



# The property of surface heterojunction performed by crystal facets for photogenerated charge separation



Zhengde Wei<sup>a</sup>, Yi Zhao<sup>a,\*</sup>, Fengtao Fan<sup>b</sup>, Can Li<sup>b</sup>

<sup>a</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

<sup>b</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, and the Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Zhongshan Road 457, Dalian 116023, China

## ARTICLE INFO

### Keywords:

Charge separation  
Surface heterojunction

## ABSTRACT

Crystal facet engineering of semiconductors has been demonstrated to be an important strategy to promote the separation of photogenerated electron-hole pair for photocatalytic activity, but the mechanism behind is still in debate. Here, density functional theory calculations are used to reveal the detailed property of surface heterojunction, one of popular concepts for charge separation, with three typical model systems of TiO<sub>2</sub>, Cu<sub>2</sub>WS<sub>4</sub> and SrTiO<sub>3</sub>. The results demonstrate that the conduction band minima and valence band maxima among different facets indeed result in surface heterojunction, thermally-kinetically favorable for spatial charge separation. However, these surface heterojunctions, caused by the surface dangling bonds and the interaction between surface atoms, are only in few surface layers (about 1 nm) and may not be powerful enough to initiate the preferential flow of charges, and the other possible mechanism for charge separation should be additionally considered.

## 1. Introduction

Since the concept of photocatalytic water splitting reaction was first proposed by Fujishima [1], a great effort has been made to synthesize photocatalytic semiconductor materials and design photocatalytic reactions due to their ability of directly harvesting solar energy to address energy and environmental issues [2,3]. In a photocatalysis process, the photocatalyst initially absorbs photon from sunlight and generates electron-hole pairs, the electron-hole pairs are then separated and transferred to the photocatalyst-solution interface, and the separated electrons and holes finally activate the hydrogen evolution reaction and oxygen evolution reaction, respectively. Due to the severe recombination of photogenerated electrons and holes, however, only few electrons and holes can move to the surface and participate in surface catalytic reactions [4], resulting in poor performances and hindering industrial applications [5]. In addition of the catalytic property of surface atomic activity, how to separate electron-hole pairs efficiently is thus crucial for increasing the activity of semiconductor-based photocatalysts.

One of important strategies for the separation of electron-hole pairs is the crystal facet engineering, i.e., the photo-excited electrons and holes can be collected on different facets of a semiconductor crystal [6–13]. Since the electrons and holes are spatially separated, they may

stay on facets for enough time for reduction and oxidation reactions, and perform a better photocatalytic activity. Although the mechanism of facet-induced charge separation in single crystals is still in debate, several concepts have been proposed to explain this phenomenon [14–28]. For instance, due to the anisotropy of intrinsic electron and hole mobilities along different facet directions, the photoillumination on a semiconductor could result in the preferred migration of holes and electrons to specific crystal facets [23–26]. Especially in the semiconductors with a ferroelectric property that can polarize related atoms and orbitals, the internal electric field can separate the photo-induced electron-hole pair efficiently [19]. Alternatively, motivated by the different energy levels of valence band maximum (VBM) and conduction band minimum (CBM) for different facets, the surface heterojunction is suggested to drive charge separation [14]. A theoretical calculation [14] has demonstrated that the CBM of {0 0 1} facet of TiO<sub>2</sub> (anatase) is slightly higher than that of {1 0 1} facet, which leads to a higher reduction activity of {1 0 1} facet. With a cluster model of TiO<sub>2</sub>, the calculations [29,30] show that the HOMO and LUMO are spatially separated on different facets, and this separation is beneficial to charge separation at the early stage of photoexcitation process, and promote the photoreduction reaction on {1 0 1} facets, in turn expedite the consumption of photoelectrons and thus further reduce the chance of

\* Corresponding author.

E-mail addresses: [yizhao@xmu.edu.cn](mailto:yizhao@xmu.edu.cn) (Y. Zhao), [canli@dicp.ac.cn](mailto:canli@dicp.ac.cn) (C. Li).

electron-hole recombination.

In this work, we focus on the surface heterojunction [12,14,31,32], an acceptable concept for charge separation because it is very similar to conventional pn junction, phase junction or two-dimensional van der Waals heterostructures [33–36]. Although a theoretical calculation [14] has demonstrated that the different CBMs and VBMs of different facets can perform surface heterojunction for charge separation, it is not clear what kinds of surface factors are dominate to determine these different band edges, how the band alignment in different facet directions looks like, etc. Here, density functional theory (DFT) calculations are used to clarify these fundamental problems, significant for charge separation. In the concrete investigations, we adopt three typical semiconductor models,  $\text{TiO}_2$ (anatase) [6,14],  $\text{SrTiO}_3$  [8] and  $\text{Cu}_2\text{WS}_4$  [7] to represent tetragonal, cubic and layered materials. The results will show that the surface heterojunctions are performed by different surface band bendings along the different facet directions. However, these band bendings are only limited to a few layers behind the surfaces (about 1 nm), and they are caused by surface electronic properties and surface dangling bond interactions, obviously different from conventional band bending induced by space charge layer (about 10–100 nm). In such a case, the surface heterojunction might not have enough power to initiate the preferential flow of charges for electron-hole separation.

## 2. Computational details

The calculations are performed by using DFT method implemented in a software of Vienna Ab initio Simulation Package (VASP) [37]. The exchange correlation potential is described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA), and the projector-augmented wave method is applied to describing electron interactions [38,39]. However, a well-known drawback of the GGA results to underestimated fundamental bandgaps. The bandgap values can be further improved by using the methods with more computational-time demand, either quasiparticle GW methods beyond DFT or the advanced functionals within DFT such as DFT + U and hybrid functionals.

