

A Combined Photoelectrochemical and Theoretical Study to Understand Adsorption Properties of Organic Molecules on TiO₂ Surfaces

Tao Sun*,** Tianjian Zeng*, Yun Wang**, Huijun Zhao**, Yu Yang*

*School of Energy, Yunnan University, P. R. China, taosun8805@163.com

**Centre for Clean Environment and Energy, Griffith University, Australia, t.sun@griffith.edu.au

ABSTRACT

Titanium photocatalytical applications in clean energy generation and environmental remediation involve interactions between organic species and TiO₂ materials. Such interactions not only depend on the intrinsic properties of TiO₂, but also on their surface structures. The adsorption properties of organic species on the surface are vital for the photocatalytical performance of TiO₂. Hence, understanding adsorption properties of organic compounds on various crystalline TiO₂ surfaces is essential for the further technological development. Throughout this study, extensive investigations have been carried out on the synthesis of TiO₂ photoanodes immobilised on the conductive substrate and exposed by specific surfaces at the solid/liquid interface. The PEC measurement of organic adsorption properties and degradation kinetics on diverse TiO₂ surfaces can be conducted using these photoanodes. At the same time, the adsorption properties of organic molecules on the TiO₂ surface were studied at the atomic level. These results highlight several areas that can be further investigated. The combination of these experimental measurements and theoretical analyses can be used to investigate the adsorption properties of molecules with different functional groups on the various photocatalyst surfaces, which may benefit the development of photocatalysts with improved solar conversion efficiencies.

Keywords: TiO₂, adsorption properties, PEC analysis, DFT

1 INTRODUCTION

Titanium dioxide (TiO₂) has been widely used in industry as a photocatalyst due to its superior photoactivity, high photo- and chemical-stability, non-toxicity, abundance, and low cost. Many of its applications in clean energy generation and environmental remediation involve interactions between organic species and TiO₂ materials. Such interactions not only depend on the intrinsic properties of TiO₂, but also on its surfaces structure. Specifically, the capacity of the TiO₂ surface to adsorb organic species is vital for TiO₂ photocatalytical performance. Generally, the adsorption properties of organic molecules on the TiO₂ surface are fundamental to enhancing the efficiency of photocatalytic reactions.^[1] The adsorption properties are determined by many factors, such

as surface structure, adsorption sites, coverage, adsorption configuration, surface defects and functional groups of adsorbates.^[1-3] As a result, the mechanistic chemistry behind adsorption is complex and the understanding of the adsorption properties of the TiO₂ surface challenging. Many characterisation methods have been developed and applied to measure the adsorption properties. Thus, understanding the adsorption properties of organic compounds on various crystalline TiO₂ surfaces is essential for further technological development.

In this project, theoretical studies initially demonstrated that TiO₂ is the most photoactive all Ti-O based materials. A combined photoelectrochemical (PEC) and theoretical study was conducted to understand the adsorption properties of organic molecules on anatase (001) and rutile (111) TiO₂ surfaces. PEC measurements can provide quantitative thermodynamic and kinetic information on the adsorption properties of organic species on the TiO₂ surface under operational, practical conditions. The theoretical studies provide further information on interactions at the atomic level.

2 ANALYTICAL METHODS

To investigate the adsorption properties of organic molecules on TiO₂ surfaces at the atomic-level, density functional theory (DFT) was used in this project as DFT describes the energy of the ground state of an N-electron system as a direct function of density. All first-principles DFT computations are performed with the Vienna ab initio simulation package (VASP) with a projector-augmented wave (PAW) method.^[4] Electron-ion interactions are described using standard pseudopotentials. The kinetic energy cutoff energy of plane waves was set as 520.0 eV because this cutoff energy is 20% higher than the default values from the database, which is sufficient to obtain reliable results as per the VASP program manual. For the adsorption energy ΔE_{ad} calculation is based on the following equation:

$$\Delta E_{ad} = E_{mol/surface} - (E_{mol} + E_{surface}) \quad (1)$$

where E_{mol} is the energy of an isolated adsorbed molecule; $E_{surface}$ is the energy of clean surface; and $E_{mol/surface}$ is the total energy of the surface with adsorbed molecules. According to Eq (1), negative values of ΔE_{ad} indicate

exothermal processes. To understand the charge transfer between the adsorbed molecules and the surface, the charge values of atoms were analysed using the Bader method. Specially, for the TiO_2 surface adsorption, the van der Waals (vdW) interactions force plays an important role in a range of systems with weak interactions, such as the physisorption of organic molecules on TiO_2 surfaces, methods beyond traditional DFT are imperative. To solve this problem, a new Tkatchenko-Scheffler (TS) method based on the atoms-in-molecules (AIM) approach has been recently developed and produces accurate results for many molecular and solid systems.^[5]

