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Engineering band gap of bare titanium dioxides for visible-light activity: a theoretical prediction

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The main obstacle for the practical applications of common titanium dioxide (TiO₂) photocatalysts is that they can only absorb ultraviolet sunlight. The fluorite TiO₂ has attracted considerable interests since they may utilize more abundant visible sunlight. However, their electronic properties have not yet been confirmed according to the previous theoretical investigations. In this study, density functional theory with different exchange-correlation functionals was employed to explore the electronic structures of fluorite TiO₂ materials. Our results demonstrate that the perfect fluorite TiO₂ crystals are indirect semiconductors. The size of supercells plays an important role for the calculation outcomes due to the Brillouin zone folding. The theoretical band gap energy of fluorite TiO₂ using hybrid DFT method is 2.31 eV, which support its photocatalytic activity over visible light. The surrounding static electric fields of Ti cations of fluorite TiO₂ are responsible to the reduced band gap energies on the basis of crystal field theory. According to our theoretical deduction, possible visible-light responsive TiO₂ photocatalysts were proposed by tuning the atomic configurations of the rutile TiO₂ (110) surface.

1. Introduction

Titanium dioxide (TiO₂) photocatalysts have demonstrated capabilities to directly utilize solar energy to remediate environment or generate clean energies.¹⁻⁴ Although notable progress has been achieved in recent years, the wide band gap energies of the common TiO₂ polymorphs (> 3.0 eV) limit their photoactivity to the ultraviolet (UV) region of the sunlight spectrum, which is just 5% of the sun-light.⁵⁻⁶ To tune TiO₂ into visible-light responsive materials, various band gap engineering approaches have been developed through chemical modifications, such as cation or anion doping,⁷ alloying,⁸ sensitization by organic dye or inorganic quantum dots, and upconversion.^{3, 9-11} These approaches have succeeded in reducing the band gap energies of TiO₂ photocatalysts to realize visible-light photocatalytic activity, such as the nitrogen doped TiO₂ materials.¹¹⁻¹² However, the energy conversion efficiencies of modified TiO₂ photocatalysts are still too low for practical applications.³ One of the disadvantages of these chemical modification approaches lies on the fact that the modifiers can be the recombination or trapping centres for the photo-generated charge carriers.⁹ Therefore, synthesizing visible-light active TiO₂ photocatalysts without any chemical modifications becomes attractive.¹³⁻¹⁵

TiO₂ shows the rich phase diagram under wild or elevated pressures and temperatures, such as rutile, anatase, brookite, baddeleyite, fluorite, and cotunnite phases.¹⁶⁻¹⁷ The previous theoretical studies indicated that the pure fluorite-type TiO₂ crystals may be visible-light active.^{16, 18-20} Among all the properties of fluorite TiO₂, their electronic structures are the key

feature to determine their performance in photocatalysis or solar power generation applications. Unfortunately, the direct detection of their electronic properties is rather difficult in experiments since fluorite TiO₂ materials can only be synthesized under high pressure (> 48 GPa) around 2000K.²¹ To explore the electronic structures of the fluorite TiO₂, some theoretical studies have been performed based on the traditional density functional theory (DFT), quasi-particle approximation (GW) or quantum Monte Carlo (QMC) method.^{16, 18-20} However, the previous theoretical conclusions on their electronic properties are inconsistent. Kong *et al.*, Mattesini *et al.*, and Abbasnejad *et al.* found that the fluorite TiO₂ was an indirect semiconductor according to their band structures using the DFT, GW or QMC methods.¹⁸⁻²⁰ Conversely, Kuo *et al.* proposed that the fluorite TiO₂ was a direct semiconductor.¹⁶ Since the electronic structures are crucial in determining the photoactivity of TiO₂ materials, the precise understanding of their electronic properties is thoroughly necessary.

In the previous theoretical studies on the fluorite TiO₂, the DFT method using local (local density approximation, LDA) or semi-local (general gradient approximation, GGA) exchange correlation (XC) functionals has been employed.^{16, 19-20} These DFT calculations generally underestimate the band gap energies of semiconductors to the extent of 30%.²²⁻²⁵ While the GW and QMC methods used in the previous studies are more advanced technologies to get better electronic structures of materials, the current computation resource still limits their applications.^{18-19, 26} An alternative to deal with these issues in a first-principle manner is the hybrid DFT method, in which a component of non-local Hartree-Fock exchange is included into the XC functional.²⁷⁻²⁸ In

Fig. 1 Atomic structures of (A)anatase; (B)rutile; and (C) fluorite TiO_2 crystals along with their total density of states (TDOS) of (D) anatase; (E) rutile; and (F) fluorite TiO_2 crystals with the PBE (red) or HSE06 (blue) functional. The black frames in (A-C) represent the unit cells of crystals. Key: red-oxygen, blue-titanium.

this work, we employed the recently developed screened hybrid functionals in periodic systems to examine the electronic structures of fluorite TiO_2 materials.²⁷ Our calculations demonstrate that they are indirect semiconductors with the visible-light activity. The orientation of the Ti 3d orbitals of fluorite TiO_2 in their surrounding static electric fields plays the key role to reduce their band gap energy.

