticles. The degradation of MB showed that, in contrast to the CR degradation, the photocatalytic degradation of MB on TiO<sub>2</sub> nanoparticles is more effective in an alkaline environment (Figure 6c,d).

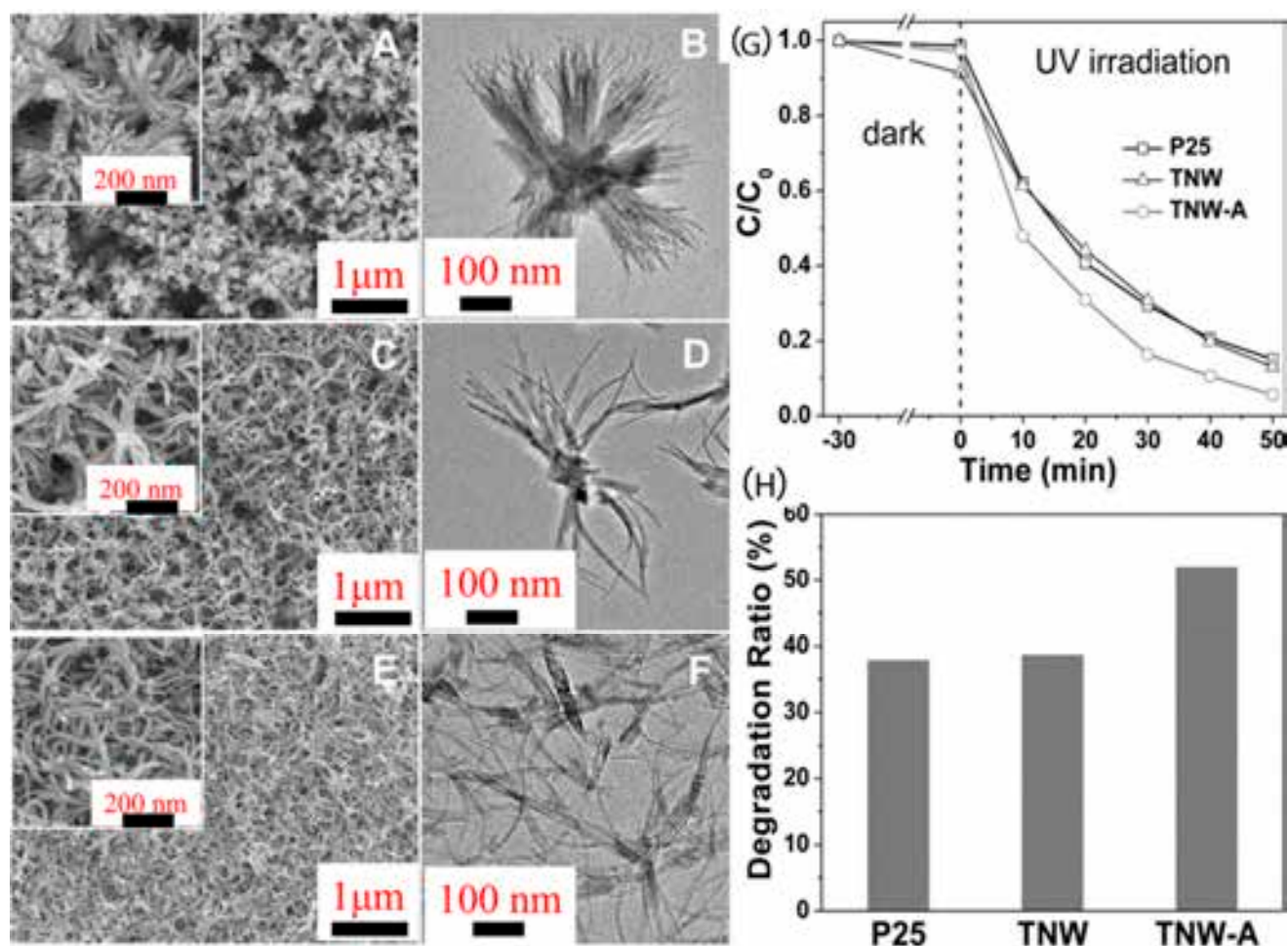


**Figure 4.** Morphological analysis (SEM and TEM images) of TiO<sub>2</sub> NWs prepared with different volumetric ratios of DMF/HAC: (A,B) 4/6, (C,D) 5/5, and (E,F) 6/4. (G) Photocatalytic degradation of RhB and (H) degradation ratio after 10 min irradiation over TNW, TNW – A, and P25. Adopted with permission from Ref. [84] Copyright 2012, Wiley.

Habibi and Jamshidi [87] conducted a study in which they synthesized TiO<sub>2</sub> in various shapes using cellulose nanofibers (CNFs) as a template and a sol-gel technique. Three different forms of TiO<sub>2</sub> were produced: hydrogel, aerogel, and alcogel (as shown in Figure 7). The hydrogel-produced TiO<sub>2</sub> nanofibers were porous and strongly entangled, while the aerogel-produced TiO<sub>2</sub> had a sheet-like structure. The alcogel-produced TiO<sub>2</sub> had a structure similar to a hydrogel, but water was replaced with isopropanol. By using the Stober method with ammonia, the sol-gel process was modified by the researchers to produce TiO<sub>2</sub> nanowhiskers and nanosheets. The morphology of the nanowhiskers transformed into nanosheets as the ammonia level was raised, as confirmed by FESEM images. Moreover, the specific surface area of the TiO<sub>2</sub> samples was found to have increased. The photocatalytic efficiency of the prepared samples was examined using methylene blue (MB) as a model pollutant. All samples exhibited high photocatalytic efficiency under UV light, with over 98% degradation of MB in 2 h. Additionally, TiO<sub>2</sub> nanowhiskers displayed higher photodegradation efficiency under visible light compared to TiO<sub>2</sub> NPs and nanosheets.

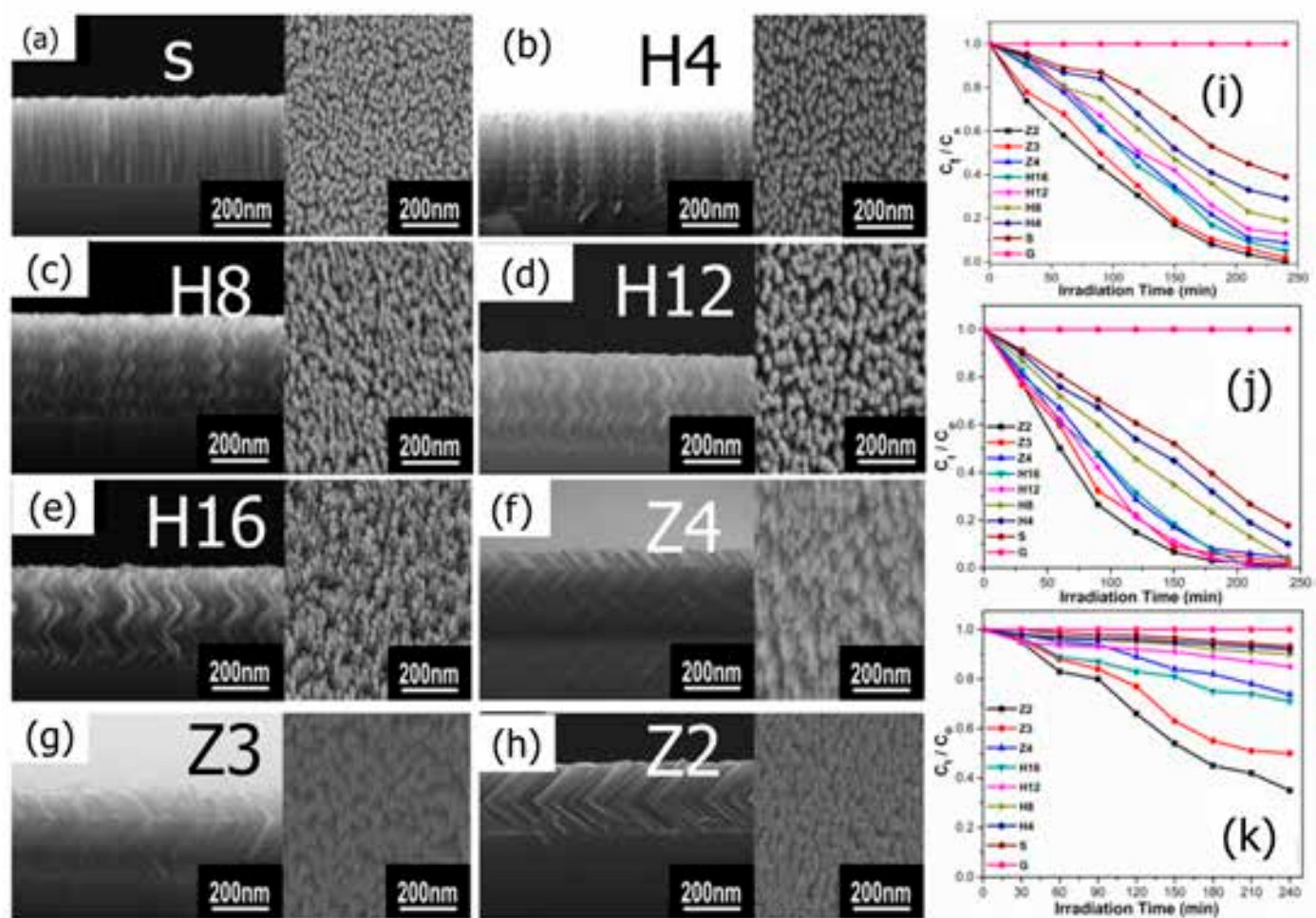


**Figure 5.** (a) SEM images (cross-sectional and top view) of TiO<sub>2</sub> nanostructures (a) Standing nanorod (b) Nanohelix-H4, (c) Nanohelix-H8, (d) Nanohelix-H12, (e) Nanohelix-H16, (f) Zigzag-Z4, (g) Zigzag-Z3, and (h) Zigzag-Z2. Pseudo-first-order kinetics (after exposure to UV-Vis light for 240 min for decolorization) of (i) MB, (j) MV, and (k) MO. Adopted with permission from Ref. [85] Copyright 2017, Elsevier.

TiO<sub>2</sub> NTs have received a lot of interest in recent years because of their one-dimensional ion exchange direction, increased surface area, and light absorption [88]. TiO<sub>2</sub> NTs can typically be made using one of three methods: hydrothermal, template, or electrochemical anodization. The most effective of these techniques, electrochemical anodization, is the least expensive and produces remarkably ordered nanotubes [89]. Additionally, the anodization technique stands out for its ability to control the morphology of nanotubes by simply changing the process parameters. In contrast to nanotubes grown over foils, Subramanian et al. [90] found that anodized TiO<sub>2</sub> NTs over titanium wires (TWs) significantly improved the photocatalytic degradation of MO.

In the presence of nanotubes grown on titanium wires, photocatalytic degradation rises from 20% to about 40%. Additionally, MO degradation in the presence of Pt-loaded TiO<sub>2</sub> nanotubes over foils matches the degradation in the presence of TiO<sub>2</sub> nanotubes on wires. This increased photoactivity is attributed to nanotubes formed in a radially outward orientation along a titanium backbone, which effectively absorb light that is reflected and refracted. Further enhancement was achieved by Rojviroon et al. [78]. In this study, electrochemical anodization was used to create TiO<sub>2</sub> nanotubes using thin titanium sheets at voltages of 20, 30, 40, and 50 V. The obtained TiO<sub>2</sub> nanotubes are shown in Figure 8a. The characterization investigation revealed that the inner diameter and depth of TiO<sub>2</sub> NTs

rose with increasing anodization voltages, but their wall thickness dropped. It seems that the TiO<sub>2</sub> NTs anodized at 50 V have shown promising photocatalytic activities towards the decolorization of indigo carmine (IC) and reactive black 5 (RB5) dyes. The decolorization efficiencies were measured to be 74.14% and 65.71%, respectively, under UV irradiation for 180 min and with an initial dye concentration of 4  $\mu$ M. These results suggest that TiO<sub>2</sub> NTs anodized at 50 V can be a potential photocatalytic material for dye wastewater treatment.

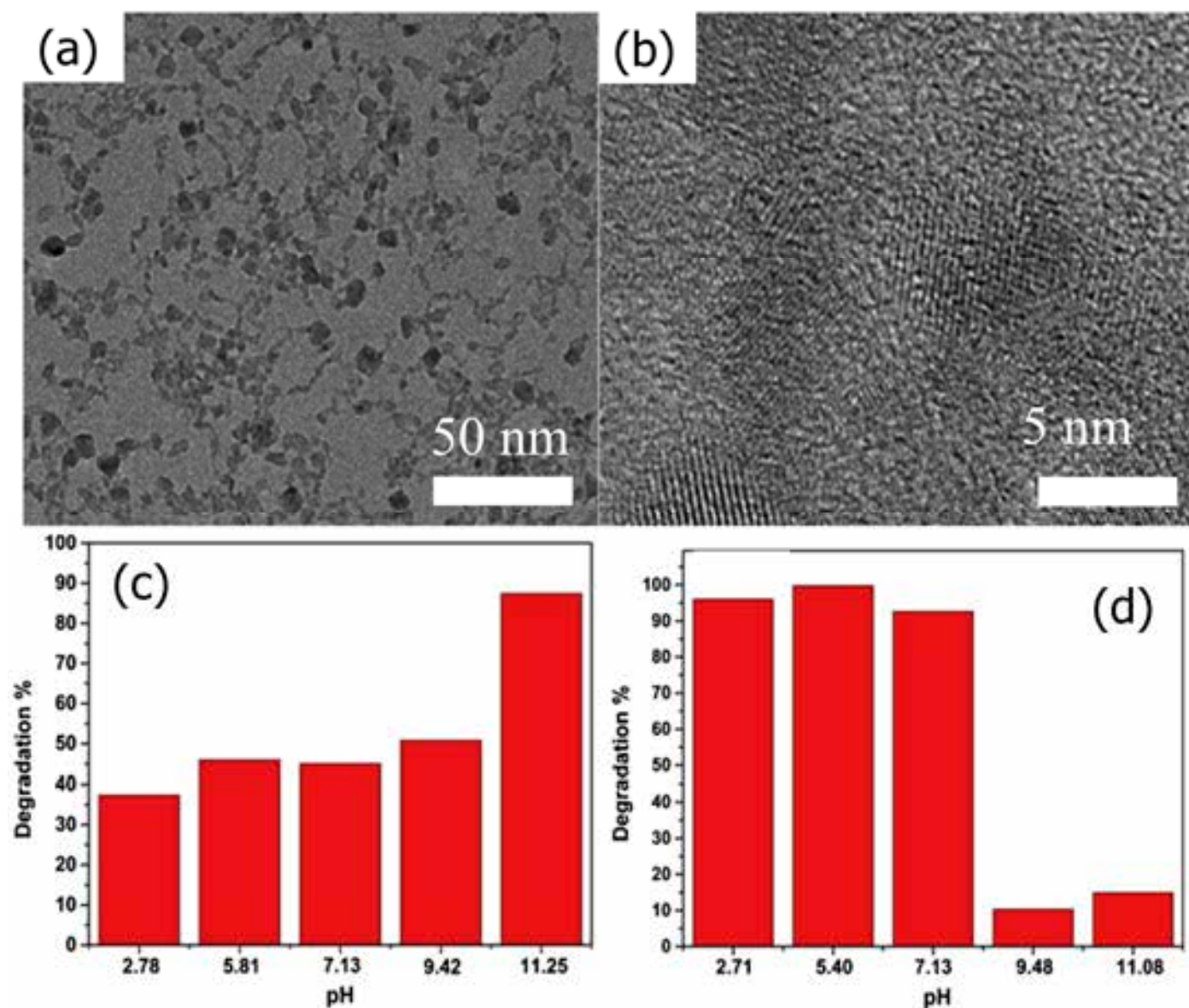


**Figure 6.** (a) TEM and (b) HR-TEM images of the prepared TiO<sub>2</sub> nanoparticles. Effect of pH on photodegradation of (c) MB and (d) CR dyes after under UV–Vis light illumination. Adopted with permission from Ref. [86] Copyright 2020, Elsevier.

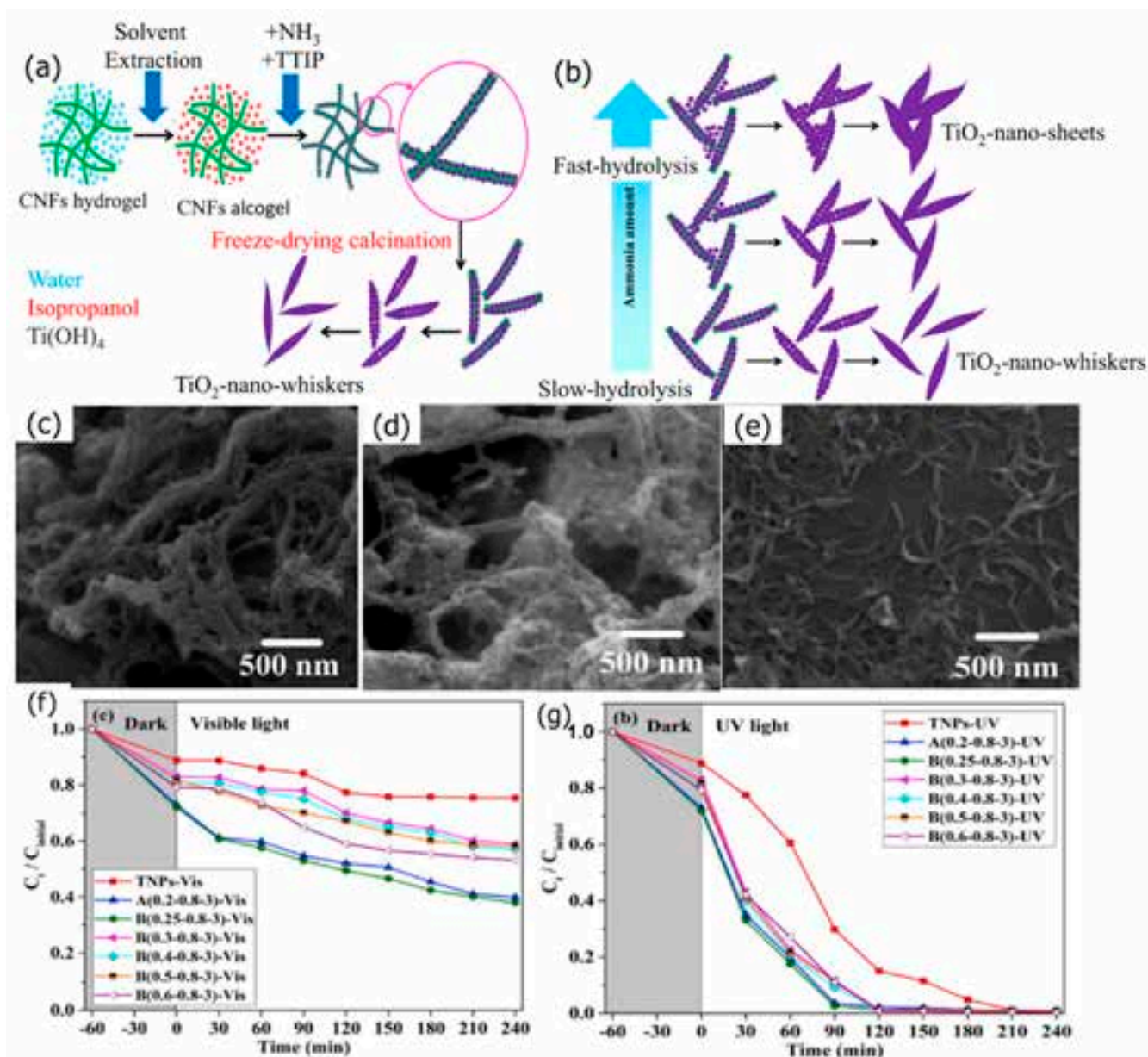


**Figure 7.** (a) Synthesis process of alcogel—TiO<sub>2</sub>, (b) the shape evolution of alcogel—TiO<sub>2</sub> with an increasing ammonia amount. FESEM images of (c) hydrogel—TiO<sub>2</sub>, (d) aerogel—TiO<sub>2</sub>, (e) alcogel—TiO<sub>2</sub>. Concentration changes in MB aqueous solution under (f) UV—and (g) visible light. Adopted with permission from Ref. [87] Copyright 2020, Elsevier.

Nozaki et al. [91] prepared TiO<sub>2</sub> nanosheet (TiO<sub>2</sub> NSs) photocatalysts for the degradation of MB when exposed to UV radiation (365 nm, 2.5 mW cm<sup>−2</sup>). Ti(OBu)<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> were both employed as starting materials, and a variety of samples with various side lengths were produced through hydrothermal synthesis by varying the F/Ti ratio between 0.3 and 2.0. Titania nanosheets produced with an F/Ti ratio of 0.3 led to the best degrading efficiency. The increase in surface area brought on by the reduction in size is what is responsible for the increased catalytic activity.

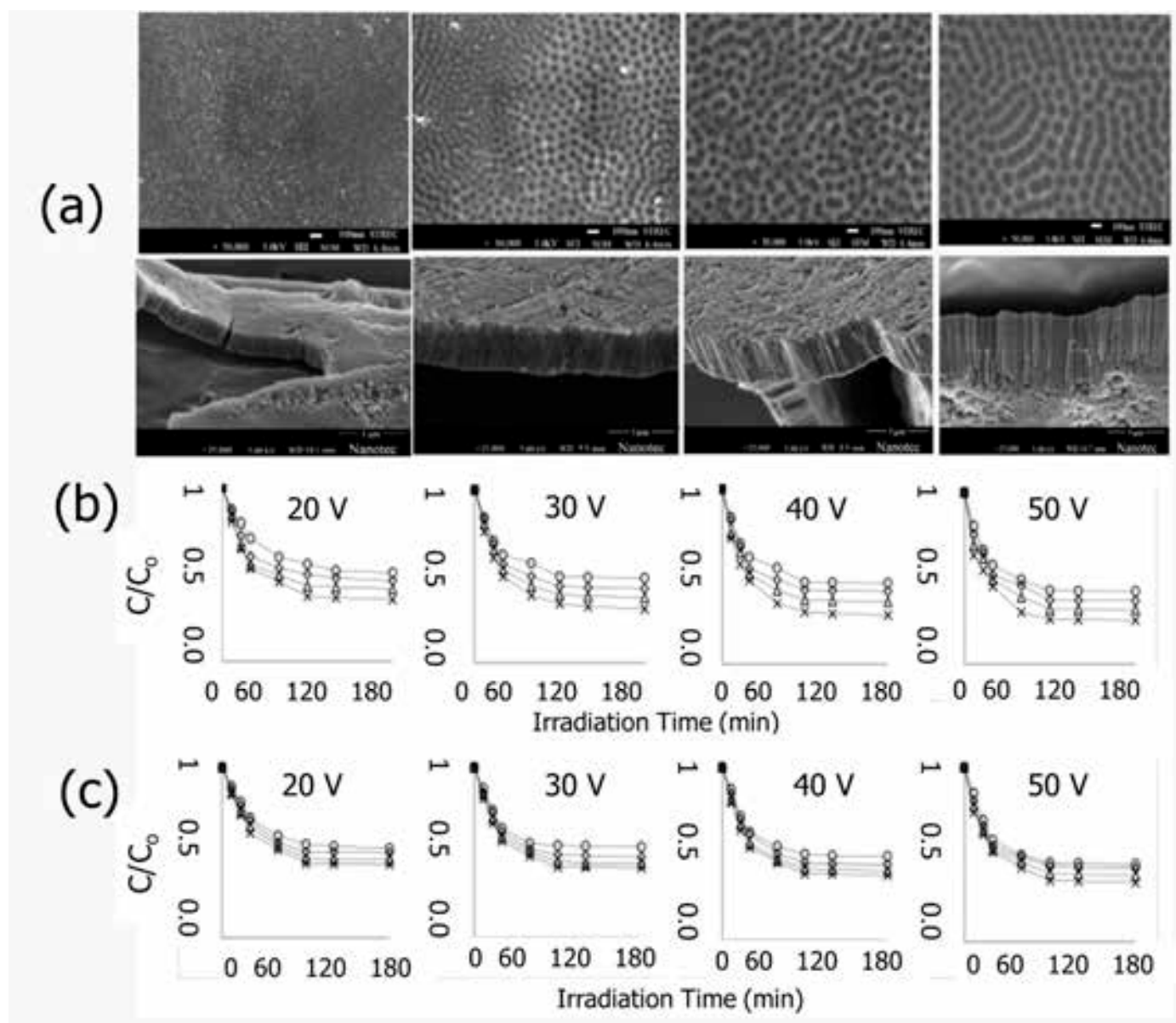


**Figure 8.** (a) FE-SEM images of TiO<sub>2</sub> NTs anodized at 20, 30, 40, and 50 V. Photocatalytic decolorization using TiO<sub>2</sub> NTs sheets anodized at 20–50 V for various initial concentrations of (b) IC and (c) RB5. Adopted with permission from Ref. [78] Copyright 2021, Elsevier.

Recently, Nair developed a floating photocatalyst to accelerate the photocatalytic degradation of a TiO<sub>2</sub> nanosheet in a cellulose acetate matrix and supplied support using ethylene vinyl acetate (Figure 9a–c) [92]. The degradation of CR dye by a floating photocatalyst made of TiO<sub>2</sub> nanosheets performed well in both UV and solar light (Figure 9d,e).

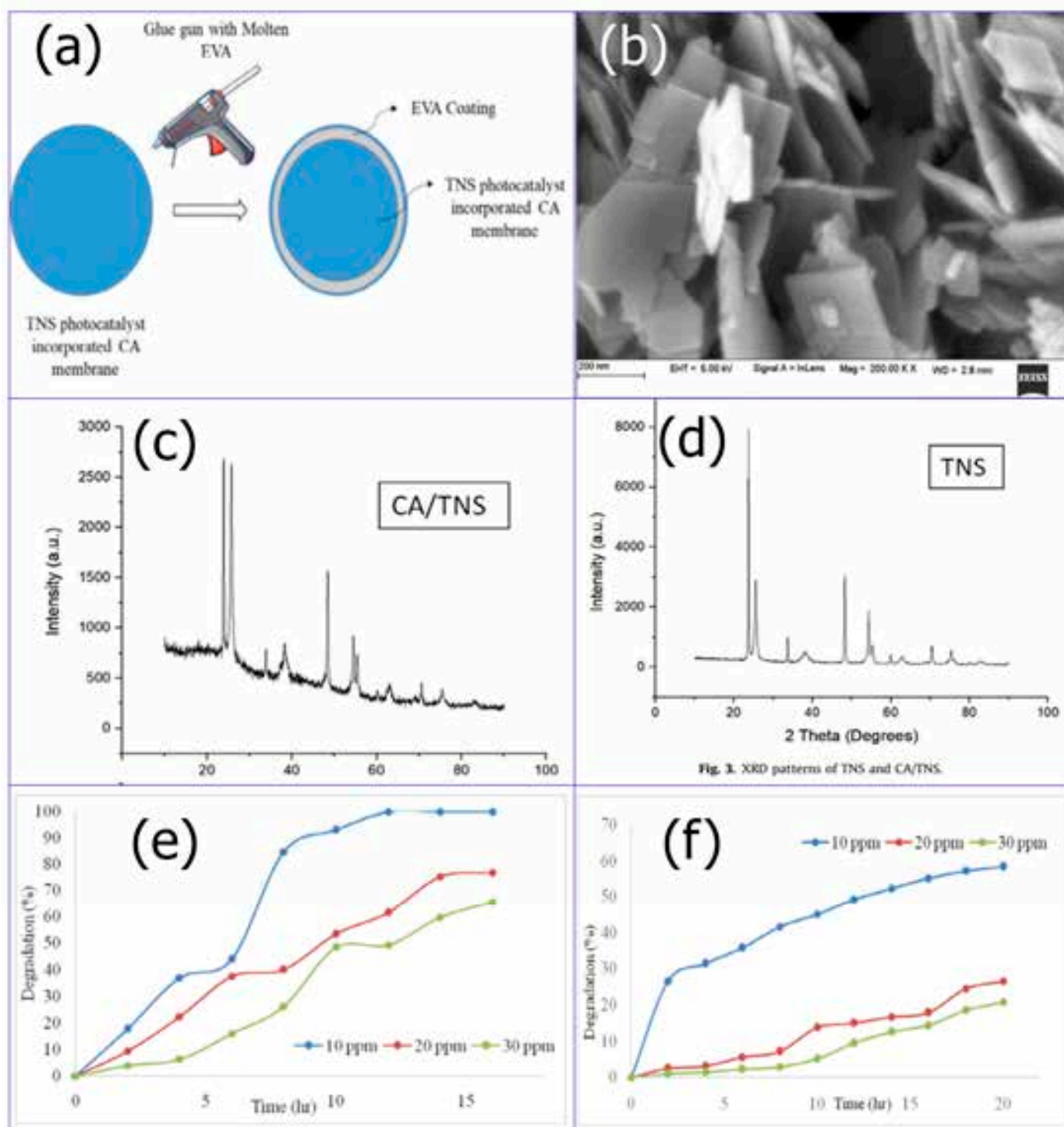


**Figure 9.** (a) Schematic representation of the synthesis of a floating photocatalyst, (b) FESEM image of TiO<sub>2</sub> NSs. XRD of TiO<sub>2</sub> NSs (c) and CA/TiO<sub>2</sub> NSs (d), (e) Solar degradation study of CR dye using a floating photocatalyst, and (f) UV degradation of CR dye using a floating photocatalyst. Adopted with permission from Ref. [92] Copyright 2021, Elsevier.

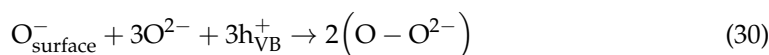
#### 4.2. Zinc Oxide Photocatalysts

ZnO is commonly found in a hexagonal wurtzite crystal structure, which has a non-centrosymmetric lattice and exhibits piezoelectric and pyroelectric properties. The crystal structure also affects the photocatalytic activity of ZnO, with the (001) crystal facet showing

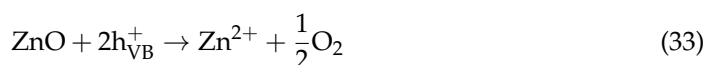
the highest photocatalytic activity due to its high surface energy and abundance of surface defects [93,94]. The photocatalytic activity of ZnO is attributed to the formation of electron–hole pairs upon the absorption of light with energy equal to or greater than its bandgap energy. The photogenerated holes can oxidize water or hydroxide ions to produce hydroxyl radicals, while the photogenerated electrons can reduce oxygen or organic molecules [95]. However, the recombination of electron–hole pairs limits the efficiency of photocatalytic reactions, and various strategies have been employed to enhance the separation of photo-generated charge carriers and improve the photocatalytic activity of ZnO, including doping with transition metals, surface modification with noble metals or semiconductors, and use of a heterostructure with other semiconductors [95,96].

Until now, various morphologies of ZnO nanomaterials such as nanorods, nanowires, nanotubes, and hollow structures have been prepared [97]. ZnO nanomaterials are usually prepared via different techniques including evaporative decomposition of solution [98], solid state reaction [99], sol-gel [100], and so on. The preparation technique shows a noticeable effect on the particle size and the morphology, which directly affects the physical and chemical properties of the prepared ZnO nanostructured materials. As reported by Singh et al., the morphology of ZnO nanostructures can be controlled by adding additives or capping agents such as triethanolamine (TEA), oleic acid, and thioglycerol [101]. The creation of ZnO nanostructures with different morphologies requires the application of many surfactants, including sodium dodecyl sulfate (SDS), tetraethylammonium bromide (TEAB), and cetyltrimethylammonium bromide (CTAB). The photocatalytic activity of ZnO is significantly influenced by its structural morphology [102,103]. This influence stems from the crystal structure, which facilitates the separation of charge carriers. However, some studies have shown that non-spherical morphologies such as nanorods and nanowires can also exhibit enhanced photocatalytic performance due to their unique crystal facets and surface areas, which can promote charge transfer and improve catalytic efficiency. Ultimately, the selection of a particular morphology for a photocatalyst relies on the specific application and the desired properties. The flake-like structure, however, exhibits comparatively lower performance [102].

Although a great deal of attention has been devoted to the photocatalytic activity of ZnO, its photocatalytic activity suffers from the following drawbacks: (i) the large bandgap of ZnO (3.37 eV), which inhibits light absorption in the UV (380 nm) range, which means ZnO cannot absorb visible light, drastically lowering photocatalytic efficiency [104,105]; (ii) the degradation reactions at the semiconductor–liquid interface are slowed down by the quick recombination of the charge carriers; (iii) the difficulties of using a traditional filtration process to recover ZnO powder from a suspension; (iv) the propensity to clump together during catalytic processes and the vulnerability to UV-induced corrosion; and (v) photocorrosion is one of the main restrictions of ZnO as a photocatalyst for wastewater treatment [106]. The following four phases describe how photocorrosion occurs [107].



The net equation for the photocorrosion of ZnO is shown below.



Therefore, the majority of ZnO photocatalytic studies have been carried out under UV radiation. Recently, various studies have been conducted on utilizing ZnO with different morphologies for the elimination of organic pollutants. To use as a photodegradation for

MO dye, Bhatia and Verma [108] synthesized ZnO nanoparticles (ZnO NPs) with varying defect concentrations by burning at 700 °C and subsequent quenching in air.

From FESEM images (Figure 10a–d), ZnO NPs are less than 45 nm in size, and an uneven grain boundary distribution was discovered in the quenching-induced defects. The improvement of the photocatalytic effectiveness of synthesized nanoparticles is greatly influenced by their various morphologies. The photodegradation of MO dye has been proven to follow a first order model through kinetic analysis, with a rate constant of  $0.0165 \text{ min}^{-1}$ . (Figure 10f). Additionally, it has been reported that approximately 100% MO degradation has been achieved in 150 min under UV irradiation (Figure 10e). Recently Doodoo-Arhin prepared ZnO NPs using the sol-gel method, with zinc acetate as a Zn source [109]. The effect of calcination temperature on the particle size of ZnO was investigated. As shown in SEM, the obtained wurtzite ZnO NPs showed crystallite sizes ranging from 16 nm to 30 nm. Increasing the calcination temperature increases the crystallite size and reduces the energy band gap of the obtained ZnO NPs. In addition, the prepared ZnO showed a rice-like microstructure morphology (Figure 10g–i). The prepared ZnO NPs were utilized as a photocatalyst toward the degradation of RhB dye under UV–light. The obtained analysis showed that ZnO NPs calcined at 400 °C obtained the highest degradation efficiency (95.41%), as shown in Figure 10h.

ZnO NPs also showed important catalytic activity under solar illumination. For example, ZnO NPs of various morphologies were developed by Saikia et al. [110] for the photodegradation of malachite green (MG) (Figure 11a–d). Under solar light, the flower-shaped homocentric bundles of hydrothermally synthesized ZnO nanorods (ZnO NRs) in the form of pencil-like structures demonstrate outstanding photocatalytic activity, as evidenced by the pseudo first-order kinetics of the Langmuir–Hinshelwood model in the photodegradation of MG dye (Figure 11e,f). Additionally, ZnO NPs and homocentric pencil-like ZNRs bundles in the shape of flowers were prepared.

Additionally, photocatalytic degradation of organic dyes by ZnO nanosheets (ZnO NSs) was also investigated. For example, Komarneni et al. [111] used a simple, ultra-rapid solution approach to create ZnO NSs with many oxygen-vacancy defects. The surface area was significantly increased from  $6.7$  to  $34.5 \text{ m}^2 \text{ g}^{-1}$  by the addition of  $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ . With a rate constant of  $0.0179 \text{ min}^{-1}$  under visible light ( $>420 \text{ nm}$ ), the as-prepared ZnO NSs showed abundant oxygen vacancies, which are crucial for improving visible light absorption and, consequently, high photocatalytic activities towards the degradation of RhB. These rates were about 13 and 11 times higher, respectively, than those of ZnO NPs with few oxygen defects.

Further enhancement with a rate constant  $k = 0.0421 \text{ min}^{-1}$  was achieved by hybridized ZnO NSs with  $\text{Ag}_3\text{PO}_4$  nanoparticles. A synergistic effect of surface oxygen vacancies and  $\text{Ag}_3\text{PO}_4$  coupling was suggested by this augmentation, which was attributed to the improved visible light absorption as well as the well-matched energy level that is responsible for effective charge transfer between oxygen-vacancy-rich ZnO NSs and  $\text{Ag}_3\text{PO}_4$ . ZnO nanowires also display a significant superior photocatalytic activity toward organic dye degradation. For example, by using a low-cost, low-temperature hydrothermal approach, Leprince-Wang et al. [112] demonstrated an effective synthesis of nontoxic, biocompatible ZnO nanostructures only on the surface of commercially available concrete and tiling pavements (Figure 12a–e).

The obtained data showed an enhancement in photocatalytic activity for degrading organic dyes in aqueous media with high photocatalytic stability (Figure 12f–h).

The degradation of Acid Red 57 (AR57) under UV irradiation was studied further by El-Bindary et al. [113]. In this study, ZnO nanowires (ZnO NWs) were prepared by a low-temperature co-precipitation technique employing zinc sulfate as a precursor. After 190 min, the effectiveness of the photocatalytic degradation of ZnO NWs produced at 400, 500, and 600 °C was 90.03, 77.67, and 72.71%, respectively. Moreover, the degradation of AR57 fitted first-order kinetics. Recently, the effect of several kinds of organic dyes as a guiding agent for the formation of ZnO NWs was described by Yang et al. [114].

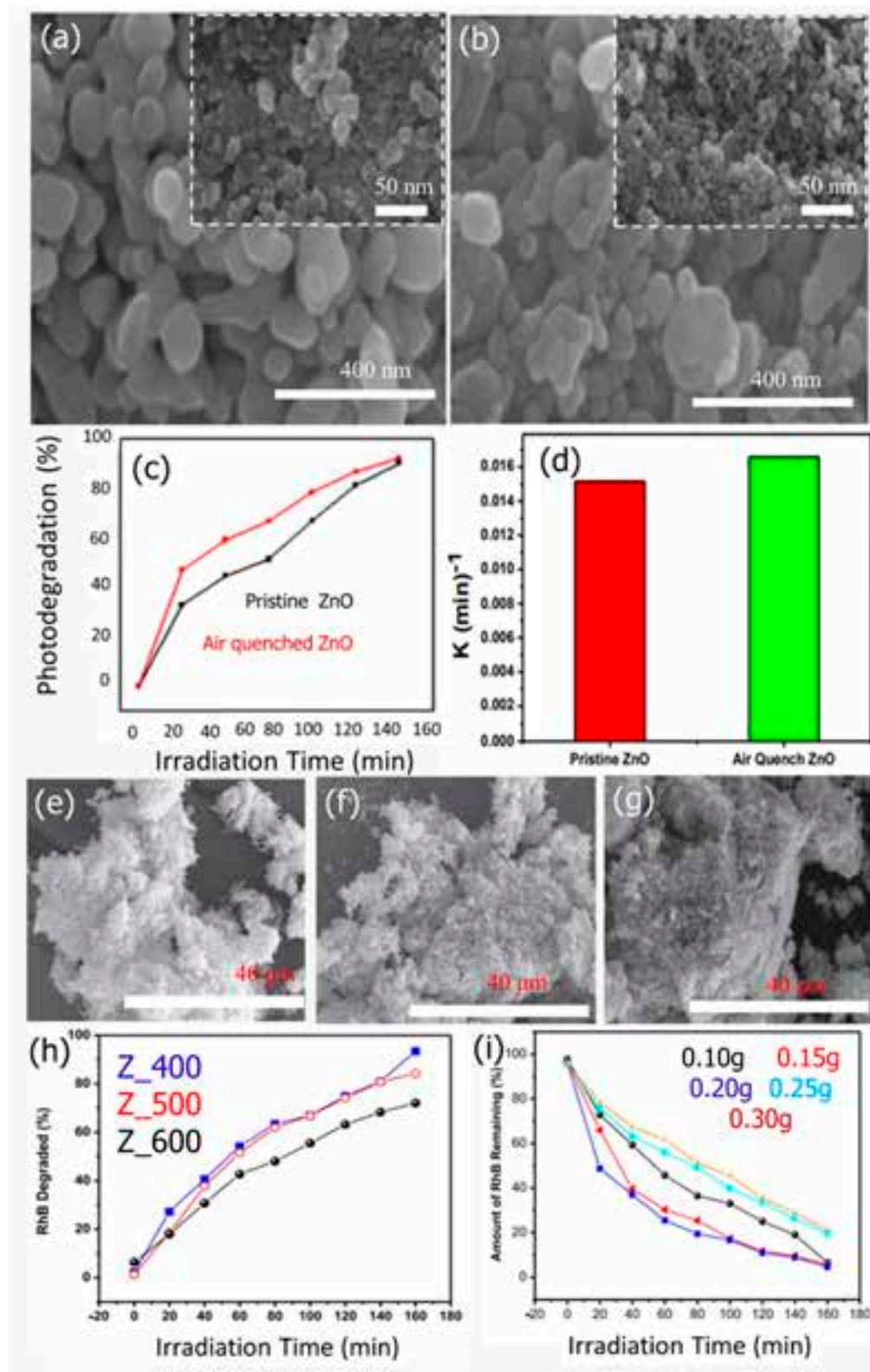


**Figure 10.** (a) Low and high magnification SEM images of ZnO, (b) air quenched ZnO, (c) photodegradation vs. irradiation time of MO dye for pristine ZnO and air quenched ZnO, (d) rate constant for after 150 min of UV exposure (Adopted with permission from Ref. [108] Copyright 2017, Elsevier), SEM images of ZnO calcined at (e) 400 °C, (f) 500 °C, and (g) 600 °C. (h) RhB degradation vs. irradiation time and (i) the effect of the catalyst load on RhB degradation (Adopted with permission from Ref. [109] Copyright 2019, Elsevier).

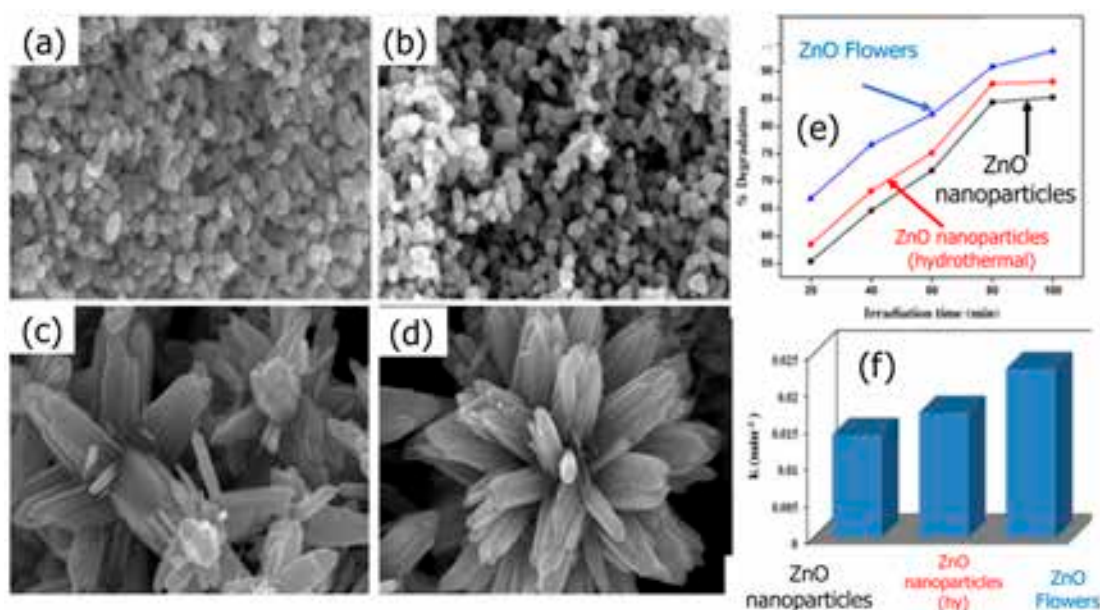


**Figure 11.** FE-SEM images of (a) ZnO NPs, (b) ZnO NPs (hydrothermal), (c) ZnO flowers, (d) one ZnO flower, (e) comparative photodegradation of MG by ZnO NPs, and (f) the estimated rate constant for photodegradation of MG by ZnO NPs under solar light. Adopted with permission from Ref. [103] Copyright 2014, Elsevier.

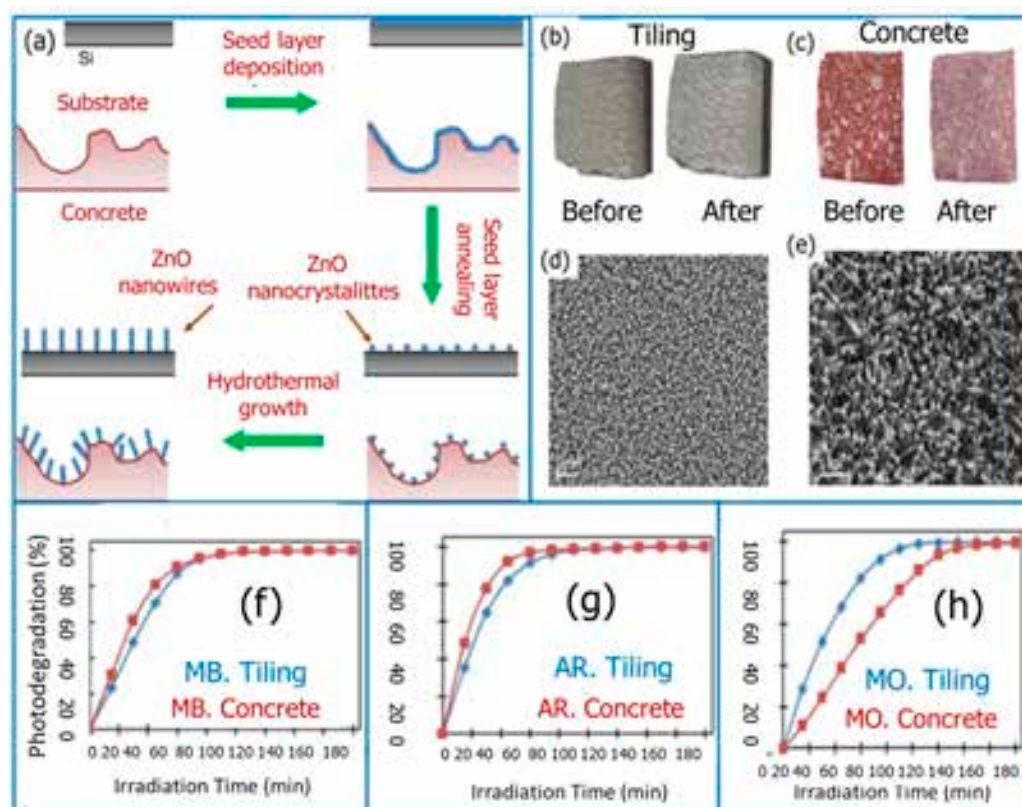


**Figure 12.** (a) Scheme of the ZnO NWs growth on a flat substrate (i.e., Si wafer) vs. a construction material (i.e., concrete), (b) top views of the gray tiling, and (c) red concrete pavement before and after the growth of ZnO nanostructures. (d) SEM top-view of ZnO NWs on the tiling surface, (e) ZnO NRs on the concrete surface, and (f–h) the photodegradation rate of MB, AR, and MO dyes vs. time. Adopted with permission from Ref. [112] Copyright 2019, Springer Nature.

EBT was found to effectively direct the growth of ZnO NWs, inhibiting their growth along the c-axis direction. Additionally, the introduction of UV light during growth significantly enhanced the photocatalytic degradation of EBT absorbed on the surface of the ZnO NWs. ZnO NWs arrays grown on glass fiber cloth with a dominant exposed polar (0001) facet exhibited superior photocatalytic performance compared to other arrays.

#### 4.3. Copper Oxide Photocatalysts

Copper (II) oxide, also known as cupric oxide (CuO), is a naturally occurring p-type semiconducting metal oxide. This is due to the presence of oxygen vacancy defects in its crystal structure. CuO has an indirect small bandgap of 1.2 eV at room temperature [115]. Copper also exists in other polymorphs such as copper (I) oxide, commonly known as cuprous oxide (Cu<sub>2</sub>O), and copper (III) oxide (Cu<sub>4</sub>O<sub>3</sub>). CuO displays higher thermal stability than Cu<sub>2</sub>O, whereas Cu<sub>4</sub>O<sub>3</sub> is a challenging metastable phase due to its mixed copper atom oxidation state, making its synthesis problematic [116,117]. CuO is a brownish-black powder that is used in various applications, such as catalysis, chemical and gas sensors, superconductors, and energy conversion and storage devices, as well as in biomedicine and textile production [118–120]. CuO has been extensively used as a heterogeneous catalyst in diverse chemical processes such as the oxidation of carbon monoxide (CO), hydrocarbons, and phenol in supercritical water, the selective catalytic reduction of nitric oxide with ammonia, and the breakdown of nitrous oxide [121].

Furthermore, CuO has been investigated as a photocatalytic material [122]. Additionally, it has been reported how the bandgap of CuO nanostructures is influenced by their morphology [123]. The subsequent section will demonstrate the effectiveness of CuO nanostructures as a photocatalyst for eliminating organic dyes from aqueous solutions, including an analysis of the removal mechanism and the impact of morphology on the removal efficiency.

CuO nanostructures are among the interesting photocatalytic materials usually utilized for the removal of various organic pollutants due to their high abundance, low cost, narrower bandgap, excellent chemical stability, and facile synthesis [124]. The narrow bandgap of CuO makes it active in the visible region of the electromagnetic spectrum. To enhance the catalytic activity of CuO, H<sub>2</sub>O<sub>2</sub> is often added to the reaction mixture. H<sub>2</sub>O<sub>2</sub> is a better electron acceptor than O<sub>2</sub>, so it quickly captures the photogenerated electrons from the photocatalyst's surface, becoming reduced and forming hydroxyl radicals (•OH) [125]. This is important for offering more active radicals, as well as reducing the rate of electron–hole recombination, which boosts the utilization of holes during the photocatalytic process. Without H<sub>2</sub>O<sub>2</sub>, CuO displays an inability to generate a sufficient amount of •OH radicals, and thus CuO is considered as an ineffective photocatalyst for degrading organic pollutants [126]. This is because the redox potential required to produce •OH radicals is higher than the VBs of CuO. Thus, CuO has weaker oxidative capabilities for the breakdown of organic contaminants and cannot produce hydroxyl radicals when illuminated. There are many works that indicate that without H<sub>2</sub>O<sub>2</sub>, CuO in different morphologies displays no catalytic activity, as reported by He et al. [127]. Recently Latief et al. prepared CuO NPs with a range of sizes between 25 and 90 nm (Figure 13a,b) to depredate CR dye from aqueous solutions. The analysis showed that the addition of H<sub>2</sub>O<sub>2</sub> to CuO NPs significantly enhanced the degradation of CR dye under UV light, as presented in Figure 13c. In addition, increases in H<sub>2</sub>O<sub>2</sub> result in improvements in the degradation rate (Figure 13d).

