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Tight-Binding Quantum Chemical Study on Absorption Spectrum of Organic Dye on Anatase Titanium Dioxide Surface

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1. Introduction

The growing demand on energy and increasing of atmospheric carbon from the combustion relating to energy generation processes have driven the research toward direct or indirect solar-based energy generation. The dye-sensitized TiO_2 based solar cell (DSSCs) attracted considerable attentions because of laboratorial relative higher solar energy to electricity conversion efficiency. Recent years, experimental and theoretical studies have proposed that TiO_2 nanoparticles with size up to ~14 Å prefer the metastable anatase phase, which exhibits higher activity in many cases, rather than the rutile form[1]. Moreover, work on different crystal facets suggests that the minority (001) surface is more reactive than the majority surfaces (101), which is the most stable surface. Therefore TiO_2 (001) surface plays a key role in the reactivity of anatase nanoparticles. Hence, in order to gain a better performance of TiO_2-based devices, it is clearly important to obtain atomic scale information on well-characterized anatase TiO_2 surface. Moreover, organic dye sensitizer which is robust, thermally stable and inexpensive hence became alternatives to metal-based dye sensitizer. Due to the diversity of organic dye sensitizers and TiO_2 surface, computational predication in advance and subsequently synthesis of the ultimately tailor dye sensitizers significantly reduce the production cost. Thus theoretical prediction in advance of structure, electronic properties of dye sensitizer and interfacial electron transfer mechanism is a research subject of DSSCs.

In the present study, we performed a tight-binding quantum molecular dynamics calculation to investigate the surface electronic structure, absorption spectra and surface electrical properties of the most reactive TiO_2 (001) surface. Moreover, the photosensitization of dye/TiO2 was studied by investigating absorption spectra of organic/TiO_2 system.

2. Computational Methods

The geometries of perylene with acrylic acid (PAA) and PAA/anatase(001) models were calculated by means of periodic boundary conditions using DFT method employing DMol^3 [2] program. The geometry optimization was performed using the VWN local correlation functional and correlation potential functional at the local density approximation (LDA) level. To eliminate the core electrons, the effective core potential (ECP) is used.

Based on the optimized structures of PAA, anatase(001), and PAA/anatase(001), tight-binding quantum chemical molecular dynamics method “Colors”[3], was performed to investigate the electronic properties of anatase TiO_2. The absorption spectrum of PAA, anatase(001), and PAA/anatase(001) were achieved by means of tight-binding quantum chemical molecular dynamics method “Colors”, which is an effective tool to explore the excitation properties even for periodic structure.

3. Results and Discussion

Anatase TiO_2(001) surface with different thickness (10, 13, 15, 18 Å) have been relaxed by using DFT method. Based on the optimum geometries of the slab models, the band gap of surface with different thickness (10, 13, 15, 18 Å) were calculated to be 2.346, 2.373, 2.378, and 2.377 eV, respectively. Apparently, band gap of TiO_2 slab increased with the increase of surface thickness and tend to a constant from 15 Å. For comparison, the band gap of bulk TiO_2 is also calculated and the obtained band gap, 3.11 eV, is in good agreement with experimental data [4]. It is evident that slab models shows smaller band gap than bulk TiO_2.

To exam the reason of band gap decrease of TiO_2 slab, projected density of states (PDOS) of TiO_2 slab and bulk were calculated and shown in Fig. 1. In comparison of PDOS of TiO_2 slab with TiO_2 bulk, the O 2*p* and Ti 3*d* are similarly distributed in top of valence band and bottom of

conduction band, respectively. However, for TiO_2 slab, new states were found just above the top of valence band and mainly composed of O 2*p* orbital. The new states appeared in the forbidden band were considered as the reason of band gap decrease.