2. Computation Methods

All calculations were performed using the Vienna *ab initio* simulation program (VASP) based on the DFT with the all-electron projected augmented wave (PAW) method in this study.²⁹⁻³¹ A plane-wave basis set was employed with a kinetic energy cut-off of 400 eV. Valence states included the Ti 3p, 4s, and 3d states, and the O 2s and 2p states. We use the PBE³² and HSE06 XC functional³³ for the GGA-level and screened hybrid DFT-level calculations, respectively. The screening parameter for exchange of the HSE06 functional was $0.2 \text{ \AA}^{-1}$.³⁴ An exchange functional of 20% exact HF exchange with 80% PBE exchange was employed in this study since calculations with such ratio accurately predicted the lattice constants and the band gap for rutile and anatase TiO_2 materials.³⁵⁻³⁶

To understand the origin of the visible-light activity of fluorite TiO_2 , the structural and electronic properties of rutile, anatase and fluorite TiO_2 polymorphs were calculated and compared. We performed Brillouin-zone (BZ) integrations using Monkhorst-

Table 1 Theoretical and experimental structural parameters and their band gap energy (E_g) for anatase, rutile and fluorite TiO_2 .

Method	a (Å)	b(Å)	c(Å)	u	E_g (eV)
anatase					
PBE	3.801	3.801	9.711	0.207	2.143
HSE06	3.770	3.770	9.626	0.206	3.341
exp. ³⁷	3.782	3.782	9.502	0.208	3.2-3.4
rutile					
PBE	4.641	4.641	2.970	0.305	1.802
HSE06	4.593	4.593	2.953	0.305	3.083
exp. ³⁷	4.593	4.593	2.959	0.305	3.0
fluorite					
PBE	4.833	4.833	4.833		1.099
HSE06	4.786	4.786	4.786		2.306
exp. ²¹	4.870	4.870	4.870		

Pack grids of special points with $(4 \times 4 \times 6)$, $(6 \times 6 \times 2)$ and $(6 \times 6 \times 6)$ meshes for rutile, anatase and fluorite TiO_2 supercells, respectively. Each supercell of rutile TiO_2 includes 6 atoms while each anatase or fluorite supercell has 12 atoms, as shown in the black frames of Fig. 1A-C. The rutile (110) surface atoms were engineered to form fluorite-type structures in this study because this surface is the most well studied one. The rutile (110) surface was modelled by a slab with the (1×1) surface cell comprising an 18 atomic layers separated by a vacuum region of 10 Å. A $(4 \times 6 \times 1)$ k-point mesh was used in this study. The reconstruction occurs in one surface of the slabs. When the geometry was optimized, all the atoms were allowed to relax. The corresponding k-mesh densities and the cut-off kinetic energy have been justified in our previous studies.³⁸⁻⁴⁰ The other calculation parameters for the hybrid DFT calculations have been validated below through the comparison with the experimental values.

3. Results and discussion

3.1 Rutile and Anatase

To validate the calculation parameters for the hybrid DFT calculations in this study, we have calculated the structural and electronic properties of rutile and anatase TiO_2 crystals firstly. Rutile and anatase are the most common polymorphs of TiO_2 in nature and practical applications. The theoretical lattice constants and band gap energies are listed in Table 1, along with the experimental data.^{16, 37} It can be found that the theoretical lattice constants calculated both with the PBE and HSE06 functionals are very close to the experimental values. The biggest discrepancy is less than 0.1 Å. However, the band gap energies of rutile and anatase materials using the PBE functional are about 40% lower than the corresponding experimental values (3.00 ~ 3.40 eV).⁴¹⁻⁴⁴ Using the HSE06 XC functional, the theoretical band gap energies are 3.08 and 3.34 eV for the rutile and anatase TiO_2 , respectively. The significant improvement through the hybrid DFT calculations confirms the advantage of this method employed in this study. The images of density of states (DOS) of rutile and anatase TiO_2 materials are also shown in Fig. 1D-E, which will be used to be compared with that of the fluorite TiO_2 . Our results are similar as those using the same level computational methods,^{35-36, 45} which demonstrates that the calculation parameters used in this study are valid.