CuO nanostructures with various morphologies, including flower-like, boat-like, plate-like, and ellipsoid-like structures, were prepared and showed excellent catalytic activity towards the degradation of MB. However, without H<sub>2</sub>O<sub>2</sub>, the degradation stopped after 15 h, highlighting the significant dependence of CuO nanostructure photocatalytic activity on H<sub>2</sub>O<sub>2</sub>. Adsorption–oxidation–desorption is the postulated possible mechanism for the photocatalytic degradation of dyes by CuO in the presence of H<sub>2</sub>O<sub>2</sub> under light illumination [127]. In this mechanism, various free radicals such as HO•, HOO•, and O<sub>2</sub><sup>•−</sup> are

mainly responsible for the degradation of dyes. The first step is adsorption of dye and  $\text{H}_2\text{O}_2$  molecules on the surface of the CuO nanostructure. The second step involves the decomposition of  $\text{H}_2\text{O}_2$  into free radicals ( $\text{HO}^\cdot$ ,  $\text{HOO}^\cdot$ , or  $\text{O}_2^{\cdot-}$ ). These free radicals display a high oxidative ability to oxidize the organic dye. The third step involves desorption of the small molecules from the CuO surface, and finally the catalyst is recovered [128].

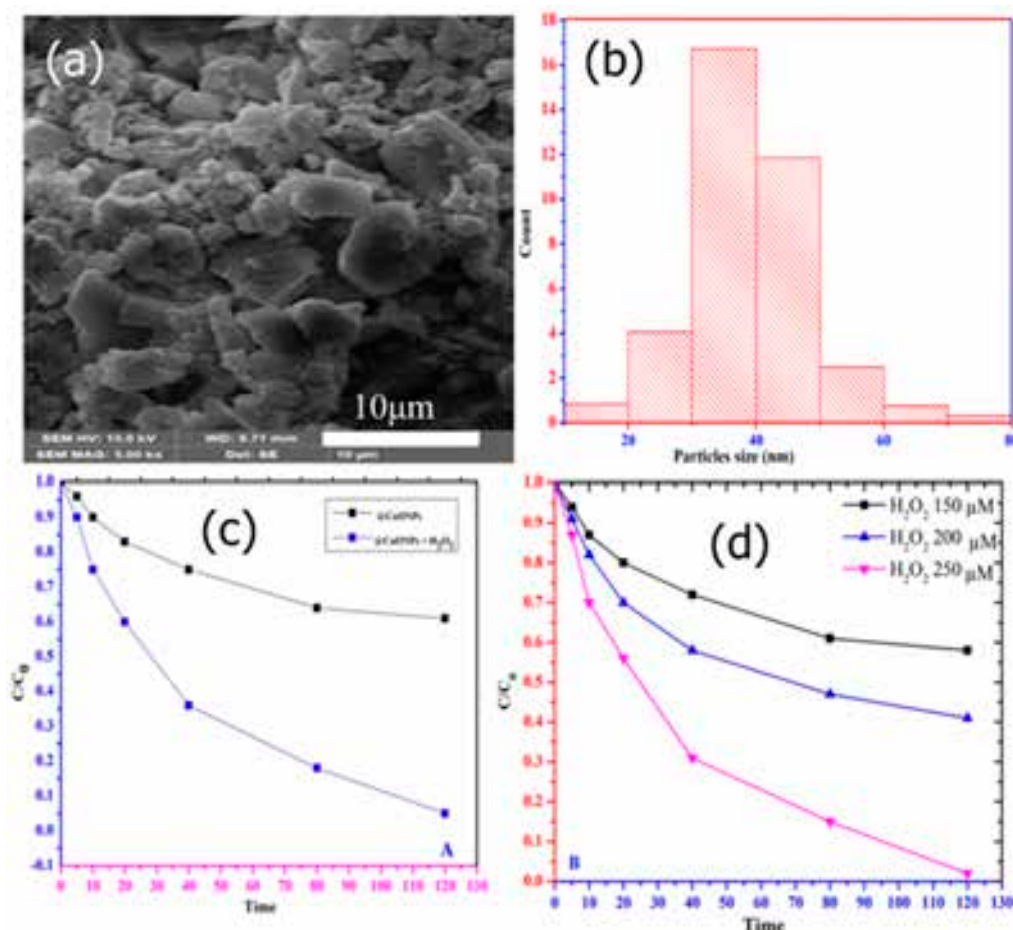


**Figure 13.** (a) SEM image of CuO NPs, (b) histogram spectrum of CuO NPs, (c) effect and removal of CR dye by UV/ $\text{H}_2\text{O}_2$ , and (d) effect of  $\text{H}_2\text{O}_2$  concentration in the degradation of CR dyes (Adopted with permission from Ref. [125] Copyright 2023, MDPI).

Morphology is a critical factor that affects the photocatalytic activity of CuO nanostructures toward the degradation of organic dyes. For example, Wang et al. reported that CuO nanowires (Figure 14a,b) showed excellent catalytic activity toward the degradation of RhB [129]. The CuO nanowires demonstrated a total degradation efficiency of 95.5% after 9 h of UV light irradiation (as shown in Figure 14c), which was significantly higher than that of commercial CuO powders (which achieved only 39.6% degradation). In addition, Sadollahkhani et al. investigated the photocatalytic performance of CuO nanoparticles with various morphologies (as depicted in Figure 14d–f) for the degradation of CR dye under UV illumination [130]. The decomposition of CR dye takes place on the surface of CuO; thus, adsorption plays a critical role in the photocatalytic degradation. Samples doped with Zn appear to have improved degradation performance (63%) according to the photocatalytic examination of the degradation of MB dye (Figure 14g). The photocatalytic studies revealed that the degradation of CR for nanorods was the highest among the other prepared materials, with a total degradation efficiency of 67% after 210 min irradiation (Figure 14h). Moreover, the CR degradation reaction follows a first order kinetics model with the three CuO morphologies. On the other hand, Anandan et al. [131] prepared

dandelion-like CuO microspheres with sizes of  $\sim 1\text{--}2\text{ }\mu\text{m}$  through the ultrasound process without any surfactants. The photocatalytic performance of the CuO nanoparticles that were synthesized was investigated for the degradation of Reactive Black-5. The study found that the CuO microspheres with a dandelion-like morphology exhibited excellent photocatalytic activity, with approximately 76% of the dye degraded in just 5 h under visible light exposure. The degradation reaction followed a pseudo-first-order kinetic model, with a rate constant of  $0.312\text{ h}^{-1}$ . Recently, George et al. prepared flowers similar to CuO 3D nanostructures doped with nickel, zinc, and iron (Figure 14h) [132].

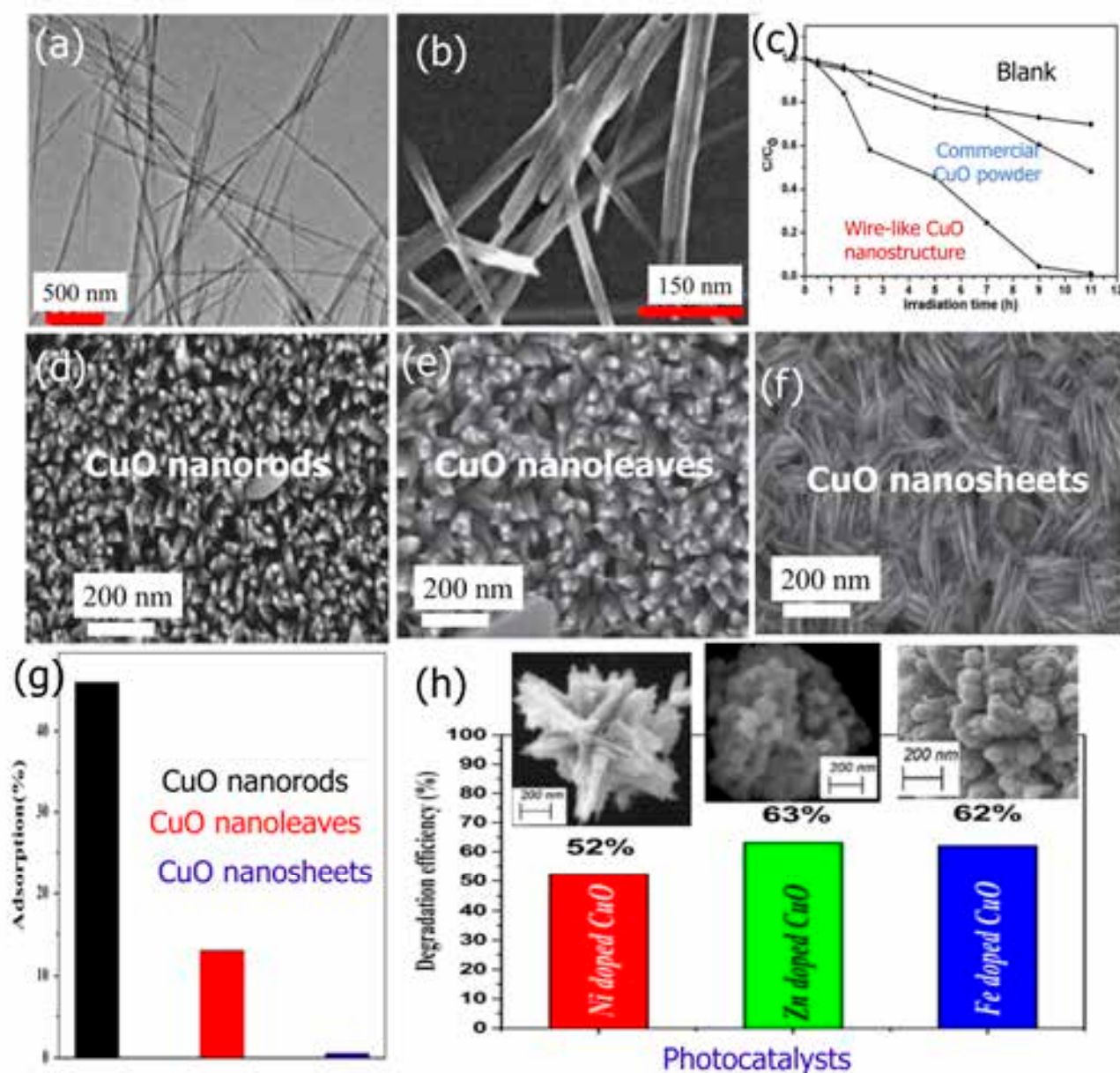


**Figure 14.** (a) TEM and (b) SEM images of CuO nanowires, (c) the photocatalytic efficiency of RhB degradation on different catalysts in the presence of CuO nanowire catalyst (Adopted with permission from Ref. [129] Copyright 2012, Elsevier), (d–f) SEM images of different CuO morphologies, (g) adsorption of CR on the surface of different morphologies of CuO [Initial CR concentration is  $20\text{ mg L}^{-1}$ , dose of CuO is  $0.05\text{ g}$ , and stirring time is  $30\text{ min}$ ] (Adopted with permission from Ref. [130] Copyright 2014, Elsevier), and (h) photocatalytic degradation efficiency of MB dye using Ni, Zn, and Fe-doped CuO (together with their SEM images) (Adopted with permission from Ref. [130] Copyright 2021, Elsevier).

Using  $\text{NaBH}_4$  as a reducing agent in an aqueous medium, Nazim et al. [133] recently synthesized porous CuO nanosheets (Figure 15a) for use as a photocatalyst towards the degradation of food dye. The optical energy band gap of the prepared CuO was found to be approximately 1.92 eV. The CuO nanosheets were tested as photocatalysts for the degradation of Allura Red AC (AR) dye and showed excellent photocatalytic degradation efficiency of around 96.99% in just 6 min under visible light irradiation at room temperature (Figure 15b,c). The photodegradation kinetics of AR followed a pseudo-first-order reaction model, with a rate constant of  $0.524 \text{ min}^{-1}$ . Additionally, the CuO nanosheets exhibited remarkable recycling ability for AR degradation (Figure 15d).

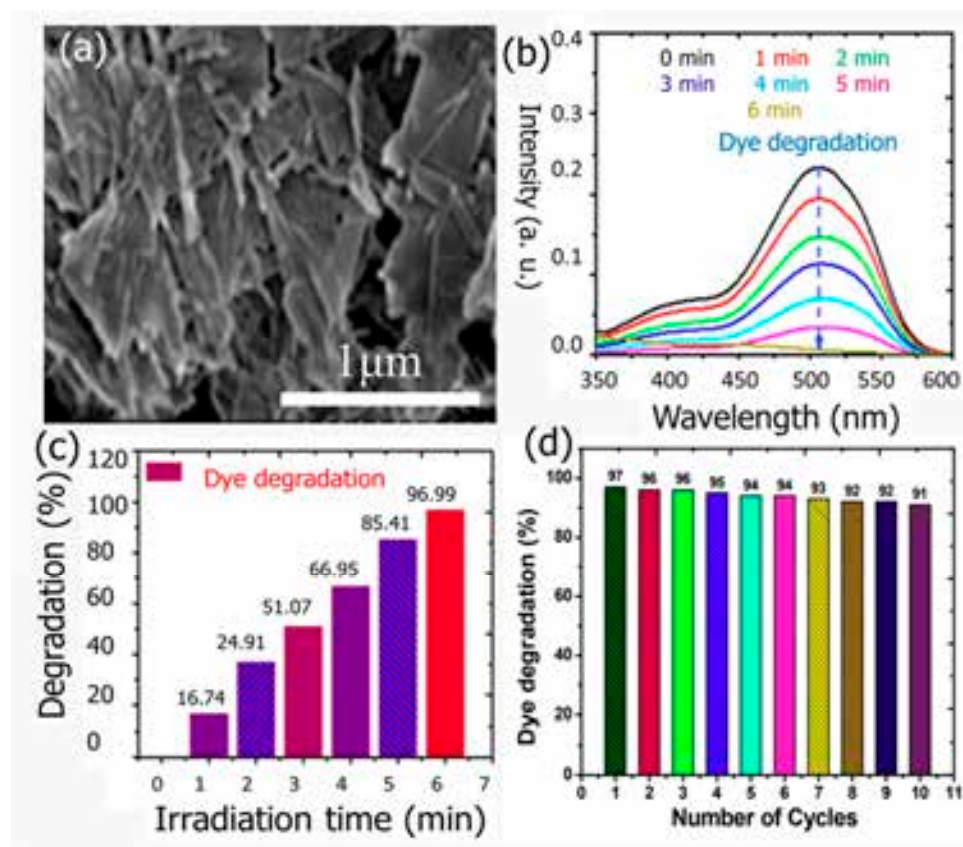


**Figure 15.** (a) FESEM images of CuO nanosheets, (b) UV-Vis spectrum of dye degradation at different times, (c) gradual degradation histogram against time of the AR dye in aqueous medium, and (d) recyclability of the CuO nanosheets after ten degradation cycles for AR dye. Adopted with permission from Ref. [133] Copyright 2021, American Chemical Society.

#### 4.4. Nickel Oxide Photocatalysts

NiO is a broad bandgap (3.6–4.0 eV) p-type semiconducting oxide. NiO has attracted a lot of attention due to its application in numerous areas, including fuel cell electrodes, battery cathodes, dye-sensitized solar cells, etc. [134–137].

In addition, NiO displays a promising ability to produce OH radicals and thus is a potential candidate toward the degradation of organic pollutants. For example, Jayakumar et al. [138] prepared NiO nanoparticles through a chemical precipitation method for use as photocatalysts for the degradation of MB dye in aqueous media. The photocatalytic degradation results showed that the NiO nanoparticles are potential photocatalysts for the degradation of MB dye.

Saeed et al. utilized a chemical reduction process to prepare NiO NPs and NiO/nanoclay nanocomposite (NiO/Nc) and evaluated their photocatalytic efficiency for the degradation of orange II dyes in aqueous solution [139]. According to the SEM examination, the

NiO NPs were spherical with variable forms and diameters in the range of 100–400 nm (Figure 16a,b). The photodegradation investigation showed that, within 20 min, orange II in aqueous medium was degraded by the NiO NPs and NiO/Nc by 93% and 96%, respectively (Figure 16c). Green methods are successfully applied for preparing NiO as a photocatalyst. For example, using the antioxidant property of *Punica granatum* L. (pomegranate) juice extract and its bio-reducing ability for MO breakdown in water, Barzinjy et al. [140] prepared NiO NPs. The biosynthesized NiO nanoparticles displayed an active catalytic ability toward the degradation of MO from media with a total degradation performance of 96%. Furthermore, Sarani et al. [141] prepared NiO nanoparticles via a green method by using extract as a stabilizing agent. The average crystal size of prepared NiO nanoparticles was approximately 54–58 nm, and the estimated energy band gap was 3–3.7. The prepared NiO nanoparticles were investigated as photocatalysts for degradation of acid orange 7 (AO7) dye in aqueous solution under visible light. The NiO nanoparticles exhibited excellent photocatalytic performance (90.2%) toward the AO7 dye and displayed excellent re-usability several times. Table 1 summarizes different metal oxide morphologies and their photodegradation performances.

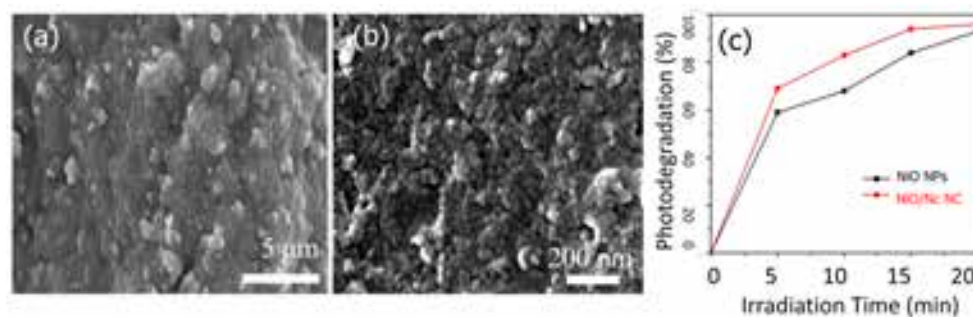


**Figure 16.** SEM image of (a) NiO NPs and (b) NiO/Nc composite, and (c) percent of degradation for orange II dye. Adopted with permission from Ref. [139] Copyright 2022, Springer Nature.

**Table 1.** Summary of different metal oxide morphologies and their photodegradation performances.

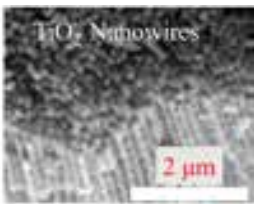
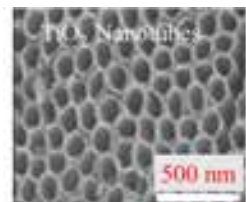
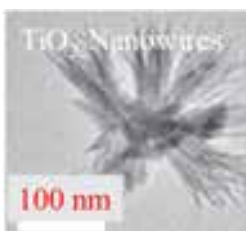
| Photocatalyst    | Morphology                                                                          | Pollutant | Degradation Conditions                                                             | Degradation Rate (%) | Ref. |
|------------------|-------------------------------------------------------------------------------------|-----------|------------------------------------------------------------------------------------|----------------------|------|
| TiO <sub>2</sub> |  | MB        | UV light<br>Time 80 min<br>Pseudo-first order<br>( $k = 0.0098 \text{ min}^{-1}$ ) | 75.00                | [83] |
|                  |  |           | UV light<br>Time 80 min<br>Pseudo-first order<br>( $k = 0.0426 \text{ min}^{-1}$ ) | 99.00                | [83] |
|                  |  | RhB       | UV light<br>Time 10 min                                                            | 50.00                | [84] |

Table 1. Cont.

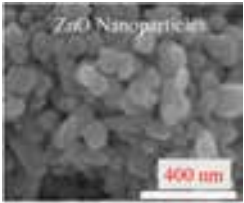
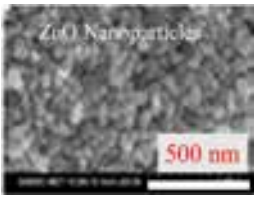
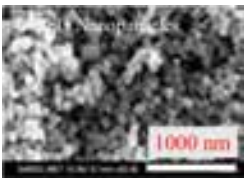
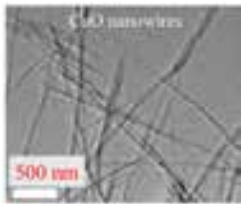
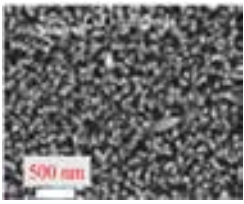
| Photocatalyst | Morphology                                                                          | Pollutant | Degradation Conditions                                                              | Degradation Rate (%) | Ref.  |
|---------------|-------------------------------------------------------------------------------------|-----------|-------------------------------------------------------------------------------------|----------------------|-------|
| ZnO           |    | MO        | UV light<br>Time 150 min<br>Pseudo-first order<br>( $k = 0.01659 \text{ cm}^{-1}$ ) | 99.00                | [108] |
|               |    | RhB       | UV light<br>Time 160 min                                                            | 95.40                | [109] |
|               |    | RhB       | UV light<br>Pseudo-first order<br>( $k = 0.014 \text{ min}^{-1}$ )                  | 80.44                | [110] |
|               |  | MG        | UV light<br>Pseudo-first order<br>( $k = 0.017 \text{ min}^{-1}$ )                  | 83.68                |       |
|               |  | MG        | UV light<br>Pseudo-first order<br>( $k = 0.023 \text{ min}^{-1}$ )                  | 90.87                | [110] |
| CuO           |  | RhB       | UV light<br>Time 9 h                                                                | 95.00                | [129] |
|               |  | CR        | UV light<br>Time 210 min                                                            | 67.00                | [130] |

Table 1. Cont.

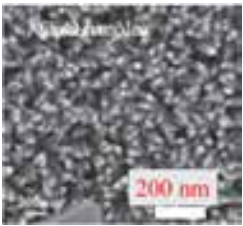
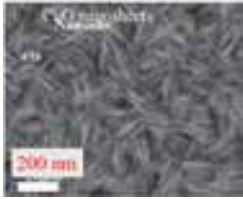
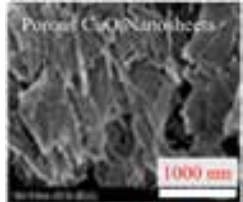
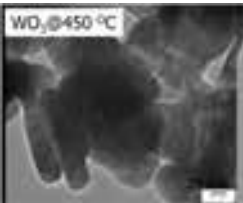
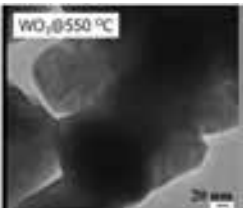
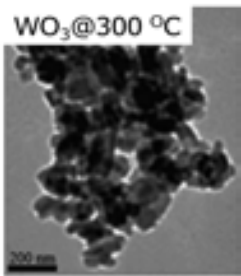
| Photocatalyst   | Morphology                                                                          | Pollutant | Degradation Conditions                                                 | Degradation Rate (%) | Ref.  |
|-----------------|-------------------------------------------------------------------------------------|-----------|------------------------------------------------------------------------|----------------------|-------|
| CuO             |    | CR        | UV light<br>Time 210 min                                               | 48.00                | [130] |
|                 |    |           | UV light<br>Time 210 min                                               | 12.00                |       |
|                 |   | AR        | UV-vis light<br>Pseudo-first order<br>( $k = 0.524 \text{ min}^{-1}$ ) | 96.99                | [133] |
| NiO             |  | O II      | UV-Vis light<br>Time 20 min                                            | 96.00                | [139] |
| WO <sub>3</sub> |  | MB        | UV light<br>Time 160 min                                               | 11.00                | [142] |
|                 |  |           | UV light<br>Time 16 min                                                | 14.30                | [142] |
|                 |  |           | UV light<br>Time 160 min                                               | 20.00                | [142] |

Table 1. Cont.

| Photocatalyst   | Morphology                                                                        | Pollutant | Degradation Conditions        | Degradation Rate (%) | Ref.  |
|-----------------|-----------------------------------------------------------------------------------|-----------|-------------------------------|----------------------|-------|
| WO <sub>3</sub> |  | RhB       | Visible light<br>Time 240 min | 96.10                | [143] |

#### 4.5. Tungsten Oxide Photocatalysts

In recent decades, tungsten-based oxides (WO<sub>3</sub>) have been the subject of substantial research, with a variety of morphologies being exhibited. A twisted WO<sub>6</sub> octahedron connects the crystal in the stoichiometric ratio of the WO<sub>3</sub> structure to generate a perovskite crystal structure. Its crystal forms are hexagonal, orthorhombic, and monoclinic. At the same time, oxygen vacancies and unsaturated, coordinated W atoms might arise from the easy loss of the oxygen lattice. Consequently, there are numerous non-stoichiometric compounds in tungsten oxide, including WO<sub>2.72</sub>, WO<sub>2.8</sub>, WO<sub>2.83</sub>, and WO<sub>2.9</sub>.

Among the low-cost semiconductors with potential photocatalytic activity is tungsten oxide (WO<sub>3</sub>) [56]. Its highly adjustable stoichiometries and structures, together with its Earth-abundance and strong sensitivity to the solar spectrum due to its low band gap of 2.5–3.0 eV [144], make it a popular choice for photocatalysis under visible light [145]. Furthermore, WO<sub>3</sub> has stable physical and chemical characteristics, little toxicity, and a strong capacity to oxidize valence band holes [39]. Nanoparticles, nanowires, nanosheets, and nanospheres are among the frequently occurring morphologies. There are many ways to produce different WO<sub>3</sub> dimensions: 0 dimensional (0D), 1D, 2D, and 3D WO<sub>3</sub>, in that order. Characteristics vary among dimensions. It is possible to create 0D WO<sub>3</sub> monodisperse monoclinic WO<sub>3</sub> quantum dots by breaking down the ammonium tungstate oxide complex, which is created hydrothermally using hydrazine hydrate and WCl<sub>6</sub> [146]. It is possible to carefully regulate the particle size distribution of WO<sub>3-x</sub> QDS within the range of 1.3–4.5 nm by varying the reaction temperature [147]. 1D WO<sub>3</sub> is widely available and simple to synthesize. Today, various structures of 1D WO<sub>3</sub> have been discovered, such as those of nanofibers, nanotubes, nanorods, and nanowires. As for 2D WO<sub>3</sub>, thin films, nanosheets, nanoplates, and so on, these have garnered a great deal of interest because of their high surface volume ratio, surface polarization, modulated surface activity, and oxygen-rich vacancies. The majority of 2D WO<sub>3</sub> structures are thin layers. As previously reported by Yin et al., 3D WO<sub>3</sub> is a layered structure made of nanoparticles, nanoplates, nanorods, and nanosheets. It can take the form of irregular structures such as mesoporous structures, microspheres, micro flowers, and sea urchin-like formations. Typically, 3D WO<sub>3</sub> displays high porosity, a large specific surface area, and a distinctive shape [148].

For photocatalytic applications, WO<sub>3</sub> shows some advantages, such as its high physico-chemical catalyst stability that is limited to photo-corrosion and has strong solar spectrum absorption. Under UV–Vis light, WO<sub>3</sub> is a highly reactive catalyst that effectively oxidizes various organic and inorganic pollutants in wastewater. WO<sub>3</sub> is a photocatalyst with a wide range of hues that can change from yellow to green to bluish to grayish depending on its oxidation state. There are many techniques that have been used to enhance the catalytic activity of WO<sub>3</sub>. For example, doping with other materials such as dyes to form dye-doped WO<sub>3</sub> as reported by Tahir et al. [149], or doping with Pt to form Pt–WO<sub>3</sub> composite [150].

One of the promising strategies is to design WO<sub>3</sub> with a different morphology, and we will present the recent progress in utilizing WO<sub>3</sub> with different morphologies in degradation some organic dyes. Ojha et al. [142] used the sol-gel method to prepare WO<sub>3</sub> nanorods

and sheets in various crystal phases. As presented in Figure 17a, they showed that the calcination temperature plays a critical role in the shapes and crystal phases of the  $\text{WO}_3$  nanostructures, and thus in the photocatalytic activity toward degradation of MB dye due to the modified electronic structure, which causes a variation in the value of the band gap (Figure 17b). The synthesized  $\text{WO}_3$  nanosheets showed improved photocatalytic activity for the photodegradation of MB dye compared to  $\text{WO}_3$  nanorods (Figure 17c). The sheet-type structure provides more active surface for the interaction of dye molecules compared to the rods.

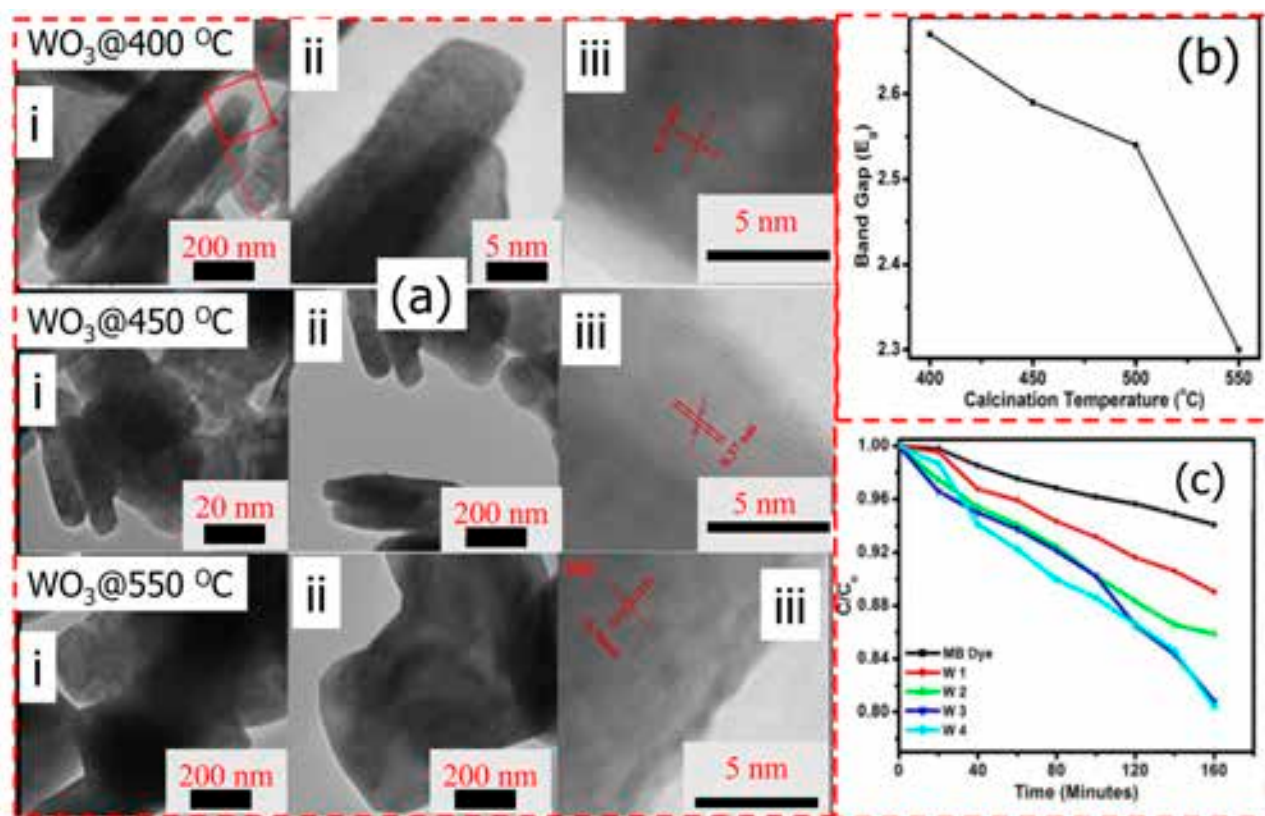


**Figure 17.** (a) TEM images with various resolutions of  $\text{WO}_3$  calcined at different temperatures, (b) variation in band gap with calcination temperature, and (c) C/Co vs. UV irradiation time plot for degradation of MB dye with W1 (at 400 °C), W2 (at 450 °C), W3 (at 550 °C), and W4 (at 550 °C). Adopted with permission from Ref. [142] Copyright 2022, Springer Nature.

Yin et al. [148] prepared  $\text{WO}_3$  photocatalyst through a hydrothermal process. The prepared  $\text{WO}_3$  nanoparticles showed promising absorption of UV, visible, and near-infrared (NIR) bandwidths.  $\text{WO}_3$  photocatalyst exhibited excellent catalytic activity toward the degradation of MB. Furthermore, they confirmed that the temperature showed different morphology (Figure 18a–d) and that the higher temperature displayed better catalytic activity (Figure 18e). Recently, Mzimela et al. [143] prepared highly agglomerated  $\text{WO}_3$  nanoparticles through the facile acid precipitation method at various temperature (Figure 18f–h) for degradation of RhB dye. The results showed that  $\text{WO}_3$  calcined at 300 °C, 5 g L<sup>-1</sup> catalyst dose, 5 ppm RhB concentration, and pH of 9.5, while the catalyst showed an excellent degradation efficiency of 96.1% after 4 h under visible light irradiation (Figure 18i). Furthermore, the degradation kinetics obeys the L–H model, which describes heterogeneous photocatalytic surface reactions.

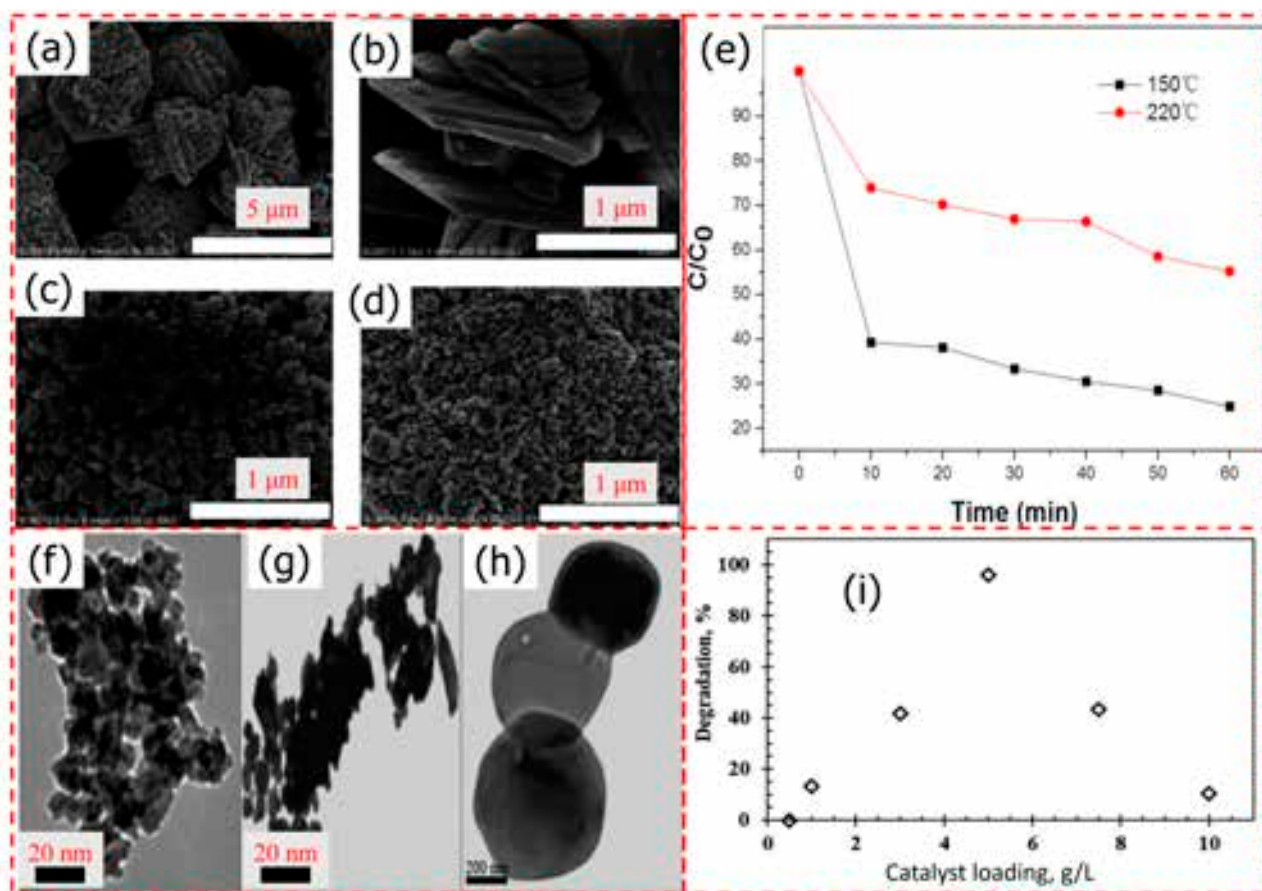


**Figure 18.** (a,b) SEM images of WO<sub>3</sub> calcined at 150 °C, and (c,d) at 220 °C. (e) The photodegradation profile of MB in the presence of the WO<sub>3</sub> photocatalyst under NIR laser irradiation. Adopted with permission from Ref. [148] Copyright 2022, Springer Nature. TEM images of WO<sub>3</sub> particles calcined at (f) 300 °C, (g) 500 °C, and (h) 700 °C, and (i) effect of catalyst loading on the photocatalytic degradation of RhB at a pH 9.5 and 5 ppm RhB at a calcination temperature of 300 °C. Adopted with permission from Ref. [143] Copyright 2022, Royal Society of Chemistry.

## 5. Conclusions and Future Perspectives

Due to the industrial revolution in the modern world, various pollutants are emitted into the environment, both directly and indirectly. Thus, great efforts have been devoted to develop advanced technology for the elimination of such environmental pollutants. One of the most promising methods for meeting global needs in an environmentally responsible manner is photocatalysis. Metal oxides are found to be potential photocatalysts because of their affordability, effectiveness, and environmental friendliness. Furthermore, metal oxides may be widely used in a wide range of applications because of their large surface area, simplicity of fabrication, and sufficient supply. Moreover, metal oxides are abundant, highly active, and could be prepared either through eco-friendly or conventional methods in large quantities. Unfortunately, a few drawbacks prevent them from being used practically, including a large bandgap, a high rate of photogenerated electron–hole pair recombination, and catalyst deactivation. Therefore, various strategies have been developed to overcome these limitations; one of these techniques is the design of metal oxides with unique morphologies. The morphology of metal oxides displayed a significant influence on the overall degradation performance, as indicated by shifting the photocatalytic degradation toward various kinds of dyes in aqueous solutions. Therefore, in the current study, the recent progress in the photocatalytic degradation of organic dyes by prominent metal oxides with different morphologies is discussed. The metal oxide nanoparticles, namely, TiO<sub>2</sub>, ZnO,

CuO, NiO, and WO<sub>3</sub>, all are widely utilized for the photodegradation of various organic dyes. The non-spherical morphologies such as nanorods and nanowires exhibit enhanced photocatalytic performance due to their unique crystal facets and surface areas, which can promote charge transfer and improve catalytic efficiency. Ultimately, the selection of a particular morphology for a photocatalyst relies on the specific application and the desired properties. The porous design and the substantial specific surface area are responsible for the increased photocatalytic activity. On the other hand, the flake-like structure exhibits comparatively lower performance.

In the future, it is highly recommended to do more research to more deeply understand the degradation mechanisms of metal oxides with different morphologies. Until now, most of the prepared metal oxides with different morphologies were obtained by using conventional methods on their appropriate precursors. Some of them are toxic or require the use of a high temperature or organic solvents during the procedure, which is not preferred for sustainability. Thus, it is important to find alternative, sustainable methods for preparing these oxides with different morphologies. Presently, there are some studies reporting the preparation of NiO using green methods; however, they are limited in number and need to be more accurate, as well as to prepare other metal oxides such as TiO<sub>2</sub>, ZnO, CuO, and WO<sub>3</sub> for organic dye degradation in aqueous solutions.

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## Article

# The Influence of Annealing Temperature on the Microstructure and Electrical Properties of Sputtered ZnO Thin Films

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**Abstract:** Thin films are the backbone of the electronics industry, and their widespread application in heat sensors, solar cells, and thin-film transistors has attracted the attention of researchers. The current study involves the deposition of a hetero-structured (ZnO/Zn/ZnO) thin film on a well-cleaned glass substrate using the DC magnetron sputtering technique. The samples were then annealed at 100, 200, 300, 400, and 500 °C. The structural, morphological, and electrical characteristics of the annealed samples as well as one as-deposited sample were then examined using atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and a Hall effect measuring apparatus. XRD analysis showed a hexagonal ZnO crystal structure for the samples annealed at 300 and 400 °C, whereas the samples annealed at 100 and 200 °C showed metallic zinc and hexagonal ZnO, and the crystallinity decreased for the sample annealed at 500 °C with pure hexagonal crystal symmetry. According to the AFM study, as the annealing temperature increases, the average roughness ( $R_a$ ) decreases. Temperature has an inverse relationship with particle size. The optimal annealing temperature was determined to be 400 °C. Over this temperature range, the average roughness and particle size increased. Similarly, when  $R_a$  decreased, the conductivity increased and the resistance decreased. A fundamental difficulty is that the heating of the heterostructure to 400 °C melts the Zn-based intermediate layer, which alters the Zn phase and disrupts the sample homogeneity.

**Keywords:** ZnO; Zn; heterostructure; annealing; sputtering



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## 1. Introduction

Semiconductor nanomaterials play a significant role in renewable energy, notably in thin-film solar cells, and have attracted the attention of scientists and researchers worldwide [1]. Many elemental and compound semiconductor nanomaterials have been investigated, with ZnO being one of the most prominent and promising [2]. ZnO is a binary II–VI compound semiconductor material having Wurtzite crystal structure, a wide and direct bandgap of 3.3 eV at ambient temperature, and an exciton binding energy of 60 meV [3–5]. It can be grown in several different types of nanoscales, thus making it possible to obtain various novel products [6]. Moreover, the properties of ZnO can be altered by fabricating thin films [7]. ZnO thin films have been extensively researched in various areas due to their high bond strength [8], good optical performance [9], severe exciton stabilisation [10], and outstanding piezoelectric properties [11], and they have many prospective applications in multiple technological areas, such as clear film/electrodes [12] in screen systems and solar energy [13]. Another benefit of ZnO compared to other metals is its substantial cost, which makes it an extremely prospective candidate for industrial applications [14]. ZnO is currently one of the leading materials used as a window layer [9], transparent conducting oxide (TCO) [15,16], and buffer layer in the solar cell industry [17].

The transparent conductive oxides (TCOs) thin films have several options in optoelectronic devices. Such thin films can be used especially for organic light-emitting diodes (OLEDs) [16], solar cells, heat sensors [18,19], and thin-film transistors (TFTs) [20]. One of the most studied and industrially used TCO is tin-doped indium oxide (ITO) [17,21]. The

latest rise in consumption by the optoelectronic devices sector ITO has become rare and more expensive [6,22]. Because of its advantages in several fields and its unique characteristics like low price, non-toxicity, and good chemical stability in maintaining plasma, an extremely successful substitute for indium tin oxide (ITO) is ZnO [21,23]. Native and extrinsic defects in ZnO nanostructures, however, are considered to reach profound concentrations that limit their application performance [24]. A detailed understanding of the type, composition, and electronic parameters of deep-level facilities is the key to understanding and controlling electronic characteristics [7,25]. Understanding surface defect behaviour is essential for ZnO to be successfully applied [26]. Inherent defects and vacancies in ZnO are mainly classified into four kinds: surface defects including O vacancies ( $V_O$ ) and Zn vacancies ( $V_{Zn}$ ) and interstitials (Zn and O), which are part of the majority of the fabric [27,28]. ZnO's large-scale development process regulates the development of its inherent flaws [29,30]. It is recognized that the number of failures depends on a post-growth sample therapy, which can change its characteristics significantly [31,32]. However, in many practical systems, no control over defects is one of the major problems in using ZnO [33,34]. Thus, one way to control point and surface defects is to post-anneal the ZnO nanoparticles to obtain high UV photodetection in a short interval of time [26,32]. Higher temperature treatment in air and  $N_2$  results in excellent monitoring of surface-related abnormalities such as  $V_O$  and  $V_{Zn}$  and decreases radiative recombination of the surface defects [22,35]. To achieve a defect-free ZnO thin film, we used the magnetron sputtering method to deposit thin film at room temperature with a ZnO/Zn/ZnO heterostructure accompanied by thermal annealing at various temperatures. The objective of the ZnO/Zn/ZnO heterostructure was to obtain a defect-free ZnO thin film by harnessing the characteristics of the intermediate Zn layer. The metallic Zn layer exhibits a 'surfactant effect', promoting recrystallization during the deposition process. In conjunction with moderate-temperature annealing, the Zn layer facilitates the 'therapy' of surrounding ZnO crystallites, enhancing the overall crystalline quality by addressing lattice mismatches and thermal expansion differences, thereby reducing defects in the ZnO layers [36,37]. Furthermore, the Zn layer facilitates grain coalescence during thermal treatment, resulting in larger grain sizes and fewer grain boundaries, which are crucial factors in achieving a high-quality, defect-free ZnO thin film.

## 2. Results and Discussion

### 2.1. Surface Morphology

#### 2.1.1. Atomic Force Microscopy (AFM) Analysis

Figure 1 shows atomic force microscopy (AFM) images of annealed thin films in comparison to as-deposited films, whereas Figure 2 describes the influence of annealing temperature on the average roughness ( $R_a$ ) of the films.  $R_a$  measures the average length between the peaks and valleys and the deviation from the mean line on the entire surface within the sampling length. From Figure 1, one can observe that  $R_a$  first increases with an increase in the annealing temperature and then decreases to a minimum value. A minimum roughness was observed for the sample annealed at 400 °C, which is about 4.95 nm. A further increase in the annealing temperature results in an increase in the  $R_a$  value. A maximum  $R_a$  value was obtained for the sample annealed at 500 °C, which is about 10.60 nm. The initial decrease in roughness with increasing annealing temperature was attributed to the coalescence of the grains. A further increase in roughness with an increase in the annealing temperature may be due to the further increase in grain size. Moreover, the heterostructure is composed of three layers; that is, Zn is sandwiched between the ZnO layers. The melting point of Zn is 420 °C, whereas that of ZnO is 1975 °C. Increasing the annealing temperature from 400 °C to 500 °C changed the Zn phase from solid to liquid. The liquid Zn layer might penetrate or percolate into the interstitial pores in the underlying ZnO layers. This penetration can lead to a disruption in the uniformity of the ZnO structure, as the liquid Zn may fill voids and create localized regions of different densities or compositions. As can be seen, an increase in the peaks and valleys in the film results in an increase in the average roughness above the optimum value of the

annealing temperature. The infiltration of liquid Zn into the ZnO layers can also promote the formation of microcracks or other structural imperfections as the film cools down and as Zn solidifies, leading to an increase in the  $R_a$  of the film. Furthermore, the increase in  $R_a$  at higher annealing temperatures can be linked to the thermodynamic instability introduced by the liquid phase of Zn. As Zn re-solidifies upon cooling, it may not return to its original crystalline orientation, leading to further imperfections and non-uniformities in the ZnO/Zn/ZnO heterostructure.

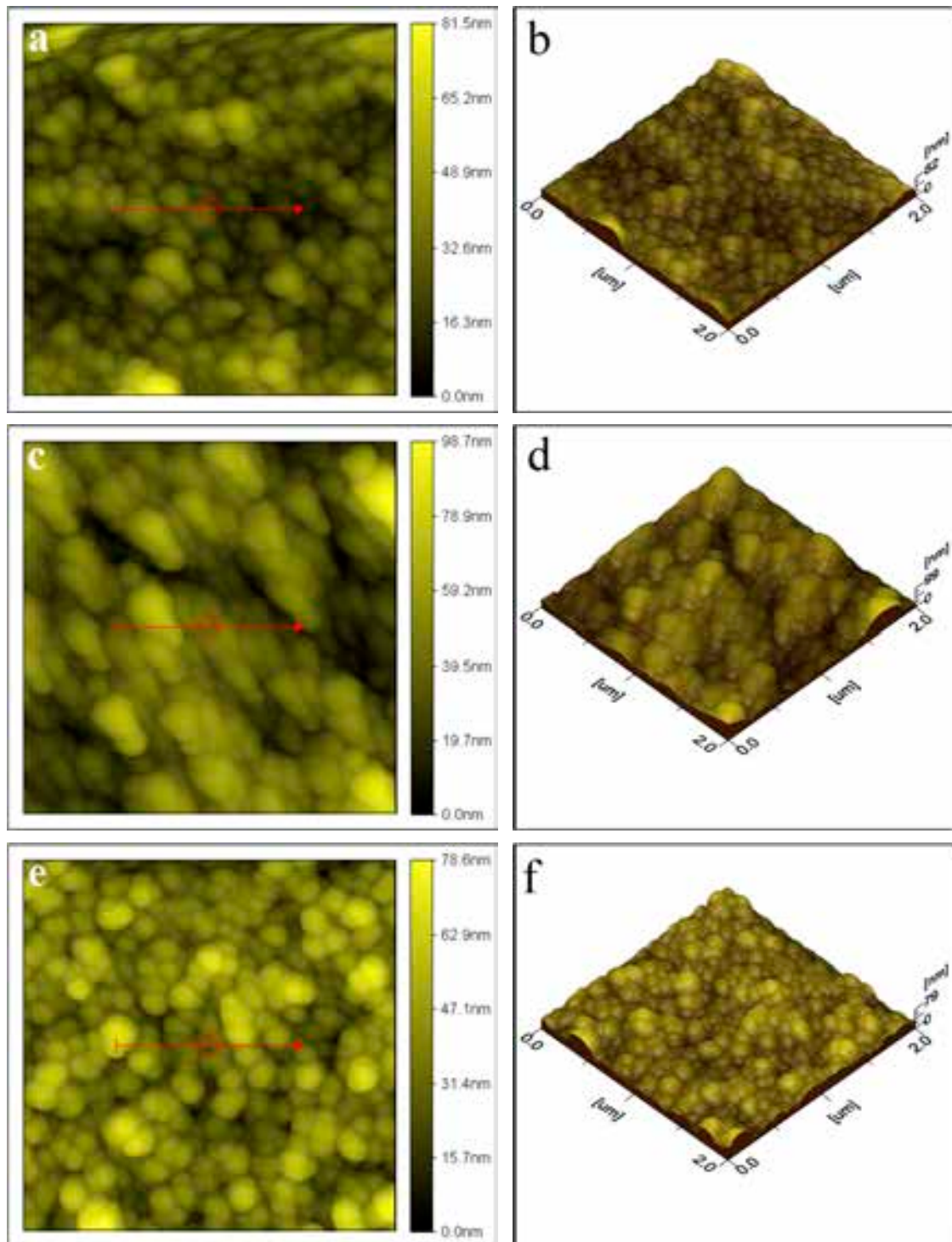


Figure 1. Cont.