The Langmuir adsorption model is used to understand the adsorption of organic compounds on TiO_2 surfaces when the concentration of reactants is low. The adsorption equilibrium constant (K) is strongly related to the adsorption affinity of the substrate to the TiO_2 surface, and is expected to remain relatively constant under various conditions.^[6] To quantify the adsorption equilibrium constant, the coverage of the adsorbates (θ) on the surface needs to be measured. the Langmuir adsorption isotherm can be rearranged to:

$$\frac{C}{Q} = \frac{1}{Q_{max}} C + \frac{1}{Q_{max} K} \quad (2)$$

there is a linear relationship between C/Q (concentration/adsorbed molecules) and concentration (C), as shown in Eq (2). The linear relationship implies that the adsorption on TiO_2 meets the requirements needed to fulfill the Langmuir adsorption model.

3 RESULTS AND DISCUSSION

This project presents a series of investigations into the adsorption properties of organics adsorbed on anatase (001) and rutile (111) surfaces. Firstly, we demonstrate that TiO_2 is the most photoactive among all Ti-O based materials, then, a combined photoelectrochemical and theoretical study has been performed to understand the adsorption properties of organic molecules on the anatase (001) and rutile (111) TiO_2 surfaces. PEC measurements offered the quantitative thermodynamic and kinetic information of adsorption properties of organic species on the TiO_2 surface under the operational conditions of their practical applications. And theoretical studies can further supply their interaction details at the atomic level.

3.1 Theoretical study of Ti-O based materials

Density functional theory computations systematically compared the physicochemical properties of Ti-O based materials including anatase TiO_2 , $\text{Na}_2\text{Ti}_3\text{O}_7$ and sodium $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Results found that their physicochemical

properties are different even though they are all comprised of TiO_6 octahedrals. The layered $\text{Na}_2\text{Ti}_3\text{O}_7$ had the highest chemical reactivity and largest bandgap energy ($E_g = 0.309$ eV).^[7] Comparatively, anatase TiO_2 was chemically inert with the highest photoactivity while the physicochemical properties of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ fell between those of anatase TiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$. Energetic analyses demonstrated that all Ti-O based materials are stable under neutral pH conditions. However, TiO_2 are more stable under acidic conditions while titanates prefer basic solutions. The theoretical results of the reaction energy predict that $\text{Na}_2\text{Ti}_6\text{O}_{13}$ can be generated by the interaction between $\text{Na}_2\text{Ti}_3\text{O}_7$ and weak acid, which indicates the potential of a novel way to produce sodium titanates with lower sodium content. According to theoretical comparisons, Ti-O based materials can be pre-screened for their different applications.

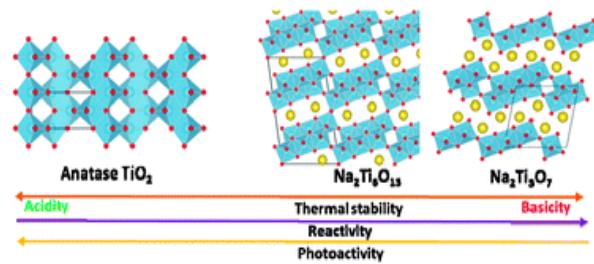


Figure 1: Structure of three Ti-O based material and the comparison of thermal stability, reactivity and photoactivity from DFT calculation. [7]

3.2 Investigation anatase (001) surface adsorption propertise

The adsorption properties of organic molecules on the anatase (001) surface have been investigated since this surface has been proposed to be highly reactive. To perform PEC measurements, an anatase photoanode with double-layer structure and largely exposed by {001} facets have been designed, synthesized and immobilized on FTO glass by combining sol-gel and hydrothermal synthesis methods. Then, the thermodynamics and kinetics of the adsorption process of oxalic acid and different functional compound aromatic on anatase photoanodes with large exposed {001} facets were measured via *in-situ* and *ex-situ* PEC methods. The adsorption properties of the {101} faceted anatase photoanode were also studied with the same approach as a comparison as Figure 2 shows.^[8] A double layered photoanode with a {101} facet dominated dense bottom layer and a {001} facet dominated top layer was purposely fabricated and successfully used for the *ex-situ* PEC determination of the adsorption constant and the instantaneous intrinsic rate constants of photocatalytic degradation of the adsorbed oxalic acid on (001) surfaces. The results indicate that the adsorption constant of oxalic acid on a facet dominated surface is 30% larger than that on a {001} facet dominated surface. The results also indicate that the average rate constant values of the slow and fast kinetic processes obtained from a photoanode with exposed

{001} facet dominated surface are 47% and 23% larger than those obtained from a photoanode with exposed {001} facet dominated surface. This confirms that anatase TiO₂ photocatalysts with {001} facets dominated surfaces possess higher photocatalytic activity than photocatalysts with {101} facets dominated surfaces. The method demonstrated in this work could be used to quantitatively investigate the photocatalytic degradation of other organic compounds. The comparative results confirm the high reactivity of the anatase (001) surface.