To demonstrate whether the relatively cheap DFT/PBE calculations can predict reasonable surface property, we also use DFT + U and DFT/HSE06 calculations in  $\text{TiO}_2$  system for comparison. As expected (the results are shown in supplementary material), DFT/HSE06 and DFT + U give bandgaps closer to experimental values than DFT/PBE results. But the DFT/PBE performs efficiently in structural optimisation and they can predicted similar results to the DFT + U method and DFT/HSE06, including the profiles of density of state (DOS) and relative energy differences among different facets, which are essential to reveal the surface heterojunction property. It should be thus reasonable to use the cheap DFT/PBE calculations in the other systems.

In the calculations, the structures are optimized until the atomic forces are less than 0.02 eV/Å and the tolerance for energy convergence is less than  $1 \times 10^{-5}$  eV. The cutoff energy is set as 450 eV, which is large enough for the present samples. Crystal surfaces are constructed from the slab model with periodic boundary conditions in the surface planes, where the vacuum spaces are set to be 20 Å to wipe out the interaction between two periodic images. The upper half part of the slab is relaxed, and the lower half part of slab is fixed. For each surface, the outermost atoms have differently possible arrangements. We try to select the most stable surfaces with the lowest surface energies to calculate their electronic properties. The models are constructed to satisfy the stoichiometric ratio and maintain the top and bottom surface symmetry. For those with asymmetrical top and bottom surfaces, the bottom side of slab is passivated by partially charged pseudohydrogen atoms to avoid spurious charge transfer from the bottom to top surface. In order to compare the energy levels of different facets, we use the oxygen atom or sulphur atom in the center of slab model, and align the energy level of its 2s or 3s orbital [20].

## 3. Results and discussion

### 3.1. Anatase $\text{TiO}_2$

$\text{TiO}_2$  is one of the most widely studied systems [40,41], and its structural and electronic properties are well discussed. It has been shown that {0 0 1} and {1 0 1} facets of anatase  $\text{TiO}_2$  are predominantly exposed and they are favorable for oxidation and reduction reactions, respectively [6]. A surface heterojunction is proposed to explain these different reaction activities [14]. Anatase  $\text{TiO}_2$  is thus one of very suitable models for the present investigation since many theoretical and experimental data are available for the comparison.

The anatase  $\text{TiO}_2$  is a tetragonal crystal with a space group of I41/amd. The optimized lattice parameters from its bulk unit cell are  $a = 3.821$  Å,  $b = 3.821$  Å,  $c = 9.671$  Å, which are very close to the experimental values of  $a = 3.789$  Å,  $b = 3.789$  Å,  $c = 9.537$  Å [42]. Based on the optimized bulk structure, we construct two slab models with {0 0 1} and {1 0 1} facets exposed [6,14]. The slab model of {0 0 1} facet contains 8 layers with 3 atoms in each layer. The slab model of {1 0 1} facet contains 10 layers with 6 atoms in each layer. For the {0 0 1} facet, the outermost atoms are 50% twofold coordinated oxygen, 50% threefold coordinated oxygen and fivefold coordinated titanium, as shown in Fig. 1(a). After optimization with Gamma

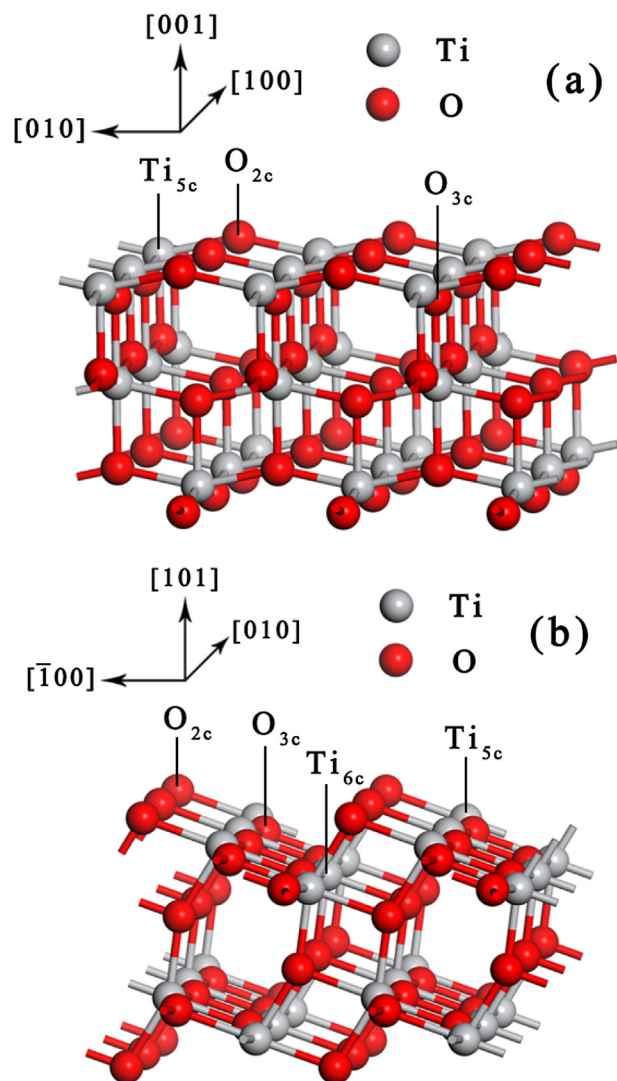


Fig. 1. The surface atomic structures of  $\text{TiO}_2$ . (a) The {0 0 1} facet. (b) The {1 0 1} facet.

Download English Version:

<https://daneshyari.com/en/article/7956822>

Download Persian Version:

<https://daneshyari.com/article/7956822>

[Daneshyari.com](https://daneshyari.com)