TiN in Aqueous Environment: a Step Towards the Experimental Complexity

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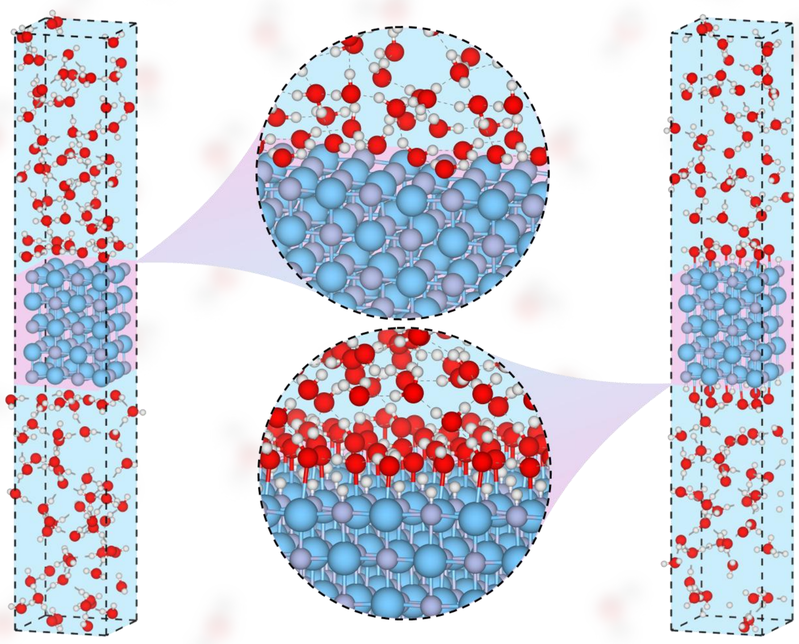
AIM OF THE STUDY

What happens on the **TiN/H_2O interface**?



Dissociation?

Molecular Adsorption?

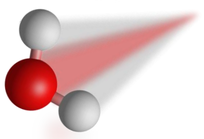
Hydrogen-bond?

Point of zero charge?

COMPUTATIONAL FRAMEWORK

Computational Details

- **GGA PBE** functional
- **PAW** pseudopotentials (core electrons) and valence electrons were expanded on a set of **plane waves**
- **Grimme's D3** parametrization
- Ab-Initio Molecular Dynamics (**AIMD**)



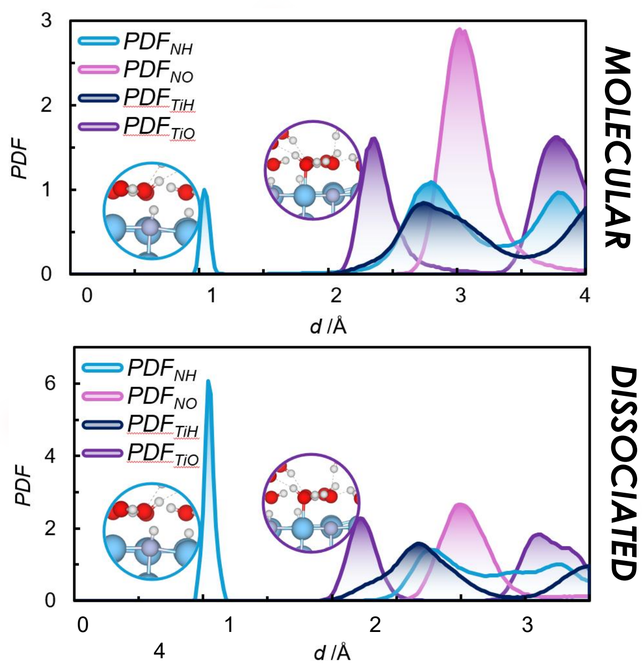
Modeling strategy

- **1fs** steps
- **2ps** of equilibration and **25ps** of AIMD
- **350K** Temperature with **Nose-Hover** thermostat