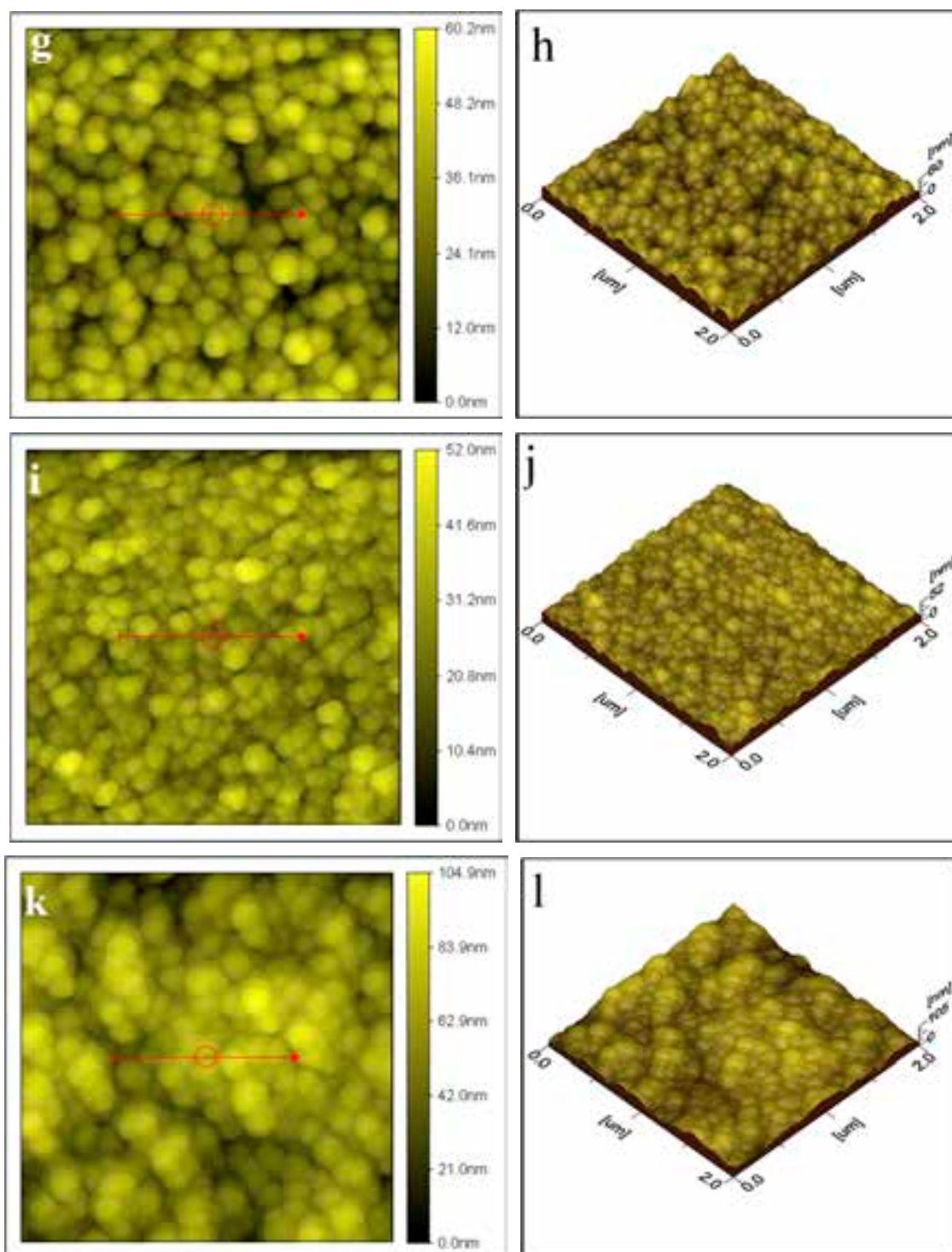


**Figure 1.** AFM 2D and 3D images of thin films: (a,b) as deposited, (c,d) annealed at 100 °C, (e,f) annealed at 200 °C, (g,h) annealed at 300 °C, (i,j) annealed at 400 °C, and (k,l) annealed at 500 °C.

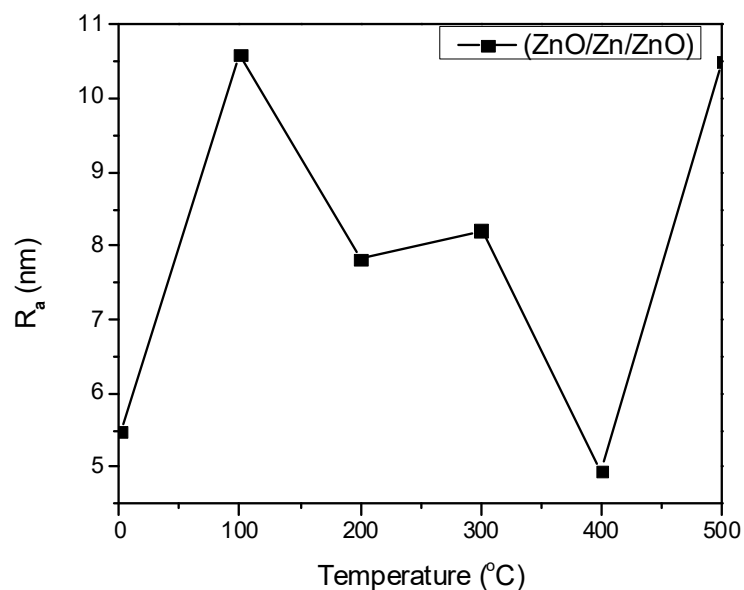


**Figure 2.** Average roughness ( $R_a$ ) vs. annealing temperature of thin films.

#### 2.1.2. Scanning Electron Microscopy (SEM) Analysis

Figure 3 shows the scanning electron microscopy (SEM) images of the ZnO/Zn/ZnO heterostructure of the as-deposited thin film in comparison with annealed thin films. The annealed samples have a smooth surface morphology compared to the as-deposited thin films. However, the surface smoothness is disturbed by the higher annealing temperature. Moreover, the average particle size also has a great impact on the annealing temperature. Table 1 lists the average particle size calculated for all the thin films along with the annealing temperature.

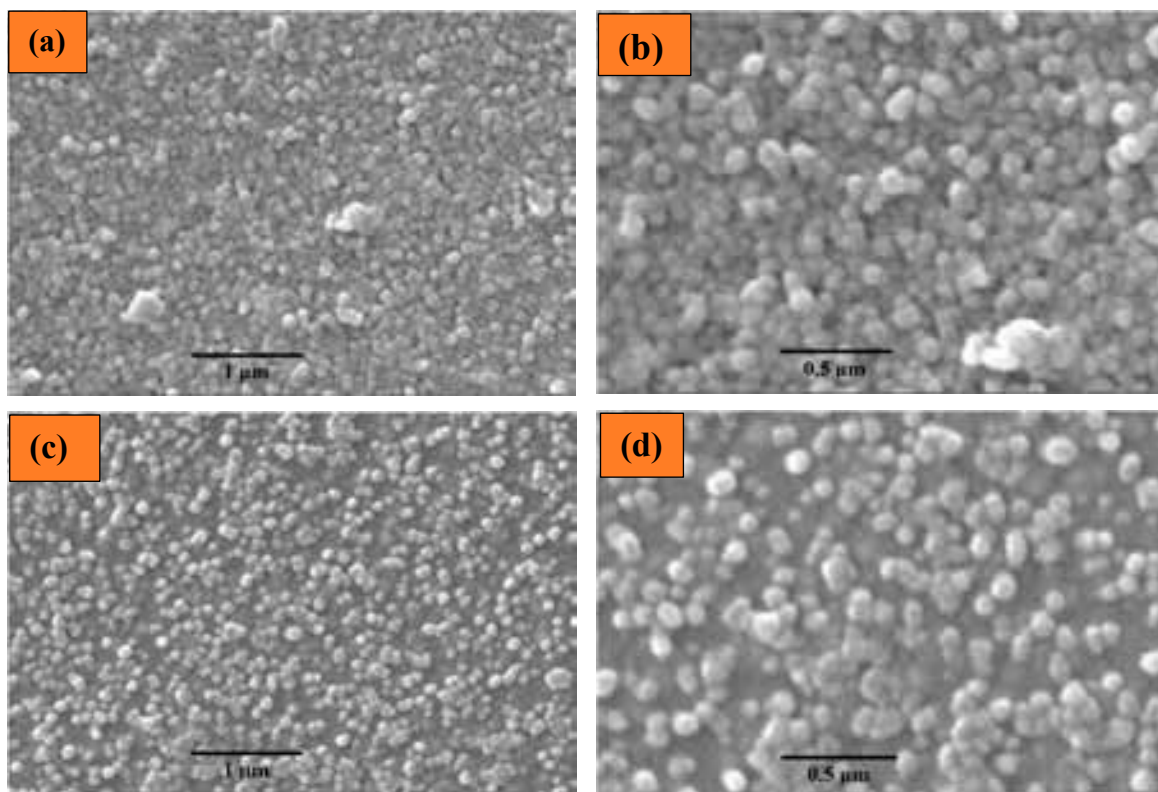


**Figure 3.** Cont.

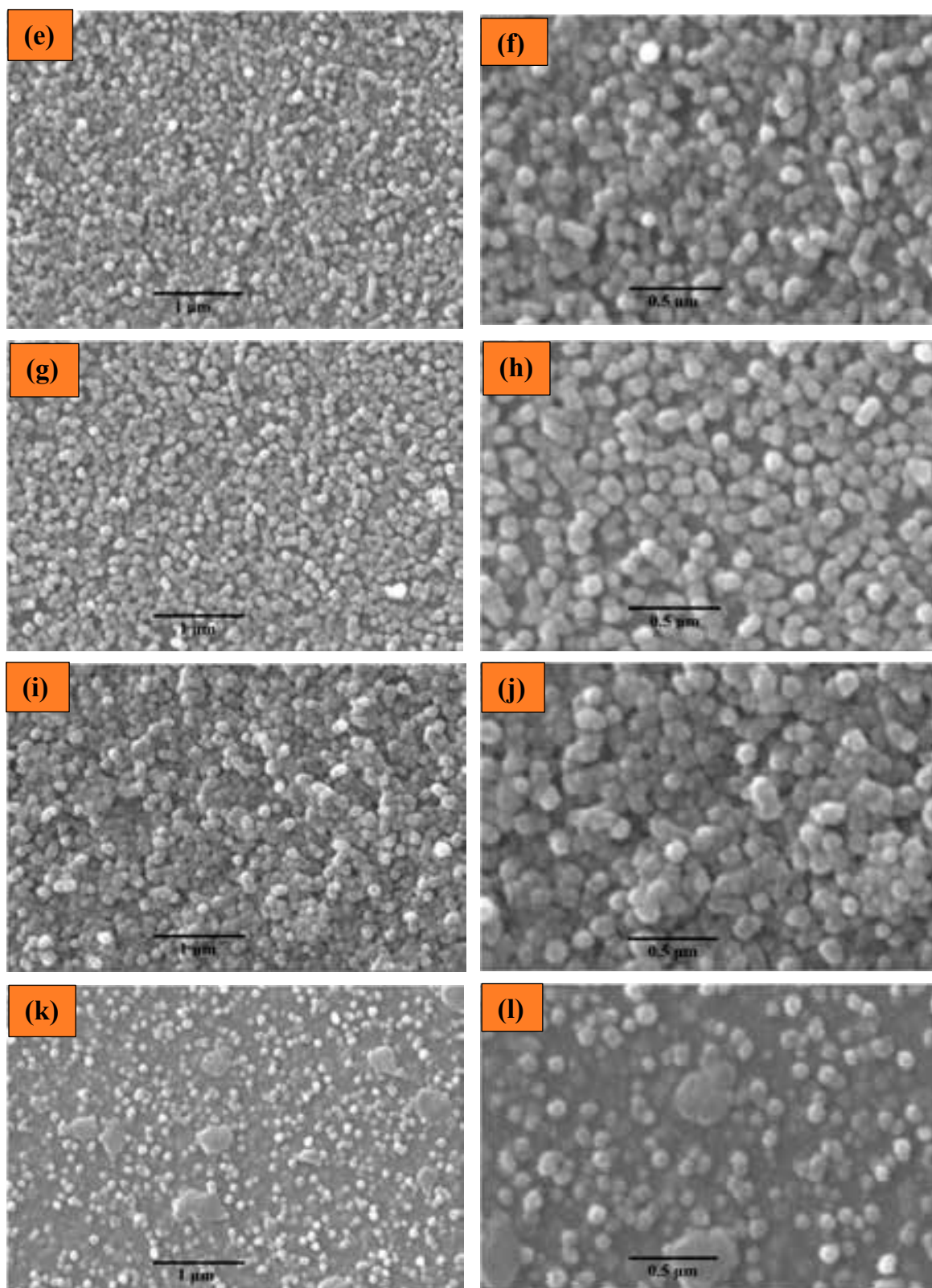
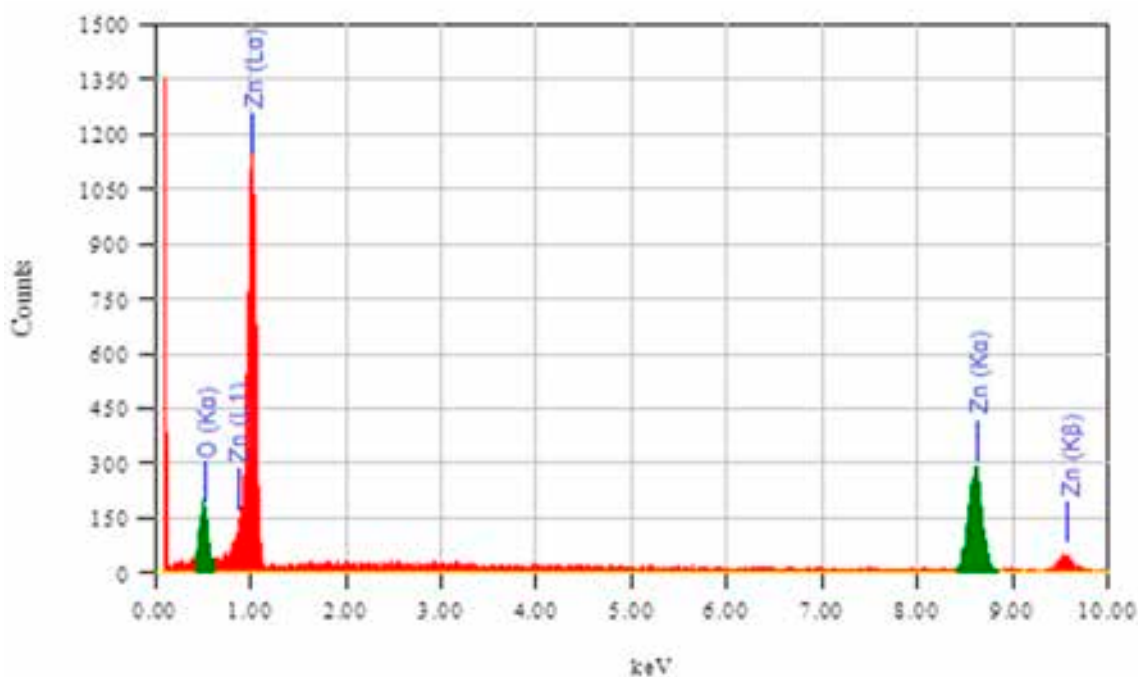


**Figure 3.** SEM images of thin films with low and high magnifications: (a,b) as deposited, (c,d) annealed at 100 °C, (e,f) annealed at 200 °C, (g,h) annealed at 300 °C, (i,j) annealed at 400 °C, and (k,l) annealed at 500 °C.

**Table 1.** Average particle size of thin films annealed at different temperatures in comparison to the as-deposited sample.

| S. No. | Thin Film    | Average Particle Size |
|--------|--------------|-----------------------|
| 1      | As deposited | $74.41 \pm 1.75$ nm   |
| 2      | 100 °C       | $78.08 \pm 1.83$ nm   |
| 3      | 200 °C       | $66.85 \pm 1.62$ nm   |
| 4      | 300 °C       | $54.46 \pm 1.23$ nm   |
| 5      | 400 °C       | $50.67 \pm 1.02$ nm   |
| 6      | 500 °C       | $163.00 \pm 2.51$ nm  |

From the table, we can see that the average particle size decreases with an increase in the post-heat treatment (annealing temperature). An optimum value of the particle size was calculated for the sample annealed at 400 °C. A further increase in temperature in the middle layer, which is comprised of Zn, affects the surface morphology and smoothness of the films. Figure 4 shows the energy dispersive X-ray (EDX) spectra of the film annealed at 400 °C, confirming that ZnO film is deposited.

**Figure 4.** EDX spectra of hetero-structured ZnO/Zn/ZnO thin film annealed at 400 °C.

## 2.2. Structural Analysis

Figure 5 displays the XRD patterns of the as-prepared ZnO/Zn/ZnO thin films that were prepared and subjected to annealing temperatures of 100, 200, 300, 400, and 500 °C. XRD offers valuable information regarding the crystalline structure and phase composition of the samples at various annealing temperatures. The XRD patterns of the sample that underwent annealing at 100 °C indicated the existence of a zincite hexagonal crystal structure. The diffraction peaks observed in the figure match those of the hexagonal zincite ZnO. However, there was also an extra peak corresponding to metallic Zn. This suggests that a portion of the Zn still existed in its metallic form. The XRD spectrum of the sample annealed at 200 °C exhibited peaks corresponding to both Zn and ZnO. The identification of the ZnO peaks provides evidence for the creation of the hexagonal structure of zincite, whereas the Zn peak indicates that a portion of the zinc did not undergo conversion at this particular temperature. The samples annealed at 300 and 400 °C displayed XRD patterns indicative of pure ZnO with a hexagonal crystal structure. There were no discernible peaks in the spectra corresponding to metallic Zn. This indicates the complete transformation

of Zn into ZnO, leading to the formation of a ZnO crystal structure with only one phase. Significantly, the strength of the diffraction peaks increased as the annealing temperature increased, culminating in the highest intensity at 400 °C. These findings indicate that the quality of the ZnO crystal structure is enhanced as the temperature increases, reaching its peak at 400 °C. However, the sample annealed at 500 °C exhibited a reduction in the intensity of the ZnO diffraction peaks in comparison to the sample annealed at 400 °C while still maintaining the pristine hexagonal structure of ZnO. The decrease in the maximum intensity at 500 °C can be ascribed to various factors. At elevated temperatures, excessive grain growth occurs, as discussed in the SEM and AFM results, and the particle size and roughness increase, resulting in the formation of imperfections within the crystal structure. The presence of these imperfections causes X-rays to disperse more widely, resulting in a decrease in the overall intensity of the diffraction patterns. Extended exposure to elevated temperatures can generate thermal stress in the thin film, which may lead to the formation of microcracks or other structural flaws that diminish the crystalline quality of the material.

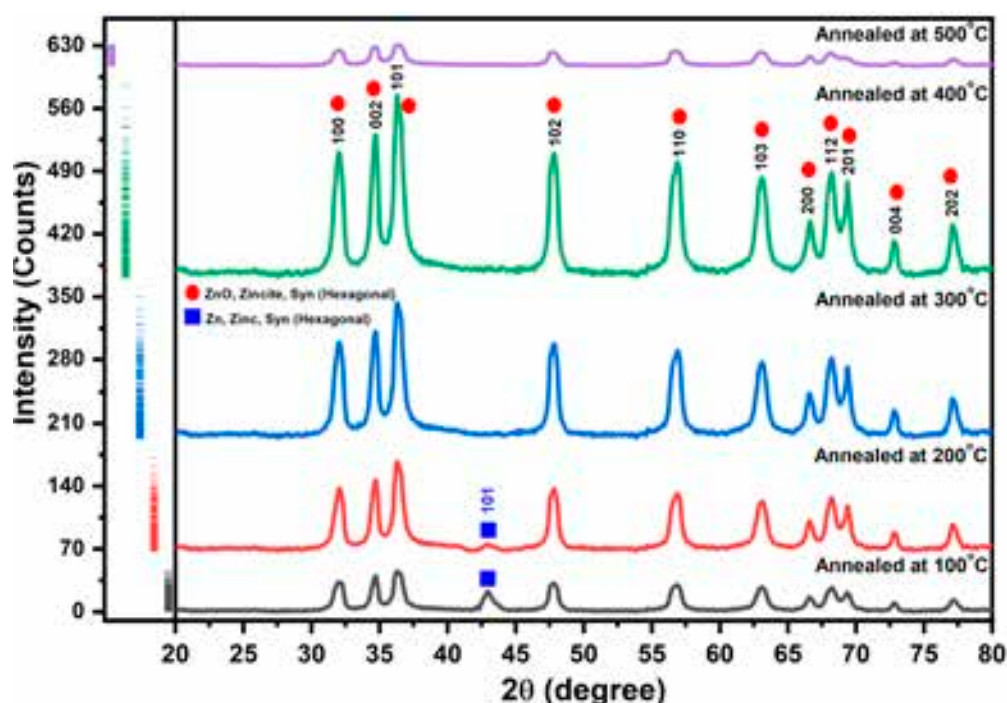


**Figure 5.** XRD spectra of ZnO/Zn/ZnO thin film annealed at 100, 200, 300, 400, and 500 °C.

### 2.3. Electrical Properties

Figure 6 shows the electrical resistivity and conductivity of the thin films annealed at different temperatures. In addition, Table 2 lists the electrical resistivity and conductivity values of the annealed and deposited thin films. From the figure and table, we can see that the electrical resistivity/conductivity of the film changes with an increase in the annealing temperature. The electrical behaviour demonstrates a complex relationship among particle size, surface roughness, and electrical conductivity, which is closely connected to the microstructural evolution during thermal annealing. The electrical conductivity of the thin films exhibited a substantial increase from the as-deposited state to a thin film annealed at 400 °C, as displayed in Figure 6. This improvement in conductivity is linked to the reduction in particle size and enhancement in crystalline quality, as demonstrated by the XRD analysis, as well as a corresponding decrease in surface roughness, which facilitates crystalline quality. The decrease in surface roughness from the as-deposited thin film to the 400 °C annealed film indicates a smoother film surface, which minimizes scattering sites for charge carriers, thus enhancing conductivity. Smaller particle sizes and improved crystal structures decrease the number of grain boundaries, which are known to act as

scattering centres for charge carriers (electrons and holes) [38–40]. The reduction in grain boundary scattering allows for more efficient carrier transport, thereby increasing the electrical conductivity of the films. However, a significant change occurred at 500 °C, where the particle size increased dramatically and the conductivity dropped sharply. This decline in conductivity can be ascribed to the formation of larger grains, which may introduce structural imperfections such as microcracks. These imperfections likely result from thermal stress or excessive grain growth, which disrupts the crystal structure and increases the scattering of carriers, ultimately leading to a higher electrical resistance [41]. This phenomenon aligns with the established understanding that while smaller grains typically increase resistance due to grain boundary scattering, excessively large grains can introduce new defects that also adversely affect conductivity.

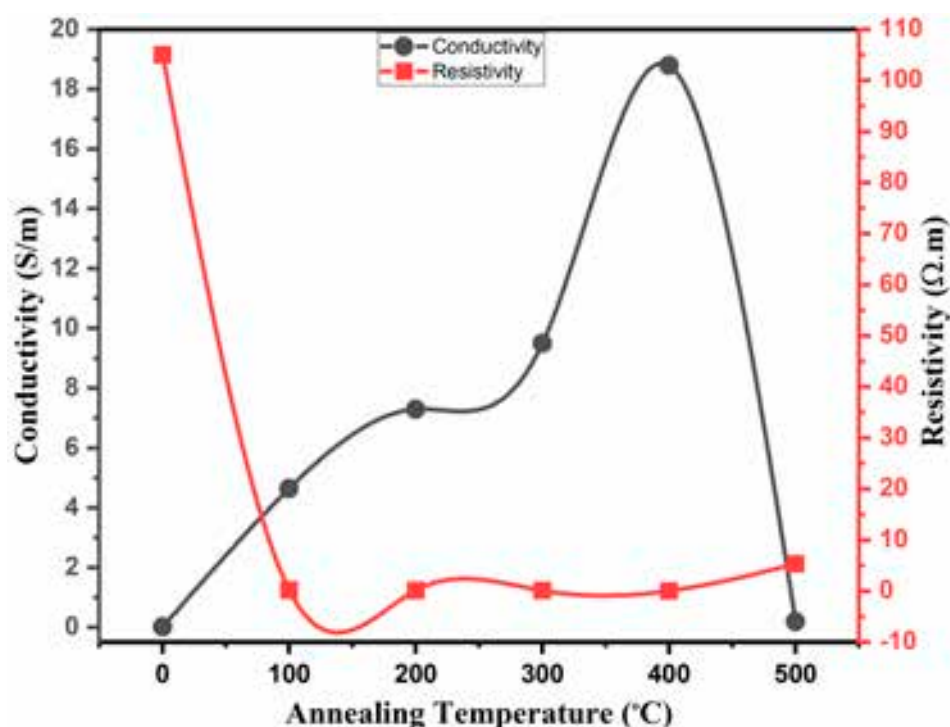


**Figure 6.** Resistivity/conductivity vs. annealing temperature of thin films.

**Table 2.** Electrical resistivity and conductivity values of thin films annealed at different temperatures in comparison to a deposited thin film.

| S. No. | Thin Film    | Electrical Conductivity (S/m) | Electrical Resistivity (Ω.m) |
|--------|--------------|-------------------------------|------------------------------|
| 1      | As deposited | 0.0095                        | 105                          |
| 2      | 100 °C       | 4.637                         | 0.2157                       |
| 3      | 200 °C       | 7.292                         | 0.1371                       |
| 4      | 300 °C       | 9.49                          | 0.105                        |
| 5      | 400 °C       | 18.79                         | 0.05321                      |
| 6      | 500 °C       | 0.187                         | 5.348                        |

### 3. Conclusions

In summary, magnetron sputtering was used to deposit hetero-structured (ZnO/Zn/ZnO) thin films on clean glass substrates. The resulting samples were annealed in an inert environment at 100, 200, 300, 400, and 500 °C. XRD analysis confirmed the presence and highly crystalline hexagonal structure of ZnO at 300 and 400 °C, whereas at other annealing temperatures, the sample either possessed metallic zinc or low crystallinity. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to effectively study the surface morphology and particle size. A Hall effect measurement device was used to analyse the

electrical characteristics. The annealed thin-film data were plotted in comparison with the deposited thin film. AFM analysis indicated that the average roughness (Ra) of the film decreased with an increase in the annealing temperature, reaching an optimum value of 4.95 nm for the sample annealed at 400 °C, and then increased with a further increase in the annealing temperature. SEM analysis showed that the particle sizes initially decreased with increasing annealing temperature but increased at higher temperatures. The Hall effect measurement system showed that the electrical resistivity decreased for the annealed samples. In addition, the resistivity showed a good relationship with the surface roughness of the thin films; the lower the surface roughness with lower scattering centres of charge carriers, the lower the resistivity. The sample annealed at 400 °C exhibited the lowest resistivity.

#### 4. Experimental

This section discusses the fabrication process of a hetero-structured (ZnO/Zn/ZnO) thin film and its thermal annealing at different temperatures and gives the description used to analyse the morphological, topographical, structural, and electrical properties of the samples. Magnetron sputtering was used to deposit a hetero-structured (ZnO/Zn/ZnO) thin film on a glass substrate, which was subsequently annealed at 100, 200, 300, 400, and 500 °C.

##### 4.1. Films Deposition

###### 4.1.1. Substrate Preparation

The cleanliness of the substrate is crucial for achieving high-quality thin films. Soda-lime glass slides (SLG) (cat. No. 7105) were cut into small squares (10 cm × 10 cm × 1 cm) using a diamond saw cutter. The cleaning process involved several steps. First, the substrates were immersed in methanol and cleaned ultrasonically for 30 min to remove organic residues. Washing with the soap solution was then carried out, followed by rinsing in deionised water. Subsequently, the substrates were immersed in a chromic acid solution for 20 min. Finally, the substrates were ultrasonically cleaned with water for 30 min. Subsequently, the substrate surface was dried by blowing pressurised inert gas and immediately transferred to the deposition chamber.

###### 4.1.2. Sputtering System and Film Deposition Process

Deposition of ZnO and Zn thin films over SLG substrates was performed using a disk-shaped ZnO and Zn target (100 mm diameter, 8.25 mm thickness) in a magnetron sputtering system (Alliance Concept, DP650, Annecy, France). The system consisted of mechanical and turbomolecular pumps, sputtering guns, RF and DC power supplies, and heating and bias capabilities for substrate support. Each film deposition cycle included the following steps: After loading the substrates, the chamber was evacuated to a base pressure of a few microtorr, followed by the introduction of argon gas. The argon flow rate was maintained at 20 sccm to achieve a pressure of 10 mTorr. The DC power was then turned on, and its value was adjusted to the desired level. Initially, the target was sputtered with its shutter closed for approximately 15 min to remove any native oxide layer present on its surface. Subsequently, ZnO (bottom layer), Zn (middle layer), and ZnO (top layer) film deposition was performed to fabricate films with a thickness of 1.5 µm, 30 nm, and 75 nm, respectively. The base pressure was maintained at  $7.49 \times 10^{-6}$  bar, and a 300 W DC power source was employed to keep the potential difference between the target and glass substrate constant. During growth, the film thickness was monitored using a quartz crystal microbalance. The sputtered samples were annealed in an inert argon atmosphere for 1 h at 100, 200, 300, 400, and 500 °C. The deposition parameters are listed in Table 3.

**Table 3.** Deposition parameters of ZnO/Zn/ZnO thin films heterostructure.

| Deposition Parameters                        |     | ZnO               | Zn    | ZnO   |
|----------------------------------------------|-----|-------------------|-------|-------|
| Pressure (mTorr)                             |     | 25                | 50    | 50    |
| Power (Watt)                                 |     | 300               | 300   | 300   |
| Thickness                                    |     | 1.5 $\mu\text{m}$ | 30 nm | 75 nm |
| Annealing Temperature ( $^{\circ}\text{C}$ ) |     |                   |       |       |
| 100                                          | 200 | 300               | 400   | 500   |

#### 4.2. Characterization Tools

The surface morphologies of the as-grown and annealed multilayer structures were examined using scanning electron microscopy (SEM) (JSM-840, JEOL, Tokyo, Japan) with an operating voltage of 15–20 kV, spot size of 30–50 nm, and working distance of 10 mm. For SEM analysis, samples were coated by sputtering 100 nm gold, and small silver strips were placed on the sample to make it conductive. Atomic force microscopy (AFM) (JEOL SPM-5200) was used to examine the topography and measure the surface roughness of the multilayer structure while operating in the non-contact mode with scan sizes of  $(10 \times 10)$  and  $(3 \times 3) \mu\text{m}^2$ . X-ray diffraction (XRD) was used to determine the structural and phase purity of the prepared samples using a D8 ADVANCE, Bruker, Germany instrument over the range of  $20$ – $80^{\circ}$  with Cu  $K\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ) and a step size and dwell time of 0.041 and 3 s, respectively. The electrical conductivity was measured using either a four-point electrical resistance probe or a Hall automated measuring system utilizing the Van-Der-Pauw method (Ecopia HMS-5000, Bridge Technology, USA). Four electrodes of gold paste were placed at four different equal points, and four needle tips were placed to measure the voltage and current.

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**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the author.

**Conflicts of Interest:** The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Article

# Synthesis and Redox Properties of Iron and Iron Oxide Nanoparticles Obtained by Exsolution from Perovskite Ferrites Promoted by Auxiliary Reactions

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**Abstract:** Nanoparticles of iron and iron oxides, as well as their composites, are of great scientific and technological interest. However, their properties and sustainability strongly depend on the preparation methods. Here, we present an original approach to synthesizing Fe and FeNi<sub>x</sub> metal nanoparticles by exsolution, in a reducing environment at elevated temperatures from perovskite ferrites (La<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3-γ</sub>, CaFeO<sub>2.5</sub>, etc.). This approach is made possible by the auxiliary reactions of non-reducible A-site cations (in ABO<sub>3</sub> notation) with the constituents of reducing compounds (h-BN etc.). The nanoparticles exsolved by our process are embedded in oxide matrices in individual voids formed in situ. They readily undergo redox cycling at moderate temperatures, while maintaining their localization. Fe nanoparticles can be obtained initially and after redox cycling in the high-temperature γ-form at temperatures below equilibrium. Using their redox properties, a new route to producing hollow and layered oxide magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/La<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3-γ</sub>), by separating the oxidized exsolved particles, was developed. Our approach provides greater flexibility in controlling exsolution reactions and matrix compositions, with a variety of possible starting compounds and exsolution degrees, from minimal up to ~100% (in some cases). The described strategy is highly important for the development of a wide range of new functional materials.

**Keywords:** transition metal-embedded nanoparticles; metal exsolution; <sup>57</sup>Fe Mössbauer spectroscopy; redox behavior; hollow and layered oxide nanoparticles; cup-shaped nanoparticles; nano zero valent iron (nZVI) particles; γFe nanoparticles



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## 1. Introduction

Nanomaterials based on nanoparticles of transition metals and/or their oxides are of great interest from both scientific and practical viewpoints. Their applications are very diverse and include catalytic, magnetic, electronic, sorption, and pharmaceutical functional materials, utilizing various types of nanoparticles (supported, embedded, individual nanoparticles of various shapes) [1–3]. Many transition metal nanoparticles are chemically active and, therefore, suffer from a lack of stability, which is further exacerbated by their tendency for recrystallization, agglomeration, and growth, etc., especially at elevated temperatures. Supported/embedded nanocomposite materials have the potential to combine useful properties of both nanoparticles and matrices and maintain long-term stability and durability [1,3,4]. Moreover, those materials can develop new features due to the synergy between nanoparticles and the support, which is attributed to the intrinsic properties of the components and the strength of their interaction [4–7].

There are a wide variety of ways to produce these diverse nanoparticle-based nanomaterials [5,8,9]. One of the actively developing strategies for the synthesis of nanocomposite materials with stronger metal nanoparticle–substrate interactions (and, therefore, enhanced functionality and stability) is based on the thermal decomposition of complex oxides under

reducing conditions. This kind of decomposition can be complete or partial and, especially the latter, is termed metal exsolution. In this approach, the complex oxides must contain both reducible and non-reducible metals under conditions of synthesis [10–13]. The main progress in this field is associated with the use of perovskite-related oxides of transition metals. It is a vast family of oxides with various stoichiometry ( $\text{ABO}_3$ ,  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$  Ruddlesden–Popper (RP) phases, etc.), whose crystal structures are based on  $[\text{AO}_3]$  close-packed layers, where the main constituents of A-sites are non-reducible rare-earth or alkaline-earth cations, while B-sites, in the interstices, can contain reducible cations of transition metals (Fe, Co, Ni, Cu, etc.) [14,15]. A series of  $\text{Ln}_2\text{O}_3/\text{M}$  nanocomposites, obtained by complete redox decomposition of the perovskite precursors of easily reducible transition metals ( $\text{M} = \text{Ni}, \text{Co}$ , etc.), were reported as metal nanoparticle-supported catalytic materials with enhanced productivity and stability [16,17]. However, the synthesis of nanocomposites by partial redox decomposition of perovskites requires methods to control the processes of metal nanoparticle exsolution and matrix transformations. Several approaches are proposed in the literature to facilitate metal exsolution in this manner [10–12,18]. One approach includes modification of the initial oxides, such as introducing an A-site deficiency [19,20], doping of B-sites with easily reduced cations [19,21,22], and promoting the formation of RP phases by adjusting the composition of A-sites [13], as well as others. Another approach is to use special reduction conditions, such as lattice strains, voltage biasing, and plasma assistance, as well as varying the temperature and  $\text{pO}_2$  [13,18].

Metal reduction and exsolution is accompanied by changes in the parent perovskite matrices, which can occur in different ways. One such change is that the starting A-site-deficient perovskites are converted into stoichiometric ones, with minimal topotactical changes [21,23]. Another possible change is the formation of the corresponding oxides of non-reducible metals ( $\text{La}_2\text{O}_3$ , etc.) [17]. Yet another change is that the initial  $\text{ABO}_3$ -based perovskites can be transformed into RP phases, with different A to B ratios for some A-site compositions (containing  $\text{Sr}^{2+}$ , etc.) [13].

Although the metal exsolution process is widely employed to enhance surface properties, it can also be used to modify the bulk properties of functional nanocomposites [24–26]. The exsolution at the interior grain and phase boundaries, together with the simultaneous transformation of host oxide matrices, provide a new pathway for the modification of a wide range of electrical, optical, and magnetic properties [25,26].

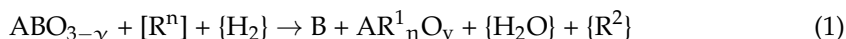
Overall, metal exsolution is a smart and effective strategy, with great potential for the preparation of new functional materials, with enhanced and unique properties. Its implementation, however, largely depends on the specific parent perovskite oxides and the appropriate reaction conditions [10,13,25]. Consequently, further development of methods for tuning the properties of the resulting nanocomposites, by controlling the exsolution process, is needed.

Herein, we present a novel approach to metal exsolution using perovskite-related ferrites, where B-metal exsolution is promoted by the additional auxiliary reactions involving non-reducible A-site cations. We have explored the behavior of a number of La and Ca-based ferrites in this new type of reaction, resulting in the formation of nanocomposites with nanoparticles embedded in individual voids, which are significantly different from the exsolved materials reported previously. The unique properties of the nanoparticles obtained in this manner, as well as the transformation of oxide matrices, will be discussed. It was shown that exsolved metal nanoparticles can be reversibly transformed into oxides in redox cycling, while maintaining their location inside the matrices. Moreover, the use of the chemical properties of nanocomposite matrices derived from alkaline earth-based ferrites makes it possible to separate and investigate the oxide nanoparticles obtained by the oxidation of exsolved metal nanoparticles.

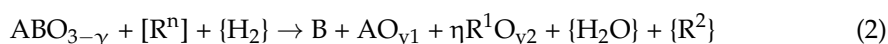
## 2. Results and Discussion

### 2.1. The Main Concept of Metal Exsolution Promoted by Auxiliary Reactions

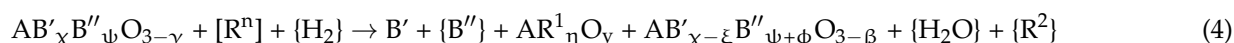
In this study, the synthesis of Fe-containing nanoparticles and nanocomposites is based on a specially developed process for metal exsolution from complex perovskite-related oxides of reducible transition metals (Fe, Ni, etc.). Our new strategy is to facilitate B-site reducible metal exsolution through additional auxiliary reactions (ARs) of non-reducible A-site (in the  $ABO_3$  notation) cations with the constituents of reducing compounds, resulting in new complex oxides. This strategy, in a general simplified form, is described by schematic reaction (1):



Here,  $[R^n]$  is a reducing compound that reduces B cations, and at the same time, some (or all) of its constituents ( $R^1$ ) form new complex oxides with non-reducible A-site cations that do not contain reducible B cations. In general,  $[R^n]$  ( $R^1R^2$ , etc.) compounds can have a different chemical nature and aggregate states. For clarity of the explanation, the overall reaction can be nominally split into two consecutive pseudo-reactions, (2) and (3):



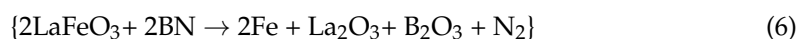
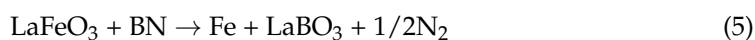
Chemical reactions for the formation of complex oxides containing  $R^1$  and non-reducible A-site cations (1b type) are designated here as auxiliary reactions. Curly brackets  $\{\}$  denote possible compounds. The reaction proceeds at elevated temperatures and under low  $pO_2$  conditions, which are required for the formation and preservation of the B components in metal form. An important feature of reaction (1) is that the main source of oxygen for the formation of the resulting oxides is the initial oxides. This imposes limitations on the possible ratios of  $R^1$  and A cations in the resulting complex oxides. If the initial oxides include two or more different B cations, then reaction (1) will be more complex depending on the B cation properties, as shown schematically below:



Reaction (4) illustrates that all the different B cations can be exsolved to various degrees, or that the irreducible or less reducible ones can remain in perovskite oxides. The exsolved metals can also form alloys.

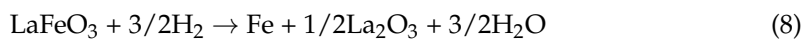
### 2.2. $LaFeO_3$ and $Ca_2Fe_2O_5$ -Based Nanocomposites

For  $LaFeO_3$  as a starting material and hexagonal BN as a reducing compound, the A-site cation AR (ACAR)-promoted exsolution can be written as reaction (5) (for clarity purposes, along with the nominal pseudo-reactions (6) and (7)):



Herein, the processes involving reaction (5) were carried out at elevated temperatures of 700–750 °C, in a reducing atmosphere, provided by a 10%  $H_2$ /Ar flow. Although hydrogen is not formally involved in the reaction, its role here is to maintain low  $pO_2$  conditions, essential for the existence of metal Fe nanoparticles. The formation of lanthanum borate  $LaBO_3$  provides an additional driving force for the reduction of  $LaFeO_3$  and decreases the reaction temperature compared to a reduction with hydrogen. The

specified temperatures of reaction (5) are below the decomposition temperature of  $\text{LaFeO}_3$  in a hydrogen-containing atmosphere, which is reported to be  $>850^\circ\text{C}$  [27,28]. Thus, its decomposition, described by reaction (3), does not occur under these conditions.



It is important to maintain reaction (5) as a main process. It should be noted that the higher temperature stability under reducing conditions makes ferrites more preferable starting materials compared to other perovskite-like compounds of reducible transition metals (cobaltites, nickelates, cuprates, etc.) [27].

Moreover, h-BN has a number of properties making it suitable for reactions of type (1, 5). First of all, it has decent reactivity in reactions of type (1, 4) with rare-earth (La, Y, etc.) and alkali-earth (Ca, Sr, etc.) perovskite-related ferrites. At the same time, it is exceptionally stable in inert and reducing atmospheres, and is also quite resistant to oxidation at moderate temperatures in air.

Figure 1 shows the powder XRD patterns of the  $\text{LaFeO}_3$  ferrite-based samples after interaction with h-BN at  $\sim 750^\circ\text{C}$  with different amounts of exsolved Fe, depending on the  $\text{LaFeO}_3/\text{h-BN}$  ratio. As the reaction proceeds, the peaks corresponding to  $\text{LaBO}_3$  and metal Fe appear in patterns, which are consistent with reaction (5) (Figure 1(a1)). The metal Fe peaks are distinguishable, but they strongly overlap with the  $\text{LaBO}_3$  ones. The corresponding Mössbauer spectra are shown in Figure 1(b1,b2). Each of the spectra consist of two magnetically split sextet components and a paramagnetic singlet component. All the components are well resolved and do not broaden. According to their hyperfine parameters (Table 1), the first of two sextets with an isomer shift ( $\delta$ ) of  $0.37\text{ mm s}^{-1}$  and a hyperfine magnetic field ( $H_{\text{hf}}$ ) of 52.4 T correspond to  $\text{LaFeO}_3$  and the second, with  $\delta \sim 0\text{ mm s}^{-1}$  and  $H_{\text{hf}} = 33\text{ T}$ , correspond to  $\alpha\text{Fe}$ . The paramagnetic singlet, according to its hyperfine parameters ( $\delta \sim -0.1\text{ mm s}^{-1}$  at 298 K), corresponds to metal  $\gamma\text{Fe}$ . Moreover,  $\gamma\text{Fe}$  is a high-temperature paramagnetic form, with a close-packed fcc crystal structure. It is important to note that  $\gamma\text{Fe}$  is metastable at temperatures below  $910^\circ\text{C}$  [29], while the synthesis temperature was  $\sim 750^\circ\text{C}$ . The metal  $\gamma\text{Fe}$  nanoparticles, however, may be undetectable in the XRD patterns (Figure 1(a2,b3)). The SEM images of  $\text{LaFeO}_3$  after the ACAR exsolution display smooth surfaces, without distinguishable metal Fe nanoparticles distributed on them (Figure 2a). Figure 2b,c shows typical TEM images of such samples. For the samples at the low or moderate extent of reaction (Figure 2b,c), the images reveal agglomerated grains of different contrast, probably due to variations in thickness, but exsolved metal Fe particles are not clearly distinguishable. For the samples at the high extent of reaction  $>40\%$ , obtained after prolonged heating for more than 15 h, the metal Fe particles are also largely undistinguishable, but some whisker-like metal Fe agglomerates are visible (Figure 2d) in small amounts with respect to the reaction extent. Additionally, the EDX analysis revealed numerous La-rich oxide grains, which, according to the XRD analysis, are actually  $\text{LaBO}_3$ , since boron is undetectable. Therefore, the metal Fe particles are embedded in the oxide matrix after the ACAR-promoted exsolution, which makes them hard to distinguish, except for the formation of whiskers, if any.

**Table 1.** Hyperfine parameters of Mössbauer spectra of the  $\text{LaFeO}_3/\text{h-BN}$ -derived nanocomposites measured at RT (except Figure 1(b2) at 78 K):  $\delta$ —isomer shift,  $\Delta\text{EQ}$ —quadrupole splitting,  $H$ —hyperfine magnetic field,  $A$ —relative area, —linewidth.

| Sample          | Component | $\delta$<br>( $\text{mm s}^{-1}$ )<br>$\pm 0.01$ | $\Delta\text{EQ}$<br>( $\text{mm s}^{-1}$ )<br>$\pm 0.01$ | $H$<br>(T)<br>$\pm 0.1$ | $A$<br>(%)<br>$\pm 0.5$ | ( $\text{mm s}^{-1}$ )<br>$\pm 0.01$ | Comments                                  |
|-----------------|-----------|--------------------------------------------------|-----------------------------------------------------------|-------------------------|-------------------------|--------------------------------------|-------------------------------------------|
| In Figure 1(b1) | s11       | 0.37                                             | −0.07                                                     | 52.4                    | 71                      | 0.26                                 | $\text{Fe}^{3+}$ oct. in $\text{LaFeO}_3$ |
|                 | s21       | −0.01                                            | −0.01                                                     | 33.0                    | 18                      | 0.24                                 | $\alpha\text{Fe}$                         |
|                 | d11       | −0.10                                            | 0.00                                                      | —                       | 11                      | 0.25                                 | $\gamma\text{Fe}$                         |

Table 1. Cont.

| Sample                  | Component | $\delta$<br>(mm s <sup>-1</sup> )<br>±0.01 | $\Delta EQ$<br>(mm s <sup>-1</sup> )<br>±0.01 | H<br>(T)<br>±0.1 | A<br>(%)<br>±0.5 | (mm s <sup>-1</sup> )<br>±0.01 | Comments                                                 |
|-------------------------|-----------|--------------------------------------------|-----------------------------------------------|------------------|------------------|--------------------------------|----------------------------------------------------------|
| In Figure 1(b2)<br>78 K | s12       | 0.48                                       | −0.07                                         | 56.2             | 71               | 0.25                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s22       | 0.11                                       | 0.01                                          | 33.8             | 18               | 0.25                           | αFe                                                      |
|                         | d12       | 0.01                                       | 0.00                                          | -                | 11               | 0.25                           | γFe                                                      |
| In Figure 1(b3)         | s13       | 0.37                                       | −0.07                                         | 52.4             | 46               | 0.27                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s23       | 0.00                                       | 0.00                                          | 33.0             | 45               | 0.24                           | αFe                                                      |
|                         | d13       | −0.10                                      | 0.00                                          | -                | 8                | 0.25                           | γFe                                                      |
| In Figure 1(b4)         | s15       | 0.37                                       | −0.07                                         | 52.3             | 72               | 0.25                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s25       | 0.00                                       | 0.00                                          | 33.0             | 28               | 0.24                           | αFe                                                      |
| In Figure 3(1)          | s123      | 0.37                                       | −0.06                                         | 52.4             | 68               | 0.27                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s223      | 0.00                                       | 0.01                                          | 33.1             | 23               | 0.23                           | αFe                                                      |
|                         | d123      | −0.10                                      | 0.00                                          | -                | 9                | 0.26                           | γFe                                                      |
| In Figure 3(2)          | s124      | 0.37                                       | −0.07                                         | 52.2             | 70               | 0.26                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s224      | −0.01                                      | 0.01                                          | 33.0             | 17               | 0.21                           | αFe                                                      |
|                         | d124      | −0.10                                      | 0.00                                          | -                | 13               | 0.23                           | γFe                                                      |
| In Figure 3(3)          | s125      | 0.37                                       | −0.07                                         | 52.2             | 71               | 0.25                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s225      | 0.35                                       | −0.17                                         | 51.0             | 5                | 0.33                           | Fe <sup>3+</sup> oct. in αFe <sub>2</sub> O <sub>3</sub> |
|                         | s325      | 0.00                                       | 0.01                                          | 33.0             | 23               | 0.23                           | αFe                                                      |
|                         | d125      | −0.10                                      | 0.00                                          | -                | 1                | 0.26                           | γFe                                                      |
| In Figure 3(4)          | s126      | 0.37                                       | −0.07                                         | 52.2             | 69               | 0.26                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s226      | 0.00                                       | 0.00                                          | 33.0             | 30               | 0.22                           | αFe                                                      |
|                         | d126      | −0.12                                      | 0.00                                          | -                | 1                | 0.25                           | γFe                                                      |
| In Figure 3(5)          | s127      | 0.37                                       | −0.08                                         | 52.3             | 70               | 0.25                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s227      | 0.38                                       | −0.18                                         | 51.4             | 30               | 0.25                           | Fe <sup>3+</sup> oct. in αFe <sub>2</sub> O <sub>3</sub> |
| In Figure 3(6)          | s128      | 0.37                                       | −0.06                                         | 52.2             | 70               | 0.26                           | Fe <sup>3+</sup> oct. in LaFeO <sub>3</sub>              |
|                         | s228      | 0.00                                       | 0.00                                          | 33.0             | 14               | 0.21                           | αFe                                                      |
|                         | d128      | −0.10                                      | 0.00                                          | -                | 16               | 0.24                           | γFe                                                      |

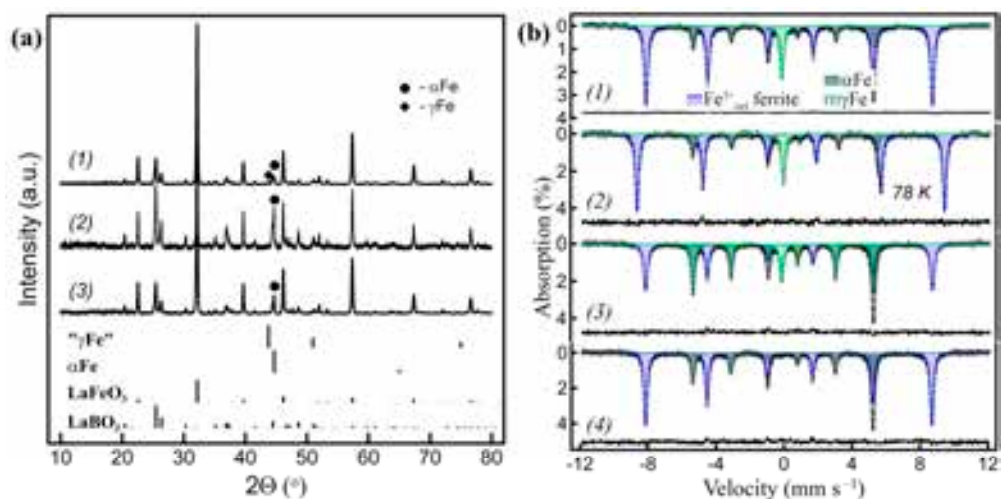


**Figure 1.** (a) Powder XRD patterns of the LaFeO<sub>3</sub>/h-BN-derived nanocomposites: (a1) 29% of the total Fe amount exsolved, where 11% is in γ form; (a2) 54% of Fe exsolved (8% γFe); (a3) sample (a1) oxidized at 300 °C and subsequently reduced at 700 °C, all 29% of Fe exsolved is in α form (all the Fe contributions were evaluated by Mössbauer spectroscopy). (b) Corresponding Mössbauer spectra: (b1,b2) of sample (a1) at RT and 78 K, respectively; (b3) of sample (a2); (b4) of sample (a3) at RT.