3.2 Structural and electronic properties of fluorite TiO_2

Fig. 2 Illustrations of (A) the cubic $[\text{TiO}_8]$ in fluorite TiO_2 and (B) octahedral $[\text{TiO}_6]$ in rutile or anatase TiO_2 . Key: red-oxygen, blue-titanium, black-orientation of Ti $3d t_{2g}$ orbitals, and green-orientation of Ti $3d e_g$ orbitals.

Compared with rutile and anatase TiO_2 , the fluorite-type crystals show higher symmetry. The atomic structure of fluorite TiO_2 crystals belongs to the cubic $Fm\bar{3}m$ space group, as shown in Fig. 1C.²¹ After the structure optimization, the theoretical lattice constants are 4.833 and 4.786 Å for PBE and HSE06 functional, respectively (see Table 1). Our results are in agreement with to the previous theoretical values, but slightly less than the experimental data.^{16, 18-21} It should be noted that the experimental data was not directly measured since the fluorite TiO_2 can only be stable at the high pressure and high temperature.²¹ The experimental lattice constant was extrapolated according to the lattice constants measured under 10-55 Gpa pressure.²¹ Thus, the theory-experiment discrepancy may be not fully ascribed to the computation accuracy. According to our PBE results, the average volume per TiO_2 unit in fluorite crystals is 28.2 Å³, which is at least 13.3% smaller than those in rutile and anatase crystals. It matches the experiments that the fluorite phase can only be produced under the high pressure.²¹

From Table 1, the theoretical band gap energy with PBE functional is 1.10 eV, which is 1.21 eV lower than that with HSE06 functional. Our PBE value is close to the previous ones obtained using the same level functionals.^{16, 20} And the band gap energy obtained through the screened hybrid DFT method is similar to that using GW (2.37 eV)¹⁹ or QMC (2.44 eV)¹⁸ methods. Since the computation costs of the screened hybrid DFT method are much less than that by using GW and QMC methods, the great advantage of the screened hybrid DFT method used in this study is shown.

On the basis of our calculations, the band gap energy of fluorite TiO_2 is about 1.0 eV lower than those of rutile and anatase phases. The reduced band gap energy of fluorite TiO_2 is mainly due to the change of the surrounding chemical environments of Ti atoms.¹⁶ In rutile and anatase TiO_2 crystals, the coordination number (CN) of Ti atoms is six through the formation of $[\text{TiO}_6]$ octahedra with the D_{2h} symmetry. In fluorite crystals, the CN of Ti atoms is eight in the perfect $[\text{TiO}_8]$ cubes with the O_h symmetry (see Fig. 2). According to the crystal field theory, the five degenerate Ti $3d$ orbitals split into t_{2g} and e_g orbitals by the interactions between the Ti $3d$ electrons and their static electric fields generated by the surrounding O anions. In the $[\text{TiO}_8]$ cubes, the Ti $3d t_{2g}$ orbitals point to the edge of the cubes (the green squares in Fig. 2A). And the Ti $3d e_g$ orbitals points to the face centres of the cubes (the black squares in Fig. 2A). As a result, the shorter distances from Ti $3d e_g$ orbitals to the oxygen atoms ($0.5d_{\text{O-O}}$, and the $d_{\text{O-O}}$ is the shortest O-O distance in

Fig. 3 Partial density of states (PDOS) of Ti (orange lines) and O (green lines) atoms in fluorite TiO_2 with the (A) PBE or (B) HSE06 functional

crystals.) lead to the stronger repulsion between the electrons in Ti $3d t_{2g}$ orbitals and the surrounding O anions. Such repulsion leads that the energy levels of Ti $3d t_{2g}$ orbitals are lower than those of e_g orbitals.^{16, 20} The partial DOS (PDOS) images of Ti and O atoms in fluorite TiO_2 have been calculated with different functionals, as shown in Fig. 3. The PDOS images confirm the order of conduction bands in fluorite TiO_2 according to the deduction of the crystal field theory.