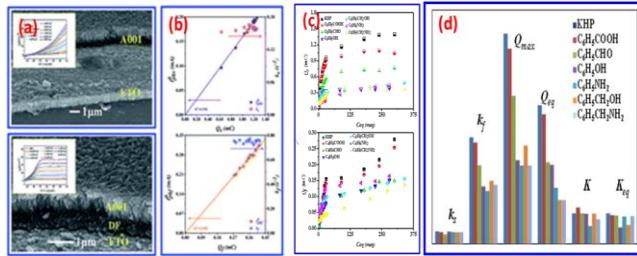


Figure 2: (a) SEM and CV curves of un-/immobilized A001 photoanodes, (b) PEC measurement for the kinetics of adsorbed oxalic acid degrades on {001} surface;[8] (c) Kinetics constants of aromatics with various functional compounds in two degradation processes, (d) Comparison of adsorption and degradation constants for different aromatics.

3.3 Theoretical analysis of oxalic acid adsorbed on the anatase (001) surface

The theoretical analysis of the adsorption properties of oxalic acid on the anatase TiO₂ (001) surface further revealed the adsorption configurations and oxidation mechanism of oxalic acid on the anatase (001) surface at the atomic level. Figure 3 shows that various possible adsorption configurations are considered by diversifying the connectivity of carboxylic groups with the surface in the first-principles theoretical study. It is found that the adsorption of oxalic acid on the anatase (001) surface prefer the dissociative state.[9] A novel double-bidentate configuration has been found due to the structural match between oxalic acid and the anatase (001) surface. More charge is transferred from the adsorbed oxalic acid to the surface with the double-bidentate configuration when comparing with other adsorption structures, which suggests a positive correlation relationship between the transferred charge amount and the interfacial bond numbers when oxalic acid adsorbs on the anatase TiO₂ (001) surface. The adsorption energies with dispersion corrections have demonstrated that the van der Waals interactions play an important role in the adsorption of oxalic acid, especially when adsorbates are close to the surface.

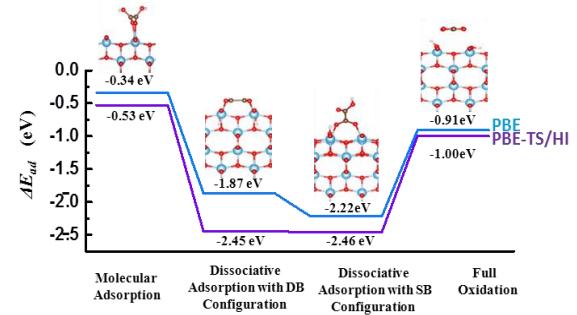


Figure 3: Theoretical study for adsorption properties of oxalic acid in different adsorb configuration and full oxidation on anatase TiO₂ (001) surface.[9]

3.4 Geometric structure of rutile (111) surfaces

The adsorption of organic molecules on the rutile (111) surface has been studied because of the specific visible light activity of rutile photoanodes capped by {111} facets at the solid/liquid interface. Figure 4 illustrates that the surface geometrical structure of the rutile (111), which is unknown before, has been theoretically modelled.[10] Our results demonstrate that the bulk-truncated and reconstructed TiO₂ (111) surfaces possess high surface energies. Complete stabilisation is facilitated on the rutile (111) surface by the hydroxylation process. The surface energy of the hydroxylated rutile (111) surface is even lower than that of the stable hydroxylated rutile (110) surface, coinciding with experimental observation that the {111} facets are exposed at the solid/liquid interface. According to rutile {111} surface geometric structures, the fully hydroxylated {111} facets are theoretically proposed and experimentally confirmed to be chemically inert to the further adsorption of water.

