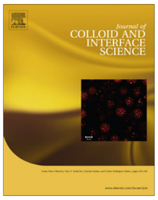
Journal of Colloid and Interface Science 454 (2015) 180–186

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

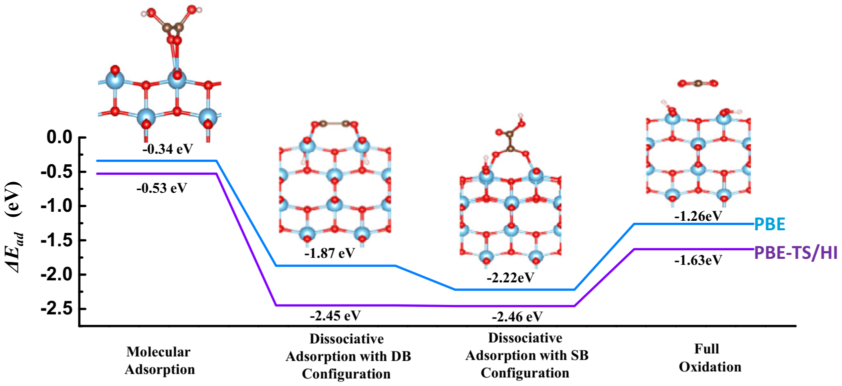


Adsorption and oxidation of oxalic acid on anatase TiO_2 (001) surface: A density functional theory study

Tao Sun [a], Yun Wang [a,*], Haimin Zhang [b], Porun Liu [a], Huijun Zhao [a,b]

[a] *Centre for Clean Environment and Energy, Griffith School of Environment, Griffith University, Gold Coast Campus, Queensland 4222, Australia*
[b] *Centre for Environmental and Energy Nanomaterials, Institute of Solid State Physics, Chinese Academy of Sciences, China*

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 April 2015
Accepted 11 May 2015
Available online 18 May 2015

Keywords:
Anatase (001) surface
Oxalic acid
Adsorption
Van der Waals interactions
Density functional theory

ABSTRACT

Anatase TiO_2 (001) surfaces have attracted great interest for photo-degradation of organic species recently due to their high reactivity. In this work, adsorption properties and oxidation mechanisms of oxalic acid on the anatase TiO_2 (001) surface have been theoretically investigated using the first-principles density functional theory. Various possible adsorption configurations are considered by diversifying the connectivity of carboxylic groups with the surface. It is found that the adsorption of oxalic acid on the anatase (001) surface prefer the dissociative states. A novel double-bidentate configuration has been found due to the structural match between oxalic acid and the (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. Thus, there is a positive correlation relationship between the transferred charge amount and the interfacial bond numbers when oxalic acid adsorbs on the anatase TiO_2 (001) surface. The adsorption energies with dispersion corrections have demonstrated that the van der Waals interactions play an important role in the adsorption, especially when adsorbates are close to the surface.

1. Introduction

Effective degradation of small organic species, such as oxalic acid (HOOCCOOH), is important for the treatment of wastewater and polluted air. Among all degradation techniques, photocatalysis

---

* Corresponding author.
E-mail address: yun.wang@griffith.edu.au (Y. Wang).

http://dx.doi.org/10.1016/j.jcis.2015.05.016
0021-9797/

by titanium dioxide (TiO_2) semiconductors is a feasible approach due to its low cost, non-toxicity and photo-stability [1–3]. The photocatalytic degradation of oxalic acid by TiO_2 has been widely investigated both theoretically and experimentally as a model reaction [4–8]. This is because oxalic acid is easy to be oxidized with the low potential of the redox couple $(COOH)_2(aq)/CO_2(g)$ as −0.49 V [9]. The mineralization of one oxalic acid molecule requires only two electrons and involves the least number of intermediates, which makes its overall photocatalytic degradation process simple. Additionally, oxalic acid is one kind of main water pollutants from some industrial treatment processes. Some of the previous studies have focused on the overall degradation efficiencies of oxalic acid by TiO_2 photocatalysts [7,9–11]. However, interactions between oxalic acid and TiO_2 surfaces should be more important because they determine several key steps during the photo-degradation processes, such as adsorption and heterogeneous electron transfer [1,2,12,13]. To this end, more studies have been carried out to address the adsorption properties and oxidation of oxalic acid on specific TiO_2 surfaces recently.

Jiang et al. once used photoelectrochemical (PEC) approaches investigated the photo-degradation kinetics of oxalic acid on anatase TiO_2 porous films mainly exposed by {101} facets [6]. And the adsorption properties of oxalic acid on clean anatase (100) and rutile (110) surfaces have been detected by Mendive et al. using combined infrared (IR) measurements and semi-empirical theoretical calculations [8,14,15]. These studies have demonstrated the adsorption properties of oxalic acid are strongly dependent on surface configurations. Thus, the employment of reactive TiO_2 surfaces, such as the anatase (001) surface, may benefit the degradation of small organic species.