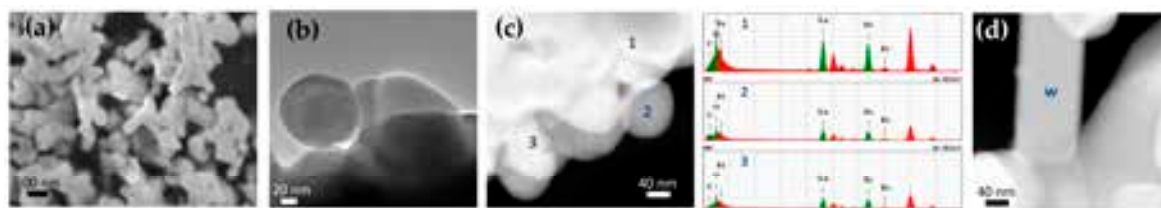


**Figure 2.** SEM and TEM images of the  $\text{LaFeO}_3/\text{h-BN}$ -derived nanocomposites: (a,b) SEM and bright field (BF) TEM images of the nanocomposites with  $\sim 45\%$  of Fe total exsolved; (c,d) high-angle annular dark-field scanning TEM (HAADF-STEM) image and energy-dispersive X-ray (EDX) elemental analysis in selected locations of the nanocomposites with  $\sim 12\%$  of Fe total ( $\sim 10\%$   $\gamma\text{Fe}$ ); (e) formation of the Fe whisker (w) in sample (a,b).

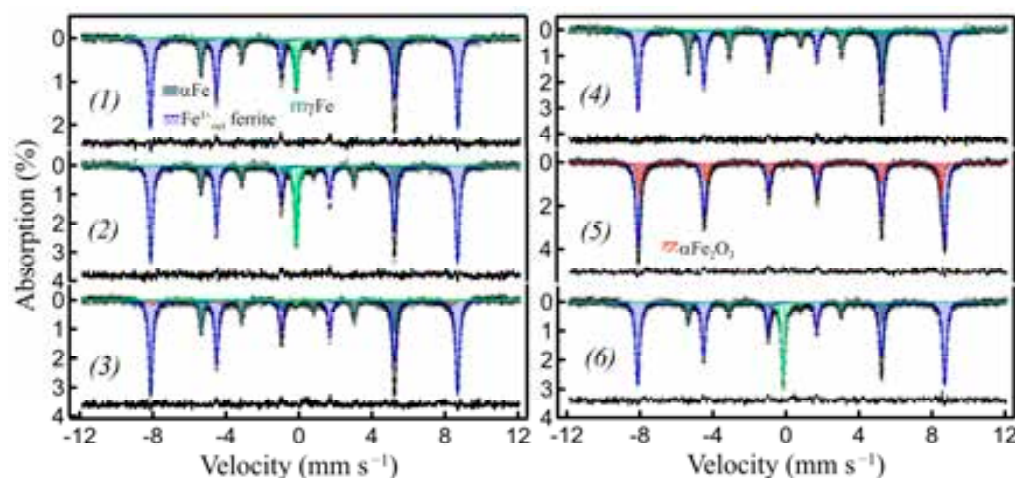


**Figure 3.** RT Mössbauer spectra of the  $\text{LaFeO}_3/\text{h-BN}$ -derived nanocomposites during redox cycling: (1) as prepared with  $32\%$  of Fe exsolved ( $\sim 9\%$   $\gamma\text{Fe}$ ); (2) sample (1) after consecutive oxidation (air,  $500^\circ\text{C}$ ) and reduction ( $10\% \text{H}_2/\text{Ar}$ ,  $700^\circ\text{C}$ ) ( $\sim 30\%$  of Fe total,  $\sim 13\%$   $\gamma\text{Fe}$ ); (3) sample (2) after oxidation at  $300^\circ\text{C}$  in air ( $\sim 23\%$   $\alpha\text{Fe}$ ,  $\sim 1\%$   $\gamma\text{Fe}$ ,  $\sim 5\%$   $\alpha\text{Fe}_2\text{O}_3$ ); (4) after reduction of sample (3) ( $10\% \text{H}_2/\text{Ar}$ ,  $700^\circ\text{C}$ ) ( $\sim 30\%$   $\alpha\text{Fe}$ ); (5) after oxidation of sample (4) (air,  $500^\circ\text{C}$ ) ( $\sim 30\%$   $\alpha\text{Fe}_2\text{O}_3$ ); (6) after reduction ( $10\% \text{H}_2/\text{Ar}$ ,  $700^\circ\text{C}$ ) of sample (5) ( $\sim 30\%$  of Fe total,  $\sim 16\%$   $\gamma\text{Fe}$ ).

This is rather different from the metal exsolution from the A-site-deficient perovskites or the high-temperature hydrogen reduction of stoichiometric perovskite oxides reported previously, where the exsolved metal nanoparticles are typically clearly visible on the surfaces of oxide matrixes [10–13]. In these processes, the reducible metal cations migrate toward the outer and inner grain surfaces, which are exposed to the reducing environment, and reduce to metal, with subsequent agglomeration, grain growth, etc. The oxide matrices, in turn, undergo shrinkage because of a loss of oxygen and metal constituents, promoting socketing of the exsolved nanoparticles [5,10,12,23]. In our ACAR-promoted exsolution process, metal reduction/exsolution is accompanied by the formation of other complex oxides of two or more elements instead of the initial perovskite oxide, even those of lower density, i.e.,  $\text{LaBO}_3$  vs.  $\text{LaFeO}_3$ . Their formation begins in the contact areas between the initial ferrite grains and the reducing reagents. These newly formed Fe-free oxides (viz.  $\text{LaBO}_3$ ) on the top of the initial perovskite grains presumably create a diffusion barrier for the Fe species. Consequently, the exsolved metal Fe nanoparticles do not appear on top of the oxide grain surfaces, but instead localize underneath their surfaces in generated in situ voids.

Perovskite-like ferrites of alkaline-earth elements, such as  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{Sr}_2\text{Fe}_2\text{O}_5$ , can also be used in reaction (1, 4) to produce metal nanoparticle-bearing composites. Because Ca is lighter than La and Sr, it may be more favorable for microscopic investigations in terms of the nanoparticle–matrix contrast. As stated above, the starting ferrite is the main source

of oxygen for the formation of the resulting oxides in ACAR-promoted exsolution processes involving reaction (1, 4). Consequently, in the case of La ferrite, other La borates, such as  $\text{LaB}_3\text{O}_6$ , cannot be formed from the  $\text{LaFeO}_3$  precursor due to a lack of oxygen. For  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and h-BN as starting materials, the formation of several Ca borates is possible, viz.  $\text{Ca}_2\text{B}_2\text{O}_5$  and  $\text{Ca}_3\text{B}_2\text{O}_6$  (without/with  $\text{CaB}_2\text{O}_4$ ). The powder XRD patterns of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  after the ACAR-promoted exsolution reactions with h-BN and the corresponding Mössbauer spectra are shown in Figure 4. According to Figure 4(a2), the main complex oxide product is  $\text{Ca}_3\text{B}_2\text{O}_6$  and, therefore, the primary reaction can be written as follow:

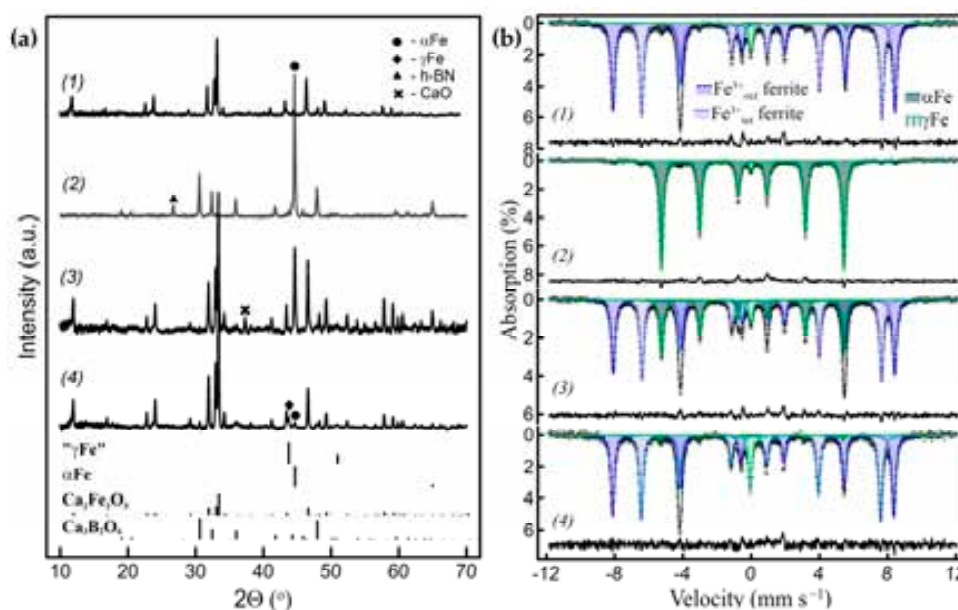
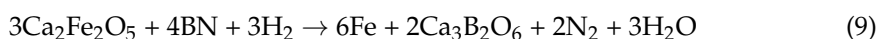


**Figure 4.** (a) Powder XRD patterns and, (b), corresponding Mössbauer spectra of the  $\text{Ca}_2\text{Fe}_2\text{O}_5$ /h-BN-derived nanocomposites with different amounts of metal Fe exsolved: (1) 7% of the total Fe amount exsolved, where 4% is in  $\gamma$  form; (2) 97% of Fe exsolved (2%  $\gamma$ Fe); (3) 28% of Fe exsolved (3%  $\gamma$ Fe); (4) after oxidation–reduction of sample (3), 10% of Fe exsolved (7%  $\gamma$ Fe).

Hydrogen, in addition to maintaining the low  $p\text{O}_2$ , reacts with excessive oxygen in this case. It is worth noting that no diffraction peaks corresponding to  $\text{Ca}_3\text{B}_2\text{O}_6$  and/or other possible resulting oxides were observed at the low extent of reaction, indicating that the oxide products were X-ray amorphous (Figure 4(a1)).  $\text{Ca}_2\text{Fe}_2\text{O}_5$  is more active in this type of reaction compared to  $\text{LaFeO}_3$  and is less stable in reducing conditions as well, so minor additional peaks of CaO can be observed in the patterns of some samples depending on the preparation and reduction conditions (Figure 4(a3)). The Mössbauer spectra of the  $\text{Ca}_2\text{Fe}_2\text{O}_5$ -derived samples are shown in Figure 4b. The spectra are comprised of three magnetically split sextet components and a paramagnetic singlet component. The  $\text{Ca}_2\text{Fe}_2\text{O}_5$  ( $=\text{CaFeO}_{2.5}$ ) has a brownmillerite structure, which is oxygen deficient compared to  $\text{ABO}_3$  perovskites with fully ordered oxygen vacancies at room temperature, where  $\text{Fe}^{3+}$  cations equally occupy distorted octahedral and tetrahedral oxygen polyhedra. Consequently, two of the sextets of nearly equal spectral contributions, according to their hyperfine parameters, correspond to the brownmillerite subspectrum, i.e.,  $\text{Fe}^{3+}_{\text{tet}}$  ( $\delta \sim 0.19 \text{ mm s}^{-1}$  and  $H_{\text{hf}} = 43.4 \text{ T}$ ) and  $\text{Fe}^{3+}_{\text{oct}}$  ( $\delta \sim 0.37 \text{ mm s}^{-1}$  and  $H_{\text{hf}} = 51.2 \text{ T}$ ) in  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . The third sextet ( $\delta \sim 0 \text{ mm s}^{-1}$  and  $H_{\text{hf}} = 33 \text{ T}$ ) and a singlet ( $\delta \sim -0.1 \text{ mm s}^{-1}$ ) correspond to metal Fe in  $\alpha$  and  $\gamma$  forms, respectively, i.e., to the metal Fe subspectrum (Table S2). Like in the  $\text{LaFeO}_3$  case, at  $\sim 650\text{--}730^\circ\text{C}$ , the temperatures during the ACAR-promoted exsolution process were much lower than  $910^\circ\text{C}$ . Both the Fe forms can be distinguished in the powder XRD patterns (Figure 4a). Similar to the previous case, the SEM images of the  $\text{Ca}_2\text{Fe}_2\text{O}_5$ -derived samples

display smooth surfaces, without distinguishable metal Fe particles (Figure 5a). The TEM images (Figure 5b,c) show agglomerates of different contrasts, without metal Fe particles being clearly visible on the surfaces. At the same time, a small number of Fe whiskers can be observed in some samples (Figure 5d). However, as it follows from Figure 5c, the EDX mapping in several locations shows areas of Fe segregation, which, taking into account the distributions of other elements, can be identified as Fe-embedded nanoparticles. These exsolved, embedded Fe nanoparticles, identified by the EDX analysis, were about 15–25 nm in size. The EDX analysis also displays Ca-rich O-containing agglomerates (i.e.,  $\text{Ca}_3\text{B}_2\text{O}_6$ , etc.).

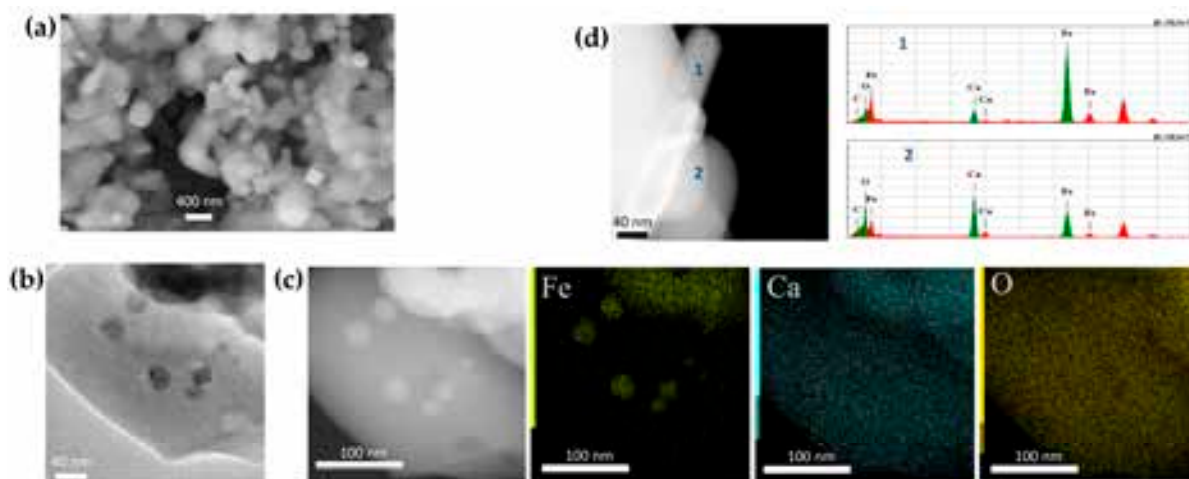


**Figure 5.** SEM and TEM images of the  $\text{Ca}_2\text{Fe}_2\text{O}_5/\text{h-BN}$ -derived nanocomposites with ~23% of metal Fe exsolved (~9%  $\gamma\text{Fe}$ ): (a) SEM image; (b,c) BF TEM and HAADF-STEM images with the corresponding EDX compositional map; (d) HAADF-STEM image, with EDX analysis of the Fe whisker.

The data show that the  $\text{Ca}_2\text{Fe}_2\text{O}_5/\text{h-BN}$  system demonstrates similar behavior to the  $\text{LaFeO}_3/\text{h-BN}$  system in the exsolution reactions facilitated by ACARs. In both the systems, the exsolved metal Fe nanoparticles, which can be determined by EDX analysis, are mostly located within oxide matrices, consisting of initial ferrites and newly formed iron-free borates, in the generated in situ voids. Presumably, the reaction zones and, hence, the adjacent voids are somehow connected to the low  $p\text{O}_2$  environment, otherwise, in most cases, the metal reduction reaction will not proceed to any significant extent. Metal Fe in the exsolved nanoparticles can exist in two forms, namely metastable at temperatures  $<910^\circ\text{C}$   $\gamma\text{Fe}$  and stable  $\alpha\text{Fe}$ , the latter can also form whiskers in some cases. The interior particle growth in a confined space in voids appears to be a key factor, along with a nanosized dimension, for the  $\gamma\text{Fe}$  formation at temperatures well below  $910^\circ\text{C}$ . The fcc close-packed crystal structure of  $\gamma\text{Fe}$  is denser than the bcc structure of  $\alpha(\delta)\text{Fe}$  [30,31], so that the compressive strain developed when the particles of nano-scale dimensions grow under confined conditions is conducive to the formation of  $\gamma\text{Fe}$  nanoparticles and their subsequent stabilization upon cooling. The strain-induced formation of  $\gamma\text{Fe}$  nanoparticles, smaller than  $\sim 20\text{ \AA}$ , under confined conditions in oxide matrices ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ), which are stable at an ambient temperature, has been reported previously [32,33]. The stabilization of  $\gamma\text{Fe}$  was also observed in iron coatings produced by arc plasma deposition on porous alumina substrates, when Fe was localized inside pores with a diameter  $<160\text{ nm}$  [34]. Note that in this case, the deposited Fe layers only covered the inner walls of the pores and did not completely fill their interior space, leaving central gaps.

The  $\gamma\text{Fe}/\alpha\text{Fe}$  ratio depends on the reaction conditions and extent: the contributions of  $\gamma\text{Fe}$  are larger in the initial stages and at the low extent of reactions. However, the nanocomposites containing only  $\gamma\text{Fe}$  have not been obtained using individual  $\text{Ca}_2\text{Fe}_2\text{O}_5$  or  $\text{LaFeO}_3$  ferrites.  $\text{Ca}_2\text{Fe}_2\text{O}_5$  is more active during the described process than  $\text{LaFeO}_3$  and

reacts at lower temperatures, and the reaction can proceed almost completely, whereas for  $\text{LaFeO}_3$ , its extent is limited to ~50–60% (based on the Fe content in coexisting phases obtained from the Mössbauer spectra).

### 2.3. ACAR-Promoted Metal Exsolution Using the Substituted Ferrites

The properties of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  or  $\text{LaFeO}_3$  ferrites can be significantly modified by substitutions. Accordingly, the effect of cation substitution on ACAR-promoted metal exsolution and  $\gamma\text{Fe}$  formation was investigated. Rare-earth and alkaline-earth  $\text{ABO}_{3-\gamma}$  perovskite ferrites allow substitution in both A- and B-sites and a wide variation in oxygen content of  $0 \leq \gamma \leq 0.5$  [14,15]. Figure 6b shows the powder XRD patterns of A and B double-substituted compounds,  $\text{Ca}_{1.4}\text{Y}_{0.6}\text{Fe}_{1.8}\text{Zn}_{0.2}\text{O}_{5.2}$  ( $=\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$ ), after ACAR-promoted exsolution using h-BN. Y was chosen as the lightest rare-earth 3+ cation. The  $\text{Ca}_{1-x}\text{Y}_x\text{FeO}_{3-\gamma}$  solid solutions have not been studied in detail in the literature, but for our process it is important that they belong to a pseudobinary system, i.e., no additional phases other than the perovskite solid solutions coexist. The solubility ranges from both the Ca side (the brownmillerite type solid solutions with oxygen excess) and the Y side (the  $\text{LaFeO}_{3-\gamma}$  type ones with mainly disordered oxygen vacancies) are not well defined and, presumably, depend on the temperature [35]. Similar to the case of unsubstituted Ca ferrite, the resulting borates can only be correctly identified at relatively large reaction extents, such as in the sample in Figure 6(b2), with ~29% of Fe exsolved, according to the Mössbauer spectrum shown in Figure 6(a2). The XRD phase analysis revealed that substitution with Y increases the number of oxide products formed, and the ACAR-promoted exsolution process in this case can be written in a simplified form as follows:

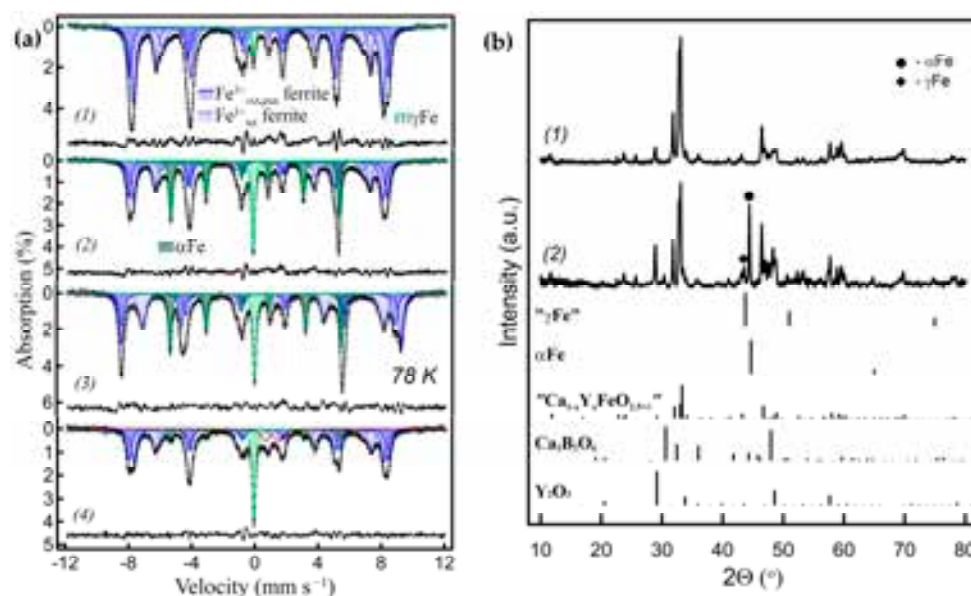
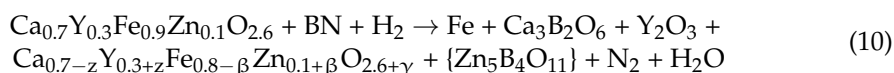


**Figure 6.** (a) RT Mössbauer spectra of the  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$ /h-BN-derived nanocomposites with different amounts of metal Fe exsolved: (a1) 3.5% of  $\gamma\text{Fe}$  exsolved; (a2) 29% of Fe exsolved (~9%  $\gamma\text{Fe}$ ); (a3) the same sample (a2) measured at 78 K; (a4) after oxidation–reduction of sample (a2), 18.5% of Fe exsolved (14%  $\gamma\text{Fe}$ ). (b) Powder XRD patterns, (b1) of the initial  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$  ferrite and, (b2) of sample (a2).

The main oxide products are  $\text{Ca}_3\text{B}_2\text{O}_6$  and  $\text{Y}_2\text{O}_3$  ( $\text{Zn}_5\text{B}_4\text{O}_{11}$  could be a minor phase). The Mössbauer spectra (Figure 6(a2,a3)) show that 29% of the Fe total content was exsolved in this sample, where  $\gamma\text{Fe}$  accounted for ~9% and  $\alpha\text{Fe}$  for 20%. The substitution

manifests itself in a significant broadening of lines in the Mössbauer spectra, due to the introduction of local distortions and the disruption of the magnetic superexchange interactions. Consequently, the components of the brownmillerite subspectrum that correspond to the tetrahedral and octahedral plus pentagonal positions in the ferrite structures were fitted with combinations of several Zeeman sextets. Sextets with  $\delta \sim 0.34\text{--}0.37\text{ mm s}^{-1}$  and  $H_{\text{hf}} \sim 49\text{--}51\text{ T}$  correspond to  $\text{Fe}^{3+}$  cations in octahedral and pentagonal positions (poorly resolved at RT), while those with  $\delta \sim 0.18\text{--}0.20\text{ mm s}^{-1}$  and  $H_{\text{hf}} \sim 40\text{--}43\text{ T}$  correspond to the tetrahedral ones. The two other components with narrow lines correspond to the metal Fe subspectrum, comprising of the  $\alpha\text{Fe}$  sextet with  $\delta \sim 0\text{ mm s}^{-1}$  and  $H_{\text{hf}} \sim 33\text{ T}$  and the  $\gamma\text{Fe}$  singlet with  $\delta \sim -0.1\text{ mm s}^{-1}$ . The Mössbauer measurements at 78 K result in the narrower lines of the components, but the spectral contributions of the subspectra remain about the same. At a lower exsolution level of  $\sim 3\text{--}6\%$ , all metal Fe was in the  $\gamma$  form (Figure 6(a1), Table S3). The TEM images of the latter samples are shown in Figure 7. Similar to the unsubstituted  $\text{Ca}_2\text{Fe}_2\text{O}_5$ -derived samples, it was difficult to differentiate the Fe particles among the agglomerates with different contrasts. However, the Fe nanoparticles  $< 50\text{ nm}$  in size embedded in the oxide matrix were clearly identified by the EDX analysis and mapping (Figure 7a,c). The HAADF-STEM images, together with the Fourier transform imaging, confirmed that the exsolved nanoparticles are metallic  $\gamma\text{Fe}$  (Figure 7b). The EDX mapping also shows some degree of Y and O segregation on the scale of tens of nanometers, which is consistent with the XRD phase analysis.

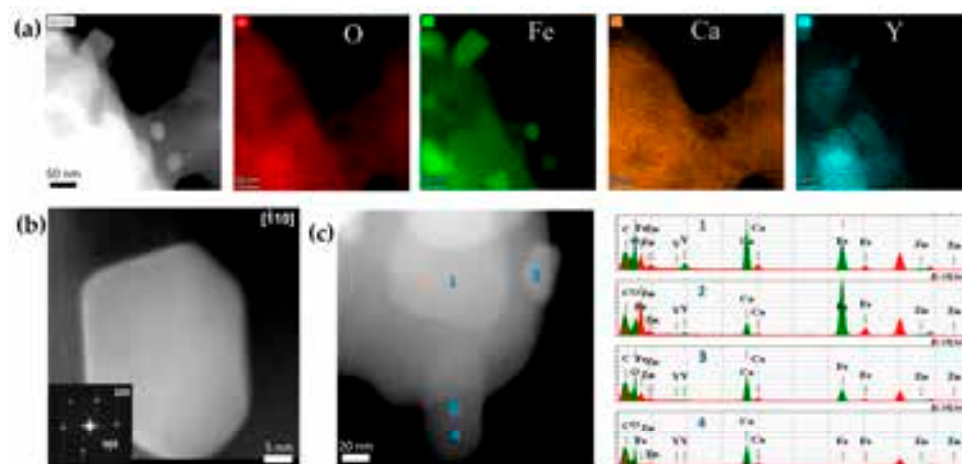


**Figure 7.** (a) HAADF-STEM images with the corresponding EDX compositional maps of the  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}/\text{h-BN}$ -derived nanocomposites with 3.5% of  $\gamma\text{Fe}$  exsolved (Figure 6(a1)). (b)  $[110]$  HAADF-STEM image of the  $\gamma\text{Fe}$  nanoparticle, along with the Fourier transform. (c) HAADF-STEM image with EDX analysis of other  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}/\text{h-BN}$ -derived nanocomposites with 6% of  $\gamma\text{Fe}$  exsolved.

Since Ca is more active in the exsolution reactions than Y, the remaining Ca–Y ferrite can also be enriched in Y despite the formation of  $\text{Y}_2\text{O}_3$ . This can be seen from the spectra of the samples with high degrees of exsolution, as shown in Figure S1 and Table S4. They reveal that the contributions of spectral components corresponding to  $\text{Fe}^{3+}$  in tetrahedral coordination decrease significantly because of the transformation of Ca ferrite-based  $\text{Ca}_{1-x}\text{Y}_x\text{FeO}_{3-\gamma}$  solid solutions with  $x = 0.3$  to Y ferrite-based solid solutions (presumably with  $x > 0.6$  [35]).

Preferable formation of Ca-rich borates was similarly observed for the La-substituted  $\text{Ca}_{1-x}\text{La}_x\text{FeO}_{3-\gamma}$  starting ferrites. This system is also pseudobinary. Within this system, the  $\text{Ca}_2\text{LaFe}_3\text{O}_8$  Grenier phase, with a crystal structure intermediate between brownmillerite and perovskite types, was reported. In addition, the formation of microdomains of close compositions is possible at different values of  $x$  and  $\gamma$  [36–38]. The main oxide product in ACAR-promoted exsolution reactions of Ca–La ferrites with h-BN is  $\text{Ca}_3\text{B}_2\text{O}_6$ , like for  $\text{Ca}_{0.7}\text{La}_{0.3}\text{FeO}_{2.65}$  in Figure 8(a2,a3)), while the formation of  $\text{La}_2\text{O}_3$  was not ob-

served. At higher exsolution degrees, double borate  $\text{Ca}_3\text{La}_3(\text{BO}_3)_5$  was additionally formed (Figure 8(a3)). Since La is retained more in the  $\text{Ca}_{0.7-z}\text{La}_{0.3+z}\text{FeO}_{2.65+\delta}$  solid solution, its content increases, as does the oxygen index value. At some level of La content, the resulting ferrite solid solution loses oxygen vacancy ordering, i.e., it becomes the  $\text{La}_{0.3+z}\text{Ca}_{0.7-z}\text{FeO}_{3-\gamma}$  type perovskite-like solid solution. This is reflected in the Mössbauer spectra as the disappearance of  $\text{Fe}^{3+}$  tetrahedral spectral components (Figure 8(b2), Table S5). A simplified reaction is shown in (11):

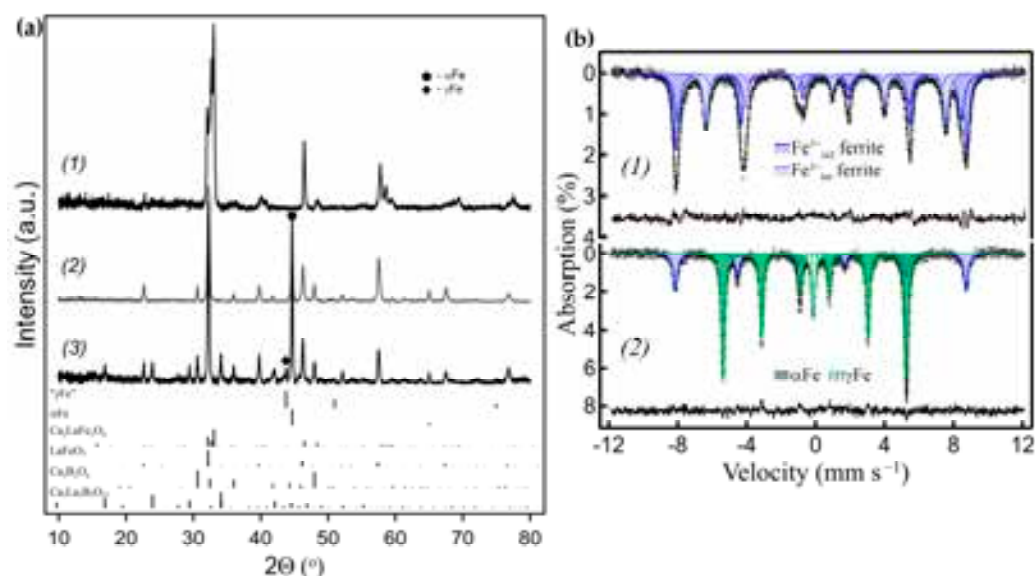
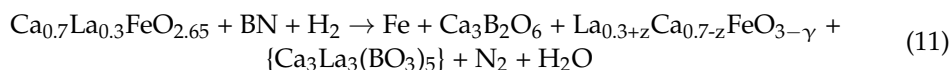


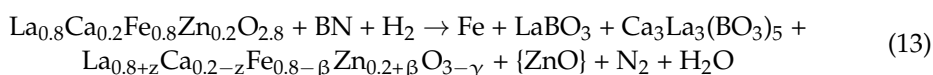
**Figure 8.** (a) Powder XRD patterns of the  $\text{Ca}_{0.7}\text{La}_{0.3}\text{FeO}_{2.65}$ /h-BN-derived nanocomposites with different amounts of metal Fe exsolved: (a1) the initial  $\text{Ca}_{0.7}\text{La}_{0.3}\text{FeO}_{2.65}$  ferrite; (a2) 66% of Fe exsolved (2%  $\gamma\text{Fe}$ ); (a3) 76% of Fe exsolved (8%  $\gamma\text{Fe}$ ). (All Fe contributions were evaluated by Mössbauer spectroscopy). (b) Mössbauer spectra (b1) of the initial  $\text{Ca}_{0.7}\text{La}_{0.3}\text{FeO}_{2.65}$  ferrite; (b2) of sample (a3).

In the case of  $\text{LaFeO}_3$ -based compounds, the substitution of  $\text{Fe}^{3+}$  cations by non-reducible cations can also lead to the formation of  $\gamma\text{Fe}$  exclusively. Figure 9 shows that the Zn-substituted solid solution,  $\text{LaFe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.9}$ , reacts with h-BN, according to the simplified reaction:



At ~8% of the total metal Fe content, all of the exsolved Fe is in the  $\gamma$  form (Figure 9(b1), Table S5). The TEM EDX mapping of this  $\text{LaFe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.9}$ -derived sample with ~8% of  $\gamma\text{Fe}$  exsolved, allowed for the identification of the embedded Fe metal nanoparticles (Figure 10a). The HAADF-STEM images, together with the Fourier transform imaging, confirmed that the exsolved nanoparticles are highly twinned metal  $\gamma\text{Fe}$  nanocrystals (Figure 10b,c).

In the case of double substitution by Ca and Zn, the ACAR exsolution with h-BN will proceed as follows (Figure S2(a2,a3,b2,b3)):



At low reaction extents only  $\gamma\text{Fe}$  will be exsolved (Figure S2(b2)). In both cases, Zn-containing phases may precipitate at high reaction extents, presumably in oxide (ZnO) or borate forms, but in most of our samples they did not appear in the XRD patterns.

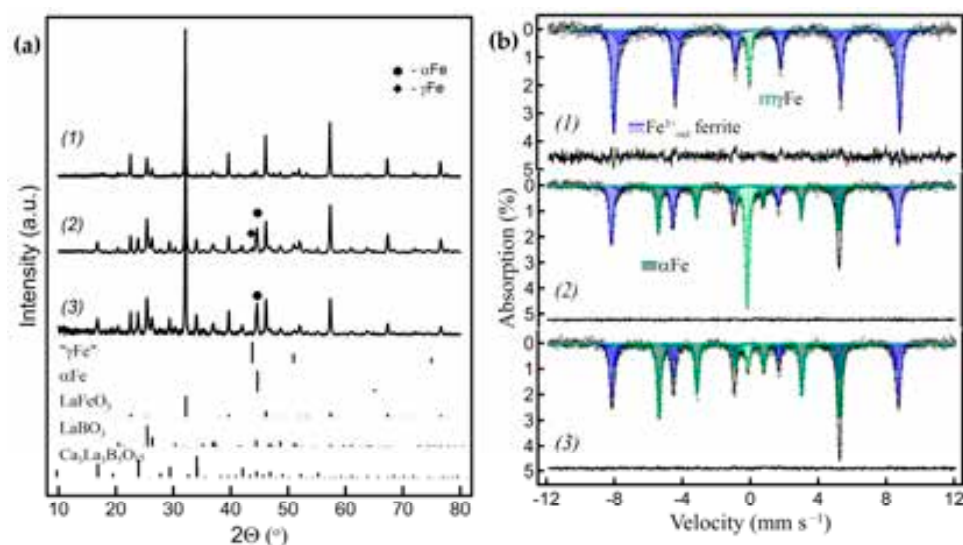


**Figure 9.** (a) Powder XRD patterns and (b) corresponding RT Mössbauer spectra of the nanocomposites obtained by the ACAR exsolution from Zn-substituted  $\text{LaFeO}_3$ : (1) from  $\text{LaFe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.9}/\text{h-BN}$  with ~8% of  $\gamma\text{Fe}$  exsolved; (2) from  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.8}/\text{h-BN}$  with ~50% of Fe exsolved, where ~20%— $\gamma\text{Fe}$ ; (3) sample (2) after grinding in a mortar.

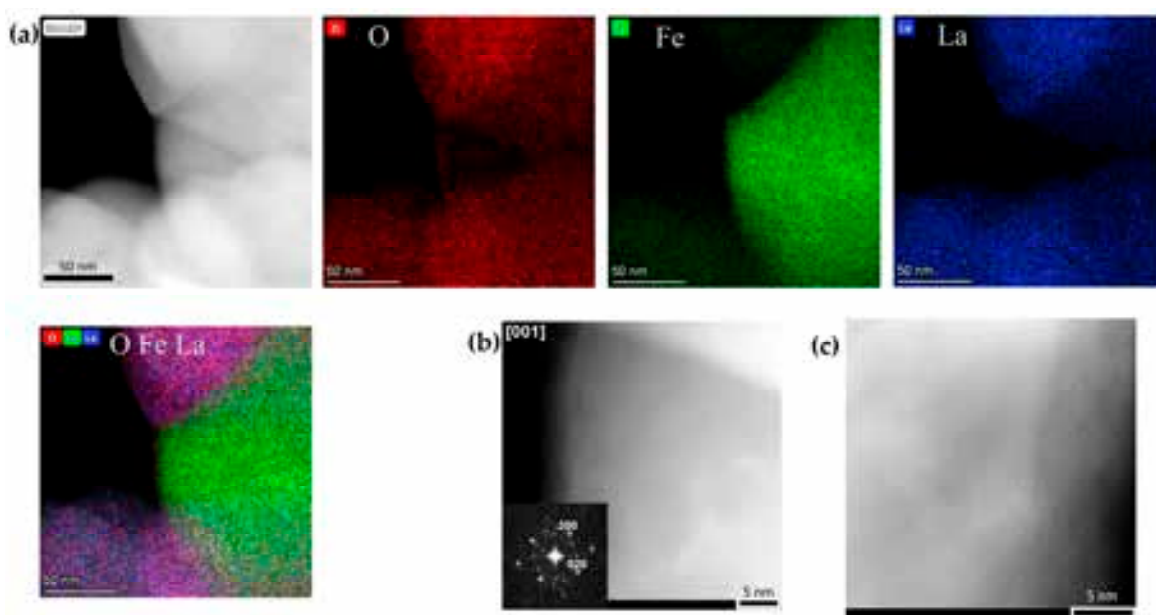


**Figure 10.** (a) HAADF-STEM image and corresponding EDX compositional maps of the  $\gamma\text{-Fe}$  nanoparticles of the  $\text{LaFe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.9}/\text{h-BN}$ -derived nanocomposites with ~8% of  $\gamma\text{Fe}$  exsolved (Figure 9(a1,b1)). (b) [001] HAADF-STEM image of the  $\gamma\text{-Fe}$  nanoparticles, along with the Fourier transform. (c) HAADF-STEM image of highly twinned  $\gamma\text{-Fe}$  nanoparticle.

The lattice parameters of the cubic fcc cell of the exsolved  $\gamma\text{Fe}$  nanocrystals can be estimated from the room-temperature powder XRD patterns, in the range of 0.357–0.358 nm. These values correspond to those calculated for austenite solid solutions at room temperature when extrapolated to pure iron [39,40]. Since the  $\gamma\text{Fe}$  nanoparticles synthesized here at 650–750 °C are crystalline and are confined in oxide/borate matrices, they are not pyrophoric in air at room temperature. Moreover, they persist during heating/cooling cycles in a reducing atmosphere. However, a mild mechanical impact on the nanocomposites with high  $\gamma\text{Fe}$  content, by gently grinding in a mortar and pestle for 1–2 min, leads to the transformation of most of the  $\gamma\text{Fe}$  into  $\alpha\text{Fe}$ , and irreversibly so

(Figures 9(a2,a3,b2,b3) and S2(a3,a4,b3,b4), Table S6). This transition is, to some extent, analogous to transformations of retained austenite caused by mechanical deformation at low temperatures [41,42].

Note that for all the substituted ferrites investigated, the formation of Fe whiskers, which is considered undesirable during the described processes, was not observed.

#### 2.4. Redox Behavior of the Exsolved Nanoparticles

The exsolved metal nanoparticles can be oxidized in air to iron oxides at elevated temperatures. The oxidation of metal nanoparticles is generally associated with a decrease in density and an increase in volume. As it was shown in [23], for CoNi exsolved, socketed nanoparticles, these volume changes lead to their migration from the initial sites under redox cycling conditions. In addition, redox cycling can cause the growth and coarsening of oxidized metal nanoparticles or their reintegration into perovskite matrices during oxidation [10,43,44]. For all the nanocomposites obtained herein, the embedded nanoparticles are also completely oxidized to  $\alpha\text{Fe}_2\text{O}_3$  at 500 °C and above, in air. The  $\gamma\text{Fe}$  nanoparticles are oxidized first, and at lower temperatures of 200–300 °C, and their oxidation is accompanied by the transition of residual  $\gamma\text{Fe}$  into the  $\alpha$  form (Figure 3(3,5), Table 1). However, the nanocomposites produced by ACAR-promoted exsolution exhibited peculiar behavior during redox cycling, or at least at the temperatures investigated. In these nanocomposites, the initial metal nanoparticles, after complete oxidation into  $\alpha\text{Fe}_2\text{O}_3$  at 500 °C and above, can revert back to the metallic state by subsequent reduction in 10%  $\text{H}_2/\text{Ar}$  at 650–750 °C and, remarkably, the metal  $\gamma\text{Fe}$  nanoparticles can be reinstated in the  $\gamma$  form through such a reduction of  $\alpha\text{Fe}_2\text{O}_3$ . Moreover, the  $\gamma\text{Fe}$  fractions may increase compared to the initial content, especially when  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and its solid solutions have been used (Figures 3(1,2) and 4(a3,a4,b3,b4)). To our knowledge, the formation of  $\gamma\text{Fe}$  nanoparticles from Fe oxides by hydrogen reduction at temperatures below 910 °C has not been reported previously. Like the formation of the initial  $\gamma\text{Fe}$  nanoparticles, this is presumably a compressive strain-driven behavior, which can be attributed to the preservation of the localization of all the nanoparticles, i.e., initially exsolved metallic-derived oxide and restored metallic oxide, within the voids, along with their strong binding to the void walls during the redox cycles. The  $\gamma\text{Fe}$  formation can, thus, be considered as a kind of indicator of the localization of nanoparticles inside the voids during these processes. Note that at the same time, there should also be free space inside the voids close to nanoparticles, sufficient to compensate for the metal/oxide volume difference, otherwise the matrix may be destroyed.

Using the above assumption on the nanoparticle redox behavior, the reversible transformation of  $\gamma\text{Fe}$  into  $\alpha\text{Fe}$ , and vice versa, through redox cycling at different oxidation temperatures can be realized (Figure 3, Table 1). The sample of the  $\text{LaFeO}_3/\text{h-BN}$  based nanocomposite with ~30% of Fe exsolved was subjected to a preliminary oxidation (at 500 °C)/reduction cycle to maximize the  $\gamma\text{Fe}$  contribution (Figure 3(1,2), Table 1 (d123, d124)). To convert most of the Fe into the  $\alpha$  form, the first stage involved oxidation at a low temperature of ~300 °C, where more chemically active  $\gamma\text{Fe}$  nanoparticles were partially oxidized/partially converted into  $\alpha\text{Fe}$  (Figure 3(3)), but the resulting oxides did not sufficiently sinter with the matrix. In the second stage, subsequent reduction at 700 °C yields  $\alpha\text{Fe}$  (Figure 3(4), see also Figure 1(a3,b4)). To regenerate  $\gamma\text{Fe}$ , the obtained  $\alpha\text{Fe}$  nanoparticles were first completely oxidized at 500 °C (Figure 3(5)), which provides sufficient sintering of the formed  $\alpha\text{Fe}_2\text{O}_3$  particles and the matrix. Subsequent reduction, at the same temperature of 700 °C, regenerated the  $\gamma\text{Fe}$  nanoparticles (Figure 3(6)). According to the Mössbauer spectra, the  $\text{Fe}^0$  (metal)/ $\text{Fe}^{3+}$  (in matrix) ratio remained approximately the same during redox cycling (Table 1).

The TEM images of the reduced sample with ~11% of  $\gamma\text{Fe}$  and ~6% of  $\alpha\text{Fe}$ , obtained by the ACAR-promoted exsolution reaction of  $\text{Ca}_{0.7}\text{Y}_{0.3}(\text{Fe}_{0.9}\text{Zn}_{0.1})\text{O}_{2.6}$  with h-BN, after an oxidation–reduction cycle demonstrate features similar to uncycled (only exsolved) nanocomposites: using EDX analysis, the Fe nanoparticles can be identified in some locations, embedded in the oxide matrix, along with some Y segregation (Figure S3).

## 2.5. ACAR-Promoted Exsolution of FeNi<sub>x</sub> Alloys

It is well-established that the existence of a region of the  $\gamma$  form can be significantly extended to lower temperatures by creating an Fe alloy with certain elements, such as Ni [29]. The exsolution of NiFe alloy nanoparticles from Ni and Fe-containing perovskite-like oxides has also been reported [10,16,21], so the formation of FeNi<sub>x</sub> alloys was expected during our process as well. Ni is less chemically active and more reducible compared to Fe, so Ni additions to La, and especially Ca, ferrites significantly decrease their stability in a reducing H<sub>2</sub>-containing atmosphere [27]. For this reason, the starting ferrites with low Ni content were used herein, to avoid decomposition. According to the XRD patterns shown in Figure 11a, the ACAR-promoted exsolution with h-BN from LaFe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>2.9</sub>, La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>2.8</sub>, and La<sub>0.5</sub>Ca<sub>0.5</sub>Fe<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>2.7</sub> can be written as follows:

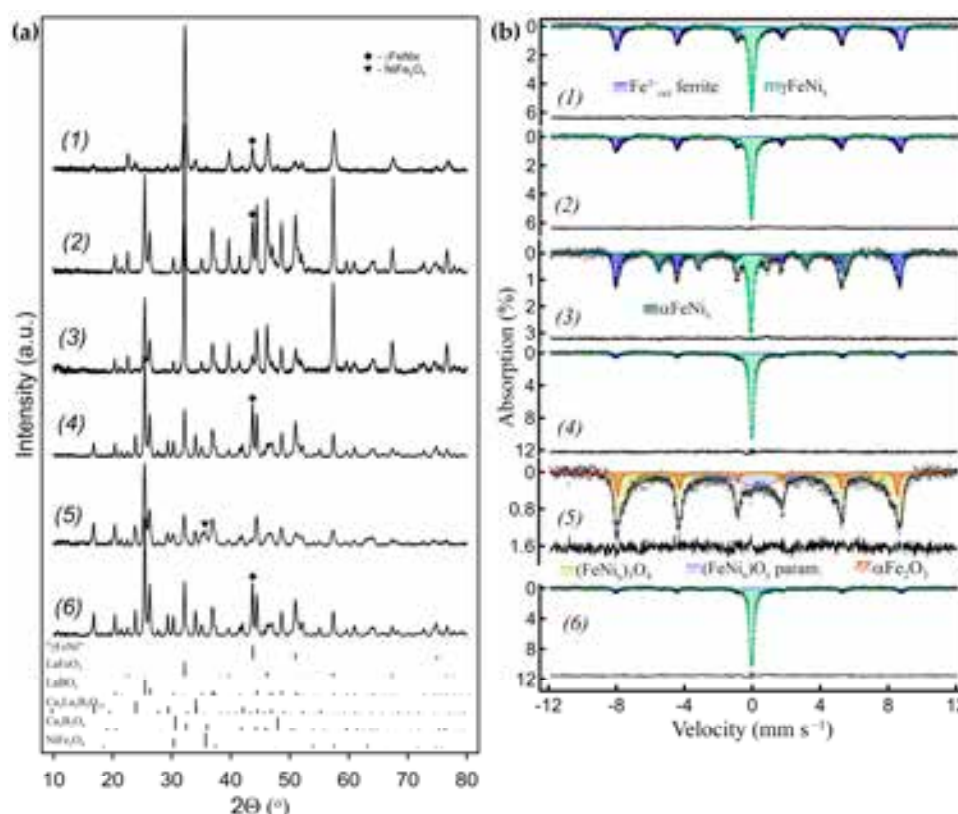
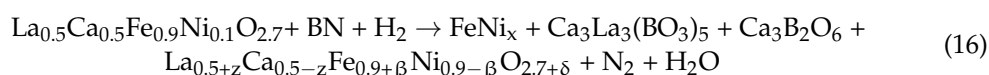
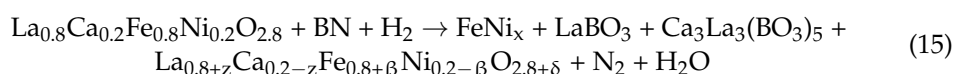
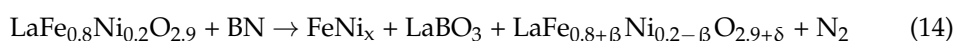


**Figure 11.** (a) Powder XRD patterns and (b) corresponding RT Mössbauer spectra of the nanocomposites obtained by the ACAR-promoted exsolution from Ni-substituted ferrites: (1) La<sub>0.5</sub>Ca<sub>0.5</sub>Fe<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>2.7</sub>/h-BN with ~41% of  $\gamma$ FeNi exsolved; (2) from LaFe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>2.9</sub>/h-BN with ~53% of  $\gamma$ FeNi exsolved; (3) sample (2) after grinding in a hand mortar (~25%  $\gamma$ FeNi, ~29%  $\alpha$ FeNi); (4) from La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>2.8</sub>/h-BN with ~82% of  $\gamma$ FeNi exsolved; (5) sample (4) oxidized at 500 °C (~44%—NiFe<sub>2</sub>O<sub>4</sub>, ~16%  $\alpha$ Fe<sub>2</sub>O<sub>3</sub>, ~13% superparamagnetic phase); (6) after reduction of sample (5) (10% H<sub>2</sub>/Ar, 700 °C) (~83%  $\gamma$ FeNi).