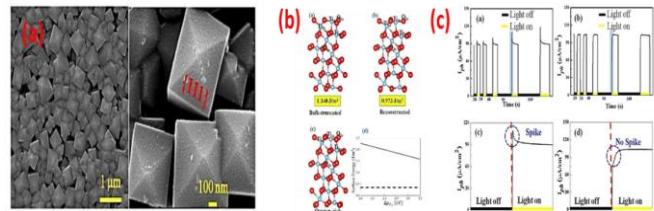


Figure 4: SEM of rutile TiO₂ photoanode with full exposed (111) surface, (b) atom structure and surface energies of bulk truncated and reconstructed (111) surface, (c) PEC measurement photocurrent-time profile of R111 and A101 photoanode for surface hydroxylation provident.[10]

3.5 Selective adsorption of aldehyde on Rutile {111} faceted TiO₂ film

The further *in-situ* PEC measurements on the adsorption properties of organic molecules with different functional groups demonstrate a highly selective adsorption behaviour of aldehydes on {111} faceted rutile photoanodes. The

adsorption strength of aldehyde on the rutile (111) surface has been investigated through the analysis of the thermodynamic and kinetic properties of photo-degradation processes using *ex-situ* PEC measurements. The comparative results with rutile {111} and anatase {101} faceted electrodes demonstrate that there is a strong selective adsorption of aldehyde on the rutile (111) surface. The high ability of the rutile (111) surface for selective adsorption of aldehyde can therefore be utilized as a new approach to separate and purify aldehyde in industry.

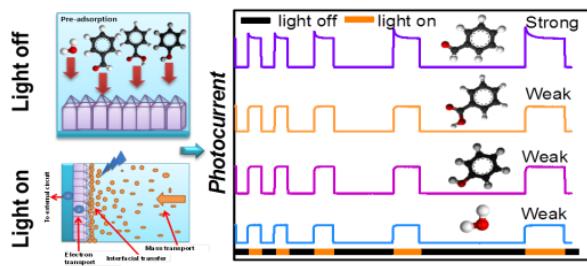


Figure 5: Scheme of three major steps of a typical PEC process and I_{ph} -time profile obtained from *in-situ* PEC measurement contains different aromatic with various functional compounds.[11]

4 CONCLUSION

Throughout this study, extensive investigations have been carried out on the synthesis of TiO_2 photoanodes immobilised on the conductive substrate and exposed by specific surfaces at the solid/liquid interface. The PEC measurement of organic adsorption properties and degradation kinetics on diverse TiO_2 surfaces can be conducted using these photoanodes. At the same time, the adsorption properties of organic molecules on the TiO_2 surface were studied at the atomic level. These results highlight several areas that can be further investigated.

It has demonstrated that PEC measurements and theoretical calculations could be a facile and effective path for the understanding of adsorption properties on the surface of photoanodes. The combination of these experimental measurements and theoretical analyses can be used to investigate the adsorption properties of molecules with different functional groups on the various photocatalyst surfaces, which may benefit the development of photocatalysts with improved solar conversion efficiencies.

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REFERENCES

- [1]. Diebold, U., *The Surface Science of Titanium Dioxide*. Surface Science Reports, 2003. **48**(5-8): p. 53-229.
- [2]. Gong, X.Q. and A. Selloni, *Reactivity of anatase TiO_2 nanoparticles: The role of the minority (001) surface*. Journal of Physical Chemistry B, 2005. **109**(42): p. 19560-19562.
- [3]. Thomas, A.G. and K.L. Syres, *Adsorption of organic molecules on rutile TiO_2 and anatase TiO_2 single crystal surfaces*. Chemical Society Reviews, 2012. **41**(11): p. 4207-17.
- [4]. Dong, X., et al., *Symmetry Breaking of Graphene Monolayers by Molecular Decoration*. Physical Review Letters, 2009. **102**(13): p. 135501.
- [5]. Bucko, T., et al., *Tkatchenko-Scheffler van der Waals correction method with and without self-consistent screening applied to solids*. Physical Review B, 2013. **87**(6): p. 064110.
- [6]. Xu, Y. and C.H. Langford, *Variation of Langmuir adsorption constant determined for TiO_2 -photocatalyzed degradation of acetophenone under different light intensity*. Journal of Photochemistry and Photobiology A: Chemistry, 2000. **133**(1-2): p. 67-71.
- [7]. Sun, T., et al., *Structure, reactivity, photoactivity and stability of Ti-O based materials: a theoretical comparison*. Physical Chemistry Chemical Physics, 2012. **14**(7): p. 2333-2338.
- [8]. Sun, T., et al., *Photoelectrochemical Determination of Intrinsic Kinetics of Photoelectrocatalysis Processes at {001} Faceted Anatase TiO_2 Photoanode*. RSC Advances, 2015.
- [9]. Sun, T., et al., *Adsorption and oxidation of oxalic acid on anatase TiO_2 (001) surface: A density functional theory study*. Journal of Colloid and Interface Science, 2015. **454**: p. 180-186.
- [10]. Sun, T., et al., *Geometric structure of rutile titanium dioxide (111) surfaces*. Physical Review B, 2014. **90**(4).
- [11]. Sun, T., et al., *Rutile {111} Faceted TiO_2 Film with High Ability for Selective Adsorption of Aldehyde*. Journal of Physical Chemistry C, 2015. **119**(31): p. 17680-17686.