The anatase (001) surface has been found to be highly reactive in photocatalytic decomposition of various harmful organic compounds. Based on the studies by Gong et al. about the adsorption properties of formic acid on the clean anatase (001) surface, they proposed that the clean anatase (001) surface places a key role in the reactivity of anatase TiO_2 nanoparticles degradation performance [16]. The strong adsorption of formaldehyde molecules on the bare anatase (001) surface has been demonstrated by using density functional theory (DFT) calculations by Liu et al. [17]. Recently, we have measured the adsorption properties and intrinsic degradation kinetics of oxalic acid on the photoanode mainly exposed by {001} facets using PEC techniques [18]. The high degradation efficiency of oxalic acid on anatase TiO_2 (001) surfaces have also be confirmed. However, up to our knowledge, there is no study on the adsorption properties and oxidation mechanisms of oxalic acid on the reactive anatase (001) surface at the atomic level. To better understand the interactions of oxalic acid with the anatase TiO_2 (001) surface, we presented first-principles DFT calculations to systematically analyze the adsorption geometries, energetics and electronic properties. A novel double-bidentate configuration is found, which is proposed to be the intermediate species for the full oxidation of oxalic acid on the anatase (001) surface based on our computational results. And the role of van der Waals forces in the adsorption was also addressed using the latest dispersion correction method.

2. Computational details

All first-principles DFT computations were performed with the Vienna *ab initio* simulation package (VASP, version 5.3.5) with a projector-augmented wave (PAW) method [19–21]. Electron-ion interactions were described using standard pseudopotentials [22,23], with valence configurations of $3p^63d^24s^2$ for Ti (Ti_sv_GW), $2s^22p^4$ for O (O_GW), $2s^22p^2$ for C (C_GW), and $1s^1$ for H (H_GW). The kinetic energy cut-off for the plane waves was set to 520.0 eV. For the electron–electron exchange and correlation interactions, the functional of Perdew, Burke and Ernzerhof (PBE) [24], a form of the general gradient approximation (GGA), was used to optimize structures and calculate the energies of systems. The anatase (001) surface was modeled by a slab with the (2×2) surface cell comprising a 12 atomic layers separated by a vacuum region of 15 Å. When the geometries were optimized, the atoms in the bottom 6 atomic layers of surfaces were fixed at the bulk position; and all other surface atoms and the adsorbates were allowed to relax until the Hellmann–Feynman forces were smaller than 0.001 eV/Å. The convergence criterion for the electronic self-consistent loop was set to 10^{-5} eV. We performed Brillouin-zone integrations using a $(4 \times 4 \times 1)$ Monkhorst-Pack *k*-point grid for the anatase TiO_2 (001)-(2×2) surface. Our selected cut-off kinetic energy and density of *k*-point meshes were similar as previous theoretical studies [25–27]. The adsorption energy ΔE_{ad} was calculated as following [28],

$$\Delta E_{ad} = E_{mol/surf} - (E_{mol} + E_{surf})$$

where E_{mol} is the energy of an isolated oxalic acid molecule; E_{surf} is the energy of clean (001) surface slab; and $E_{mol/surf}$ is the total energy of the surface with adsorbed oxalic acid molecules. A $15 \times 15 \times 15$ Å^3 unit cell was used for the calculations on the isolated oxalic acid molecule using a Γ-only *k*-point grid. According to the equation to calculate the adsorption energy, a negative value of ΔE_{ad} indicates an exothermal process. To investigate the charge transfer between the oxalic acid and the surface, the charge values of atoms were calculated using the Bader method [29,30].

3. Results and discussion

3.1. Clean surface and isolated oxalic acid

The atomic structures of the bare anatase TiO_2 (001) (2×2) surface and the isolated oxalic acid molecule are shown in Fig. 1. It can be found that the anatase TiO_2 (001) surface is flat. In a (2×2) surface cell unit, there are four $[TiO_6]$ octahedra, each of which has one of the oxygen vertices truncated, leaving behind "defected" octahedra with fivefold coordination (Ti_{5c}). Four twofold-coordinated O atoms (O_{2c}) are each bonded to two Ti_{5c} atoms in the surface, giving one dangling Ti—O bonds forming a Ti_{5c}—O_{2c}—Ti_{5c} angle of 144.9°. And the rest four surface O atoms are each bonded to three Ti atoms (O_{3c}), which is same as those in the bulk. The calculated parameters of the anatase TiO_2 (001)

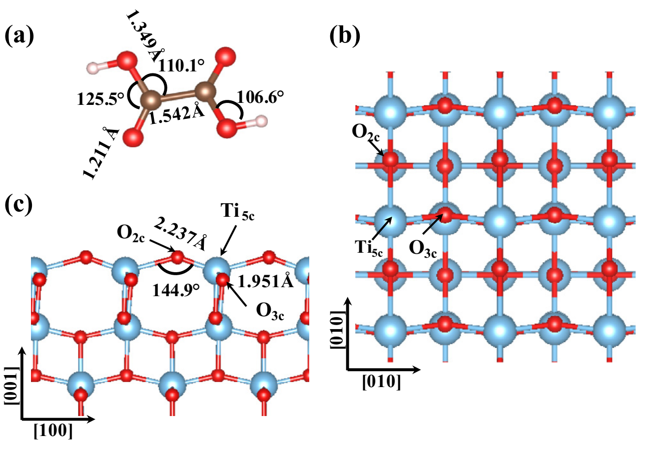


Fig. 1. Optimized structures of (a) oxalic acid, (b) top view of clean anatase TiO_2 (001) surface, and (c) side view of clean anatase TiO_2 (001) surface. Key: Brown-C, blue-Ti, red-O, and pink-H. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)