In these reactions, the resulting borates are the same as for the Ni-free ferrites described before (Figure 11(a1,a2,a4)). Note that while it is difficult to achieve exsolution levels of

more than ~50% using metal Fe for the Ni-free ferrites due to cation mobility limitations, the reaction extent can be significantly higher for Ni-containing ferrites. As follows from the Mössbauer spectra shown in Figure 11(b1,b2,b4) and Table S7, Ni additions effectively stabilize the fcc structure of the exsolved nanoparticles. Their spectra are mainly comprised of two subspectra. The first, magnetically split with broad lines, correspond to  $\text{Fe}^{3+}$  cations in ferrites. It was fitted as a set of sextets, with  $\delta \sim 0.37 \text{ mm s}^{-1}$  and  $H_{\text{hf}} \sim 49\text{--}53 \text{ T}$ . The second subspectrum, which was fitted as a paramagnetic singlet with  $\delta \sim -0.07 \text{ mm s}^{-1}$ , corresponds to Fe in  $\gamma\text{FeNi}_x$  alloys. According to the Fe–Ni phase diagram, at temperatures close to ambient, the  $\alpha\text{Fe}$ -based bcc phase  $\alpha\text{FeNi}_x$  coexists with intermetallic compounds of  $\text{Fe}_3\text{Ni}$  and  $\text{FeNi}$  fcc types in the Fe-rich region; although, the phase boundaries at these temperatures are difficult to determine [29]. The thermodynamically stable phases of  $\text{FeNi}_x$  alloys, viz. the Fe-rich bcc and the Ni-rich fcc alloys, are magnetically ordered at room temperature [45]. At elevated temperatures, there is a continuous solid solution of  $\gamma\text{FeNi}_x$  with the eutectoid temperature of  $\sim 345\text{--}400^\circ\text{C}$  at  $\sim 50 \text{ at\%}$  of Ni. At  $\sim 10\text{--}20 \text{ at\%}$  of Ni, which matches the initial ferrite stoichiometry, the transition temperature is about  $\sim 650\text{--}700^\circ\text{C}$ . Since Ni is more reducible than Fe, the alloys at low degrees of exsolution will be enriched in Ni and their transition temperatures will be even lower. These temperatures are below the temperatures of  $700\text{--}750^\circ\text{C}$  at which reactions (14, 15, and 16) were carried out. When cooled to room temperature, the XRD patterns show that all the exsolved  $\text{FeNi}_x$  nanoparticles retained their  $\gamma$  structure at room temperature (Figure 11(a1,a2,a4)). The Mössbauer subspectra corresponding to the  $\text{FeNi}_x$  nanoparticles consist of singlets with  $\delta \sim -0.1 \text{ mm s}^{-1}$  (Figure 11(b1,b2,b4)), evidencing that they are paramagnetic. It is consistent with their  $\gamma$  form, since paramagnetic behavior at room temperature has been reported for metastable  $\gamma\text{FeNi}_x$  alloys with high Fe content [46,47]. The stabilization of the most exsolved  $\gamma\text{FeNi}_x$  nanoparticles in  $\gamma$  form upon cooling, which can be explained by the strain developed due to their localization in voids, suggests that this is the main type of localization. Similar to  $\gamma\text{Fe}$  exsolved nanoparticles, a large part of  $\gamma\text{FeNi}_x$  nanoparticles can be transformed into ferromagnetic  $\alpha\text{FeNi}_x$  (Figure 11(b3)) by gently grinding in a mortar and pestle for 1–2 min. This treatment significantly reduced the  $\text{FeNi}_x$  reflections visually, in the XRD pattern of those samples (Figure 11(a3)). The mechanical stress-induced martensite  $\gamma$  to  $\alpha$  transformation in Fe-rich Fe–Ni bulk alloys at room temperature has been previously reported in the literature [48,49].

The exsolved  $\gamma\text{FeNi}_x$  nanoparticles can be completely oxidized at  $500^\circ\text{C}$  and above, to the spinel solid solution  $\text{Ni}_{1\pm x}\text{Fe}_{2\pm x}\text{O}_4$  (Figure 11(a5,b5)). Subsequent reduction in  $10\% \text{ H}_2/\text{Ar}$  atmosphere at  $650\text{--}700^\circ\text{C}$  will restore the  $\gamma\text{FeNi}_x$  metal nanoparticles (Figure 11(a6,b6)). It is noteworthy that the exsolution level for this sample was  $>80\%$  (Table S7).

The TEM images of Ni-containing samples after the ACAR exsolution from  $\text{La}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{2.7}$  ferrite, with  $\sim 41\%$  of Fe exsolved (Figure 11(a1,b1)), are shown in Figure 12a–d. Similar to other samples, the images show agglomerates of different contrast (Figure 12a–c). The embedded  $\text{FeNi}_x$  nanoparticles  $<30 \text{ nm}$  in size, however, can be identified by EDX analysis, e.g., like in locations 2, 3, and 4 in Figure 12d. The alloy nanoparticles contained approximately about  $\sim 30 \text{ at\%}$  of Ni at this exsolution degree. Figure 12e shows the TEM images of this sample after gently grinding in a mortar with a pestle. There is not much difference compared to the unground ones, except for some rounded agglomerates of  $<25\text{--}30 \text{ nm}$  located on the grain surfaces enriched in Fe and Ni, which can be identified as alloy nanoparticles (Figure 12e, loc. 2). Figure 12f shows the TEM images of the same unground sample after the oxidation (at  $500^\circ\text{C}$ , air)/reduction ( $700^\circ\text{C}$ ,  $10\% \text{ H}_2/\text{Ar}$ ) cycle. Here again, it looks similar to the original sample with embedded  $\text{FeNi}_x$  nanoparticles, which were identified by EDX analysis (Figure 12f, loc. 2).

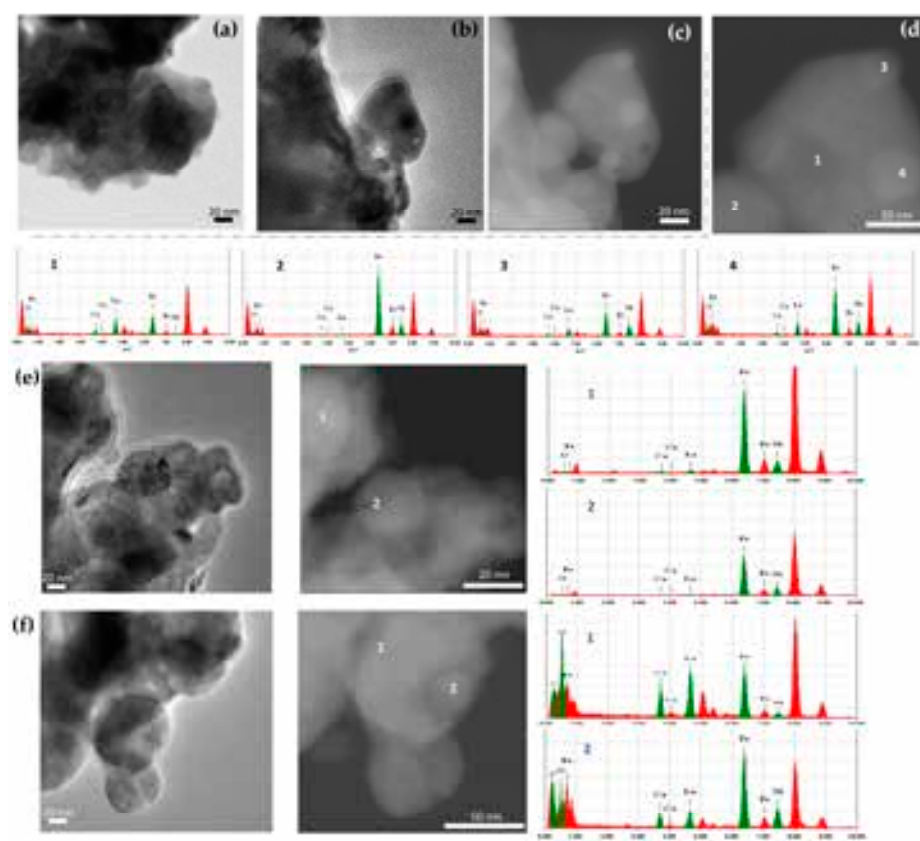


**Figure 12.** (a,b) BF TEM, (c) HAADF-STEM images, and (d) EDX elemental analysis in the selected locations of the  $\text{La}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{2.7}/\text{h-BN}$  nanocomposite with ~41% of  $\gamma\text{FeNi}$  exsolved (Figure 11(1)) at different locations; (e) BF TEM and HAADF-STEM images and EDX elemental analysis in the selected locations after mortar grinding; (f) BF TEM and HAADF-STEM images and EDX elemental analysis of the same sample (a–d) in the selected locations of the sample after the oxidation/reduction cycle.

## 2.6. Separation of the Individual Nanoparticles

The reversible oxidation/reduction of metallic nanoparticles, while maintaining their localization within the in situ-created individual voids, is a remarkable feature of the nanocomposites produced by ACAR-promoted exsolution. It makes it possible to transform the initial metallic nanoparticles into various oxides, viz.  $\text{Fe}_{1-x}\text{O}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\alpha/\gamma\text{Fe}_2\text{O}_3$  etc., while preventing their agglomeration. The components of matrices, viz. the starting and resulting ferrites, resulting borates, etc., in turn, have very diverse chemical properties depending on their composition. In particular, unsubstituted, and certain substituted, Ca ferrites are susceptible to hydrolysis and dissolve in dilute mineral acids like HCl.  $\text{Ca}_3\text{B}_2\text{O}_6$  is also soluble in dilute acids. Since  $\text{Fe}_3\text{O}_4$  (and  $\gamma\text{Fe}_2\text{O}_3$ ) particles can dissolve reasonably slowly in dilute acidic aqueous solutions at RT, the crystallized and sintered Fe oxide nanoparticles, produced by the oxidation of the exsolved metal nanoparticles, can be separated from such oxide matrices by acid hydrolysis.

The TEM and SEM images of the nanoparticles separated from the  $\text{Ca}_2\text{Fe}_2\text{O}_5/\text{h-BN}$  and  $\text{Ca}_2\text{FeAlO}_5/\text{h-BN}$ -derived nanocomposites (~30–35% of Fe exsolved) are shown in Figures 13 and S5.  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$  ferrites of the brownmillerite type, including  $\text{Ca}_2\text{FeAlO}_5$ , obtained by the isovalent substitution of  $\text{Fe}^{3+}$  cations with  $\text{Al}^{3+}$ , are also prone to hydrolysis as unsubstituted  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . They react with h-BN, similar to  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , according to the simplified reaction (17), where Al is mainly retained in the ferrite phase (Figure S4):



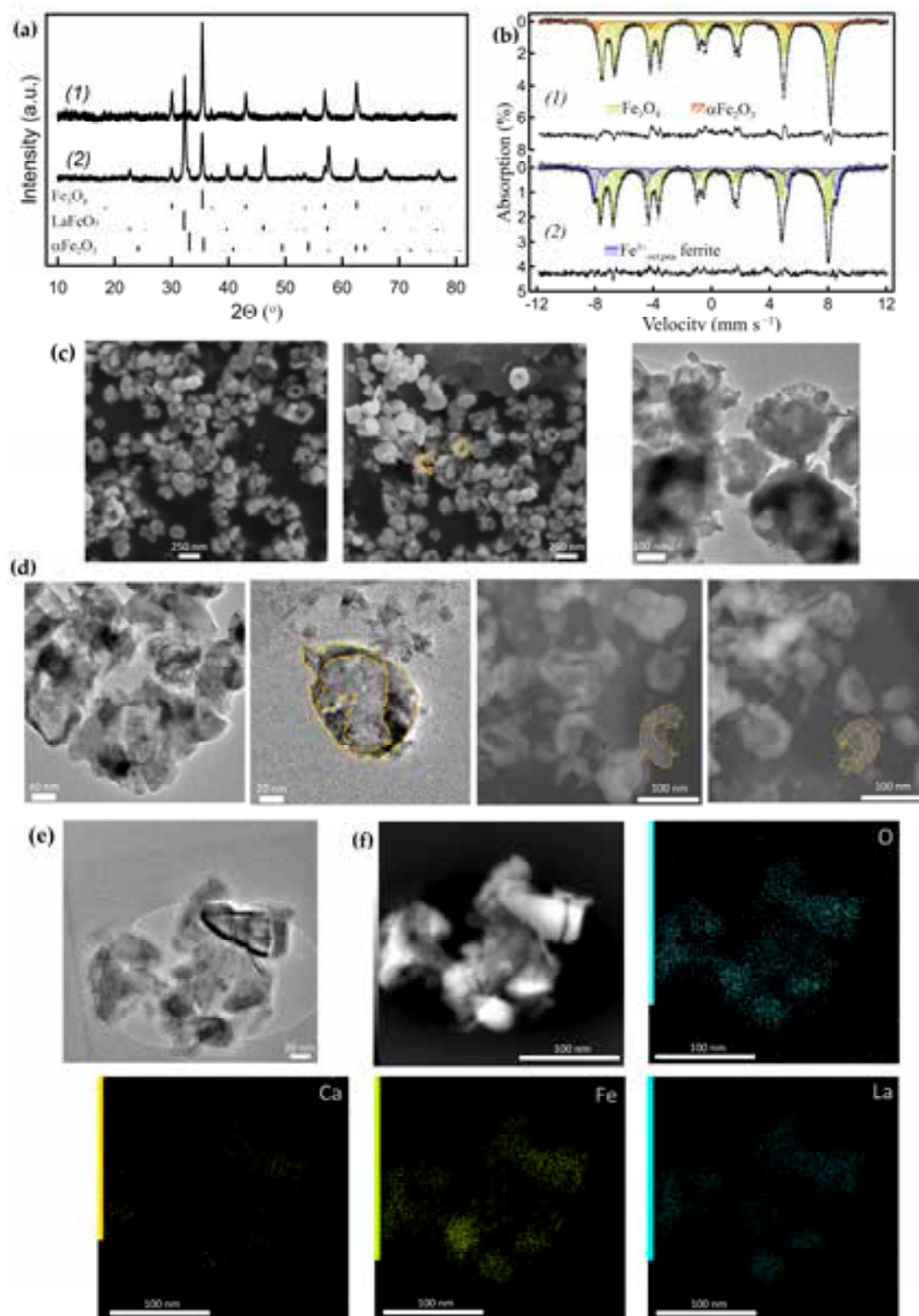


**Figure 13.** Separated nanoparticles: (a) powder XRD patterns and (b) corresponding RT Mössbauer spectra of the nanoparticles obtained from the  $\text{Ca}_2\text{FeAlO}_5/\text{h-BN}$ -derived nanocomposite (a1,b1) and from the  $\text{Ca}_{0.8}\text{La}_{0.2}\text{FeO}_{2.6}/\text{h-BN}$  derived nanocomposite (a2,b2). (c) SEM and BF TEM images of the  $\text{Fe}_3\text{O}_4$  nanoparticles obtained from the  $\text{Ca}_2\text{Fe}_2\text{O}_5/\text{h-BN}$ -derived nanocomposite. (d) BF TEM and HAADF-STEM images of the  $\text{Fe}_3\text{O}_4$  nanoparticles obtained from sample (a1,b1) (dashed lines indicate the cup shape of the particles). (e) BF TEM and (f) HAADF-STEM images with corresponding EDX compositional map of the  $\text{Fe}_3\text{O}_4/\text{La}_{0.2+z}\text{Ca}_{0.8-z}\text{FeO}_{3-\gamma}$  nanoparticles obtained from sample (a2,b2).

The RT Mössbauer spectrum of the  $\text{Ca}_2\text{FeAlO}_5/\text{h-BN}$ -derived nanocomposite is shown in Figure S4(1). The subspectrum corresponding to  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$  is significantly broadened and unresolved due to the magnetic dilution by diamagnetic  $\text{Al}^{3+}$  cations. Therefore, the spectral contribution of exsolved Fe, which totaled ~35% (~5%  $\gamma\text{Fe}$ ), was evaluated from the 78K Mössbauer spectra (Figure S4(2)).

Figure 13(a1,b1) shows the powder XRD patterns and Mössbauer spectra (Table S8) of the  $\text{Fe}_3\text{O}_4$  nanoparticles separated from the  $\text{Ca}_2\text{FeAlO}_5/\text{h-BN}$ -derived nanocomposite. The transformation of metal Fe nanoparticles into  $\text{Fe}_3\text{O}_4$  nanoparticles was carried out by their oxidation to  $\alpha\text{Fe}_2\text{O}_3$  at 500 °C, followed by their reduction in 10%  $\text{H}_2/\text{Ar}$  flow at 460–480 °C. The matrices were dissolved in 0.5–1.5% HCl aqueous solutions at RT. The  $\text{Fe}_3\text{O}_4$  nanoparticles were magnetically separated and washed thoroughly with distilled water. It is worth noting that the leaching process of  $\text{Fe}_3\text{O}_4$  can be carried out with high yields. This is facilitated by the fact that the particles were produced at relatively high temperatures at both stages of synthesis, viz. at oxidation of the metallic particles to  $\text{Fe}_2\text{O}_3$  and at their subsequent reduction to  $\text{Fe}_3\text{O}_4$  and were, therefore, crystallized and sintered well, which should reduce their solubility in diluted acids. Similar acid leaching in diluted aqueous HCl solutions has previously been successfully utilized to extract  $\text{SrFe}_{12}\text{O}_{19}$ -based nanoparticles, during high-temperature glass–ceramic synthesis [50].

The HAADF-STEM and SEM images of the separated nanoparticles obtained from the  $\text{Ca}_2\text{Fe}_2\text{O}_5/\text{h-BN}$  and  $\text{Ca}_2\text{FeAlO}_5/\text{h-BN}$ -derived nanocomposites (~30–35% of Fe exsolved) reveal that most of them are cap-shaped (hemispherical) hollow nanostructures with sizes below ~200 nm and ~100 nm, respectively (Figures 13c,d and S5). According to Figures 13 and S5, the wall thickness of the oxide nanoparticles is of the order of a few nm, thus the wall thickness of the parent metallic nanoparticles should be of the same scale.

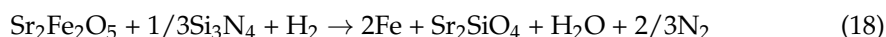
The separated nanoparticles provide insight into the shape and size of the parent metal nanoparticles within the matrices. These hollow cap-shaped oxide nanoparticles indicate that the exsolved metal nanoparticles are formed as an inner layer in individual voids generated in situ within the matrices. This particle shape can potentially provide free space sufficient to accommodate the volume increase during oxidation, if the hollow particles are not completely filled with other reaction products. At the same time, these shapes and locations appear to play an important role in creating the conditions necessary for the development of compressive strain in metal nanoparticles sufficient to stabilize  $\gamma\text{Fe}$ , which is somewhat analogous to the  $\gamma\text{Fe}$  formation in cylindrical pores [34].

The extracted nanoparticles were different when La-substituted  $\text{Ca}_{1-x}\text{La}_x\text{FeO}_{2.5+\delta}$  ferrite was used as the starting material in the ACAR-promoted exsolution process. Figures 13e,f and S6 show the TEM images of the oxide nanoparticles extracted from the nanocomposite obtained by the reaction of  $\text{Ca}_{0.8}\text{La}_{0.2}\text{FeO}_{2.6}$  with h-BN (~35% of Fe exsolved). Metallic Fe nanoparticles were converted into  $\text{Fe}_3\text{O}_4$  nanoparticles in a similar manner as described above. According to reaction (14), the La content in the remaining perovskite oxide  $\text{Ca}_{0.8-z}\text{La}_{0.2+z}\text{FeO}_{2.6+\delta}$  increases and, thus, its solubility in the dilute HCl aqueous solution decreases.

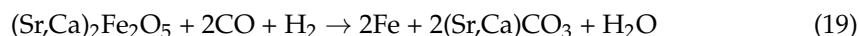
Using Mössbauer spectroscopy and XRD analyses, it was found that the extracted nanoparticles consisted mainly of spinel  $\text{Fe}_3\text{O}_4$  and perovskite  $\text{La}_{0.2+z}\text{Ca}_{0.8-z}\text{FeO}_{3-\gamma}$  phases (Figure 13(a2,b2), Table S8). The TEM with EDX analysis revealed that the  $\text{La}_{0.2+z}\text{Ca}_{0.8-z}\text{FeO}_{3-\gamma}$  crystallites were segregated around  $\text{Fe}_3\text{O}_4$  nanoparticles (Figures 13e,f and S6). Most of them were almost completely covered by the resulting La–Ca ferrite, forming open shells. The size of the  $\text{Fe}_3\text{O}_4$  nanoparticles was estimated to be smaller (<40–50 nm) than in the previous case. The composition and microstructure of the extracted nanoparticles reflect the relative arrangement of the metal/resulting ferrite phases in the parent nanocomposites. They show that the growth of exsolved metal nanoparticles in matrices is accompanied by the formation of shells, consisting of the resulting La-rich ferrites.

### 2.7. Variety of ACAR-Promoted Metal Exsolution Reactions

The new approach we have developed is not limited to the aforementioned ferrites and h-BN as starting compounds. The range of suitable compounds is wider and includes, but is not limited to, for example, Sr-containing ferrites and some other nitrides like  $\text{Si}_3\text{N}_4$ , etc. In particular, Figure S7 (Table S9) illustrates the ACAR-promoted exsolution of metal Fe nanoparticles from  $\text{Sr}_2\text{Fe}_2\text{O}_5$ , with  $\text{Si}_3\text{N}_4$  as a reducing agent, according to the simplified reaction (18):



Even CO gas can be utilized in reactions of this type with Ca and Sr ferrites, when it is added to 10% $\text{H}_2$ /Ar flow at  $\sim 650^\circ\text{C}$ , according to reaction (19):



This reaction also leads to embedded metal  $\alpha$  and  $\gamma$  Fe nanoparticles, as shown in Figure S8 [51].

The chemical activity of reducing reagents in ACAR processes is different, so that  $\text{Si}_3\text{N}_4$  and CO are active with Ca and Sr-based ferrites, forming the corresponding silicates or carbonates, but are inactive towards La-based ferrites.

### 2.8. In Situ Reactions of Exsolved Nanoparticles

The exsolved metallic nanoparticles and their oxides can also be converted into other functional compounds, directly inside the matrices. For instance, embedded  $\alpha\text{Fe}_2\text{O}_3$  nanoparticles obtained by the oxidation of exsolved metallic nanoparticles inside (La-based ferrite  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.8}$ )/h-BN-derived nanocomposites (Figure 14(1)) can be converted into embedded  $\chi\text{-Fe}_5\text{C}_2$  (Hagg carbide) nanoparticles by the reaction with gaseous CO at  $300\text{--}350^\circ\text{C}$  (Figure 14(2), Table S10), according to the scheme in Figure S9. This carbide is considered to be an active phase in Fischer–Tropsch synthesis [52–54]. Its Mössbauer subspectrum at RT consists of three broad Zeeman sextets, with  $\delta$  of  $0.18\text{--}0.25\text{ mm s}^{-1}$  and  $H_{\text{hf}}$  of  $10\text{--}22\text{ T}$ , providing reliable identification [52]. The matrix, consisting of La ferrites and La borates, does not react with CO under the above conditions and remains unchanged. The  $\alpha$  and, more significantly,  $\gamma$  Fe metallic nanoparticles can then be regenerated by the oxidation of carbide to  $\alpha\text{Fe}_2\text{O}_3$  at  $500^\circ\text{C}$ , followed by reduction to metal (Figure 14(3)), indicating that the metal/oxide/carbide nanoparticles retain their localization in the voids.

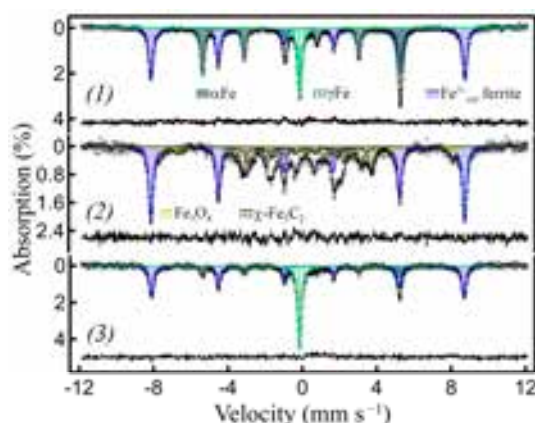


**Figure 14.** RT Mössbauer spectra of the  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.8}$ /h-BN-derived nanocomposites during redox cycling involving CO: (1) as prepared with  $\sim 51\%$  of Fe exsolved ( $\sim 14\%$   $\gamma\text{Fe}$ ); (2) sample (1) after oxidation (air,  $500^\circ\text{C}$ ) following by the reaction with CO at  $350^\circ\text{C}$  ( $\sim 46\%$  of Fe in  $\chi\text{-Fe}_5\text{C}_2$  carbide); (3) the same sample after the oxidation (air,  $500^\circ\text{C}$ )–reduction (10% $\text{H}_2$ /Ar,  $700^\circ\text{C}$ ) cycle ( $\sim 47\%$  of metal Fe total,  $\sim 30\%$   $\gamma\text{Fe}$ ).

### 3. Materials and Methods

#### 3.1. Materials Preparation

The initial perovskite-like compounds used for the nanocomposite syntheses were prepared using a sol–gel routine from the respective nitrate precursors and citric acid as a complexing agent. All the chemicals were of reagent grade, from commercial sources (AO Reachem, Moscow, Russia). The aqueous solution of metal nitrates in the calculated amounts were mixed with concentrated citric acid solutions in the molar ratio of citric acid to metals at ~1.1. The pH of the solution was adjusted by a dilute ammonia solution to values of ~5–7. Several samples, mostly Sr-containing ones, were synthesized using ethylenediaminetetraacetic acid (EDTA) as a complexing agent. In this case, the respective nitrate solution was dropwise added to an EDTA solution in diluted aqueous ammonia and then the pH was adjusted to ~8. The water was evaporated from the mixed solution and the resulting viscous gels were heated to ~200 °C to yield porous brownish materials. The materials were ground and then calcined in air at 500 °C (heating rate was 5 °C/min) for 4 h. The samples were then calcined in air for 8–10 h at 700–900 °C. The substituted perovskites, usually containing Fe<sup>4+</sup> and/or Fe<sup>(3+δ)+</sup> cations in mixed oxidation states, were additionally treated in 10% H<sub>2</sub>/Ar gas flow at 600 °C for 1 h to reduce them to Fe<sup>3+</sup>.

The nanocomposites with exsolved particles were synthesized through the solid-state method. The required amounts of perovskite powders and h-BN (PlasmoTherm, Moscow, Russia) or other reducing reagents were dry grounded in an agate mortar until homogeneous for 20–30 min. The mixture powders were placed into a silica reactor in alumina crucibles and heated in 10% H<sub>2</sub>/Ar gas flow of ~1–4 mL/min. The synthesis temperatures were ~650–700 °C and ~700–780 °C for the Ca- and La-based ferrites, respectively. For most of the samples used in this work, the exsolution reactions were carried out in a single step over ~10–16 h to reach completeness or a steady state. The experimental conditions for the synthesis of the nanocomposites are summarized in Table S1. The different extents of the exsolution reactions in this work were mainly predetermined by the ferrite/(h-BN, etc.) ratio, and the final amounts of exsolved Fe were quantified experimentally using Mössbauer spectroscopy.

#### 3.2. Materials Characterization

The phase composition of the nanocomposites was characterized by X-ray powder diffraction (XRD), with a Huber G670 Image Plate Guinier diffractometer (CuK<sub>α1</sub> radiation, curved Ge monochromator, image plate detector) (Huber Diffractionstechnik GmbH & Co., Ltd., Rimsting, Germany).

The <sup>57</sup>Fe Mössbauer spectra were recorded in terms of the transmission geometry on a commercial MS-1104EM spectrometer, using a <sup>57</sup>Co(Rh) source (13.5 mCi), equipped with a custom liquid nitrogen bath cryostat (77–320 K) (ZAO, Kordon, Russia). The fitting procedure was performed with a special original least-squares fitting software developed at Lomonosov MSU. All the isomer shift values refer to αFe at room temperature (RT).

Scanning electron microscopy (SEM) analysis was performed using a Quattro S scanning electron microscope (LaB6 field emission cathode, Thermo Fisher Scientific, Bleiswijk, The Netherlands). Transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) spectra were obtained with a JEOL 2100 F/Cs, operated at 200 kV and equipped with a JEOL system for EDX analysis (JEOL Ltd., Tokyo, Japan), and using an aberration-corrected Titan Themis Z transmission electron microscope at 200 kV (Thermo Fisher Scientific, The Netherlands), equipped with a Super-X system for EDX analysis. For the TEM studies, the powder samples of the nanocomposites were prepared by dispersing in ethanol or heptane without additional grounding to avoid sample destruction, and then depositing a few drops of the suspension on special grids.

#### 4. Conclusions

The novel approach to metal exsolution using  $\text{ABO}_{3-\gamma}$  ( $\text{B} = \text{Fe}, \text{Ni}, \text{etc.}$ ) complex perovskite oxides of reducible transition metals has been developed to produce Fe-containing metal and metal oxide nanoparticles and nanocomposites. Our strategy is based on the additional auxiliary reactions of irreducible alkaline-earth and/or rare-earth A-site cations of the parent perovskite oxides with the constituents of reducing compounds resulting in the formation of complex oxides, which facilitate the exsolution of reducible transition metals from the B-sites of perovskites. The approach was applied mainly to Ca- and La-based unsubstituted and substituted ferrites as starting compounds and h-BN as a reducing compound. The metal nanoparticles exsolved by the described approach are largely localized within oxide matrices, in individual voids generated in situ. Moreover, the metal nanoparticles of Fe and  $\text{FeNi}_x$  alloys can be formed and stabilized in  $\gamma$  form, presumably due to induced compressive strain that develops in such locations.

The redox behavior of the exsolved nanoparticles was investigated. It was shown that they readily undergo redox cycling at moderate temperatures, where they maintain localization in the voids. The latter allows, under certain conditions, the regeneration of  $\gamma\text{Fe}$  and  $\gamma\text{FeNi}_x$  from oxides during redox cycling. The nanoparticles can be chemically modified by reagents inside the matrices, while maintaining their localization.

The oxide matrices consist of unreacted initial perovskites and reaction products (borates, silicates, resulting perovskites, etc.) in various combinations and exhibit a wide variety of chemical and physical properties. They undergo significant transformation during the exsolution process, and their phase and chemical compositions depend on various factors, such as the composition of the initial ferrites and reducing reagents, the extent of reactions, and the reaction conditions, etc.

For certain Ca and Sr ferrite-based nanocomposites, a method has been developed for the separation oxide nanoparticles produced by the oxidation of the initially exsolved metal nanoparticles. The separated  $\text{Fe}_3\text{O}_4$  nanoparticles (which can also be  $\gamma\text{Fe}_2\text{O}_3$ , etc.), obtained using Ca ferrites as starting materials, had a cup-shaped hollow shape. The separated nanoparticles obtained using La-substituted Ca ferrites were composite  $\text{Fe}_3\text{O}_4$ /(La-based resulting ferrite) layered particles. The separated nanoparticles provide insight into the shape, size, and relative arrangement of the phases of the parent metal nanoparticles within the matrices. This approach provides a new high-temperature templateless route for the synthesis of hollow and layered nanoparticles of Fe oxides and related compounds.

Our proposed strategy is applicable to a wide range of both perovskite-like oxides and reducing compounds. The developed approach provides greater flexibility in controlling the reaction extent, as well as the composition and properties of the resulting nanocomposites and nanoparticles. The approach can also be applied to the surface modification of perovskite oxide ceramics, since the starting perovskite compounds are considered stable under the reaction conditions. Our novel strategy is expected to be viable for the development of various new functional materials.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12080223/s1>, Figure S1. RT Mössbauer spectra of the  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$ /h-BN-derived nanocomposites with 57% of Fe exsolved ( $\sim 11\%$   $\gamma\text{Fe}$ ); Figure S2. (a) Powders XRD patterns of the nanocomposites obtained by the ACAR exsolution from Zn-substituted  $\text{LaFeO}_3$ : (a1) from  $\text{LaFe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.9}$ /h-BN with  $\sim 8\%$  of  $\gamma\text{Fe}$  exsolved; (a2) from  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.8}$ /h-BN with  $\sim 5\%$  of  $\gamma\text{Fe}$  exsolved; (a3) from  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{2.8}$ /h-BN with  $\sim 50\%$  of Fe exsolved, where  $\sim 20\%$ — $\gamma\text{Fe}$ ; (a4) sample (a3) after grinding in a mortar; (a5) sample (a3) oxidized at  $500^\circ\text{C}$  (all Fe contributions are evaluated by Mössbauer spectroscopy) and (b) corresponding RT Mössbauer spectra: (b1) of sample (a1); (b2) of sample (a2); (b3) of sample (a3); (b4) of sample (a4); (b5,6) of sample (a5) at RT and 78K, respectively; Figure S3. (a) BF TEM image of the  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$ /h-BN-derived nanocomposites ( $\sim 18\%$  of Fe) after the oxidation–reduction cycle; (b) HAADF-STEM images with corresponding EDX compositional maps of the sample in (a); Figure S4. The powder XRD pattern (a) and the corresponding RT Mossbauer spectrum (b) of the  $\text{Ca}_2\text{FeAlO}_5$ /h-BN-derived nanocomposite with  $\sim 35\%$  of Fe exsolved ( $\sim 5\%$  of  $\gamma\text{Fe}$ ); Figure S5. TEM

images of the separated  $\text{Fe}_3\text{O}_4$  nanoparticles obtained from the  $\text{Ca}_2\text{FeAlO}_5/\text{h-BN}$ -derived nanocomposites: (a) BF TEM; (b) HAADF-STEM images and EDX elemental analysis in the selected locations; Figure S6. TEM images of the separated  $\text{Fe}_3\text{O}_4/\text{La}_{1-y}\text{Ca}_y\text{FeO}_{2.5+\delta}$  nanoparticles obtained from the  $\text{Ca}_{0.8}\text{La}_{0.2}\text{FeO}_{2.6}/\text{h-BN}$ -derived nanocomposite: (a) HAADF-STEM images with the corresponding EDX compositional map; (b) HAADF-STEM images and EDX elemental analysis in the selected locations; Figure S7. The powder XRD pattern (a) and the corresponding RT Mössbauer spectrum (b) of the  $\text{Sr}_2\text{Fe}_2\text{O}_5/\text{Si}_3\text{N}_4$ -derived nanocomposite with ~60% of Fe exsolved (~9% of  $\gamma\text{Fe}$ ); Figure S8. The RT Mössbauer spectrum of nanocomposites by ACAR-promoted by CO exsolution reactions: (1) from  $\text{Sr}_2\text{Fe}_2\text{O}_5/\text{CO}$  with ~16% of Fe exsolved (~5%  $\gamma\text{Fe}$ ); (2) from  $\text{Ca}_2\text{Fe}_2\text{O}_5/\text{CO}$  with ~12% of Fe exsolved (~3%  $\gamma\text{Fe}$ ); Figure S9. Scheme of transformations of the exsolved Fe nanoparticles during the redox cycle involving CO treatment; Table S1. Experimental conditions for the synthesis of nanocomposites by ACAR-promoted metal exsolution; Table S2. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure 4b; Table S3. Hyperfine parameters of the RT Mössbauer spectra of the  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$ -derived nanocomposites in Figure 6a; Table S4. Hyperfine parameters of the RT Mössbauer spectra of the  $\text{Ca}_{0.7}\text{Y}_{0.3}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_{2.6}$ -derived nanocomposites in Figure S1; Table S5. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure 9b; Table S6. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure S2b; Table S7. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure 11b; Table S8. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure 13d; Table S9. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure S7b; Table S10. Hyperfine parameters of the RT Mössbauer spectra of the samples in Figure 14.

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## Article

# Mesoporous Titania Nanoparticles for a High-End Valorization of *Vitis vinifera* Grape Marc Extracts

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**Abstract:** Mesoporous titania nanoparticles (NPs) can be used for encapsulation polyphenols, with applications in the food industry, cosmetics, or biomedicine. TiO<sub>2</sub> NPs were synthesized using the sol-gel method combined with solvothermal treatment. TiO<sub>2</sub> NPs were characterized through X-ray diffraction, FTIR spectroscopy, the N<sub>2</sub> adsorption method, scanning and transmission electron microscopy, and thermal analysis. The sample prepared using Pluronic F127 presented a higher surface area and less agglomerated NPs than the samples synthesized with Pluronic P123. Grape marc (GM), a by-product from wine production, can be exploited for preparing extracts with good antioxidant properties. In this regard, we prepared hydroethanolic and ethanolic GM extracts from two cultivars, Feteasca Neagra (FN) and Pinot Noir. The extract components were determined by spectrometric analyses and HPLC. The extract with the highest radical scavenging activity, the hydroethanolic FN extract, was encapsulated in titania (FN@TiO<sub>2</sub>) and compared with SBA-15 silica support. Both resulting materials showed biocompatibility on the NCTC fibroblast cell line in a 50–300 µg/mL concentration range after 48 h of incubation and even better radical scavenging potential than the free extract. Although titania has a lower capacity to host polyphenols than SBA-15, the FN@TiO<sub>2</sub> sample shows better cytocompatibility (up to 700 µmg/mL), and therefore, it could be used for skin-care products.

**Keywords:** mesoporous titania; grape marc extract; mesoporous silica; extract encapsulation; antioxidant properties; phenolic compounds; biocompatibility



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## 1. Introduction

An effective carrier for biologically active molecules should meet the following conditions: a high specific surface area and pore volume, tunable pore size, good biocompatibility and no toxicity, and the possibility to adjust the interactions between biologically active molecules and the support. The most used inorganic matrix for the encapsulation of biologically active compounds is mesoporous silica, which presents outstanding porosity (up to 1200 m<sup>2</sup>/g specific surface area and 1.5 cm<sup>3</sup>/g pore volume), good biocompatibility depending on particle size and shape, surface properties, concentration, etc. [1–3]. Silica nanoparticles are generally assessed as safe and biocompatible by the US Food and Drug Administration (FDA) and have been employed as additives in cosmetics and foods [4].

Among functional inorganic materials, nanostructured titania is of particular interest due to its remarkable features: good chemical and thermal stability, low cost, biocompatibility, resistance to photochemical erosion, and excellent optical and electrical properties.

Titania is used intensively in environmental applications to remove pollutants from both air and water [5]. Titania, which has already been successfully applied as an implant material or in cosmetic formulations, can also be employed as a carrier for biologically active compounds [6]. For example, in 2012, mesoporous titania was tested as a carrier for ibuprofen [7].

Titania exhibits photocatalytic properties under UV irradiation but has a lower adsorption capacity than mesoporous silica, so by combining the properties of both silica and titania, titania–silica composites have been successfully applied as photocatalysts for environment purification [8], as well as for biomedical applications [9]. Titania nanoparticles (NPs) are poorly soluble in biological fluids and thus pose challenges when used in biomedical applications. However, titania NPs have been applied in photodynamic therapy for the tumors' treatment [10,11]. There are reports that showed that titania NPs help to neutralize bacterial or fungal strains [12].

Unlike silica, mesoporous titania exhibits lower porosity values (up to 250 m<sup>2</sup>/g specific surface area and 0.4 cm<sup>3</sup>/g pore volume) and a lower concentration of surface OH groups that can be involved in functionalization reactions, but it could interact with biologically active substances through donor–acceptor bonds.

Typically, mesoporous titania is produced by the soft-templated sol-gel method based on the hydrolysis and condensation reactions involving the cooperative assembly of titanium precursor, usually, titanium isopropoxide or titanium butoxide, with the structure directing agent in the presence of a complexation agent that slows down the rate of hydrolysis and condensation reactions. The sol-gel process of Ti precursors differs from that of silicon alkoxides because of their higher chemical reactivity, resulting from the lower electronegativity of titanium and its ability to spontaneously enhance the coordination number with water molecules, with the hydrolysis rate of titanium alkoxide being five times faster than silicates, hindering the cooperative assembly of inorganic species with surfactant molecules [13].

Red *Vitis vinifera* L. grape marc (GM) resulting from winemaking is an affordable source of polyphenols, including anthocyanins, flavonoids, stilbenes, flavan-3-ols, and phenolic acids, which have antioxidant, anti-inflammatory, antidiabetic, and cardioprotective properties, antiproliferative effects [14], and potent broad virucidal activity [15]. For instance, Balea et al. [16] reported that Feteasca Neagra extract prepared in 70% ethanol from fermented grape pomace exhibited antiproliferative activity on A549 lung carcinoma, MDA-MB-231 human breast adenocarcinoma, and B164A5 murine melanoma, with the best results being obtained for the last cell line.

There are studies on phenolic compounds in wines. For example, malvidin glycosides are formed during wine maturation [17]. Goldberg et al. [18] highlighted that climate influences the concentration of quercetin, as wines originating from areas with a warmer climate and greater exposure to sunlight had a higher concentration of quercetin. The presence of p-coumaric acid in wines seems to be more random than that of quercetin, with this phenolic acid being important because it acts as a precursor of flavonols, flavan-3-ols, and trihydroxy stilbenes [17].

Lately, the demand for natural extracts with antioxidant properties for cosmetics and nutraceuticals is of growing interest and the use of an abundant waste such as grape marc from wine production can contribute to the sustainability of this field [19]. Wasilewski et al. [20] reported a shower gel formulation enriched with compounds extracted from grape pomace, which was safe for utilization as natural cosmetics.

The recovery of biologically active substances from GM is done by extraction, with the yield and chemical profile depending on the type of solvent, the extraction technique and its parameters, and the quality of the grape pomace, which in turn is strongly influenced by the climate, etc. [21–23].

Herein, we report the synthesis of a series of mesoporous titania NPs by combining the sol-gel process and solvothermal treatment using two metal precursors, titanium(IV) isopropoxide and titanium(IV) butoxide, and two nonionic surfactants, the triblock copoly-

mer EO20-PO70-EO20 (Pluronic P123) or EO99-PO70-EO99 (Pluronic F127), in various molar ratios, 2-propanol or n-butanol, as the solvent and acetic acid was used to delay the hydrolysis rate of the metallic alkoxide. Titania NPs with the best features were used to encapsulate a hydroethanolic extract prepared from red grape marc, and the resulting material was compared with the material obtained by incorporating the same extract in mesoporous SBA-15 silica. We also evaluated the chemical profile of several ethanolic or hydroethanolic extracts prepared from the red grape marc from two varieties: Feteasca Neagra and Pinot Noir.

## 2. Results

### 2.1. Obtaining and Characterization of Mesoporous Matrices

A series of mesoporous titania nanoparticles were synthesized by the sol-gel method assisted by solvothermal treatment using as a template agent either the triblock copolymer, EO20-PO70-EO20 (Pluronic P123) or the nonionic surfactant EO99-PO70-EO99 (Pluronic F127). The scheme showing the steps of obtaining the titania samples can be seen in Figure 1, while Table 1 lists the titanium precursor, the solvent, the molar ratio between the titanium precursor and template agent used in the synthesis of titania NPs, and how the samples are denoted. Titania samples obtained after solvothermal treatment and purified through Soxhlet extraction (samples labeled Sn\_E) or calcined at 400 °C (samples labeled Sn\_C) were characterized by wide-angle powder X-ray diffraction (XRD), FTIR spectroscopy, thermal analysis, scanning electron microscopy, transmission electron microscopy, and porosity evaluation based on N<sub>2</sub> adsorption–desorption isotherms.

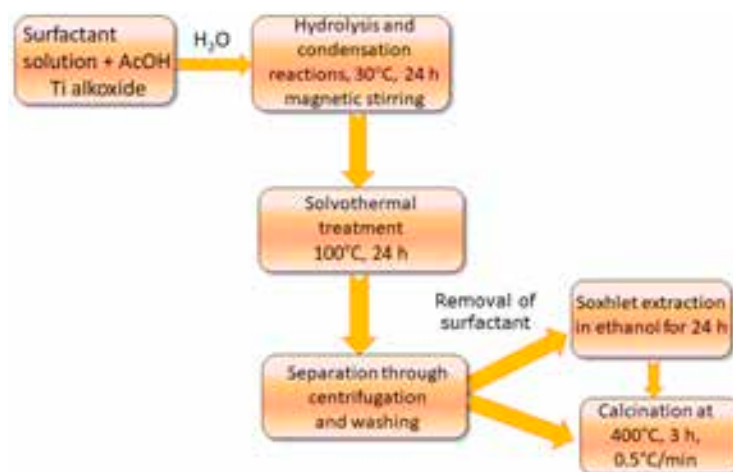


**Figure 1.** Main steps of the titania samples preparation.

**Table 1.** Synthesis conditions for mesoporous titania obtaining.

| Sample | Solvent    | Titania Precursor              | Template Agent | Ti Precursor/Template Agent Molar Ratio |
|--------|------------|--------------------------------|----------------|-----------------------------------------|
| S1     | n-butanol  | Ti(O <i>n</i> Bu) <sub>4</sub> | P123           | 1/0.017                                 |
| S2     | n-butanol  | Ti(O <i>n</i> Bu) <sub>4</sub> | P123           | 1/0.034                                 |
| S3     | 2-propanol | Ti(O <i>i</i> Pr) <sub>4</sub> | P123           | 1/0.017                                 |
| S4     | 2-propanol | Ti(O <i>i</i> Pr) <sub>4</sub> | P123           | 1/0.034                                 |
| S5     | 2-propanol | Ti(O <i>i</i> Pr) <sub>4</sub> | F127           | 1/0.017                                 |
| S6     | n-butanol  | Ti(O <i>n</i> Bu) <sub>4</sub> | F127           | 1/0.017                                 |

#### 2.1.1. X-ray Diffraction

The XRD patterns of the titania samples demonstrated the formation of an anatase crystalline phase, having tetragonal symmetry for all samples irrespective of the structure directing agent, titanium precursor, or quantity of the surfactant used in the synthesis. The thermal treatment determined the preservation of the anatase phase (JCPDS no. 21-1272) and an increase in its crystallinity, with a crystallite size of D<sub>101</sub> = 8 nm, calculated using

Rigaku PDXL software version 1.8 from the most intense diffraction peak at  $2\theta = 25.27^\circ$  for uncalcined materials (Figure 2A), and  $D_{101} = 10$  nm for the samples obtained at  $400^\circ\text{C}$  (Figure 2B).

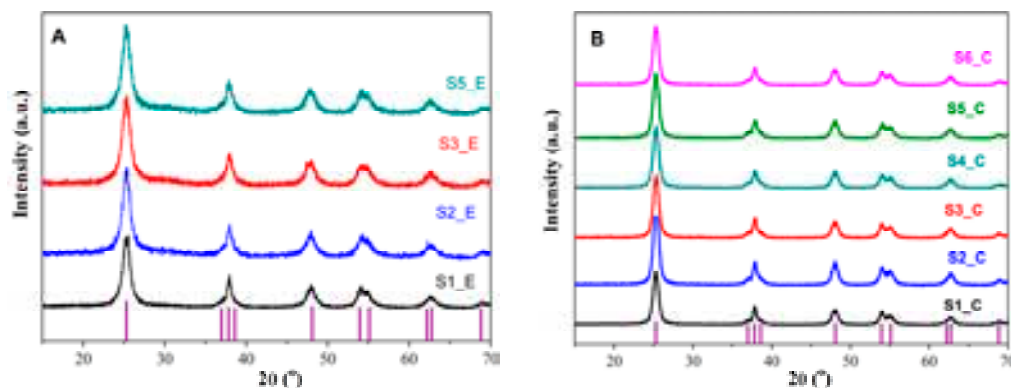


**Figure 2.** XRD patterns of titania samples obtained after solvothermal treatment and purified by Soxhlet extraction (A) and for  $\text{TiO}_2$  samples calcined at  $400^\circ\text{C}$ , 3 h. (B) The JCPDS no. 21-1272 for anatase phase is shown as reference.

### 2.1.2. Morphology of Mesoporous Inorganic Matrices

The morphology of titania samples was investigated by scanning and transmission electron microscopy (Figure 3). The use of titanium(IV) butoxide as a precursor yielded more agglomerated nanoparticles (Figure 3A,B,D) than in the case of titanium(IV) isopropoxide (Figure 3C,E). TEM investigation demonstrated the crystalline nature of  $\text{TiO}_2$  NPs and the interparticle pores formation (Figure 3F,G). Titania samples present polyhedral nanoparticles with around 10 nm dimension, which are agglomerated. The particle sizes of the calcined S3\_C (Figure 3F) and S5\_C (Figure 3G) samples observed on the TEM investigation were consistent, with the crystallite size found based on XRD analyses. Mesoporous SBA-15 silica presents rod-type particles with an average diameter of 447 nm and a length/diameter ratio in the range of 2.04–2.20 (Figure 3H).