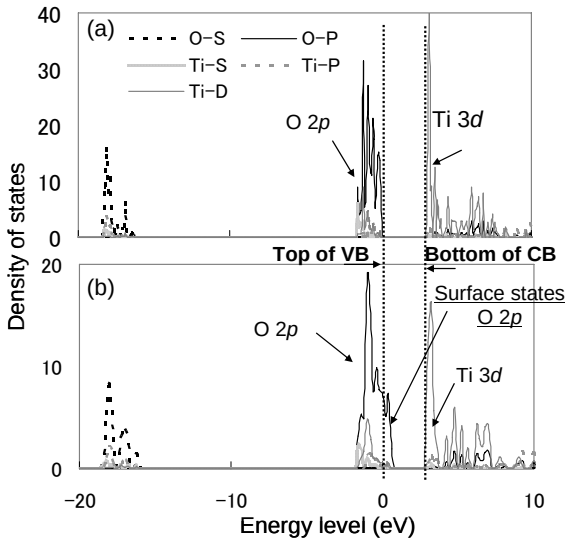

Figure 1 Projected partial density of states of anatase TiO_2 (a) bulk and (b) (001) surface.

Meanwhile, the absorption spectra of periodic TiO_2 slab and bulk, shown in Figure 2, were calculated successfully using theoretical approach for the first time. The absorption edge of bulk anatase TiO_2 was measured in 398 nm, which is close to experimental data. While the absorption edge of anatase TiO_2 slab was obtained around 521 nm. Compared to bulk TiO_2, the absorption edge of TiO_2 slab shifted to longer wavelength region (visible-light region). A red shift of TiO_2 slab was observed from the absorption spectra and considered to be caused by the decrease of band gap of TiO_2 slab.

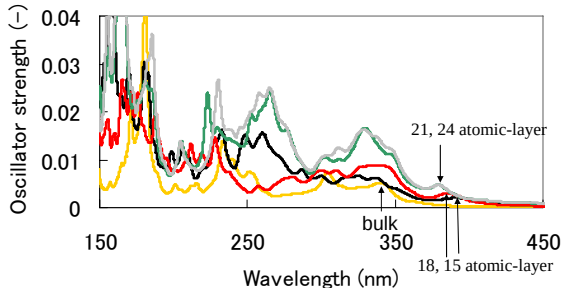

Figure 2 Absorption spectra of anatase bulk and slabs

Meanwhile, the electronic structure, charge, bond population, density of states of PAA was investigated by using Colors" program and DFT method, respectively. A 2.65 eV band gap was achieved by "Colors" calculation, which is very close to previous theoretical data [5]. As active dye sensitizer, the electronic absorption spectrum of PAA is of importance. Hence, the "Colors" program was performed to explore the electronic absorption spectrum of PAA. The first absorption shown in Fig. 3 can be observed around 469 nm. This result is very close to previous theoretical work [5]. Moreover, the absorption mode and absorption spectra of optimized PAA/ anatase(001) systems were also studied. The absorption edge of PAA/anatase(001) system shows good UV-vis light photosensitization. This result demonstrate that PAA/anatase(001) may be a candidate of DSSCs. Our results conformed that in-house program "Colors" is an effectively tool to study spectra properties for both molecular and periodic systems.

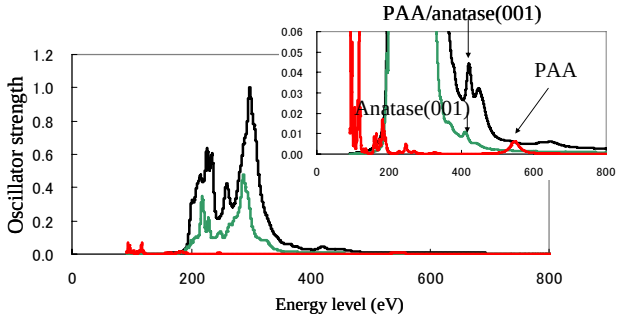

Figure 3 UV-vis absorption spectrum PAA/anatase(001) system.

4. Conclusions:

A theoretical calculation on the effect of surface states on the absorption spectra, electronic and electrical properties of anatase(001) surface were carrier out by tight-binding quantum chemical molecular dynamics method. The existence of surface states lead to the decrease of band gap and red-shift of absorption peak. The results have shown that anatase(001) surface with a thickness of 1.0 nm is promising for its application in photocatalyst and solar cell field. A significant red-shift was observed from the UV-vis absorption spectrum of PAA/anatase periodic systems calculated by "Colors" program. This result suggests that a PAA/anatase(001) may be potential candidate for the application of solar cell. This study also proposed an effective computational tool Colors" to study of the electronic excitation properties even for adsorbed system.

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