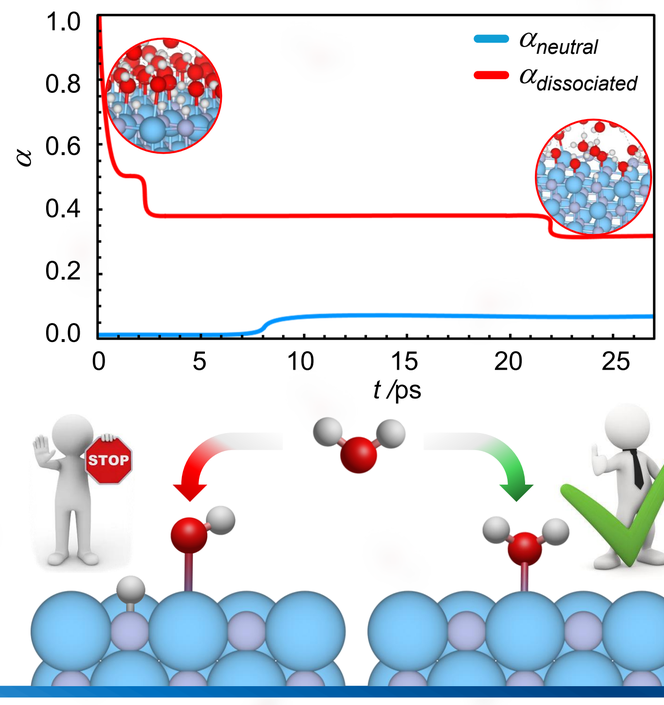
RESULTS

Interaction on the surface

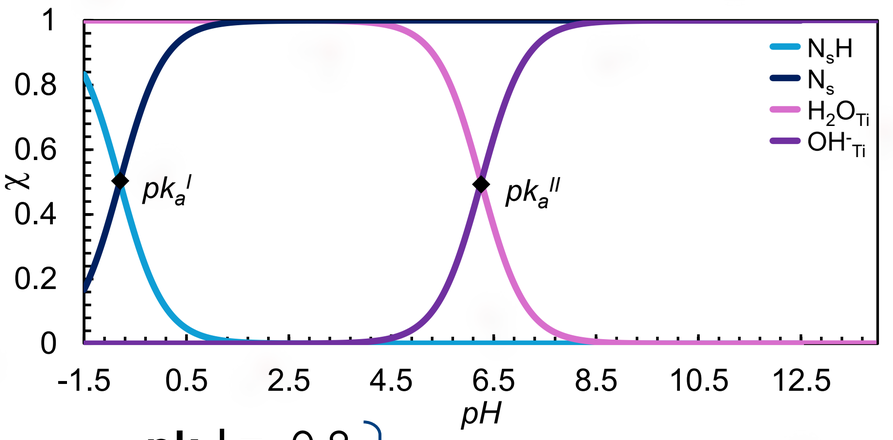
Total **absence** of **Hydrogen-bonds**



Molecular adsorption is preferred



pH-dependency



pk_a^I = -0.8
pk_a^{II} = 6.4

Acidic behavior

Calculated pHzc 2.73
Experimental pHzc
between **2** and **4**

IN CONCLUSION…

Titanium nitride (**TiN**) is increasingly used as a catalytic surface and support material, yet its **interfacial behavior** in aqueous environments remains poorly understood. In this study, we employed density functional theory-based **Ab-Initio Molecular Dynamics** to investigate the TiN(100)/H_2O interface under varying pH conditions[1]. Our simulations show that TiN does not form hydrogen bonds with water and preferentially stabilizes molecular adsorption over dissociative modes. These findings suggest limited surface reactivity toward water, with implications for catalytic selectivity and **stability**. Moreover, the calculated Point of Zero Charge is consistent with available experimental data[2,3], validating our approach and offering insights into the electrochemical behavior of TiN in solution.

REFERENCES

1. **Maleki, Farahnaz**, Giovanni Di Liberto, and Gianfranco Pacchioni. "pH-and facet-dependent surface chemistry of TiO2 in aqueous environment from first principles." *ACS Applied Materials & Interfaces* 15.8 (2023): 11216-11224.
2. **Shih, Chi-Jen**, Bor-Hwa Lung, and Min-Hsiung Hon. "Colloidal processing of titanium nitride with poly-(methacrylic acid) polyelectrolyte." *Materials chemistry and physics* 60.2 (1999): 150-157.
3. **Wang, Yan**, et al. "All solid-state pH electrode based on titanium nitride sensitive film." *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis* 18.15 (2006): 1493-1498.

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