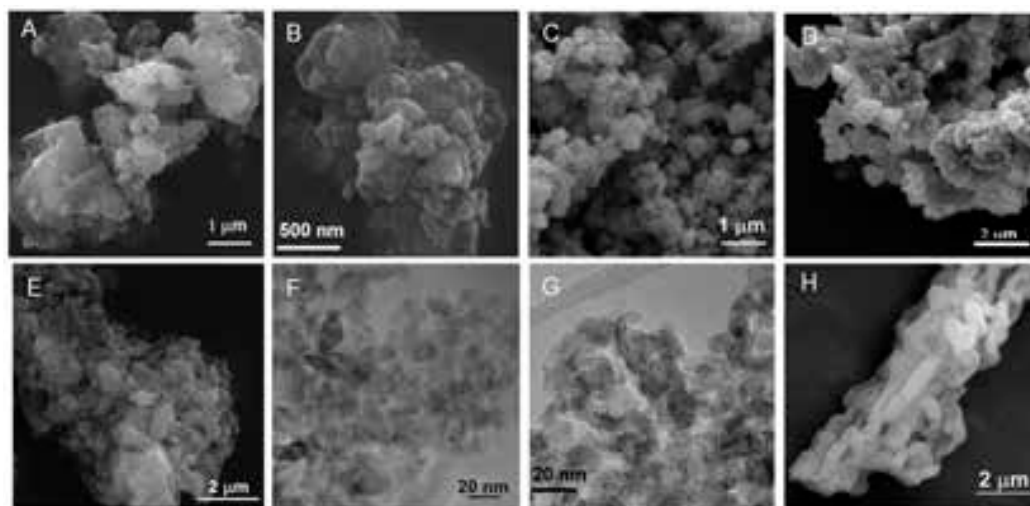


**Figure 3.** SEM micrographs for the following samples: S1\_E (A) and S6\_E (B) purified by Soxhlet extraction, S5\_C (C), S2\_C (D) and S4\_C (E) titania samples obtained at  $400^\circ\text{C}$ , TEM images of S3\_C (F) and S5\_C (G) calcined samples, and SEM image of SBA-15 silica (H).

### 2.1.3. FTIR Spectroscopy

In the FTIR spectra of the titania samples isolated after solvothermal treatment (S3 and S5), one can notice the characteristic bands of methyl and methylene groups in the range of  $2850\text{--}2930\text{ cm}^{-1}$ , as well as the ether bridge vibrations ranging in the

1410–1530  $\text{cm}^{-1}$  domain that demonstrate the presence of the polymer on the surface of titanium dioxide nanoparticles (Figure 4). The extraction process in ethyl alcohol for 24 h did not completely remove the structure directing agent, as its characteristic vibrations were still present but less intense in the FTIR spectra of the samples purified by extraction, S1\_E and S3\_E (Figure 4). The calcining step at 400 °C caused the removal of the template agent regardless of the polymer type (Figure 4—spectrum of S3\_C sample). In the FTIR spectra of all  $\text{TiO}_2$  samples, irrespective of the stage in which the samples were analyzed, one can notice the specific bands of Ti–O and Ti–O–Ti bonds at 677  $\text{cm}^{-1}$  and 466  $\text{cm}^{-1}$ , respectively [24], as well as the stretching modes of vibration of hydroxyl groups with the lowest transmittance value at 3420  $\text{cm}^{-1}$  and the bending band of adsorbed water molecules at 1634  $\text{cm}^{-1}$ . The stretching vibrations of -OH groups are less intense in the case of the calcined S3\_C sample than in the spectra of the other NPs isolated after solvothermal treatment, S3 and S5, or after Soxhlet extraction, S1\_E and S3\_E (Figure 4).

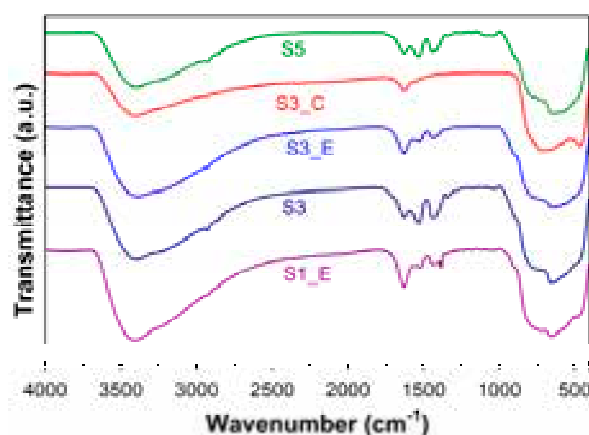


**Figure 4.** FTIR spectra of the following samples: S1\_E and S3\_E obtained after Soxhlet extraction, S3 and S5 isolated after solvothermal treatment, and S3\_C calcined at 400 °C.

#### 2.1.4. Thermal Analysis

The copolymers decompose in steps up to 400 °C. The extraction process was not very efficient, a content of about 10% (wt.) copolymer remained in the materials purified by Soxhlet extraction (Figure 5A). In agreement with FTIR spectra, the DTA-TG analysis showed that the thermal treatment at 400 °C for 3 h completely removed the surfactant, as no effect was recorded on the DTA traces of the calcined samples (Figure 5B).

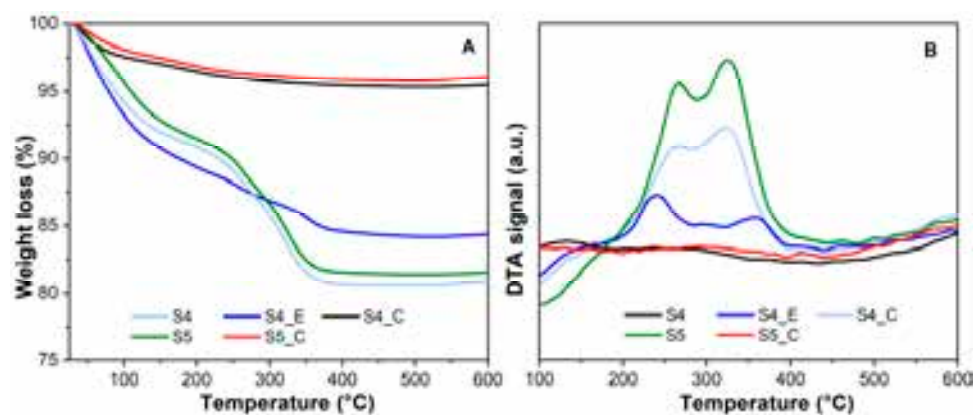


**Figure 5.** (A) TG analyses performed in synthetic air for S4 and S5 samples isolated after solvothermal treatment, S4\_E purified by Soxhlet extraction and S4\_C and S5\_C calcined at 400 °C, 3 h. The TG curves for calcined samples were included to evaluate the content of hydroxyl groups attached to the titania surface that was subtracted when the content of the polymer was determined. (B) Corresponding DTA curves.

### 2.1.5. Evaluation of the Porosity for Mesoporous Inorganic Matrices

The textural properties of the titania samples were determined from nitrogen adsorption–desorption isotherms, recorded at liquid nitrogen temperature, that are type IV with hysteresis at  $P/P_0 > 0.5$ , characteristic for mesoporous materials with wormlike pores. The porosity of the titania samples is mainly due to interparticle pores, evidenced by a sharp increase in the volume of adsorbed gas in the region of high  $P/P_0$  values (Figures 6A,B and S1). Table 2 gathered the parameters determined from nitrogen adsorption–desorption isotherms: specific surface area,  $S_{\text{BET}}$ , determined by applying BET theory, total pore volume measured at relative pressure,  $P/P_0 = 0.985$ , and average pore diameter,  $d_{\text{BJH}}$ , calculated from the desorption branch of the isotherms with BJH method. The uncalcined titania samples have a higher specific surface area,  $S_{\text{BET}}$ , than the calcined materials (312 and 274  $\text{m}^2/\text{g}$  for S2\_E and S4\_E, respectively, and 154  $\text{m}^2/\text{g}$  in the case of S4\_C), probably because of the contribution of remaining copolymer on titania nanoparticles surface (Table 2). When  $\text{Ti}(\text{OnBu})_4$  was used as the precursor in the synthesis, this resulted in higher values of average pore size (6.3 nm for S6\_C in comparison with 5.4 nm for S5\_C for which  $\text{Ti}(\text{OiPr})_4$  was used), although the specific surface area and total pore volume did not change significantly (153  $\text{m}^2/\text{g}$  and 0.33  $\text{cm}^3/\text{g}$  for S5\_C and 153  $\text{m}^2/\text{g}$  and 0.31  $\text{cm}^3/\text{g}$  for S6\_C–Table 2). The use of the copolymer F127 instead of Pluronic P123 for titania nanoparticles synthesis did not have an important contribution to the porosity of the resulting materials. A higher copolymer quantity introduced in the synthesis led to a diminution of the pore size (7.4 nm and 5.8 nm for S3\_C and S4\_C, respectively, Table 2). SBA-15 silica had higher porosity than all titania NPs with the following textural features:  $S_{\text{BET}} = 984 \text{ m}^2/\text{g}$ ,  $V = 1.31 \text{ cm}^3/\text{g}$ , and the average diameter of the mesopores computed from the desorption branch of isotherm,  $d_{\text{BJH}} = 6.3 \text{ nm}$ .

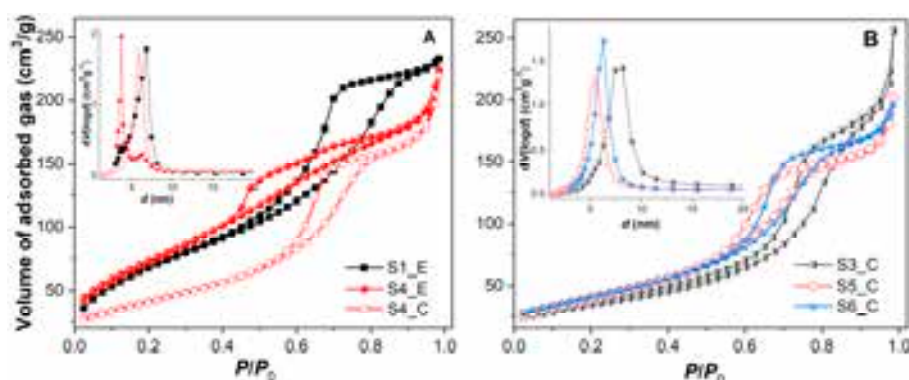


**Figure 6.** Nitrogen adsorption–desorption isotherms recorded at liquid nitrogen temperature of S1\_E and S4\_E samples purified by Soxhlet extraction and S4\_C (A), S3\_C, S5\_C, and S6\_C calcined at 400 °C (B). The corresponding pore distribution curves calculated with BJH model from desorption branch of the isotherms are inserted in both figures. All samples were outgassed in vacuum at 120 °C for 17 h.

**Table 2.** The textural parameters computed from  $\text{N}_2$  adsorption–desorption isotherms for mesoporous inorganic matrices.

| Sample | $S_{\text{BET}}$<br>( $\text{m}^2/\text{g}$ ) | V<br>( $\text{cm}^3/\text{g}$ ) | $d_{\text{BJH}}$<br>(nm) |
|--------|-----------------------------------------------|---------------------------------|--------------------------|
| S1_E   | 258                                           | 0.34                            | 6.8                      |
| S2_E   | 312                                           | 0.43                            | 3.7                      |
| S2_C   | 142                                           | 0.42                            | 6.8                      |
| S3_C   | 126                                           | 0.42                            | 7.4                      |
| S4_E   | 274                                           | 0.30                            | 3.7                      |
| S4_C   | 154                                           | 0.36                            | 5.8                      |
| S5_C   | 153                                           | 0.33                            | 5.4                      |
| S6_C   | 153                                           | 0.31                            | 6.3                      |
| SBA-15 | 984                                           | 1.31                            | 6.3                      |

## 2.2. Obtaining and Characterization of Red GM Extracts

The polyphenols extraction was carried out using *Vitis vinifera* L. red grape marc (GM) from two cultivars, Feteasca Neagra (FN) and Pinot Noir (PN), from the Research Station for Viticulture Murfatlar (Constanta County, Romania). The extracts were obtained by conventional technique at reflux using FN and PN grape pomace samples collected after wine production in 2018 or 2019 and ethanol or 50% ethanol aqueous solution as solvent.

For all extracts, the following data were determined by UV-vis methods: the total polyphenols index (TP) expressed as gallic acid (GA) equivalents based on the chemical reaction between phenolic substances and Folic Ciocâlteu reagent, the total flavonoids index (TF) expressed as quercetin (Q) equivalents, based on the chemical reaction between flavonoids and the aqueous solution of  $AlCl_3$ , and the total anthocyanin pigments (TA) expressed as cyanidin-glucoside (CG) equivalents using the method described by Lee et al. [25]. All these data are presented in Table 3. The radical scavenging activity (RSA) was expressed as Trolox (T) equivalents using two assays: DPPH and ABTS.

**Table 3.** Solvents used for extraction, yield values, and spectrometric data expressed per gram of dry extract for prepared extracts.

| Extract | Year, Solvent     | Yield (%) | TP (mgGA/g)   | TF (mgQ/g)   | TA (mg CG/g) |
|---------|-------------------|-----------|---------------|--------------|--------------|
| FN      | 2019, 50% ethanol | 13.2      | 295.46 ± 1.33 | 14.82 ± 0.51 | 7.35 ± 1.89  |
| FN(E)   | 2018, ethanol     | 0.4       | 71.02 ± 0.22  | 12.31 ± 0.64 | 20.42 ± 4.26 |
| FN(E-W) | 2018, 50% ethanol | 6.5       | 147.71 ± 8.6  | 5.06 ± 0.12  | 3.56 ± 0.24  |
| PN      | 2019, 50% ethanol | 11.8      | 138.49 ± 3.49 | 11.94 ± 0.03 | 4.29 ± 0.00  |
| PN(E)   | 2018, ethanol     | 1.3       | 47.09 ± 0.99  | 13.34 ± 4.11 | 2.86 ± 0.00  |

All spectrometric measurements were performed in triplicate.

Upon first glance at the data in Table 3, one can observe that the type of red GM and the harvest year strongly influenced the quantity of phenolic compounds in the extracts. The extract richest in polyphenols is the hydroethanolic FN extract prepared from Feteasca Neagra GM collected in 2019. Both GMs used in this study from 2018 were very poor in phytochemicals, probably because the climate has altered the quality of these wastes. For all extracts prepared from GMs collected in 2018, we obtained very low yields (in the range of 0.4–6.5%) and TP index values (47.09–147.71 mgGA/g extract). Regarding the solvent, the 50% ethanol aqueous solution was more effective in the recovery of polyphenols (147.71 for FN(E-W) vs. 71.02 mgGA/g extract for FN(E) extract) than absolute ethanol, which was better at extracting flavonoids (12.31 and 5.06 mgQ/g extract for FN(E) and FN(E-W), respectively, or 13.34 and 11.94 mgQ/g extract for PN(E) and PN, respectively).

Figure 7 shows the radical scavenging activity (RSA) expressed as Trolox equivalents (TE) using two assays: DPPH and ABTS. The FN sample prepared from GM collected in 2019 has the highest value for antioxidant activity assessed by both DPPH and ABTS assays, ( $566.00 \pm 13.08$  and  $572.37 \pm 5.78$  mgTE/g extract, respectively), followed by the other hydroethanolic FN extract obtained from GM collected in 2018 ( $316.92 \pm 21.6$  and  $267.11 \pm 9.04$  mgTE/g extract, respectively). Both ethanolic extracts prepared from GMs collected in 2018 had weak radical scavenging activity ( $35.18 \pm 4.88$  and  $47.89 \pm 7.12$  mgTE/g extract for FN(E) and PN(E), respectively), which could be correlated with the low amount of polyphenols, though the FN(E) sample has the highest index of TA ( $20.42 \pm 4.26$  mgCG/g extract)—Table 3.

Phenolic substances present in the extracts were quantified using reverse-phase high-performance liquid chromatography and the data are listed in Table 4. The chromatograms can be seen in Figure S2. We identified in all the extracts the following phenolic acids: gallic, protocatechuic, vanillic, and syringic acids from the class of flavonoids, rutin and quercetin, and catechin (except for the FN(E) sample) and (-) epicatechin (except the extracts prepared in absolute ethanol) from the flavan-3-ol class. The only extract in which delphinidin ( $0.593 \pm 0.010$  mg/g extract) and the esterified phenolic acid—caftaric acid ( $0.050$  mg/g

extract)—were quantified was FN(E-W), while *p*-coumaric acid was found only in the FN(E) sample. Being poorly soluble in water but soluble in ethanol, *trans*-resveratrol was quantified in higher amounts in the ethanolic extracts: FN(E) and PN(E) (Table 4).

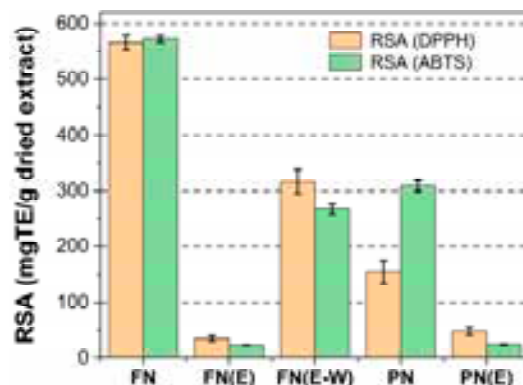


**Figure 7.** Radical scavenging activity expressed as Trolox equivalents per mass of the dried extract using DPPH and ABTS methods.

**Table 4.** Chemical profile of prepared extracts determined by HPLC-PDA analysis.

| Phenolic Substance        | Concentration (mg/g Dried Extract) |               |               |               |               |
|---------------------------|------------------------------------|---------------|---------------|---------------|---------------|
|                           | FN                                 | FN(E)         | FN(E-W)       | PN            | PN(E)         |
| Gallic Acid               | 1.150 ± 0.004                      | 0.594 ± 0.001 | 0.437 ± 0.000 | 0.238 ± 0.008 | 0.723 ± 0.000 |
| Protocatechuic acid       | 0.541 ± 0.001                      | 0.714 ± 0.000 | 0.078 ± 0.002 | 0.367 ± 0.001 | 1.748 ± 0.001 |
| Catechin                  | 0.087 ± 0.001                      | nd            | 5.978 ± 0.000 | 1.164 ± 0.002 | 0.504 ± 0.001 |
| Caftaric acid             | nd                                 | nd            | 0.050 ± 0.000 | nd            | nd            |
| Vanillic acid             | 1.091 ± 0.003                      | 0.826 ± 0.000 | 0.334 ± 0.007 | 1.424 ± 0.004 | 0.309 ± 0.000 |
| Syringic acid             | 2.492 ± 0.004                      | 1.490 ± 0.000 | 0.674 ± 0.000 | 2.043 ± 0.006 | 1.869 ± 0.003 |
| <i>p</i> -Coumaric acid   | nd                                 | 0.083 ± 0.000 | nd            | nd            | 0.035 ± 0.001 |
| (-) Epicatechin           | 2.755 ± 0.006                      | nd            | 4.757 ± 0.001 | 0.644 ± 0.002 | nd            |
| Delphinidin               | nd                                 | nd            | 0.593 ± 0.010 | nd            | nd            |
| Rutin                     | 0.582 ± 0.001                      | 0.191 ± 0.001 | 0.702 ± 0.001 | 0.427 ± 0.000 | 0.139 ± 0.000 |
| <i>trans</i> -Resveratrol | 0.023 ± 0.001                      | 0.082 ± 0.000 | nd            | nd            | 0.080 ± 0.000 |
| Quercetin                 | 0.160 ± 0.001                      | 0.370 ± 0.000 | 0.133 ± 0.000 | 0.073 ± 0.001 | 0.280 ± 0.000 |

nd—not determined.

### 2.3. Characterization of Materials Containing FN Extract

The hydroethanolic FN extract with the best antioxidant potential (572.37 mgTrolox/g extract) was selected to be encapsulated into mesoporous SBA-15 silica with an ordered pore framework with hexagonal symmetry determined by small-angle X-ray diffraction (Figure S3) and in S5\_C titania nanoparticles through the impregnation method, followed by solvent evaporation under low pressure (3 mbar) according to the procedure described elsewhere [26].

The resulting materials containing FN extract were analyzed by TG-DTA analysis to evaluate the amount of phenolic compounds incorporated in mesoporous inorganic matrices. The main feature influencing the quantity of phenolic compounds that can be encapsulated in the mesopores of inorganic matrices is the total pore volume. The extract amount from the considered inorganic supports was computed based on the weight loss for materials containing extract, taking into account the weight loss of hydroxyl groups during the support heating, and the removal of moisture, which corresponds to the first endothermic event of the DTA curve for each sample subjected to the analysis (Figure 8). As expected, the quantity of encapsulated phenolic substances was lower in the case of FN@TiO<sub>2</sub>, 20% (wt) (Figure 8A) than for FN@SBA-15 material, 39% (wt) (Figure 8B). Another observation from the thermal analyses is that the temperature at which the polyphenol decomposition rate reached the maximum, 312 °C, was higher in the

case of FN@SBA-15 (Figure 8B, black dash-dot curve) than 281 °C for FN@TiO<sub>2</sub> (Figure 8A, red dash-dot line), which could be explained by the bigger exposure of biologically active compounds to oxidation in the case of their embedding in mesoporous titania since its mesopores are interparticle pores, and the polyphenols were on the titania NPs' surfaces, unlike in the case of the SBA-15 matrix, which has cylindrical channels of mesopores.

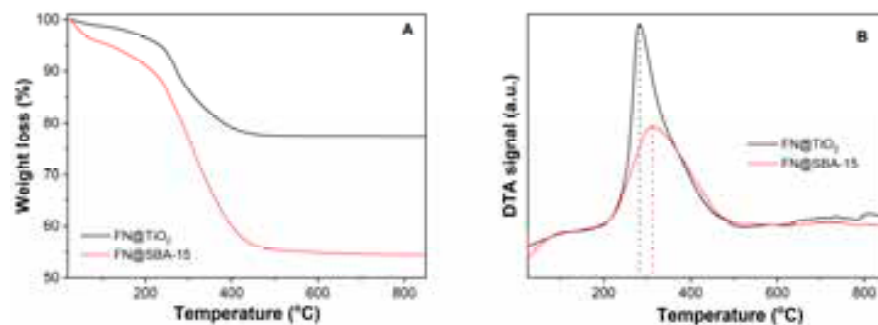


**Figure 8.** TG analyses of FN@TiO<sub>2</sub> and FN@SBA-15 samples (A) and the corresponding DTA curves (B) performed in air flow.

The sharp decrease in the porosity of materials with encapsulated extract demonstrated the presence of phytocompounds in the mesopores of the inorganic matrices (Figure S4). In the case of FN@SBA-15 material, the values of  $S_{\text{BET}}$  and  $V$  decreased from 984 m<sup>2</sup>/g and 1.31 cm<sup>3</sup>/g, respectively, for SBA-15, to 209 m<sup>2</sup>/g and 0.36 cm<sup>3</sup>/g, respectively. In the case of FN@TiO<sub>2</sub>, practically all pores were filled with FN extract ( $V = 0.01$  cm<sup>3</sup>/g), though the extract quantity was lower than in the case of FN@SBA-15.

FTIR spectroscopy highlighted the presence of phenolic components in the spectra of the FN extract and FN@SBA-15 and FN@TiO<sub>2</sub> samples (Figure 9A) through the presence of the asymmetric stretching vibrations of C=O bonds belonging to the carboxylic groups at 1726 cm<sup>−1</sup>, asymmetric and symmetric stretching bands of C–H bonds of methylene groups at 2929 cm<sup>−1</sup> and 2843 cm<sup>−1</sup>, respectively. The stretching vibration of C–O bonds overlapped with the deformation band of O–H groups linked on aromatic rings from 1391 cm<sup>−1</sup> and the vibration mode of aromatic C–H bonds at 1100 cm<sup>−1</sup>, the last band being superimposed the very intense asymmetrical stretching band of the Si–O–Si bonds of the SBA-15 matrix in the case of FN@SBA-15 material. In all the spectra, including that of mesoporous inorganic matrices, the broad band with the minimum transmittance at 3470 cm<sup>−1</sup> due to hydroxyl groups, which belong either to the phenolic substances or the inorganic matrices, and the bending vibration of adsorbed water at 1627 cm<sup>−1</sup> can be observed [27].

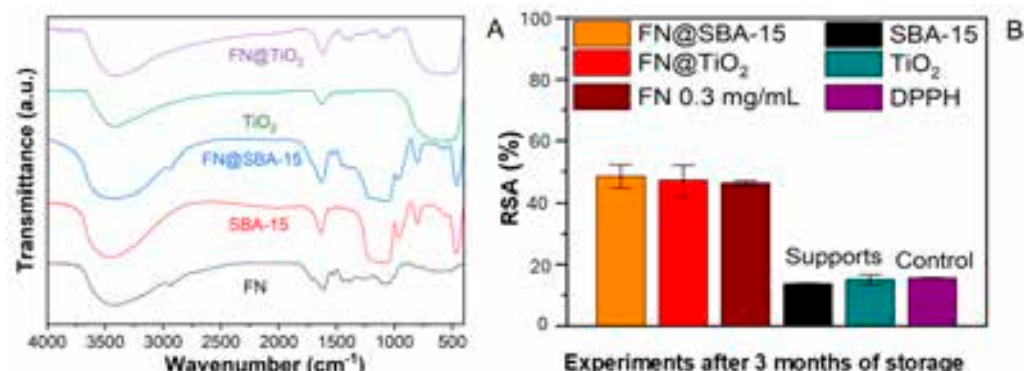


**Figure 9.** FTIR spectra of FN extract, SBA-15 matrix, FN@SBA-15 material, TiO<sub>2</sub> support, and FN@TiO<sub>2</sub> sample (A). Radical scavenging activity assessed by DPPH assay for FN@TiO<sub>2</sub> and FN@SBA-15 in comparison with FN extract alone and corresponding inorganic matrices, TiO<sub>2</sub> and SBA-15, in the same quantities as in the FN-loaded supports (B).

Spectrometric determinations of radical scavenging activity (DPPH method) for materials containing FN extract showed the preservation of this property over time (Figure 9B). The antioxidant potential was also determined for the FN extract after three months of storage in dark conditions, in a refrigerator, and for mesoporous inorganic matrices, which showed no contribution to the radical scavenging potential of FN@TiO<sub>2</sub> and FN@SBA-15.

#### 2.4. Assessment of Cytocompatibility of the Polyphenolic Extract, Materials Containing Extract, and Corresponding Mesoporous Supports

The cytocompatibility of FN and PN extracts, FN extract encapsulated in SBA-15 and TiO<sub>2</sub>, and the corresponding inorganic materials was assessed on NCTC clone L929 murine fibroblasts cell line at 24 h and 48 h incubation times using MTT assay. All samples were tested in triplicate.

Both extracts, FN and PN, are biocompatible at concentrations lower than 300 µg/mL, either after 24 h or 48 h of incubation. PN extract showed lower cytotoxicity than FN extract at 700 µg/mL concentration, and in the case of FN extract, cell viability decreased to 35.86% at 24 h and 19.47% after 48 h, while for PN extract, cytotoxic effects were observed only after 48 h of incubation (69.17% cell viability). Cell viability decreased sharply at a treatment dose of 1000 µg/mL for both FN and PN extracts to 15.64% and 47.71%, respectively after 24 h and 7.59% and 15.64%, respectively, after 48 h of incubation (Figure 10A).

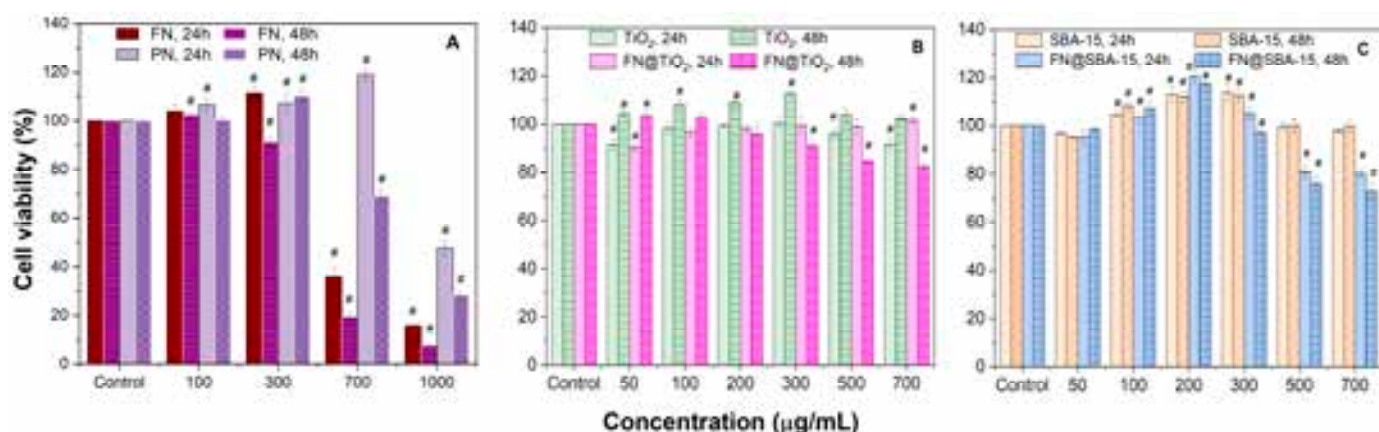


**Figure 10.** Cell viability of normal L929 cells for the free hydroethanolic PN and FN grape pomace extracts (A) and FN extract encapsulated in TiO<sub>2</sub> (B) and SBA-15 matrices compared to the corresponding supports, TiO<sub>2</sub> and SBA-15, assessed using MTT assay (C). Results are presented as average value of three replicates  $\pm$  standard deviation ( $n = 3$ ). # ( $p < 0.05$ ) shows significant differences between the fibroblasts incubated with samples in comparison to control. Treatments with samples of cells are not considered toxic when cell viability is higher than 80%.

The FN extract encapsulated in TiO<sub>2</sub> NPs, FN@TiO<sub>2</sub>, showed biocompatible behavior for all tested concentrations, between 50 µg/mL and 700 µg/mL, with cell viability values in the range of 104.22–82.89%. TiO<sub>2</sub> NPs also showed no cytotoxic effect on NCTC fibroblasts at concentrations up to 700 µg/mL (Figure 10B). FN@SBA-15 showed cytocompatibility at concentrations in the range of 50–300 µg/mL after both incubation periods. At high concentrations, 500 and 700 µg/mL of FN@SBA-15, the cell viability decreased to 75.95% and 72.91%, respectively. SBA-15 support presents no cytotoxicity at the tested concentrations (Figure 10C).

### 3. Discussion

Antioxidants are very important for cellular health because they help neutralize free radicals and thus can prevent various inflammation-based diseases. In recent years, many interdisciplinary research groups have studied their biological effects on human health, their recovery from various sources, including plant waste [28–30], and how to preserve or

enhance their effectiveness by developing new approaches, such as including antioxidants in various formulations with improved features and benefits [26,31,32].

Grape pomace, a by-product from wine production, is a source of antioxidants and antimicrobial agents, especially against foodborne bacteria strains, which can be used in various fields, such as fertilizers, the food industry, cosmetics, and supplements, after their recovery by solid–liquid extraction [33–35]. Grape pomace extracts can improve the antibacterial activity of antibiotics because they inhibit biofilm formation and could be used in the treatment of resistant-biofilm-related infections [35]. Until now, this valuable source of antioxidants and antimicrobials has not been very well exploited.

We valorized fermented dried grape marc from two cultivars, Feteasca Neagra and Pinot Noir from Constanta County, Romania, collected in two years, by preparing extracts through conventional extraction technique in non-toxic solvents: 50% ethanol aqueous solution and absolute ethanol for further application in cosmetics. We observed that the quantity of phenolic compounds is very different depending on the variety and the harvest year of the grapes. The extracts obtained from Feteasca Neagra were generally richer in polyphenols and had more total anthocyanins expressed per mass of dried extract than those prepared from Pinot Noir GM, results that are in agreement with the data reported by Balea et al. [16].

Thus, the richest extract in bioactive compounds obtained in this study was the hydroethanolic FN extract with  $39.00 \pm 0.17$  mg GA/g GM, followed by hydroethanolic PN extract with  $16.34 \pm 0.41$  mg GA/g GM, with the TP index values being in the domain of total phenolic content reported by Constantin et al. [36] for the extracts prepared in water at 28 °C from Feteasca Neagra grapes, Galati County, Romania (0.77–83.62 mg/g dried mass). They reported the following distribution of phenolic compounds: 3%, 1%, and 96% in grape pulp, skins, and seeds, respectively. This study and previous results demonstrated that the climatic conditions and cultivar strongly influence the content of phenolic compounds in not only wines but also in fermented GM, and thus, if exploited, the quality of extracts. For instance, we reported for a polyphenolic extract prepared in the same way as the PN sample in this study, but using GM collected in 2020, values for TP of 43.16 mgGA/g GM and RSA of 689.09 mgTE/g extract, which are 2.6 and 2.2 times higher, respectively, than those of the hydroethanolic PN extract from reference [26]. If we compare the ethanolic FN(E) extract with our previous results from an extract obtained from the same GM variety but collected in 2017, the TP index and antioxidant potential are 3.9 and 3.4 times lower for the FN(E) sample than for the FN extract (GM from 2017) [23]. Previously, we also prepared and characterized Cabernet Sauvignon extract for which the TP index was  $265.21 \pm 4.97$  mg GA/g extract and the RSA value was 344 mgTE/g extract (DPPH assay), with both values being lower than those of FN extract (295.46 mg GA/g extract and 566.00 mgTE/g extract, respectively) discussed here.

With respect to the TA index expressed as CG equivalents per mass of dry extract, all the extracts prepared from Feteasca Neagra had higher TA index values, especially the ethanolic extract (20.42 for FN(E) vs. 7.35 and 3.56 mgCG/g for FN and FN(E-W), respectively) than extracts obtained from Pinot Noir (2.86 and 4.29 mgCG/g for PN(E) and PN, respectively). Also, for the Pinot Noir extracts, for the preparation of which we used GM collected in 2020, we determined a lower value of the TA index, 4.52 mgCG/g extract, [23] than for Feteasca Neagra extracts.

Nevertheless, bioactive substances derived from plants are susceptible to degradation. Hence, one approach to enhance their chemical stability and thus their shelf-life is to encapsulate bioactive compounds in various carriers. In this regard, Castro et al. [37] proposed formulations for a grape seed extract using microdispersion based on soy lecithin and pectin with a very good yield of the entrapment and controlled delivery of the extract polyphenols. Raschip et al. [38] reported the embedding of Feteasca Neagra and Merlot extracts in ice-templated 3D xanthan–PVA composites. They showed that the polymeric films containing Feteasca Neagra extract presented a high antioxidant potential, while the Merlot extract embedded in xanthan–PVA composites exhibited a better antibacterial poten-

tial against Gram-positive or Gram-negative bacterial strains than the samples containing FN extract or samples without extract. By microencapsulation through the freeze-drying method of grape pomace extracts in sodium alginate with gum Arabic coated with gelatin, an improved in vitro bioaccessibility of polyphenols was demonstrated [39].

Reports on polyphenols, like quercetin- or resveratrol-based delivery systems for cancer therapy have emerged in recent years [40–42]. For example, functional lipid–polymer nanoparticles with high biocompatibility have been developed as carriers for bioactive substances from *Curcuma zedoaria* and *Platycodon grandiflorum* to treat breast cancer metastases [43], in addition to quercetin-loaded lipid nanoparticles with improved release properties for anticancer therapy, thus mitigating the side-effects of chemotherapy [40].

Among carriers, mesoporous inorganic materials, especially silica, have been used for embedding various extracts, the resulting extract-loaded materials exhibiting improved stability, radical scavenging potential or anti-inflammatory properties, and desirable biocompatibility [23,44,45]. Usually, mesoporous silica nanoparticles increase the solubility of poorly water-soluble bioactive compounds due to their nanoconfinement in mesopores in amorphous state, improving their bioavailability [46].

In our previous papers, we showed the improved properties of the extracts when loaded on supports based on mesoporous MCM-41 silica, depending on the surface functionalization [47,48]. For example, we reported that the hydroethanolic Pinot Noir extract (GM collected in 2020) presented better anti-inflammatory properties when encapsulated in fucoidan-coated aminopropyl functionalized MCM-41 silica than that of corresponding free extract or reference drugs [26]. We carried out a stability study of polyphenolic extract from wild bilberries free and encapsulated in mesoporous silica. During the accelerated degradation study, the free extract lost a part of the polyphenols, while when it was incorporated in mesoporous silica, better stability in time was observed [48].

Herein, for the first time, we tested mesoporous SBA-15 silica as a carrier for phenolic compounds, which has a larger pore volume and wider pore diameter than MCM-41. We demonstrated that SBA-15 silica has desirable cytocompatibility, being suitable for use as a matrix for the incorporation of bioactive compounds (with the FN@SBA-15 sample having a high content of polyphenols, 39% wt.). The FN@SBA-15 formulation showed non-toxic effects up to 300 µg/mL on NCTC fibroblast cells (Figure 10C). Also, the encapsulation of FN extract in SBA-15 support did not alter the radical scavenging properties of the extract (Figure 9B). Also, liposomal formulations of sea buckthorn and grape pomace extracts showed an enhanced antioxidant activity of extracts due to the protective effect of liposomes against acidic degradation [49].

The use of titania NPs is approved by the Food and Drug Administration and the EU Commission in cosmetics and sunscreen formulations [11,50]. The challenge in using TiO<sub>2</sub> NPs for biomedical applications is related to their poor solubility in water and biological fluids, but titania can be used for topical applications.

Previously, we reported the use of titania NPs as support for common sage and wild thyme extracts [51]. TiO<sub>2</sub> NPs, used to incorporate these extracts, were obtained by sol-gel method, followed by an aging step of the reaction mixture at reflux using Pluronic P123 as a template agent. Finally, titania was calcined at 450 °C. In this study, we report the synthesis of a series of titania nanoparticles synthesized through the sol-gel technique combined with a solvothermal treatment, showing the parameters that influence the textural features of NPs.

We demonstrated that both Pluronic P123 and Pluronic F127 can be used for mesopore formation. By using this method, we obtained smaller pore diameters ranging from 3.7 to 7.4 nm versus 10.5 nm and higher S<sub>BET</sub> in the range of 126–312 m<sup>2</sup>/g (Table 2) compared to 115 m<sup>2</sup>/g [51], 112 m<sup>2</sup>/g for a sample also prepared in the presence of Pluronic F127 in ethanol [52], or 39 m<sup>2</sup>/g [53]. The use of Pluronic F127 led to less aggregated TiO<sub>2</sub> NPs, the formed spherical agglomerates having nanometric size (100–400 nm). In this study, we selected the titania sample obtained in the presence of F127 copolymer, which was thermally treated at 400 °C/3 h to encapsulate the hydroethanolic FN sample, the resulting sample being denoted as FN@TiO<sub>2</sub>. The biocompatibility of titania support and FN@TiO<sub>2</sub>

was assessed on NCTC fibroblasts, and the results demonstrated no cytotoxic effects of either titania NPs or the FN@TiO<sub>2</sub> sample for all tested concentrations, in the range of 50–700 µg/mL after 24 h and 48 h incubation time periods (Figure 10B). As in the case of FN@SBA-15 sample, titania nanoparticles containing FN extract preserved the radical scavenging capacity of the extract (Figure 9B). Our findings are in agreement with the literature data that showed a good in vitro biocompatibility of titania nanostructures on various cell lines [54–56].

Regarding the morphology of titania NPs prepared in the presence of both Pluronic F127 and P123, small crystals of 10 nm average size with polyhedral shape were obtained. Samsudin et al. observed that Pluronic F127 acts as a crystallographic controlling agent favoring the formation of {0 0 1} anatase facet that finally led to truncated octahedral bipyramidal particles, while the {1 0 1} facets led to the formation of almost spherical particles [53]. During TEM investigation, a similar particles shape was observed of titania NPs synthesized in the presence of either Pluronic F127 or Pluronic P123, so both triblock copolymers probably favor the formation of the {0 0 1} anatase facet.

#### 4. Materials and Methods

All chemicals utilized for the red GM polyphenolic extracts preparation and analyses, as well as for the synthesis of the mesoporous inorganic matrices, are provided in the Supplementary Materials.

##### 4.1. Obtaining of Mesoporous Inorganic Matrices

The first step of the synthesis of titania nanoparticles consisted of dissolving 1.25 g of the structure directing agent (Pluronic P123 or Pluronic F127) in 50 mL of solvent (2-propanol or n-butanol) at 40 °C, under magnetic stirring. Then, 1.5 mL of glacial acetic acid were added dropwise to slow down the hydrolysis reaction of the titanium precursor. A volume of Ti(IV) isopropoxide or Ti(IV) n-butoxide was poured into the reaction mixture kept at 40 °C, under magnetic stirring. After 1 h, in the resulting solution, 1 mL of deionized water was dropped to promote the hydrolysis and condensation reactions of titanium alkoxide. The reaction mixture was maintained under magnetic stirring at 40 °C for 24 h. Then, the resulting mixture was transferred into a reactor under autogenous pressure for a solvothermal treatment carried out at 100 °C for 24 h. After cooling, the solid was separated by centrifugation, washed with corresponding solvent, water, and ethanol, and then dried at 60 °C. The removal of the structure directing agent was carried out by Soxhlet extraction in ethanol for 24 h. Then, a part of each sample was calcined at 400 °C for 3 h with a heating rate of 0.5 °C/min.

Mesoporous SBA-15 silica was synthesized by an established procedure [57] starting with 2.5 g of Pluronic P123 dissolved at room temperature in 92.8 mL aqueous solution of hydrochloric acid (prepared by adding 13.8 mL HCl 37% (wt) in 79 mL deionized water), and then tetraethyl orthosilicate (5.9 mL) was added to the solution of the structure directing agent. The resulting mixture was stirred at 35 °C for 24 h and then was solvothermally treated in static conditions under autogenous pressure for another 24 h at 100 °C. The solid was filtered off, washed 3 times with 25 mL ethanol and 3 times with 50 mL deionized water, and dried at room temperature overnight. Finally, SBA-15 silica was thermally treated at 550 °C for 5 h.

##### 4.2. Materials Characterization

The materials were investigated through X-ray diffraction in the range of  $2\theta = 10\text{--}70^\circ$  and at a scanning rate of  $2^\circ/\text{min}$  and  $0.01^\circ$  step (Miniflex 2, Rigaku Holdings Corporation, Tokyo, Japan), FTIR spectroscopy using 64 scans, a resolution of  $2\text{ cm}^{-1}$  in  $4000\text{--}400\text{ cm}^{-1}$  range (KBr pellets technique; Bruker Tensor 27, Bruker Corporation Optik GmbH, Bremen, Germany), thermogravimetric analysis coupled with differential thermal analysis carried out in air flow ( $50\text{ mL/min}$ ), with a heating rate of  $10^\circ/\text{min}$  in the temperature range of  $20\text{--}850^\circ\text{C}$  (DTA-TG, Mettler Toledo GA/SDTA851e, Greifensee, Switzerland),

scanning electron microscopy (Tescan Vega 3 LMH microscope, Brno, Czech Republic), and transmission electron microscopy (FEI TECNAI F30 G2 S-TWIN, Hillsboro, OR, USA), as well as N<sub>2</sub> adsorption–desorption isotherms recorded at liquid nitrogen temperature after outgassing of the samples at 120 °C for 17 h (Quantachrome Autosorb iQ<sub>2</sub>, Quantachrome Instruments, Boynton Beach, FL, USA).

#### 4.3. Extracts Preparation

The grape marc (GM) samples were collected after fermentation stage during wine-making process. The fermented GM was dried in fresh air, in a thin layer, at ambient temperature on metallic mesh. Every 24 h, the GM was aerated by turning to facilitate the evaporation of water and ethylic alcohol and to avoid the development of bacteria and fungi because of the moisture. The dry GM was grounded in a food processor to increase the contact surface between vegetal waste and solvent.

For all extracts, a maceration step of 18 h was carried out at room temperature, under magnetic stirring before the three steps of 60 min, performed by refluxing the mixture containing red GM (3 g) and solvent (18 mL), adding on each stage a new solvent volume, and keeping the same ratio between the vegetal waste mass and solvent volume (1/6 g/mL). All three fractions obtained after extraction were put together, and then the solvent was completely evaporated using a DLAB RE100-Pro rotary evaporator (DLAB SCIENTIFIC Co., Ltd., Beijing, China).

#### 4.4. Characterization of Polyphenolic Extracts

Total polyphenols index, total flavonoids content, total amount of anthocyanins, and radical scavenging potential (DPPH and ABTS assays) were determined using UV-vis spectroscopy (Shimadzu UV-1800 spectrophotometer, Shimadzu Corporation, Kyoto, Japan), the methods being described in reference [23]. The components of the extracts from twenty-three standard substances (see Supplementary Materials) were quantified by reverse-phase HPLC-PDA (Shimadzu Nexera X2 with SPD-M30A detector) operating in the wavelength range of 250–600 nm and using a Nucleoshell® C18 column 4.6 × 100 mm (2.7 µm) (Macherey-Nagel GmbH & Co. KG, Düren, Germany). The details of the HPLC method were provided elsewhere [23].

#### 4.5. Cytocompatibility Evaluation

The cytocompatibility of FN and PN extracts, as well as of nanoparticles containing FN extract compared to that of mesoporous inorganic matrices in which FN extract was incorporated, was evaluated on NCTC clone L929 murine fibroblasts obtained from the European Collection of Authenticated Cell Cultures. The samples were sterilized under UV irradiation for 2 h, and then stock suspensions/solutions of 1 mg/mL were prepared in culture medium, which contained 10% fetal bovine serum and 1% antibiotics. The stock solutions/suspensions were incubated at 37 °C for 24 h in humid atmosphere containing 5% carbon dioxide. After 24 h, the stock suspensions were dispersed in ultrasounds for at least 1 h, and the extract solutions were filtered off through 0.22 µm Millipore membrane. Mouse NCTC fibroblast cells were seeded in sterile 96-well culture plates ( $4 \times 10^4$  cells/mL) in culture medium. Fibroblasts were treated with the tested samples and incubated for 24 h and 48 h. The in vitro testing of biocompatibility of the samples was carried out at the following concentrations: 100, 300, 700, and 1000 µg/mL for the free FN and PN extracts and 50, 100, 200, 300, 500, and 700 µg/mL for encapsulated FN extract in TiO<sub>2</sub> NPs and SBA-15 silica (FN@TiO<sub>2</sub> and FN@SBA-15) and corresponding supports (TiO<sub>2</sub> and SBA-15). The determination of cell viability (MTT assay, Sigma-Aldrich, Merck Company, Darmstadt, Germany) was performed after 24 h and 48 h incubation periods of the cells with samples. The experiments were performed according to the procedure described in reference [58]. The spectrophotometric determinations were performed on a Berthold Mithras LB 940 Multimode Plate Reader (Berthold Technologies GmbH & Co., Bad Wildbad, Germany),

at 570 nm wavelength. Untreated cells were considered the control with 100% cellular viability, based on which were calculated the cell viability for the samples.

Experiments were performed in triplicate, and the results were presented as mean  $\pm$  standard deviation. Student's *t*-test was performed for the statistical analysis, using two-tailed distribution and two-sample equal variance, in Microsoft 365 Excel software. Statistical differences were considered for  $p < 0.05$ .

## 5. Conclusions

We report the parameters that influenced the morphology of mesoporous titania NPs synthesized by sol-gel method combined with solvothermal treatment. The use of Pluronic F127 as a porogenic agent in the synthesis showed the formation of less agglomerated TiO<sub>2</sub> nanoparticles based on SEM and TEM investigation with higher  $S_{\text{BET}}$  and lower pore diameter (153 m<sup>2</sup>/g vs. 126 m<sup>2</sup>/g and 5.4 nm vs. 7.4 nm, respectively) than in the case of Pluronic P123.

We determined the chemical profiles of several extracts prepared from two types of red GM (Feteasca Neagra and Pinot Noir), and we could conclude that it depended on the cultivar and solvent. The extract with the best antioxidant properties, hydroethanolic FN extract prepared from GM collected in 2019, was encapsulated in TiO<sub>2</sub> NPs and compared with the resulting material obtained by the incorporation of FN extract in SBA-15 silica support.

We have successfully obtained and characterized materials containing FN extract, FN@TiO<sub>2</sub>, and FN@SBA-15, with desirable cytocompatibility on NCTC clone L929 murine fibroblasts in the concentration range of 50–300 µg/mL after 24 h and 48 h of incubation time and radical scavenging properties.

A long-term stability study for the FN extract alone and encapsulated in titania nanoparticles must be performed to obtain data regarding shelf-life. Also, further *in vivo* studies should be carried out for the safe use of the proposed extract-loaded nanoparticles in skincare products.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12100263/s1>. Figure S1. N<sub>2</sub> adsorption–desorption isotherms for S2\_E and S2\_C samples recorded at 77 K. Inset the corresponding pore size distribution curves calculated with BJH model from desorption branch; Figure S2. Chromatograms for the following extracts: hydroethanolic FN extract (A), ethanolic FN(E) extract (B), hydroethanolic PN extract (C), and ethanolic PN(E) extract; Figure S3. Small-angle X-ray diffraction of mesoporous SBA-15 silica; Figure S4. N<sub>2</sub> adsorption–desorption isotherms for FN@SBA-15 sample (a) and SBA-15 silica (b).

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## Article

# Precipitative Coating of Calcium Phosphate on Microporous Silica–Titania Hybrid Particles in Simulated Body Fluid

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**Abstract:** Titania and silica have been recognized as potential drug delivery system (DDS) carriers. For this application, controllable biocompatibility and the suppression of the initial burst are required, which can be provided by a calcium phosphate (CP) coating. However, it is difficult to control the morphology of a CP coating on the surface of carrier particles owing to the homogeneous nucleation of CP. In this study, we report the development of a CP-coating method that homogeneously corresponds to the shapes of silica–titania (SiTi) porous nanoparticles. We also demonstrate that controlled surface roughness of CP coatings could be achieved in SBF using SiTi nanoparticles with a well-defined spherical shape, a uniform size, and a tunable nanoporous structure. The precipitation of CP was performed on mono-dispersed porous SiTi nanoparticles with different Si/Ti molar ratios and pore sizes. The pore size distribution was found to significantly affect the CP coating in SBF immersion; the surfaces of the nanoparticles with bimodal pore sizes of 0.7 and 1.1–1.2 nm became rough after CP precipitation, while those with a unimodal pore size of 0.7 nm remained smooth, indicating that these two pore sizes serve as different nucleation sites that lead to different surface morphologies.