On the other hand, the symmetry of the $[\text{TiO}_6]$ octahedra in rutile and anatase TiO_2 is different from that of the $[\text{TiO}_8]$ cubes. The distances from the Ti $3d e_g$ orbitals in the $[\text{TiO}_6]$ octahedra are shorter since they points to the edge of the $[\text{TiO}_6]$ octahedra (the black squares in Fig. 2B). Thus, the energy levels of Ti $3d t_{2g}$ bands in the rutile and anatase TiO_2 are lower than those of e_g bands. Such electronic structure is reverse to that in the fluorite TiO_2 .^{16, 20} In addition, the distance from the Ti $3d t_{2g}$ orbitals to O anions is $0.577d_{\text{O-O}}$ in the $[\text{TiO}_6]$ octahedra, which is shorter than that in the $[\text{TiO}_8]$ cubes ($0.707d_{\text{O-O}}$). As a result, the Ti $3d e_g$ bands in the $[\text{TiO}_8]$ cubes shift towards the Fermi energy level because of the relatively weaker repulsion between the electrons in Ti $3d e_g$ and O anions. (see Fig. 1). The band gap energy of fluorite TiO_2 , therefore, reduces. The theoretical band gap energy (2.31 eV) of the fluorite TiO_2 supports that they can absorb visible sunlight with wavelength less than 537nm.

3.3 Comparison between different functionals

The data in Table 1 show that the calculations both with the PBE and HSE06 functionals can give accurate structural properties of TiO_2 materials. The crucial improvement using the screened hybrid DFT method is the band gap energies of systems.

Fig. 4 Band structures of fluorite TiO_2 crystals from Γ to X symmetric points with (A) PBE and (B) HSE06 functional. And band structures from W-L- Γ -X-W-K of fluorite TiO_2 crystals with (C) a conventional unit cell including four Ti atoms and eight O atoms, or (D) a primitive cell (it includes one Ti atom and two O atoms) using the PBE functional.

Comparing the DOS images in Fig. 1 and 3, it can be found that the position of the conduction bands by using the GGA/DFT is about 1.0 eV lower than that and screened hybrid DFT methods, which leads to the underestimation of the band gap energies of all TiO_2 materials. This discrepant value (~ 1.0 eV) has been used in GGA/DFT calculations to adjust the band gap energies while it is totally empirical.¹⁶ Another difference related to the functionals is the width of the bands. According to our calculations, the widths of bands with the PBE functional are smaller than the counterparts with HSE06 functional. One example is that the width of upper valence band is 7.4 eV with PBE functional for the fluorite TiO_2 , which is about 0.7 eV smaller than that with HSE06 functional. From Fig. 3, the Ti $3d$ t_{2g} band width with the HSE06 functional is almost twice as that using the PBE functional. However, the DOS images in Fig. 1 and 3 also indicate that the order and shapes of the various bands of TiO_2 are similar. Such similarities suggest that we may still use the GGA/DFT methods, which can reduce computation costs significantly to study more complicated systems, to approximately analyze the electronic properties of TiO_2 materials.

3.4 Nature of electronic structure

The main discrepancy of previous theoretical studies is whether fluorite TiO_2 materials are direct semiconductors or not. Kong *et al.*, Mattesini *et al.* and Abbasnejad *et al.* have proposed that the fluorite TiO_2 is an indirect semiconductor. The indirect transition is from the conduction band minimum (CBM) at the Γ point to the valence band maximum (VBM) at X as the minimum band gap.¹⁸⁻²⁰ On the contrary, Kuo *et al.* found that fluorite TiO_2 is a direct semiconductor with the minimum band gap at the Γ symmetry point based on their GGA/DFT calculations.¹⁶ Since the hybrid DFT calculation can improve the prediction of band gap energies as those using the GW and QMC methods, the calculations using the hybrid DFT calculations are expected to repeat the conclusion using the GW or QMC methods. In this regard, we have calculated the band structure of fluorite TiO_2 from the Γ point to the X point using both traditional DFT and screened hybrid DFT approaches, as shown in Fig. 4A-B.

Fig. 5 (A) Atomic structure of regular rutile (110) surface; (B) Atomic structure of the reconstructed rutile (110) surface with $[\text{TiO}_8]$ octahedra (shown in the black rectangular frame); (C) TDOS of the fluorite TiO_2 crystal (purple line), and the regular rutile (110) surface (green line) and the reconstructed rutile (110) surface (black line); and (D) TDOS of the reconstructed rutile (110) surface (black line), PDOS of eight-coordinated Ti atoms (magenta line) and six-coordinated Ti atoms in the bulk (orange line). Key: red-oxygen, blue-titanium.

Unfortunately, the results suggest that the nature of band structures is independent to the choices of the functionals. The fluorite TiO_2 is a direct semiconductor with the minimum band gap at the Γ symmetry point both with the PBE and HSE06 functionals. There must be another factor causing the discrepancy found in the previous studies.