**Keywords:** bioceramic nanoparticles; simulated body fluid; nanopore; CP precipitative coating; silica–titania nanohybrid



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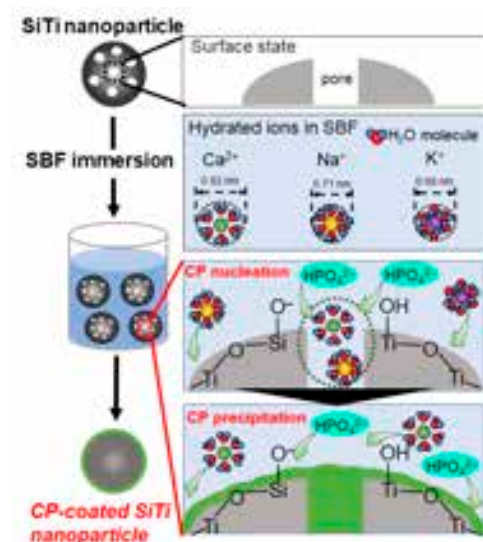
## 1. Introduction

Various nanomaterials composed of bioinert ceramics have been synthesized for use as artificial joints, implants, and drug delivery system (DDS) carriers [1,2]. In these applications, a DDS carrier needs to fulfill many requisites, including not only the inherent biocompatibility of bioceramic-based materials but also other properties including being of a uniform shape, size, and size distribution and possessing high affinity for aqueous media in order to form a stable suspension [3–5]. A sol–gel method based on the hydrolysis and condensation of a metal alkoxide has been used to synthesize a variety of biocompatible metal oxide nanoparticles with controlled morphologies, for which titania and silica have been extensively studied [6–8]. For example, amorphous titania in nanotube form has been investigated with respect to its use as a DDS carrier [9,10]. Since the surface of titania exhibits a Zeta potential of  $-18$  mV [11] in water (at pH 7.4), serious aggregate formation can occur depending on the experimental conditions. By contrast, amorphous silica shows a higher Zeta potential of  $-60$  mV in water (at pH 7.4) [12], allowing for the formation of a relatively stable suspension [13,14]. Although mixed oxide nanoparticles composed of silica and titania (SiTi nanoparticles) [15] have been explored as another potential option, their use also poses the problems such as biotoxicity due to the release of a silicate ion elution into the biological solution [16] and difficulty in controlling drug release owing to

the initial burst [17,18]. Therefore, the surfaces of SiTi nanoparticles need to be properly designed before being used for DDS applications.

Calcium phosphate (CP) coating has been developed as a technique to improve the osteoconductivity of the surfaces of titanium implants [19–21]. The CP coating is thought to suppress the initial burst of drug molecules [22], allowing them to be released gradually over several weeks. This is due to the fact that the CP coating itself can act as a reservoir for drug molecules, which slowly dissolve and diffuse over time as the coating degrades. The general CP-coating methods are electrochemical deposition, sputtering, and plasma spraying, which are performed under unphysiological conditions such as at high temperatures to provide different chemical and crystalline states with respect to the bone hydroxyapatite [23–25], leading to lower bioactivity in vivo. The biomimetic method has attracted attention due to its potential benefits. In this approach, CP is precipitated on particles in simulated body fluid (SBF) under conditions that mimic the biological environment of a living body [26,27]. Biomimetic CP synthesized under these conditions has been found to be more bioactive than CP synthesized under higher-temperature conditions [28–30]. However, biomimetic CP has generally only been coated on flat substrates [31–35]. In the case of nanoparticles, uniform nucleation occurs at different positions from the particle surfaces due to their high curvature and lower ability to induce heterogeneous nucleation. Therefore, a coating technique that adapts to the shapes of nanoparticles and provides a uniform coating has not been developed.

In this study, we demonstrate that controlled surface roughness of CP coatings can be achieved in SBF by using SiTi nanoparticles with a well-defined spherical shape, a uniform size, and a tunable nanoporous structure (Scheme 1). We synthesized SiTi nanoparticles using a microfluidic approach [15], which allowed us to design their size and shape so that they were suitable for DDS, and used them as a scaffold for the CP coating. The SiTi nanoparticles serve two critical functions in the SBF: they (1) provide CP nucleation sites that promote the substitution of phosphate ions with silicate ions and (2) create nanopores that induce the selective adsorption of hydrated ions in SBF. As described, the silicate ions elute readily into biological fluids [36,37] and can be replaced by phosphate ions [38], facilitating  $\text{Ca}^{2+}$  ion adsorption and subsequent CP nucleation. Moreover, the hydrated ions in SBF, including  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , can be adsorbed into the nanopores in their hydrated states and their sizes differ from each other. We prove that SiTi nanoparticles with tunable nanostructures can effectively function as an ion (molecular) sieve [39,40] that enables the selective adsorption of  $\text{Ca}^{2+}$  from SBF, leading to the formation of CP coatings. We also discuss the effect of nanopore sizes on the surface roughness of CP coatings.



**Scheme 1.** Illustration of the CP precipitation process of the SiTi nanoparticles via immersion in SBF.

## 2. Results and Discussion

### 2.1. Synthesis Result of XSiTi Nanoparticles

The Si/Ti molar ratios were measured via XRF and the values were X, and the sample was named as XSiTi (X = 0, 0.1, 0.7, and 1.2). The FE-SEM images and size distributions of the XSiTi nanoparticles are shown in Figure 1. All the SiTi nanoparticles exhibited spherical and mono-dispersed states. The diameter of the particles was around 150–200 nm, which is considered a size that does not induce cytotoxicity [41,42].

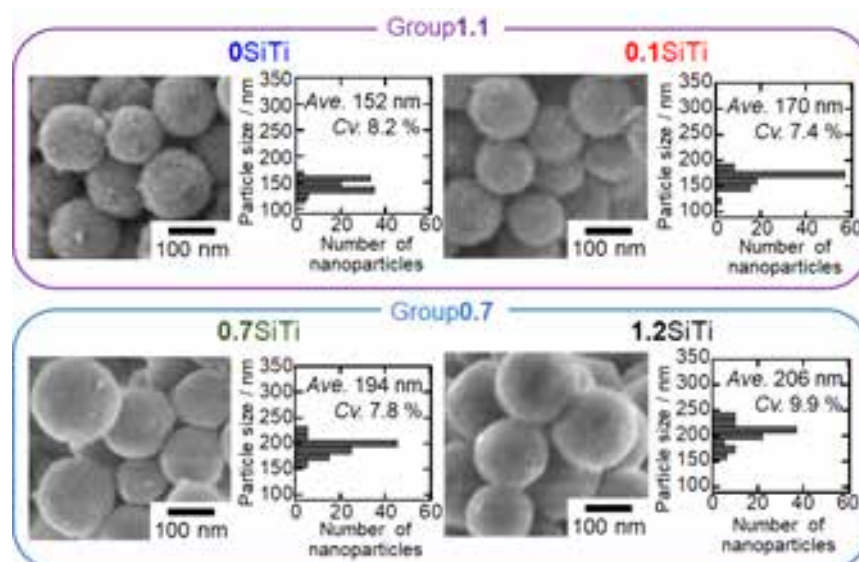


**Figure 1.** FE-SEM images and particle size distributions of the SiTi nanoparticles.

The XRD patterns (Figure S1) of the XSiTi nanoparticles indicated that all the nanoparticles were amorphous. Comparing the properties of these particles (e.g., particle shape, particle size, and CV value) with those of previously reported particles [15], we confirmed that they were identical and that equivalent particles were synthesized.

Figure 2 shows the N<sub>2</sub> adsorption and desorption isotherms of the SiTi nanoparticles. In the results regarding the specific surface area calculated using the  $\alpha$ s-plot (Figure 2a), it is evident that the surface area increased with the increase in the Si/Ti molar ratio. According to the nanopore size distributions based on the MP (micropore) method in the results regarding the XSiTi nanoparticles (Figure 2b,d), 0SiTi and 0.1SiTi exhibited bimodal nanopore sizes of 0.7 and 1.1–1.2 nm, and 0.7SiTi and 1.2SiTi exhibited only monomodal pores of 0.7 nm. The different nanopore sizes occurred due to the increase in the Si/Ti molar ratio. We propose that the hydrated ions of SBF were potentially diffused and adsorbed into the nanopores (Figure 2c,e). We suggest that nanopores 0SiTi and 0.1SiTi, with pore sizes of 1.1–1.2 nm, enable the diffusion and adsorption of the hydrated Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> ions, while 0.7SiTi and 1.2SiTi, with a pore size of 0.7 nm, only allows for the diffusion and adsorption of the hydrated Na<sup>+</sup> and K<sup>+</sup> ions. According to the nanopore size distribution, 0SiTi and 0.1SiTi were defined as Group1.1, while 0.7SiTi and 1.2SiTi were defined as Group0.7. By comparing these nanopore diameters with those of previously reported particles [15], we confirmed that they are identical and that comparable particles had been synthesized.

### 2.2. Results Regarding the SBF-Immersed SiTi Nanoparticles

The chemical element (Ca, Na, and K) amounts adsorbed by the SiTi nanoparticles through immersion in SBF were evaluated via XRF (Figure 3). The adsorbed elements increased with an increased immersion time. Referring to the results regarding the change in the amount of Ca on the nanoparticles (Figure 3a), the amount in Group1.1 was clearly larger than that in Group0.7 at the initial stage, indicating that Ca was preferentially

adsorbed on the nanoparticles in Group1.1. By observing the amount changes of Na and K adsorbed on the nanoparticles (Figure 3b,c), it is evident that those of Group0.7 were significantly larger than those in Group1.1 at the initial stage, indicating that Na and K were preferentially adsorbed on the nanoparticles in Group0.7. These differences are thought to be due to the difference in the nanopore sizes between Group1.1 and Group0.7. The diameters of the hydrated ions that could diffuse and be adsorbed inside the nanopores were determined as shown in Figure 2. The adsorption of Ca in Group1.1 reached equilibrium within 1 day of immersion, while the other ions in Group0.7 did not reach equilibrium even after 3 days. In addition, most of the adsorption of Na and K for Group0.7 reached equilibrium within 1 day of immersion, whereas that for Group1.1 did not reach equilibrium until 3 days.

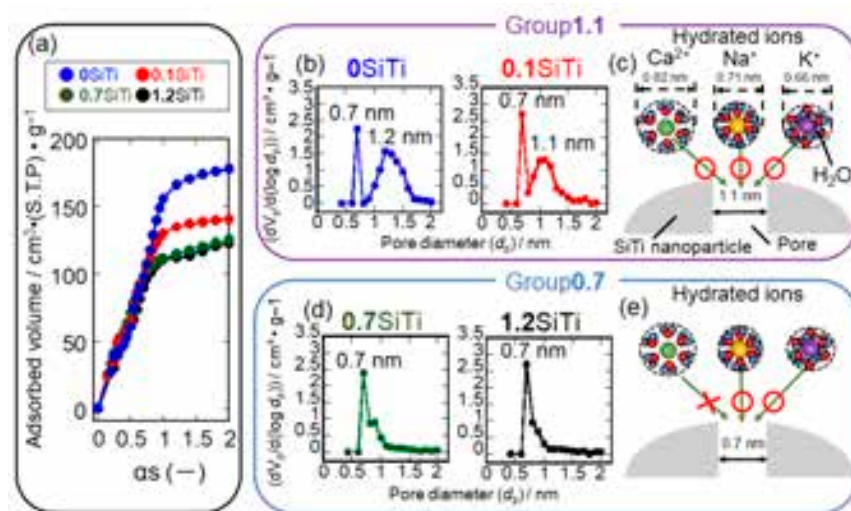


**Figure 2.** (a) N<sub>2</sub> adsorption (●) and desorption (○) isotherms of the SiTi nanoparticles; (b,d) the MP pore size distributions; and (c,e) illustrations of the hydrated ion interactions with the micropores. The specific surface areas of 0SiTi, 0.1SiTi, 0.7SiTi, and 1.2SiTi were 382, 443, 466, and 570 m<sup>2</sup>·g<sup>-1</sup>, respectively.

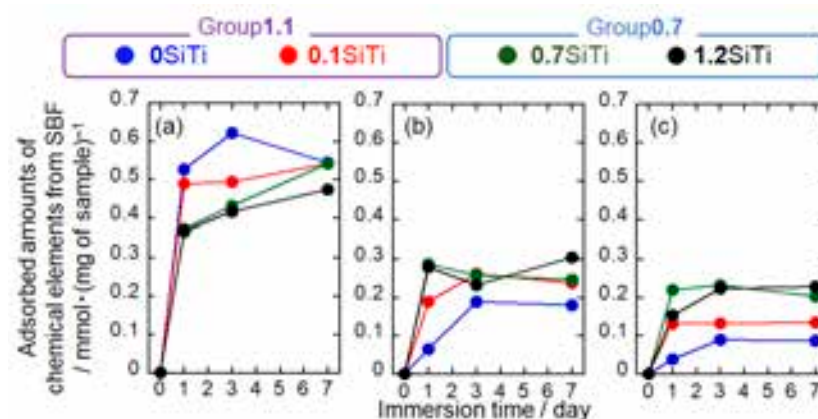


**Figure 3.** Adsorbed amount changes of the chemical elements of (a) Ca, (b) Na, and (c) K on the SiTi nanoparticles from SBF with immersion time.

The nucleation sites pertaining to the CP precipitation of SiTi nanoparticles immersed in SBF are discussed in Figure 4. Figure 4a shows the FT-IR spectra of the change in the absorbance band due to the OH group of the nanoparticles. The band intensity of Group1.1 did not change after immersion, whereas Group0.7 showed an increase in band intensity. The result of the change in the Si/Ti molar ratio of the nanoparticles after immersion is shown in Figure 4b. Group1.1 did not change in terms of its Si/Ti molar ratio, whereas Group0.7 showed a significant decrease, suggesting that the Si component was

eluted from Group0.7 into SBF. Regarding the changes in the average particle sizes of the nanoparticles following immersion (Figure 4c), all the nanoparticles showed a decrease in the size, and a significant decrease was observed in Group0.7. Group1.1 containing lower Si-content did not show a change, while Group0.7 with higher Si-content showed a change, indicating that the Si component's elution can induce CP precipitation. The mechanism behind the CP nucleation in the precipitation on Group0.7 is suggested in Figure 4d. Group0.7 preferentially absorbed the hydrated  $\text{Na}^+$  and  $\text{K}^+$  ions inside the nanopores. The Si-components in Group0.7 were eluted as the silicate ions outside the nanopores, and the phosphate ions interacting with the  $\text{H}_2\text{O}$  component in SBF were adsorbed into the eluted sites [38]. The intensity of the OH group of Group0.7 increased through immersion in SBF due to the subsequent adsorption of the hydrated  $\text{Ca}^{2+}$  ions and the consequent promotion of CP nucleation. Therefore, the outside nanopore surfaces are considered the CP nucleation sites for Group0.7.

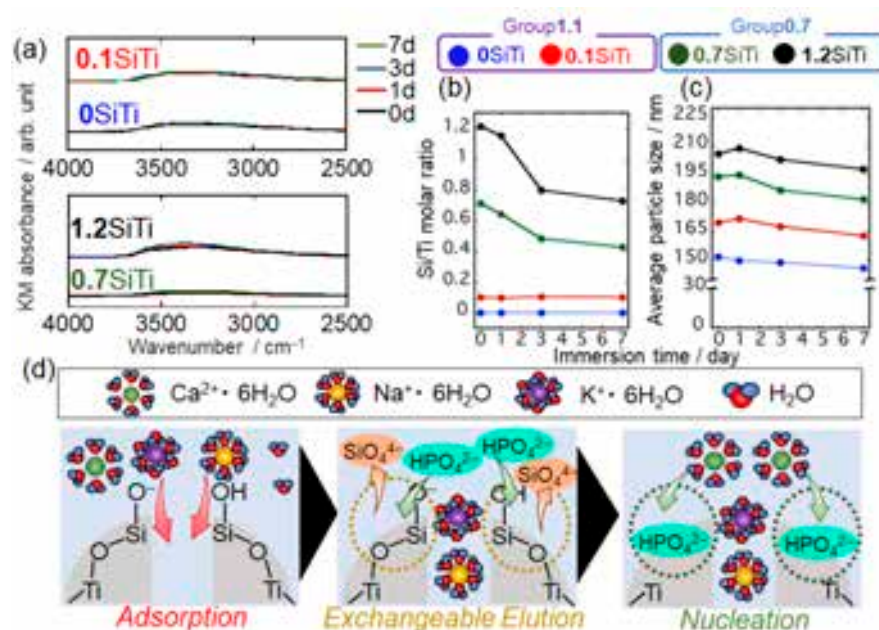


**Figure 4.** (a) FT-IR spectra, (b) Si/Ti molar ratio, and (c) average particle size changes of the SiTi nanoparticles with immersion time in SBF, and (d) illustrations of the possible interfacial reactions of Group0.7 with the ions in SBF. Xd represents the immersion time of X days (X = 0, 1, 3, and 7).

In Figure 5, the characteristics of phosphate ion adsorption for the CP nucleation sites on Group1.1 and Group0.7 are evaluated and discussed. According to the changes of the absorption band generated by phosphate ions after immersion (Figure 5a), Group1.1 and Group0.7 showed increases in the absorbance bands of the stretching vibrations due to Ti–P–O [43], P–O, and P–OH bonds [44] at 1100, 1039–997, and 866–842  $\text{cm}^{-1}$  following immersion. For Group0.7, the bands produced by Si–O–Si [45] and Si–OH [46] at 1039–997 and 866–842  $\text{cm}^{-1}$  were also included in the spectra, and the shapes were different from those of Group1.1. The amount changes in the adsorbed phosphorous components of Group1.1 and Group0.7 showed an increase in the amount after immersion (Figure 5b). In particular, Group1.1 reached the adsorption equilibrium after approximately 1 day of immersion, whereas Group0.7 showed a slower adsorption rate, suggesting that the CP precipitate emerged at a relatively earlier stage in Group1.1 compared to that of Group0.7. Figure 5c shows the possible illustrations of the nucleation sites of Group1.1 and Group0.7. In Group1.1, the hydrated  $\text{Ca}^{2+}$  ions in addition to the  $\text{Na}^+$  and  $\text{K}^+$  ions were preferentially diffused and absorbed inside the nanopores, which serve as sites for CP nucleation. In Group0.7, the hydrated  $\text{Na}^+$  and  $\text{K}^+$  ions were preferentially diffused and absorbed inside the nanopores, and the phosphate ions were replaced with the sites where the silicate ions were eluted, suggesting that the outside of the nanopores serve as CP nucleation sites.

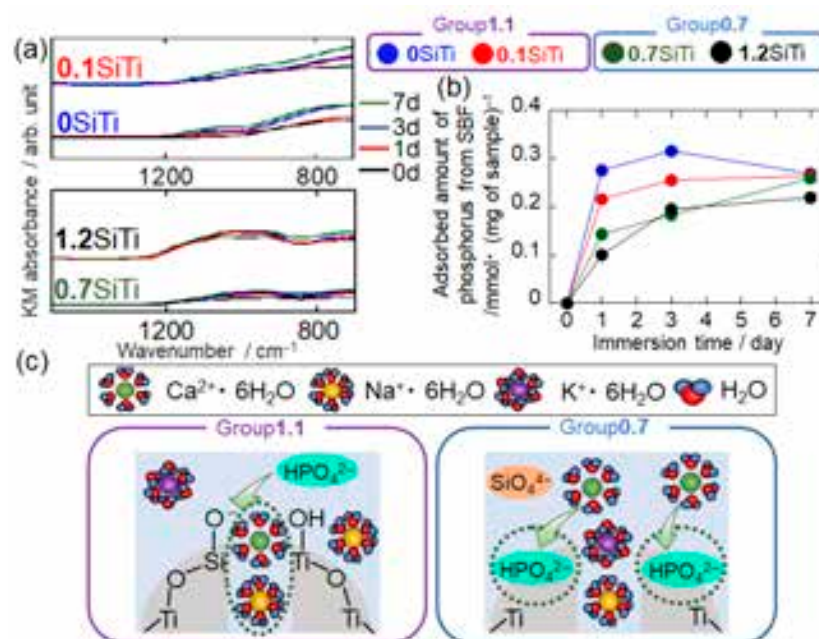


**Figure 5.** (a) FT-IR spectral changes of the SiTi nanoparticles with immersion time in SBF and (b) the adsorbed amount changes of phosphorus from SBF. (c) Illustrations of the possible calcium phosphate nucleation processes of Group1.1 and Group0.7.

According to the FE-SEM images and particle size distributions of the SiTi nanoparticles (Figure 6), even after immersion for 7 days, the particles still exhibited spherical shapes and mono-dispersed states, indicating a preserved particle size of approximately 150–200 nm. In particular, Group1.1 exhibited rough surfaces, whereas Group0.7 retained smooth surfaces. These results show that CP was roughly precipitated on Group1.1 but was smoothly precipitated on Group0.7, indicating that a smooth CP coating was achieved using Group0.7.

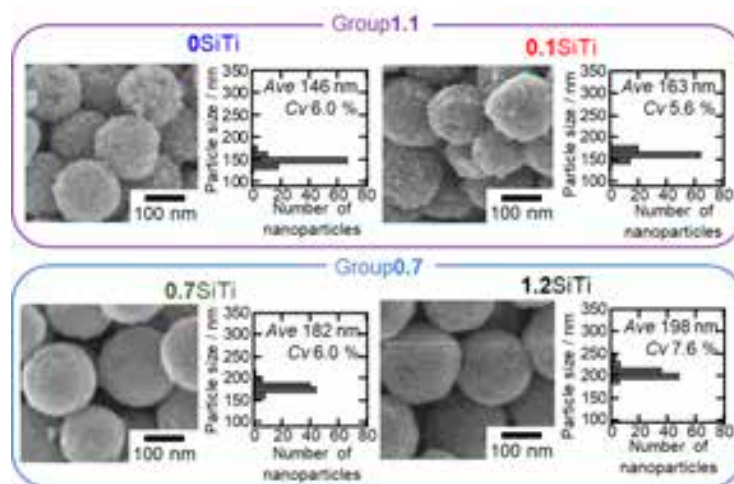


**Figure 6.** FE-SEM images and particle size distributions of the SiTi nanoparticles after immersion in SBF for 7 days.

The elemental mapping results and TEM images of 0.1SiTi and 1.2SiTi after their immersion are shown in Figure 7. The particle images (i.e., BF: STEM HAADF images) and shapes (i.e., locations) of the chemical elements were similar between Group1.1 and Group0.7 (Figure 7a,d), indicating that a homogeneous CP precipitation on the surfaces could be achieved by immersing the nanoparticles in SBF. The Ca signal for 0.1SiTi (Group1.1) was weaker than that for 1.2SiTi (Group0.7), which is possibly due to the different CP nucleation

mechanisms between Group1.1 and Group0.7 (as shown in Figure 5c). In Group1.1, the hydrated  $\text{Ca}^{2+}$  ions in addition to the  $\text{Na}^+$  and  $\text{K}^+$  ions were preferentially diffused and adsorbed inside the nanopores, which served as CP nucleation sites. The results suggested that the number of nucleation sites in Group1.1 is smaller than that in Group0.7, indicating a lower amount of the CP precipitation. The contrast of 0.1SiTi (Group1.1) was different from that of 1.2SiTi (Group0.7), indicating the presence of rough surfaces due to the CP precipitation of Group1.1 (Figure 7b,c,e,f).

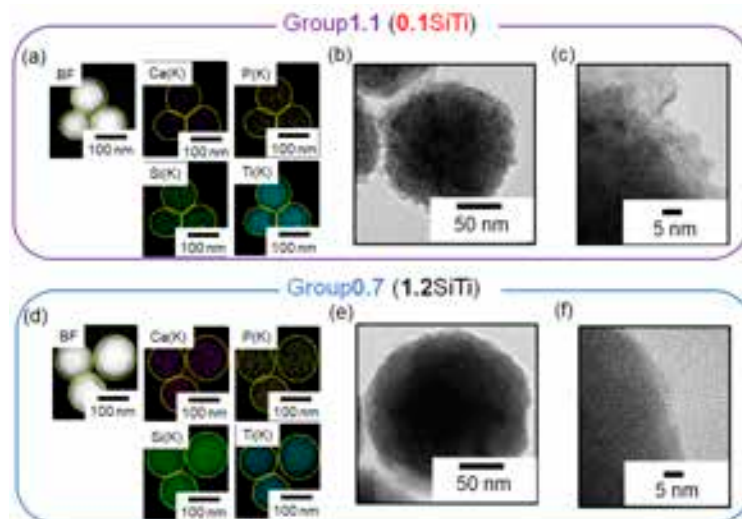


**Figure 7.** (a,d) STEM and EDS elemental mapping (Ca, P, Si, and Ti) images of the SiTi nanoparticles after immersion in SBF for 7 days. The detected energies for Ca(K), P(K), Si(K), and Ti(K) were 3.69, 2.01, 1.74, and 4.52 keV, respectively. The dotted yellow circles indicate areas where chemical elements are present. (b,c,e,f) TEM images of the SiTi nanoparticles after immersion in SBF for 7 days.

The  $\alpha$ s plots of the SiTi nanoparticles after immersion in SBF are shown in Figure S2. The changes in the specific surface area of the nanoparticles, which were determined based on the aforementioned results, are shown in Figure 8. Group1.1 and Group0.7 showed a decrease in the specific surface area following immersion, indicating the adsorption of the ions inside the nanopores. In particular, Group1.1 showed a faster rate of decrease in surface area compared with Group0.7 since nitrogen ( $\text{N}_2$ ) molecules could not enter the nanopores where CP had effectively precipitated inside. Based on Figure 8, it can be observed that Group1.1 presents a higher rate of reduction in external surface area determined from the  $\alpha$ s-plot, indicating that the effective precipitation of CP was due to pore blockage. As a result, Group1.1 exhibits a higher concentration of adsorbed phosphorous (i.e., phosphate ions). The lower reduction in the specific surface area in Group0.7 suggests lesser pore blockage through calcium ion adsorption. Since the slight reduction in the surface area is attributed to  $\text{Na}^+$  and  $\text{K}^+$  ions, it can be inferred that this reduction in surface area is less significant in the present paper. Therefore, the distribution of pores in Group 1.1 is considered a random array shape. Moreover, the peaks of Group1.1 with bimodal distributions decreased after immersion (Figure S3). The nanopores of 0SiTi at 1.2 nm decreased to 1.0 nm, while the nanopores of 0.1SiTi at 1.1 nm decreased to 0.9 nm. Figure S4 shows the  $\text{N}_2$  adsorption and desorption isotherms during immersion. According to a previous report [47], the isotherm type of Group1.1 was type IV before immersion, which changed to type I after immersion. The isotherm of Group0.7 remained type I after SBF immersion, indicating that the nanopore structures in Group1.1 were preserved upon their immersion. Regarding pore size distribution, Group1.1 shows bimodal shapes in Figure S3. It was suggested that pore blockage in the 1.1 nm sized particles of Group1.1 would occur, whereas the pores at 0.7 nm remained unblocked, thereby maintaining microporous structures. After immersion, the adsorption isotherm of Group1.1 in SBF was changed such that is similar in shape to that of Group0.7 (Figure S4).

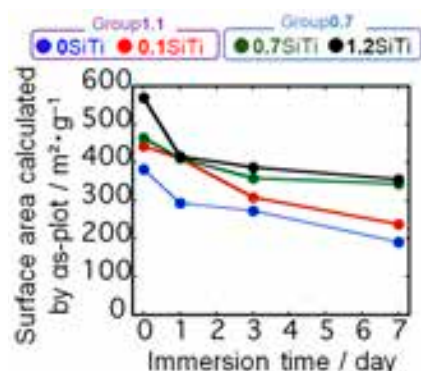
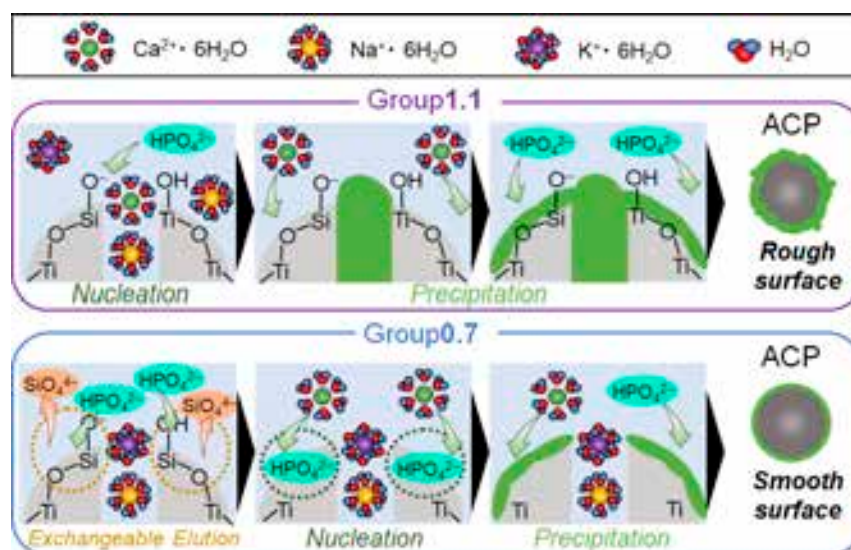


**Figure 8.** Specific surface area changes of the SiTi nanoparticles with immersion time in SBF. The reduction percentages in the surface areas of 0SiTi, 0.1SiTi, 0.7SiTi, and 1.2SiTi were 50, 46, 26, and 38%.

According to the XRD pattern results, after their immersion in SBF for 14 days, Group1.1 and Group0.7 remained amorphous (Figure S5). All of the nanoparticles showed an amorphous calcium phosphate (ACP) halo peak at  $2\theta = 30^\circ$ , indicating the precipitation of ACP on their surfaces.

### 2.3. Mechanism of ACP Precipitation on XSiTi Nanoparticles after Immersion

Based on the above results and discussion, the mechanisms of ACP precipitation in Group1.1 and Group0.7 are shown in Scheme 2. Regarding Group1.1, the  $\text{Ca}^{2+}$  ions were diffused and adsorbed inside the nanopores after immersion within one day. The  $\text{Ca}^{2+}$  ions inside the nanopores reacted with the phosphate ions in SBF, and the nanopores became the ACP nucleation sites, leading to rough ACP precipitation. For Group0.7, only the  $\text{Na}^+$  and  $\text{K}^+$  ions were diffused and adsorbed inside the nanopores after immersion for one day. The phosphate ions exchanged with the eluted silicate ions outside the nanopores and became the ACP nucleation sites. Therefore, it was determined that the ACP precipitation state was smooth without changing the surface morphology of Group0.7.



**Scheme 2.** Illustration of the precipitation processes of the SiTi nanoparticles in this study.

## 3. Materials and Methods

### 3.1. Chemicals

TEOS ( $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ : CAS No. 78-10-4) and TTIP ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ : CAS No. 546-68-9) were purchased from Tokyo Chemical Industry Co., Ltd. 2-Propanol (IPA, CAS No.

67-63-0), hydrochloric acid (HCl, 1 N, CAS No. 7647-01-0), ethanol (EtOH, 99.5 vol %, CAS No. 64-17-5), tris-hydroxymethylaminomethane (Tris,  $C_4H_{11}NO_3$ , CAS No. 77-86-1), sodium chloride (NaCl, CAS No. 7647-14-5), potassium chloride (KCl, CAS No. 7447-40-7), dipotassium hydrogenphosphate ( $K_2HPO_4$ , CAS No. 7758-11-4), magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ , CAS No. 7791-18-6), calcium chloride ( $CaCl_2$ , CAS No. 10043-52-4), and sodium sulfate ( $Na_2SO_4$ , CAS No. 7757-82-6) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. Sodium hydrogen carbonate ( $NaHCO_3$ , CAS No. 144-55-8) was purchased from Nacalai Tesque Co., Ltd. Octadecylamine (ODA,  $CH_3(CH_2)_{17}NH_2$ , CAS No. 124-30-1) was purchased from Sigma Aldrich Co., Ltd. All reagents are unpurified.

### 3.2. Synthesis

#### 3.2.1. Synthesis of SiTi Nanoparticles

In a previous report [15], SiTi nanoparticles were synthesized via microfluidic synthesis. Initially, three solutions (A–C) were prepared. Volumes of 1.63 mL of TTIP and 0, 0.187, 1.705, and 15.34 mL of TEOS were added to solution A to form Si/Ti molar ratios of 0, 0.15, 1.4, and 12, respectively, and 43.30, 43.11, 41.60, and 27.96 mL volumes of IPA were added according to the ratios. Solution B was prepared by mixing 44.60 mL of IPA and 0.277 mL of ultrapure water. Solution C was prepared by mixing 236.1 mL of IPA, 3.00 mL of ultrapure water, and 0.205 g of ODA. Solutions A and B were then mixed and reacted in a microreactor to generate nucleation via a sol–gel process, and the reaction solution was dropped into Solution C at a flow rate of 60 mL/min at 1000 rpm and left to grow the particles for 24 h under the room temperature. The liquid portion was removed via centrifugation, washed with ethanol and ultrapure water, and then dried at 60 °C for 24 h to obtain the SiTi nanoparticles with ODA (SiTi-ODA). Next, 10.2 mL of 1 N HCl and 150 mL of ethanol were added into 1 g of the dried SiTi-ODA, and the mixture was stirred at 700 rpm for 3 h at room temperature to remove ODA through solvent extraction. The solid phase was then removed via centrifugation and washed once with ethanol and once with ultrapure water. The particles were dried at 60 °C for 24 h to obtain nanoporous SiTi nanoparticles.

#### 3.2.2. Immersion of SiTi Nanoparticles into SBF

The 1.0 SBF ( $Na^+$ , 142 mM;  $K^+$ , 5.0 mM;  $Mg^{2+}$ , 1.5 mM;  $Ca^{2+}$ , 2.5 mM;  $Cl^-$ , 148.8 mM;  $HCO_3^-$ , 4.2 mM;  $HPO_4^{2-}$ , 1.0 mM;  $SO_4^{2-}$ , 0.5 mM; and Tris, 50 mM) was prepared according to the method provided in a previous report [48], and the pH value was adjusted to 7.4 with HCl. Then, 0.5 SBF and 1.5 SBF were prepared at 0.5 and 1.5 times the inorganic ion concentrations of 1.0 SBF. After the XSiTi nanoparticles were added to 0.5 SBF, the pH value was adjusted to 8.60 with Tris and kept at 37 °C for 1 day. The particles were then immersed in 1.5 SBF for 7 days. The solid phase was removed via centrifugation and dried at 37 °C for 24 h to obtain CP-coated SiTi nanoparticles.

### 3.3. Characterization

The morphologies were observed on a carbonblack-coated Cu grid using a field emission scanning electron microscope (FE-SEM: HITACHI Co., Ltd., SU-8230) at an accelerating voltage of 200 kV; the vertical size, side size, and particle size distributions of the SiTi nanoparticles' shapes were calculated by counting 150 particles, and their average (Ave.) and coefficient of variation (Cv.) values were also calculated. Size distributions of the SiTi nanoparticle images obtained through FE-SEM were calculated by randomly selecting 150 particles.

X-ray diffraction (XRD) patterns were obtained using a powder X-ray diffractometer (Rigaku Co., Ltd., Smart Lab) with  $CuK\alpha$  radiation ( $\lambda = 0.15418$  nm), a voltage of 40 kV, and a current of 200 mA.

Specific surface area and pore size distribution determined via  $N_2$  adsorption and desorption isotherms were measured at  $-196$  °C with a BELSORP-Mini II instrument

(Microtrac BEL Co., Ltd.) to estimate the total surface areas. Prior to measurement, 100 mg of each sample was degassed and pretreated at 80 °C under a vacuum. The following methods were used to analyze the nanopores. The specific surface area was evaluated using the  $\alpha$ s-plots [49], and the pore size distribution was determined using micropore analysis (MP). Furthermore,  $t$ -plots were used to calculate the specific surface area inside the pores and the adsorbed layers' thickness [50,51]; then, the pore volume was obtained. In this study, the Harkins–Jura equation representing the standard  $t$ -curve was used to investigate the standard isotherm. This curve is one of the most commonly used MP methods. Pore size was defined as  $d_p$ , which was plotted against  $dV_p/d\log d_p$  to show the pore size distribution.

Elemental composition was evaluated using an X-ray fluorescence analyzer (XRF: ZSX Primus II, Rigaku Co., Ltd.). XRF analysis was performed on sample powders in the state of pellets, which were pressurized and molded without dilution. The fundamental parameter method was conducted using software for semi-quantitative analysis (EZ Scan Program, Rigaku Co., Ltd.). Specifically, the amount of each element (Ca, Na, K, and P) adsorbed from SBF was detected and then evaluated in terms of  $\text{mmol} \cdot (\text{mg of sample})^{-1}$  on a semi-quantitative basis.

Infrared absorption spectra were measured using a Fourier transform infrared spectrometer (FT-IR: FT/IR-4600, Japan Spectroscopic Co., Ltd.) operating in the wavenumber range  $4000\text{--}500\text{ cm}^{-1}$  with a KBr background, 128 accumulation times, and a spectral resolution of  $4\text{ cm}^{-1}$ . FT-IR spectra were measured using KBr powder, and all weights were determined with 49 mg of KBr and 1 mg of sample. All the spectra were recorded after subtracting the background spectrum of KBr.

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100F transmission electron microscope. Scanning TEM high-angle annular dark-field (STEM–HAADF) images and elemental mapping energy-dispersive X-ray (EDX) spectroscopy images were recorded using a JEM-2100F and a JED-2300 instrument (EX-24200M1G2T, JEOL Ltd.) at an accelerating voltage of 200 kV. The sample suspension was dropped onto a Cu grid (a high-resolution carbon substrate on STEM 100CuP grids, Okenshoji Co., Ltd.), and the grids were dried under vacuum for a few days before each measurement. STEM and EDS elemental mapping (Ca, P, Si, and Ti) images of the SiTi nanoparticles were taken after the nanoparticles' immersion in SBF for 7 days. The detected energies for Ca(K), P(K), Si(K), and Ti(K) were 3.69, 2.01, 1.74, and 4.52 keV, respectively.

#### 4. Conclusions

We established a CP-coating method that homogeneously corresponds to the shapes of SiTi nanoparticles. CP precipitation was performed on mono-dispersed nanoporous SiTi nanoparticles with different Si/Ti molar ratios and pore sizes. The pore size distribution was found to significantly affect the CP coating in SBF immersion; the surfaces of the nanoparticles with bimodal pore sizes of 0.7 and 1.1–1.2 nm became rough after CP precipitation, while those with unimodal pore sizes of 0.7 nm remained smooth, indicating that these two pore sizes work as different nucleation sites that lead to different surface morphologies. These CP-coated SiTi nanoparticles could improve osteoconductivity while retaining the properties of SiTi nanoparticles, which we believe may be suitable for use in the DDS carriers in the future.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11060235/s1>, Scheme S1: XRD patterns of the SiTi nanoparticles.; Figure S2:  $\alpha$ s-plots of the SiTi nanoparticles with the immersion time  $X_d$  ( $X$  days,  $X=0, 1, 3, 7$ ) in SBF; Figure S3: The MP pore size distribution of SiTi nanoparticles with the immersion time in SBF; Figure S4:  $\text{N}_2$  adsorption (close marks) and desorption (open marks) isotherms of the SiTi nanoparticles with the immersion time in SBF; Figure S5: XRD patterns of the SiTi nanoparticles at the immersion time in SBF for 14 days.

**Author Contributions:** Conceptualization, R.K. and M.T.; methodology, R.K., K.F. and M.T.; software, R.K.; validation, K.F. and M.T.; formal analysis, I.Y. and K.S.; investigation, R.K.; resources, M.T.; data curation, Y.Z.; writing—original draft preparation, R.K. and Y.Z.; writing—review and editing, K.S., Y.Z., I.Y. and M.T.; supervision, K.S. and M.T.; project administration, K. S. and M.T. All authors have read and agreed to the published version of the manuscript.

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## Review

# The Story, Properties and Applications of Bioactive Glass “1d”: From Concept to Early Clinical Trials

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**Abstract:** Bioactive glasses in the CaO–MgO–Na<sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>–CaF<sub>2</sub> system are highly promising materials for bone and dental restorative applications. Furthermore, if thermally treated, they can crystallize into diopside–fluorapatite–wollastonite glass-ceramics (GCs), which exhibit appealing properties in terms of mechanical behaviour and overall bone-regenerative potential. In this review, we describe and critically discuss the genesis, development, properties and applications of bioactive glass “1d” and its relevant GC derivative products, which can be considered a good example of success cases in this class of SiO<sub>2</sub>/CaO-based biocompatible materials. Bioactive glass 1d can be produced by melt-quenching in the form of powder or monolithic pieces, and was also used to prepare injectable pastes and three-dimensional porous scaffolds. Over the past 15 years, it was investigated by the authors of this article in a number of in vitro, in vivo (with animals) and clinical studies, proving to be a great option for hard tissue engineering applications.

**Keywords:** bioactive glass; glass-ceramic; oxide system; diopside; fluorapatite; wollastonite; bone regeneration



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## 1. Introduction

The first bioactive glass composition, trade named as 45S5 Bioglass<sup>®</sup>, was designed by Larry Hench [1] in the early 1970s and addressed to bone replacement applications. After the invention of 45S5 glass, many other bioactive glasses have been reported for various medical applications like drug delivery [2], cancer treatment [3] or even soft tissue applications for organ repair [4]. The original 45S5 composition (45SiO<sub>2</sub>–24.5CaO–24.5Na<sub>2</sub>O–6P<sub>2</sub>O<sub>5</sub> in wt.%) is based on silica (SiO<sub>2</sub>) as the main glass-forming oxide and could create bonds with the living bone after in vivo implantations. A sequence of 11 reaction steps is involved in the bonding process of silicate bioactive glasses to living tissue [5], where the steps 1 to 5 are key for the formation of a hydroxyapatite-like layer on the surface of glasses.

Biomedical glasses are conventionally classified as “bioactive” based on these two mechanisms: (i) the formation of a calcium phosphate (hydroxyapatite-like) layer on the surface of the glass when it dissolves in a physiological environment (also in vitro in simulated body fluid (SBF)), and (ii) the release of biologically active ions during in vitro and in vivo testing. Hence, bioactive silicate glasses are both osteoconductive (mechanism (i)) and osteoinductive (mechanism (ii)). The interaction of bioactive glass surfaces with

body fluids begins with an exchange of ions that leads to an increment of the pH in the medium, resulting in the development of a  $\text{SiO}_2$ -rich layer and then the growth of a  $\text{CaO}/\text{P}_2\text{O}_5$ -rich layer on the glass surface. This layer is further enriched with carbonates and then crystallizes to form hydroxycarbonate apatite, which mimics the mineral phase of natural bone and ultimately helps to bond with the osseous tissue [6].

The hydroxyapatite-like layer also promotes the next biological reaction stages, including cell migration, proliferation and differentiation to form new bone with good mechanical bonds to the implant surface. The hydroxyapatite layer thickness plays a major role in the bone-bonding ability of the glass as well as on the interfacial shear strength. It was reported that an interface thickness of 20  $\mu\text{m}$  yields adequate shear strength and interfacial bonding [7].

Borate and borosilicate glasses are more reactive than silicate materials when in contact with body fluids or, in general, aqueous media; hence, they are less durable and can convert faster to hydroxyapatite compared to  $\text{SiO}_2$ -based glasses. In principle, the bioactivity mechanism is very similar except for the formation of a borate-rich gel layer, analogous to the silica gel layer in silicate systems. The apatite-formation rate can be controlled by changing the glass composition, thus varying the reaction time from hours to months [8].

Phosphate glasses have also been proposed for bone tissue engineering applications; their tendency to rapidly dissolve in aqueous media depending on the composition—and, especially, on the metal oxide content—has pushed their use towards advanced therapies mediated by controlled ions release [9].

When high-strength and/or load-bearing applications are major goals, the controlled crystallization of silicate glasses yielding bioactive glass-ceramic (GC) materials is an attractive option. For example, the commercial apatite/wollastonite (A-W)-containing Cerabone ( $\text{SiO}_2$ - $\text{CaO}$ - $\text{MgO}$ - $\text{P}_2\text{O}_5$ -F parent system) has been produced by controlled heat treatment, obtaining 38 wt.% apatite, 34 wt.% of wollastonite and 38 wt.% of residual glass phase, and used as a coating for titanium alloys, artificial vertebrae and bone fillers [10,11]. The bending strength of these A-W glass-ceramics (GCs) is typically higher than that of human cortical bone (160 MPa), but the fracture toughness is three times lower (6  $\text{MPa m}^{1/2}$ ) [12]. Interestingly, it was observed that hydroxyapatite can form on the surface of these GCs even if the silica gel on the surface is absent, as the apatite and wollastonite crystals act as sites for direct nucleation of calcium phosphate phases [13].

Other common examples of bioactive GCs include A-W Ceravital and diopside-containing products, such as apatite–diopside (AD), wollastonite–diopside (WD) and diopside–combeite (DC) GCs. Ceravital ( $\text{SiO}_2$ - $\text{CaO}$ - $\text{MgO}$ - $\text{Na}_2\text{O}$ - $\text{K}_2\text{O}$ - $\text{P}_2\text{O}_5$  parent system) [14] has an analogous bioactivity mechanism to Hench's 45S5 Bioglass<sup>®</sup>, along with good mechanical properties and better stability in the long term. After the implantation of Ceravital material, an initial degradation of the surface caused by ionic exchange was observed, followed by the formation of reaction layers that protect the implant from further chemical attacks.

The phase in common for the other GC types mentioned above is diopside, which is very appealing for biomedical applications due to its attractive mechanical performance. For example, diopside was combined with hydroxyapatite in order to increase the fracture resistance of the latter [15]. In this case, the fracture strength of the AD bioceramic was found to be 2–3 times higher compared to hydroxyapatite alone; moreover, the material was non-toxic to the body cells and promoted bone regeneration.

In wollastonite–diopside GCs, wollastonite and diopside phases form when the parent glass is thermally treated above 900 °C. Both wollastonite and diopside have good mechanical properties and the latter has a slower dissolution rate upon contact with body fluids. These bioactive GCs have been used in bulk, granular and porous forms for bone graft applications [16].

DC GCs have also been proposed for bone-contact applications; it is worth mentioning that combeite is a highly biocompatible phase, which is typically found in sintered 45S5 Bioglass<sup>®</sup> treated above 550 °C, too [17].

Therefore, all these studies witnessed that diopside was an attractive crystalline phase to have inside GC biomaterials. These results pushed scientists to design new glass-derived formulations that could originate GC products with superior biological and mechanical properties, of which the “1d” composition is a valuable example.

## 2. The Genesis of the 1d Composition

The glass composition 1d (Table 1) was designed so that, upon thermal devitrification, a final GC material containing diopside, fluorapatite and wollastonite could be obtained with high mechanical strength and excellent bioactive properties [18].

**Table 1.** Chemical composition of 1d glass and some of its derivatives (in wt.%) [18–20].

| Composition                                            | SiO <sub>2</sub> | CaO         | MgO         | P <sub>2</sub> O <sub>5</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | CaF <sub>2</sub> |
|--------------------------------------------------------|------------------|-------------|-------------|-------------------------------|-------------------|------------------|------------------|
| <i>Parent glass composition</i>                        |                  |             |             |                               |                   |                  |                  |
| <b>1d</b>                                              | <b>46.1</b>      | <b>28.7</b> | <b>8.8</b>  | <b>6.2</b>                    | <b>4.5</b>        | <b>0</b>         | <b>5.7</b>       |
| 1d-a                                                   | 41.8             | 32.85       | 8.85        | 6.24                          | 4.54              | 0                | 5.72             |
| 1d-b                                                   | 37.51            | 37.07       | 8.88        | 6.26                          | 4.55              | 0                | 5.73             |
| 1e                                                     | 43.5             | 30.4        | 8.8         | 7.2                           | 4.5               | 0                | 5.6              |
| 1e-a                                                   | 43.09            | 30.13       | 8.67        | 9.17                          | 4.44              | 0                | 4.47             |
| 1e-b                                                   | 42.71            | 29.85       | 8.59        | 11.1                          | 4.41              | 0                | 3.33             |
| 1e-c                                                   | 42.33            | 29.59       | 8.52        | 13.00                         | 4.37              | 0                | 2.19             |
| <i>K<sub>2</sub>O for Na<sub>2</sub>O substitution</i> |                  |             |             |                               |                   |                  |                  |
| <b>1d-k</b>                                            | <b>45.0</b>      | <b>28.0</b> | <b>8.60</b> | <b>6.1</b>                    | <b>0</b>          | <b>6.7</b>       | <b>5.6</b>       |
| 1e-k                                                   | 42.5             | 29.7        | 8.5         | 7.1                           | 0                 | 6.7              | 5.5              |
| <i>MgO for CaO partial substitution</i>                |                  |             |             |                               |                   |                  |                  |
| <b>1d-m</b>                                            | <b>46.6</b>      | <b>24.8</b> | <b>11.9</b> | <b>6.3</b>                    | <b>4.6</b>        | <b>0</b>         | <b>5.8</b>       |
| 1e-m                                                   | 44.00            | 26.7        | 11.8        | 7.3                           | 4.5               | 0                | 5.7              |

The 1d composition relies on the primary crystallization field of pseudowollastonite in the CaO–MgO–SiO<sub>2</sub> ternary system, in which P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O and CaF<sub>2</sub> were added. Following a melt-quenching route, 1d products can be obtained in an amorphous form (glass) but the development of the three crystalline phases mentioned above can be induced by applying a proper thermal treatment.

The 1d glass was the most promising member of a family of compositions, which were originally designed and studied by a multidisciplinary international research team and resulted in numerous publications since 2006; other sister formulations include 1e glass—having the same components as 1d in different amounts [18–20]—and 1b glass [21,22], also containing B<sub>2</sub>O<sub>3</sub> as an additional oxide.

Similarly, other glasses based on the 1d and 1e compositions have been created by replacing the components and changing the ratio of percentages by weight, such as the following:

- 1d-a and 1d-b: in which the CaO/SiO<sub>2</sub> ratio has been progressively increased [18] (Table 1);
- 1e-a, 1e-b, 1e-c: in which the P<sub>2</sub>O<sub>5</sub>/CaF<sub>2</sub> ratio has been progressively increased [18] (Table 1);
- 1d-k, 1e-k: where Na<sub>2</sub>O was replaced with K<sub>2</sub>O [19,20] (Table 1);
- 1d-m, 1e-m: where CaO was partially replaced with MgO [19,20] (Table 1).

## 3. Material Preparation and Basic Properties

The 1d glass is typically synthesized by following a melt-quenching route; several publications can be found in the literature where the basic preparative process has been applied with some modifications, as summarized in Table 2, from the reagent powders to frit production. Examples of 1d glass frit and glass powders after milling are given in Figure 1.

**Table 2.** Processes to obtain 1d glass powder from precursors powders.

| Article                      | Powders                                                                                                                                                                                                                                                  | Batch and Milling                                                         | Heat Treatment                                                                                                                                           | Frits and Glass Powders                                                                                                                                                                                                             |
|------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| I. Kansal et al. [18]        | SiO <sub>2</sub> (purity > 99.5%), CaCO <sub>3</sub> (>99.5%), MgCO <sub>3</sub> (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99%), CaF <sub>2</sub> (>99.9%), NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (>99%)                                        | Homogenous mixture of precursors of about 100 g obtained by ball milling. | Pre-heating at 900 °C for 1 h for calcination.<br>Melting in Pt crucible at 1450–1550 °C for 1 h.                                                        | Frits are obtained by quenching of melted glass in water.<br>Frits are dried and then milled in agate mill.<br>Powders are sieved to obtain a mean particle size of about 10 µm.                                                    |
| D. U. Tulyaganov et al. [22] | SiO <sub>2</sub> (purity>99.5%), CaCO <sub>3</sub> (>99.5%), 4MgCO <sub>3</sub> ·Mg(OH) <sub>2</sub> ·5H <sub>2</sub> O (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99%), CaF <sub>2</sub> (>99%), NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (>99%)   | Homogenous mixture of precursors of about 100 g obtained by ball milling. | Pre-heating at 1000 °C for 1 h for decarbonization.<br>Melting in Pt crucible at 1400 °C for 1 h.                                                        | Frits are obtained by quenching of melted glass in water.<br>Frits are dried and then milled in a porcelain mill.<br>Powders are sieved to obtain a mean particle size of 11–14 µm.                                                 |
| S. I. Schmitz et al. [23]    | SiO <sub>2</sub> (purity > 99.5%), CaCO <sub>3</sub> (>99.5%), 4MgCO <sub>3</sub> ·Mg(OH) <sub>2</sub> ·5H <sub>2</sub> O (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99%), CaF <sub>2</sub> (>99%), NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (>99%) | Homogenous mixture of precursors.                                         | Pre-heating at 1000 °C for 1 h for decarbonization.<br>Melting in Pt-crucible at 1400 °C for 1 h.                                                        | Frits are obtained by quenching of melted glass in deionized water.<br>Frits are dried and then milled in a planetary mill.<br>Powders are sieved to obtain a final particle size <32 µm.                                           |
| D. U. Tulyaganov et al. [24] | SiO <sub>2</sub> (purity > 99.5%), CaCO <sub>3</sub> (>99.5%), MgCO <sub>3</sub> (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99%), CaF <sub>2</sub> (>99%), NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (>99%)                                          | Homogenous mixture of precursors.                                         | Pre-heating at 1000 °C for 1 h for decarbonization. Melting in Pt crucible at 1400 °C for 1 h.                                                           | Frits are obtained by quenching of melted glass in water.<br>Frits are dried and then milled.<br>Powders are sieved to obtain a mean particle size of 10–15 µm.                                                                     |
| K. Dimitriadis et al. [20]   | SiO <sub>2</sub> (purity > 99.5%), CaCO <sub>3</sub> (>99.5%), Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99%), CaF <sub>2</sub> (>99%), (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> (>99%)     | Homogenous mixture of precursors of about 100 g.                          | Pre-heating at 900 °C for 1 h for decarbonization.<br>Melting in Pt crucible at 1400 °C for 1 h.                                                         | Frits are obtained by quenching of melted glass in water.<br>Frits are dried and then milled in a planetary mill.<br>Powders are sieved to obtain a final particle size <32 µm.                                                     |
| F. Baino et al. [25]         | SiO <sub>2</sub> (purity > 99.5%), CaCO <sub>3</sub> (>99.5%), MgCO <sub>3</sub> (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99%), CaF <sub>2</sub> (>99.9%), NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (>99%)                                        | Homogenous mixture of precursors of about 100 g by ball milling.          | Pre-heating at 850 °C for 1 h in an Al <sub>2</sub> O <sub>3</sub> crucible at heating rate of 2.5 °C/min.<br>Melting in Pt crucible at 1420 °C for 1 h. | Frits are obtained by quenching of melted glass in water.<br>Frits are dried and then milled in a planetary mill.<br>Powders are sieved to obtain a final particle size <56 µm.                                                     |
| K. Dimitriadis et al. [19]   | SiO <sub>2</sub> (purity > 99.8%), CaCO <sub>3</sub> (>99%), Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (>99%), Na <sub>2</sub> CO <sub>3</sub> (>99.6%), CaF <sub>2</sub> (>99%), (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> (>99%)     | Homogenous mixture of precursors of about 100 g by ball milling.          | Pre-heating at 900 °C for 1 h in an Al <sub>2</sub> O <sub>3</sub> crucible at heating rate of 1.5 °C/min.<br>Melting in Pt crucible at 1400 °C for 1 h. | Frits are obtained by rapid pouring of melted glass in water.<br>Frits are dried and then milled in a planetary ball-mill at 400 rpm for 45 min in a YSZ milling jar.<br>Powders are sieved to obtain a final particle size <32 µm. |

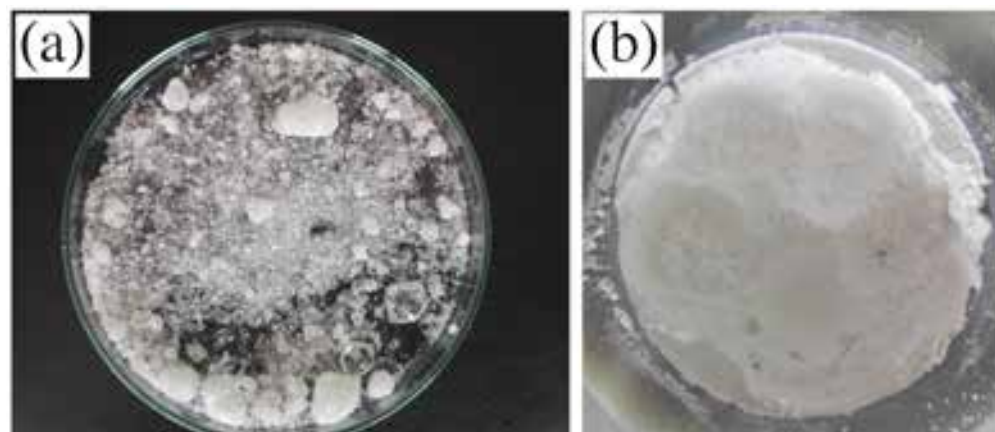


**Figure 1.** Example of (a) 1d glass frit, (b) glass powders after ball milling.

The density of 1d glass was reported to be  $2.57 \pm 0.13 \text{ g/cm}^3$ , the characteristic temperatures, i.e., glass transition ( $T_g$ ), onset of crystallization ( $T_c$ ) and peak of crystallization ( $T_p$ ), were assessed in various publications (also by using different experimental methods) and are collected in Table 3.

**Table 3.** Characteristic temperatures of 1d glass: glass transition ( $T_g$ ), onset of crystallization ( $T_c$ ) and peak of crystallization ( $T_p$ ).

| Article                      | $T_g$ (°C)   | $T_c$ (°C)  | $T_p$ (°C)   |
|------------------------------|--------------|-------------|--------------|
| K. Dimitriadis et al. [19]   | $649 \pm 9$  | $783 \pm 2$ | $815 \pm 13$ |
| F. Baino et al. [25]         | 640          | 785         | 830          |
| K. Dimitriadis et al. [20]   | $655 \pm 5$  | $783 \pm 2$ | $845 \pm 13$ |
| D. U. Tulyaganov et al. [24] | $607 \pm 7$  | -           | $815 \pm 13$ |
| D. U. Tulyaganov et al. [22] | $590 \pm 10$ | -           | -            |

#### 4. Crystalline Phases and Mechanical Properties

Powders of 1d glass have been used as-is, even in clinical trials (as discussed later [26]), or as starting materials to fabricate other products, such as 3D porous scaffolds for bone tissue engineering. To obtain these 1d-derived implants, a thermal treatment is necessary to consolidate and join the glass particles together, during which sinter-crystallization may take place. In other words, the formation of crystalline phases is promoted upon heating, leading to the material's transformation from purely amorphous to a GC state with the development of wollastonite, fluorapatite and diopside. Figure 2 shows the microstructure of 1d-derived GCs, in which the part formed by prisms corresponds to diopside, wollastonite crystals have a needle-like shape, and flakes refer to fluorapatite [19].

Table 4 illustrates the influence of heat-treatment temperatures on the mechanical properties of various 1d-derived GCs. It is known that crystallization yields an improvement in the mechanical properties of GCs compared to parent glass; accordingly, the highest increments of flexural strength, elastic modulus, hardness and fracture toughness, were achieved in the GC produced by heat treatment at  $850^\circ\text{C}$ , i.e., a temperature close to  $T_p$  (see Table 3). It was also determined that the brittleness indexes of the produced 1d- and 1e-derived GCs ranged between 3.6 and 3.7 and 3.3 and 3.5  $\mu\text{m}^{-0.5}$ , respectively. Qualitatively, machinability reflects the easiness of a material to be cut, and it can be quantified by the magnitude of brittleness [27]. The 1d- and 1e-derived GCs exhibited a brittleness index higher than 3  $\mu\text{m}^{-0.5}$  [28], thus being in the preferred range as the brittleness index for glasses and ceramics typically ranges from 3 to 9  $\mu\text{m}^{-0.5}$  [27]. This discovery holds significance for dental materials production, as these materials are often shaped using specialized cutting tools. Therefore, the aforementioned brittleness index values suggest a reduced risk of fractures or cracks occurring during these processes especially for the

1d-derived GC, since it shows a higher value on the brittleness index compared to the 1e-derived GC [28].

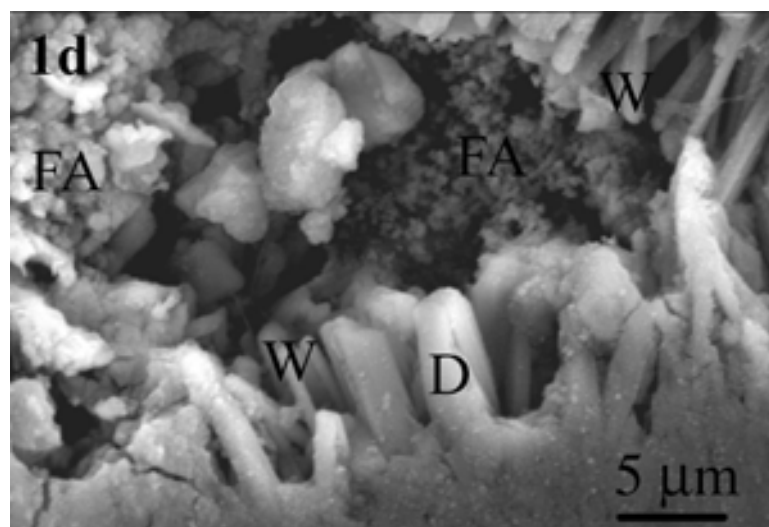


**Figure 2.** Typical microstructure of 1d-derived GCs produced by heat treatment at 850 °C for 1 h. Observation was performed after etching the polished surface with 2% HF solution (D: diopside; FA: fluorapatite; W: wollastonite).

**Table 4.** Mechanical properties of different 1d-derived GCs compared to other GCs containing diopside, wollastonite and fluorapatite as crystalline phases.

| Materials                                                        | Heat Treatment (°C)   | Flexural Strength ( $\sigma$ , MPa) | Elastic Modulus (E, GPa) | Vickers Microhardness (HV, GPa) | Fracture Toughness ( $K_{IC}$ , MPa · m <sup>0.5</sup> ) |
|------------------------------------------------------------------|-----------------------|-------------------------------------|--------------------------|---------------------------------|----------------------------------------------------------|
| 1d-derived GCs [28]                                              | 800                   | 119 ± 10                            | 24 ± 6                   | 6.0 ± 0.4                       | 1.6 ± 0.1                                                |
|                                                                  | 850                   | 171 ± 11                            | 27 ± 5                   | 6.1 ± 0.5                       | 1.7 ± 0.1                                                |
|                                                                  | 900                   | 141 ± 6                             | 22 ± 4                   | 5.2 ± 0.7                       | 1.4 ± 0.1                                                |
| GCs containing diopside and fluorapatite [29]                    | 850                   | 120–195                             | -                        | -                               | -                                                        |
| GCs containing wollastonite and quartz [30]                      | 900–1000              | 98 ± 6                              | -                        | 5.9–6.7                         | -                                                        |
| GCs containing wollastonite, hydroxyapatite and fluorite [31,32] | 700–1000              | -                                   | 89–100                   | -                               | 4.6–5.6                                                  |
| GCs containing wollastonite [33]                                 | 3100 (flame-spraying) | -                                   | 37–56                    | 2.6–5.4                         | -                                                        |
| GCs containing wollastonite and diopside [33]                    | 3100 (flame-spraying) | -                                   | 62–77                    | 2.2–6.5                         | -                                                        |

The main characteristics of these three crystalline phases contributing to mechanical properties of GCs (Table 4) are described in the following sections.

#### 4.1. Fluorapatite

Fluorapatite is a mineral that is part of the apatite family with the chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ . It is a double salt resulting from the bond between calcium phosphate and calcium fluoride. It is a highly biocompatible material and fits well with bone repair

applications. In fact, it is present in nature and is part, for example, of the mineralized phase of bones and teeth in mammals [34].

Moreover, having the fluoride ion instead of the hydroxyl ion, fluorapatite exhibits peculiar characteristics that differentiate it from hydroxyapatite; in fact, the former is much less soluble in an acidic environment, such as that of the human mouth, compared to hydroxyapatite. However, despite few differences in some physicochemical properties, the structure of both calcium phosphates is substantially the same. If in hydroxyapatite there are calcium phosphate tetrahedra arranged around hydroxyl ion columns, in fluorapatite there are tetrahedra which develop around fluoride columns (Figure 3).

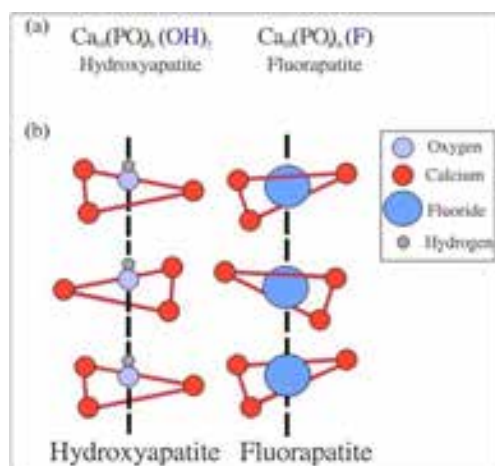


**Figure 3.** Similarities between fluorapatite and hydroxyapatite: (a) chemical formulas and (b) chemical structures. Reproduced from [35] with permission.

The crystalline structure of fluorapatite, characterised by flake-like crystals, can be visualized in the SEM image displayed in Figure 4. These morphological observations are also in agreement with theoretical expectations (see Figure 3).

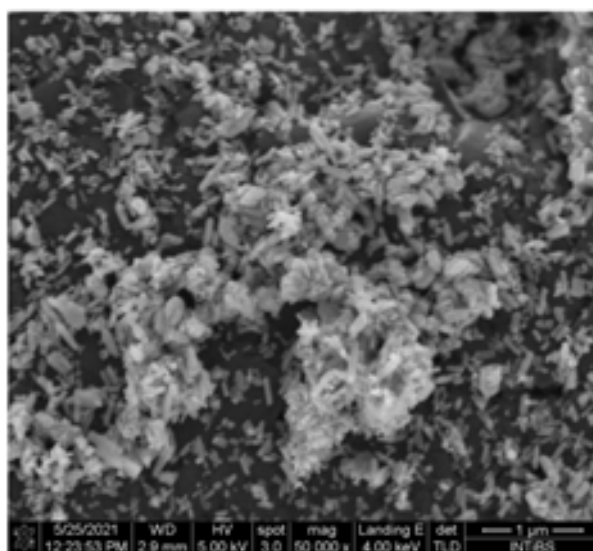


**Figure 4.** SEM image of fluorapatite. Reproduced from [36] under CC license.

#### 4.2. Wollastonite

Wollastonite is a mineral with interesting characteristics for biomedical applications, including biocompatibility, biodegradability, thermal stability/low thermal expansion, low thermal conductivity and high mechanical properties [37,38]. Given these appealing properties, in the early 1980s, Kokubo et al. [39] first produced a bioactive GC containing

both apatite and wollastonite. This new biomaterial belonged to a more complicated system than that invented by Hench one decade earlier (45S5 Bioglass®) [40]. This GC contained apatite (38%), wollastonite (24%) and residual amorphous phase (38%) [39] and has been since marketed under the commercial name of Cerabone®.

Wollastonite is a simple calcium silicate with the chemical formula  $\text{CaSiO}_3$ ; alternatively, it can be seen as a mixture of silica ( $\text{SiO}_2$ ) and lime ( $\text{CaO}$ ) having a theoretical percentage of 51.7% and 48.3%, respectively [37]. Due to its crystal structure (Figure 5), wollastonite belongs to the class of minerals known as pyroxenoids. It was reported that pyroxenoid chains are more kinked and have a great repeat distance [37].

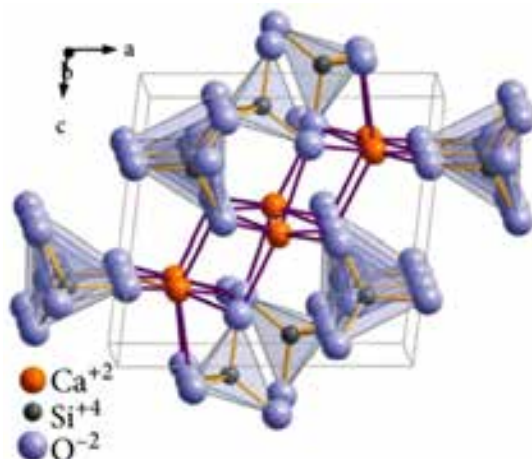


**Figure 5.** Crystalline structure of wollastonite. Reproduced from [37] under CC license.

Two polymorphs of wollastonite,  $\alpha$ -phase and  $\beta$ -phase, potentially exist in nature: the  $\beta$ -phase is the stable state at low temperatures, while the  $\alpha$ -phase is found above 1125 °C [41]. Therefore, wollastonite used in biomedical implants is typically the  $\beta$  type and has been proposed as filler in composite fabrication in orthopaedics as well as for dental restoration [37]. The needle-like shape of  $\beta$ - $\text{CaSiO}_3$  crystals is shown in Figure 6.

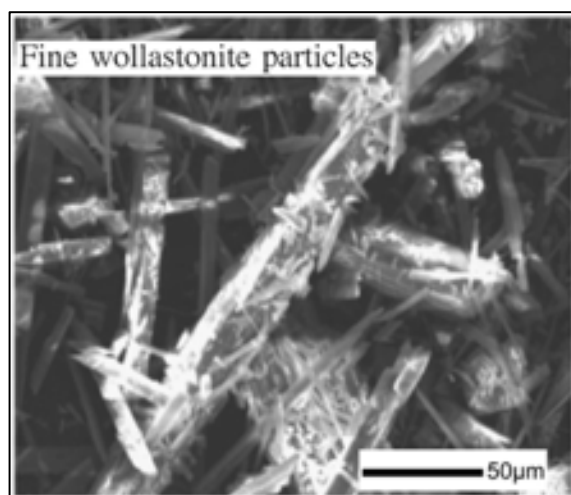


**Figure 6.** SEM image of wollastonite. Reproduced from [42] with permission.

#### 4.3. Diopside

Diopside ( $\text{CaMgSi}_2\text{O}_6$ ) is a prismatic monoclinic mineral, but it is not always possible to have this structure; on the contrary, it is easier to find granular and globular structures [43]. The crystalline structure of diopside is very similar to pyroxene, as displayed in Figure 7.

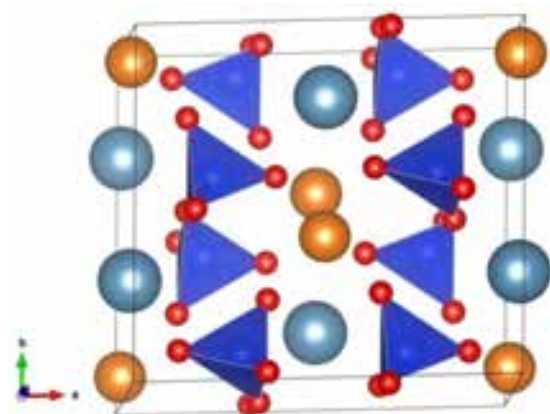


**Figure 7.** Crystalline structure of diopside found by Warren and Bragg: light blue spheres are calcium atoms, orange spheres are magnesium atoms, each tetrahedron consists of 1 silicon atom and 4 oxygen atoms (red spheres) [44].

Diopside was found to exhibit superior mechanical properties compared to other commonly used bioceramics. For example, it presents a bending strength of 300 MPa and a fracture toughness of  $3.5 \text{ MPa m}^{1/2}$ , which are higher with respect to wollastonite-containing ceramics with similar densities and exceed those of hydroxyapatite by 2–3 times [45].

Diopside was also found to be able to bond with living bone tissue. In this regard, Nonami and Tsutsumi [15] conducted a high-resolution electron microscopy study revealing the continuity between diopside implants and bone tissue in monkeys and rabbits, which was possible due to growth of new tissue at the interface. The same authors also reported that diopside had a much longer degradation time than hydroxyapatite, which was not optimal for bone regeneration; however, this can be useful in those cases where more chemical stability is required or for dental roots.

## 5. Comparison between 1d Formulation and 45S5 Bioglass®

As previously stated, bioactive glasses in the  $\text{CaO-MgO-SiO}_2$  ternary system as well as their relevant GC derivatives can indeed be designed for potential use in bone repair, but it is necessary to compare the major characteristics of these new materials with a “gold standard” reference, such as 45S5 Bioglass®. A series of studies were carried out for this specific purpose, as discussed in the next sections.

### 5.1. Chemical Composition

Table 5 highlights the quantitative differences in the composition of 1d and 45S5 glasses, in terms of amount of ingredients.

**Table 5.** Nominal compositions of 1d glass and 45S5 Bioglass®.

| Glasses               | $\text{SiO}_2$ | $\text{CaO}$ | $\text{MgO}$ | $\text{P}_2\text{O}_5$ | $\text{CaF}_2$ | $\text{Na}_2\text{O}$ |
|-----------------------|----------------|--------------|--------------|------------------------|----------------|-----------------------|
| 1d glass (wt.%)       | 46.1           | 28.7         | 8.8          | 6.2                    | 5.7            | 4.5                   |
| 45S5 Bioglass® (wt.%) | 45             | 24.5         | -            | 6                      | -              | 24.5                  |

The two bioactive glasses have a similar number of former oxides ( $\text{SiO}_2$  and  $\text{P}_2\text{O}_5$ ); the content of  $\text{CaO}$  is higher for 1d glass.

The main differences between the two bioactive glasses can be summarized in two points:

1. The content of  $\text{Na}_2\text{O}$  in 45S5 is more than five times greater when compared to 1d;
2. The 1d glass contains additional  $\text{MgO}$  and  $\text{CaF}_2$ , which are not present in the case of the 45S5 Bioglass®.

The presence of magnesium within the glass composition is useful because  $\text{Mg}^{2+}$  ions are naturally contained in bone tissue and play an active role in human bone metabolism.

Magnesium ions promote cell adhesion, proliferation and differentiation of osteoblasts [23]. Moreover, Dietrich et al. [46] noted that having an amount of MgO in the glass composition between 0.4 and 1.2 wt.% accelerates glass dissolution, consistent with its role as network modifier.

Instead, the partial substitution of Na<sub>2</sub>O with CaF<sub>2</sub> has the effect of decreasing the pH in the surrounding solution during in vitro tests, as well as the melting and glass transition temperatures of the glass; furthermore, a change in cell response was also reported [23]. In this regard, in vitro results with mesenchymal stem cells suggested an advantage of 1d glass concerning cell viability and proliferation. On the other hand, the ions released from 45S5 material appeared to have a stronger osteoinductive effect, whereas no clear superiority of either of the bioactive glasses was observed upon direct cell–glass contact [23]. Further tests are necessary to elucidate these issues, also considering that different experimental conditions could have played a role (e.g., the particle sizes used in that study: <32 µm for 1d and <56 µm for 45S5 glass).

### 5.2. Advanced Microstructural Analysis ( $Q^n$ Units)

Figure 8 shows the Fourier-transformed infra-red (FTIR) spectra of 1d and 45S5 glasses acquired in the wavenumber range of 300 to 1300 cm<sup>−1</sup>. In order to study the distribution of  $Q^n$  (i.e., the degree of polymerization of the structure inside the glass, where n indicates the number of bridging oxygens), Kansal et al. [18] focused on the range within 900–1100 cm<sup>−1</sup>, which corresponds to SiO<sub>4</sub> with a different number of bridging oxygens.

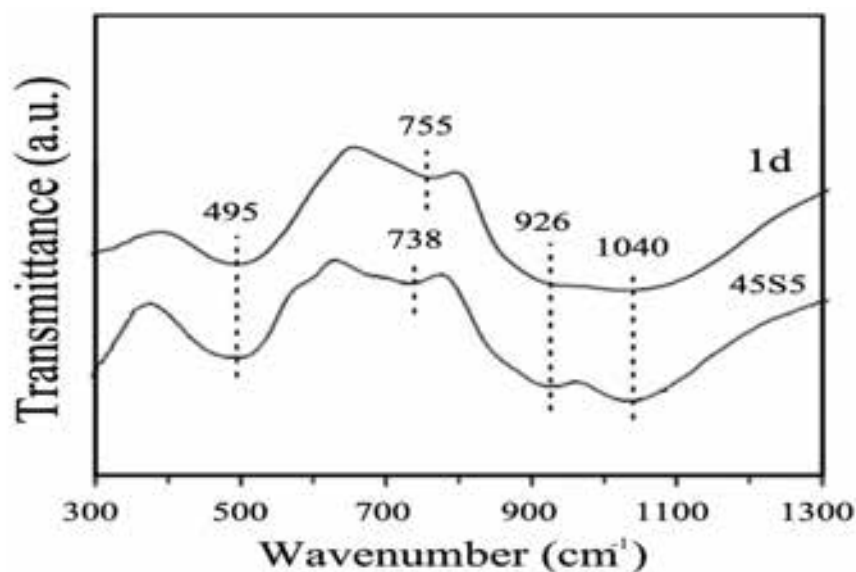


**Figure 8.** FTIR spectra of bioactive glasses 1d and 45S5. Reproduced from [18] with permission.

There were two interesting bands in this range, around 1040 cm<sup>−1</sup>, which indicate the presence of silicate  $Q^3$  units, and around 930 cm<sup>−1</sup>, which indicate the polymerization of silicate  $Q^2$  units along with some  $Q^1$  units. As reported by Tilocca [47], the highest bioactivity of phosphosilicate glasses can be expected if  $Q^n$  units are dominated by chains of  $Q^2$  metasilicates, which are sporadically cross-linked through  $Q^3$  units, whereas the chains are terminated by  $Q^1$  units. The structures of 1d and 45S5 glasses are similar since the predominant units are  $Q^2$  and  $Q^3$  for both materials; hence, a high apatite-forming ability is expected. The number of non-bridging oxygens per each tetrahedron was calculated for both 45S5 and 1d glasses, resulting to be 1.99 and 1.88, respectively. These values suggest that 1d glass has a more cross-linked structure than 45S5 Bioglass<sup>®</sup> because, although predominantly containing  $Q^2$  units, it has a larger fraction of  $Q^3$  units compared to the other glass [21].

### 5.3. pH In Vitro

Tulyaganov et al. [26] conducted immersion studies in SBF to evaluate the effect of 1d and 45S5 glasses on the pH of the solution. Over the first 300 h, there was a noticeable rise in pH in the case of 45S5 Bioglass<sup>®</sup> from 7.10 to about 7.75. This increase was due to the ion exchange mechanism already proposed by Hench [5,6,10,13] and explained above. On the contrary, a more moderate increment in pH was observed in the experiment with 1d glass, which was associated with the presence of fluoride ions that were exchanged with OH<sup>−</sup> ions from the SBF (from the dissociation of water into H<sup>+</sup> and OH<sup>−</sup>), eventually leading to a pH decrease. This was also consistent with other findings about fluoride-containing bioactive glasses [48].

Having a moderately alkaline pH around the implant (up to 7.8–8.0) carries some advantages, such as the accelerated formation of the apatite layer on the glass surface and the stimulation of the viability of osteoblasts; however, if the pH value is too high, damage to tissues and bone cells may occur as well as the inhibition of endothelial cell proliferation [26].

### 5.4. Mass Loss

Because of the different chemical compositions, there is also a different dissolution rate of 1d and 45S5 glasses in testing solutions. Tulyaganov et al. [26] reported that the mass loss was much higher in the case of Hench's glass (3.7 wt.%) when compared to the 1d composition (2 wt.%) after soaking for 120 h in Tris-HCl. For completeness, it was also reported that the pH value inside this solution increased more significantly after immersion of 45S5 when compared to 1d glass (9.7 versus 8.1, from a starting value of 7.2).

### 5.5. In Vitro Bioactivity

XRD patterns of the two different bioactive glass compositions, before and after immersion in SBF for different time frames, are reported in Figure 9.

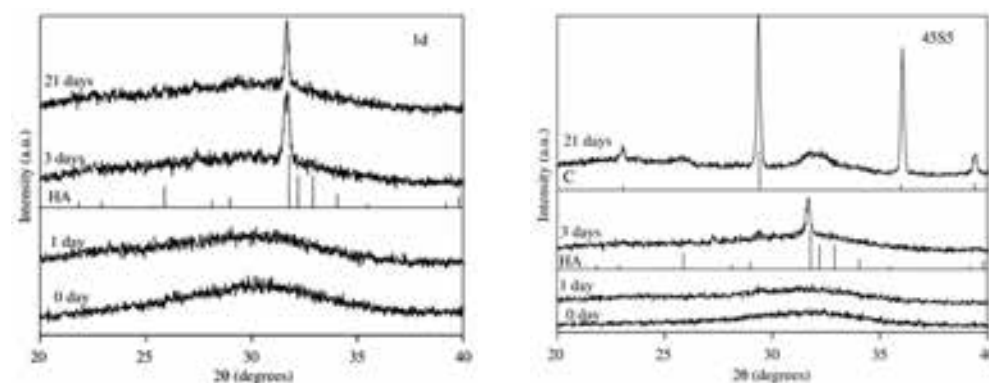


**Figure 9.** XRD patterns of 1d glass (**left**) and 45S5 Bioglass<sup>®</sup> (**right**). HA = hydroxyapatite; C = calcite. Reproduced from [26] with permission.

The common feature in both as-produced materials is the presence of the amorphous halo in the range of 28 to 35°, which is typical of silicate glasses. No detectable modifications can be seen after 1 day of immersion in SBF but, after 3 days, the characteristic peaks of hydroxyapatite—especially the main reflection (211) at ~32°—begin to develop. At this time point, the (211) diffraction peak of hydroxyapatite was sharper in the case of the 1d glass compared to 45S5 [26].

The results after 21 days show a different behaviour for the two bioactive glasses; in fact, while only hydroxyapatite was found to grow on the 1d surface, in the case of 45S5 glass, there were some peaks related to calcium carbonate (calcite), too. The coexistence of apatite and calcite was reported to occur in some in vitro studies, which may depend on multiple factors (e.g., glass particle size, volume of solution used, glass composition) not fully elucidated yet, as comprehensively discussed elsewhere [49].

### 5.6. Direct and Indirect Cell Culture

Schmitz et al. [23] performed an experiment to investigate the biological responses elicited by 45S5 and 1d glasses in two different cell-culture settings with a focus on cell proliferation, viability and osteogenic differentiation:

- (a) Indirect culture: the bioactive glasses were immersed in a solution for 24 h at body temperature and shaken to promote the release of ionic dissolution products. At the end of this first phase, the glasses were removed, and the solution was filtered and used as a culture medium for mesenchymal stem cells (MSCs). This setting is used to verify the effects of the ions released.
- (b) Direct culture: the bioactive glasses removed from the solution in the point (a) were placed in direct contact with MSCs.

The use of both settings was very useful to describe in detail both the action of the ions that were released by the bioactive glasses through the indirect culture setting and the reactions that take place once the physical contact of the materials with the cells occurs through the direct culture setting.

The major results from the two different settings can be summarized as follows:

- Indirect culture setting: 45S5 glass elicited a better osteogenic action compared to 1d glass. This behaviour was because, in the former case, there was a higher concentration of P and Si ions in the cell culture medium having osteostimulatory effects. In fact, phosphorus stimulates osteogenic differentiation and bone mineralization [50], and Si ions also activate gene families in bone cells, ultimately promoting osteogenic differentiation [51].
- Direct culture setting: there was a reversal in the trend compared to the indirect culture setting. In fact, the osteogenic action was no longer so different between the two bioactive glasses, although the expression of the specific protein OCN (marker of osteogenic differentiation) was greater in the 1d cultures. The concentration of magnesium, which was released by the 1d glass, in the first 24 h was one tenth of that detected after a week, and the concentration of Ca increased over time in the medium. This progressive, increasing release of beneficial ions is important as magnesium ions have the ability to increase cell viability [52], and calcium ions improve cell viability and proliferation [53]. These promising in vitro results on 1d glass were corroborated by in vivo tests.

The obtained results demonstrated an advantage of 1d glass in regard to cell viability and proliferation. Owing to its good osteogenic potential compared to the benchmark 45S5 glass and its higher biocompatibility, 1d glass was proposed to be an interesting alternative to 45S5 glass for bone tissue engineering applications [23].

### 5.7. Antibacterial Properties

The antibacterial properties of some experimental compositions based on 1d glass were tested against *Escherichia coli* (*E. coli*) [54]. Silver from 0.035 M, 0.077 M, 0.150 M and 0.220 M AgNO<sub>3</sub> aqueous solutions have been incorporated into the surface of 1d bioactive glass through the ion exchange approach assisted with ultrasonic treatment. Antibacterial tests showed that the silver-containing glasses inhibited the growth of *E. coli*, which exhibited a rapid decrease in its viability, reaching the limit of detection after a maximum of 2 h. Parent 1d glass induced a slight decrease in bacterial number after one hour compared with the bacterial inoculum. However, after two hours of incubation at 37 °C, the number of bacteria increased again, being comparable to the inoculum. It was observed that, according to the mid IR spectra, the structure of silver-modified glasses was similar to that of the parent 1d glass, which indicates that the treatment performed did not significantly alter the structure of the glass network and, thus, was not expected to interfere with its bioactivity mechanisms.

## 6. In Vivo Experiments and Clinical Trials

Tulyaganov et al. [26] studied the effects of bioactive glass 1d on both animals and human patients. In the first set of experiments, 1d glass particles were inserted directly into osseous defects produced in rabbit femora after being properly sterilized. Reactions in rabbits were monitored at different time points, i.e., 1 week, 2 weeks, 1 month, 2 months, 3 months, 4 months and 6 months (Figure 10).

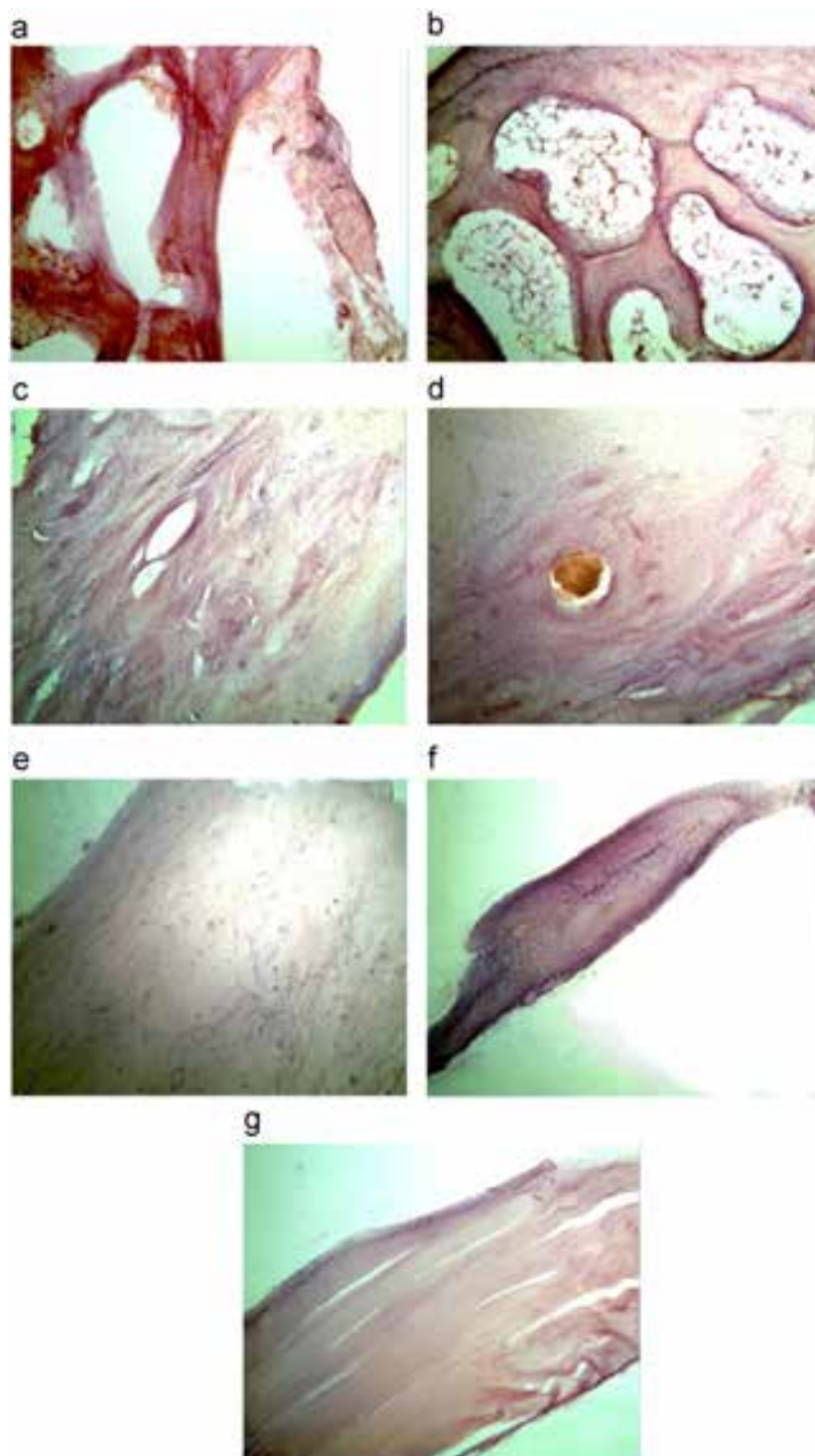


**Figure 10.** Histopathological sections of the bone in cortical area of bone (magnification 400×) after implantation for different periods: (a) 1 week; (b) 2 weeks; (c) 1 month; (d) 2 months; (e) 3 months; (f) 4 months; and (g) 6 months. Reproduced from [26] with permission.

Since the first week, the presence of low inflammatory infiltrate and an increase in the thickness of blood vessels was observed. From the first month onwards, the formation of new bone began, starting from the outside and spreading inwards. As the months passed, the bone trabeculae became thicker and thicker, and the implanted material was progressively embedded inside the newly formed bone. After 6 months, the surgically created cavities were completely filled with regenerated bone, which was mature and homogeneous. Overall, 1d glass powders were fully compatible with the surrounding tissues without eliciting any significant adverse reaction throughout the experiment duration.

The same 1d glass particulate was clinically tested over 8 months to treat jawbone defects in human patients mainly after a cystectomy operation. The test was conducted in 45 volunteers (21 males and 24 females) aged between 19 and 60. Patients were examined before and after surgery at 2 weeks, 2 months and 6 months. In this study, glass particles were inserted where there was a defect in the alveolar bone in order to avoid the progressive loss of bone over time (resorption) and assure the stability of the patient's teeth. These early clinical trials showed that the glass formed a cohesive mass with the patient's blood, thus demonstrating a homeostatic effect. Figure 11 shows that new, regenerated bone was formed after 2 months where there was the empty space of a jawbone defect before surgery. Similar results were found in all patients and, thus, these early clinical trials support the suitability of 1d glass for the conventional treatment of bone defects (highly biocompatible and bioactive filler). Figure 12 shows two other radiographs of the patient showing that after a cystectomy operation, the lesions were filled up with newly formed cancellous bone. However, in order to gain regulatory approval and consider this bioactive glass for routine surgery, it will be necessary to increase the number of patients during a further phase of clinical trials.

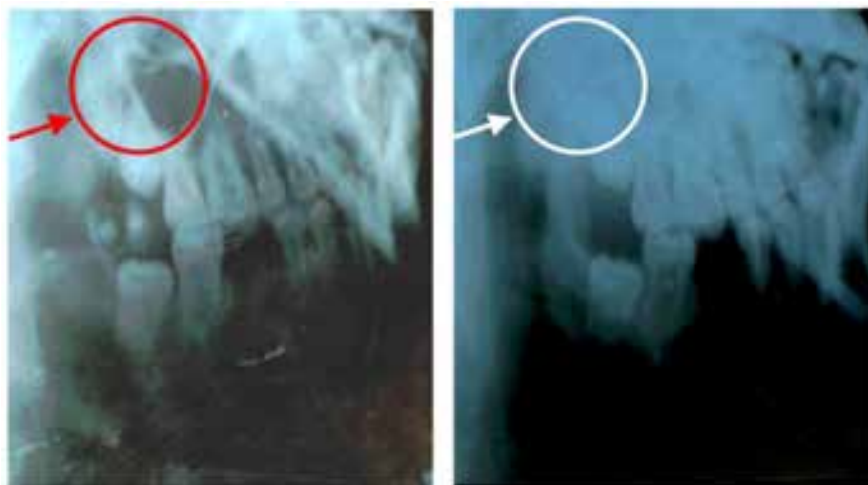


**Figure 11.** Radiographic images of jawbone defects before ((left) side) and after surgical intervention (2 months of follow-up) with implantation of 1d glass particulates ((right) side). Reproduced from [26] with permission.

In an attempt to avoid undesired losses of glass particulates during the grafting procedure and to further improve the handling properties, composites based on bioactive glass 1d and organic carriers, i.e., glycerol and polyethylene glycol (PEG), were synthesized [55]. Homogeneous mixtures were obtained that could be handled as mouldable pastes, demonstrating cohesive injectability. All pastes exhibited high apatite-forming rates after immersion in SBF, consistent with the *in vitro* bioactivity of 1d particles. The potential suitability of these materials for osteostimulatory bone healing was recently confirmed *in vivo* through implantation experiments in rabbit femoral defects [24].

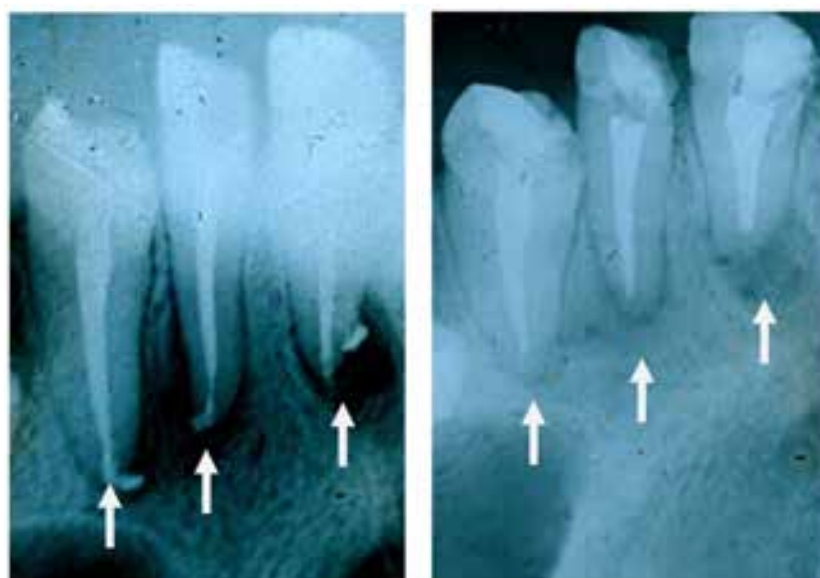


**Figure 12.** High-magnification radiographs of the patient before ((left) side) and after 2 months from operation ((right) side) showing that the lesions were filled up with trabeculae of new bone.

## 7. Towards the Future: 1d-Derived GC Dental Implants and Porous Scaffolds

### 7.1. GC Dental Implants

Dental implants rely on osteointegration through osteoinduction (whereby osteogenesis is induced) and osteoconduction, which involves the formation of hydroxyapatite [56–58]. The mechanical properties of natural tissues like the jawbone and dental hard tissue play a crucial role in the longevity of dental implants in the oral cavity [58,59]. After the placement of a prosthetic restoration, the dental implant receives the loads from the occlusal forces. When the elastic modulus and fracture toughness of the implant material align closely with those of the jawbone, the implant can effectively distribute the load to the adjacent bone, maintaining its density. However, if these properties differ significantly from those of the jawbone, then the dental implant is the only one that is loaded mechanically by the occlusal forces; as a result, the implant does not transfer the occlusal forces to the jawbone. This phenomenon is called stress shielding [60], whereby the osteocytes lose their main role (i.e., the preservation of the extracellular matrix), resulting in a reduction in the bone density of the jawbone, and eventually in the failure of the dental implant. The high elastic modulus of commonly-used dental implant materials like titanium alloys and zirconia (110 and 220 GPa, respectively) compared to the jawbone (7–30 GPa) and dentine (15–30 GPa) [31,61–64] is a common cause of implant failure and decreased bone density post-implantation. Bone grafts are utilized in various clinical scenarios when a patient's jawbone fails to meet the necessary criteria for optimal dental implant placement (specifically, due to insufficient bone quantity resulting from tooth loss) [31,62–64]. Initially, autogenous and allograft jawbone grafts were employed for their osteogenic and osteoinductive/osteoconductive properties, respectively. Subsequently, researchers redirected their focus towards synthetic materials (hydroxyapatite, tricalcium phosphates, bioactive glasses and GCs) to overcome the drawbacks associated with traditional grafts (such as patient discomfort, infection, complex surgical procedures, non-simultaneous absorption of the graft/new bone formation) and reduce costs [61–67].

According to Dimitriadis et al. [20,60], 1d-derived GCs display an excellent bioactive behaviour, yielding to spontaneous formation of hydroxyapatite on their surface after immersion in SBF at 37 °C. Besides having an adequate bioactivity, these GCs exhibited a well-sintered, dense microstructure embedding biocompatible crystalline phases that affected their mechanical properties (Table 4). These features, along with the attractive aesthetics (a white colour) [19,20], encourage further studies on such highly promising dental implant materials. More specifically, heat-treatment at 850 °C yielded GCs with

mechanical properties comparable to those of dentine (which is the biological tissue to be replaced by a dental implant) and the jawbone (which is the biological tissue put in direct contact with the material of a dental implant). Therefore, these appealing characteristics warrant further investigation regarding the suitability of 1d-based GCs in the production of dental implants.

The range of mechanical properties could be further modulated and finely tuned by combining the bioactive glass with biocompatible polymers, thus obtaining glass/polymer composites. These multiphasic biomaterials allow combining the peculiar features of bioactive glasses, such as bioactivity and osteostimulatory properties, with the added values of polymers, including flexibility [68,69]. These composites show great promise in overcoming some traditional limits of bioactive glasses such as low fracture toughness, which is a particularly critical issue in glass-derived porous scaffolds [70].

### 7.2. Glass-Derived Porous Scaffolds

Biomaterials addressed to bone repair, including bioactive glasses or GCs, are often produced in the form of porous templates with architectural characteristics mimicking the trabecular structure of cancellous bone [71]. Following this “biomimicry-guided” criterion is thought to improve the regenerative properties of the implants, which are thus dictated not only by the inherent characteristics of the material (e.g., apatite-forming ability, biocompatibility with bone cells) but also by the porous geometry, allowing biofluids to flow in and out, cells to colonize the scaffold walls and blood vessel to grow in. Macroporous 1d-derived scaffolds have been recently fabricated for the first time using the sponge replica method [25]. Upon high-temperature thermal treatment at 800 °C for 3 h, the 1d glass particles underwent sinter-crystallization, leading to the consolidation of a scaffold structure and the concurrent development of diopside, fluorapatite and wollastonite, as expected from the material design. The sintered 1d-derived GC scaffolds exhibited a 3D pore-strut architecture and total porosity (68 vol.%) comparable to those of cancellous bone, while the compressive strength (29.7 MPa) and elastic modulus (1.4 GPa) were even superior to those of trabecular bone tissue (50–500 MPa), suggesting suitability for application in load-bearing sites. The scaffolds were also highly bioactive *in vitro* as demonstrated by the formation of a calcium phosphate layer after immersion in SBF for just 48 h. In an attempt to improve the scaffold reproducibility and the scalability of the whole fabrication process, early trials using additive manufacturing technologies to process 1d glass powders are currently ongoing in the context of a research collaboration among the authors of this review article.

## 8. Conclusions

Since its invention, 45S5 Bioglass<sup>®</sup> has been implanted in millions of human patients and is currently being marketed for various dental and orthopaedic applications. This has led to a considerable effort towards understanding the fundamentals that govern the physical, chemical and biological properties of bioactive glasses based on—or inspired by—45S5 glass. On the other hand, some limitations of the 45S5 composition—e.g., the high pH environment created by a high sodium content and poor sinterability—pushed scientists to develop new bioactive glass formulations. In this regard, bioactive glasses belonging to the CaO-MgO-SiO<sub>2</sub> ternary system as well as their relevant GC derivatives that feature low sodium oxide contents can indeed be used in bone repair as an alternative to the “gold standard” reference 45S5 Bioglass<sup>®</sup>. This was demonstrated through promising *in vitro* results on 1d glass that were corroborated by *in vivo* tests. The experimental data collected over the past 15 years supports the suitability of 1d glass in a variety of clinical applications for the repair of periodontal defects, ridge preservation and sinus augmentation. The full potential of bioactive glasses and GCs based on the CaO-MgO-SiO<sub>2</sub> ternary system, with special reference to the 1d composition, is still to be fully exploited and indeed deserves further investigation in the near future.

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