The previous studies on the anatase TiO_2 revealed that the size of supercells in calculations may affect the band structures.⁴⁵ Considering the computational costs of the GW and QMC methods are very high, the primitive cell of the fluorite TiO_2 crystal may be used in those calculations. The primitive cell of the fluorite TiO_2 includes one Ti atom and two O atoms, which size is one quarter of that of the conventional unit cell used in this study before. Based on this consideration, the band structures of the systems with primitive or conventional supercells were calculated using the PBE functional (see Fig. 4C-D). When the primitive cell was employed, the band structure shows that the fluorite TiO_2 is an indirect semiconductor, which is same as those reported by Kong *et al.*, Mattesini *et al.* and Abbasnejad *et al.*¹⁸⁻²⁰ However, the system changes into a direct semiconductor when the bigger conventional supercell including four Ti atoms and eight O atoms was used. Thus, the size of supercells affects the band structures of fluorite TiO_2 . The size effect can be ascribed to the folding of the BZ.⁴⁶ Since the conventional supercell is larger than the primitive one, the first BZ of the conventional supercell is smaller. Consequently, the VBM at the X point in the first BZ of the primitive supercell is folded back onto the Γ symmetry point in the first BZ of the conventional supercell, which causes the nature of the band structure of fluorite TiO_2 materials changes. Since the band structures using the primitive supercell describe the correct electronic properties of systems, the fluorite TiO_2 are, therefore, demonstrated to be an indirect semiconductor.

3.5 Reconstructed surfaces with $[\text{TiO}_8]$

Since the change of the static electric fields of Ti cations can

tune the band gap of TiO_2 into visible-light activity, engineering the surface structures to form highly symmetric $[\text{TiO}_8]$ becomes a possible approach to avoid the high pressure required by the formation of the fluorite TiO_2 bulk. To verify this theoretical deduction, the stable rutile TiO_2 (110) surface was deliberately reconstructed to form $[\text{TiO}_8]$ in the surface. Two three-coordinated O atoms in the rutile TiO_2 (110) surface were shifted half of unit vector length along $\langle 001 \rangle$ direction to generate $[\text{TiO}_8]$ cubes, as shown in Fig. 5A-B. After the atomic optimization, the $[\text{TiO}_8]$ in the surface are not with perfect O_h symmetry, but very close to it. Such atomic structure can lead to the same electronic structures as that of the fluorite TiO_2 since the static electric fields of Ti cations in both systems are similar. As a result, the similar visible-light activity can be expected.

The total DOS (TDOS) images shown in Fig. 5C demonstrate that the CBM of the reconstructed surface indeed shift towards the Fermi energy level. The location of CBM is close to that of the fluorite TiO_2 crystal. The further PDOS analysis of the Ti atoms in the reconstructed surface (see the magenta line in Fig. 5D) reveals that the shift of the CBM is ascribed to the formation of the eight-coordinated surface Ti atoms in $[\text{TiO}_8]$. As a comparison, the CBM of PDOS of six-coordinated Ti atoms in the bulk (the orange line in Fig. 5D) locates at the similar position of those of bulk rutile. The shift of CBM of the reconstructed surface demonstrates that the visible-light response of the bare TiO_2 photocatalysts can be achieved through the surface engineering to change the static electric fields of Ti cations in the surface. Recently, Etacheri *et al.* found that the oxygen-rich anatase TiO_2 surfaces possessed visible-light activity.¹⁴ At the same time, the reconstructed rutile (011) surface under the oxidizing condition was also found to be visible-light active without any doping.¹³ Such uncommon visible-light response may also be explained the formation of $[\text{TiO}_8]$ cubes under the oxygen-rich conditions. The recent experiments to use the hydrofluoric acid as a facet controlling agent to produce high-energy anatase (001) surface can be used as the model to synthesize visible-light active surfaces with $[\text{TiO}_8]$ cubes.^{40, 47-48}

4. Conclusions

In this study, we have studied the rutile, anatase and fluorite TiO_2 crystals using both the GGA/DFT and the screened hybrid DFT methods. The employment of the screened hybrid DFT methods improves the prediction of the band gap energies of TiO_2 photocatalysts significantly. The theoretical values with the HSE06 functional are almost identical to the experimental values. Through our calculations, the fluorite TiO_2 materials have been confirmed to be indirect semiconductors with minimum band gap from the CBM at the Γ point to the VBM at the X point as the minimum band gap. The band gap energy as low as 2.31 eV supports that the fluorite TiO_2 phase is visible-light active. Such visible-light response is related to the structure change of TiO_2 by the formation of $[\text{TiO}_8]$ cubes. The change of the static electric fields of Ti cations can tune the band gap energies of TiO_2 on the basis of the crystal field theory. To this end, the TiO_2 photocatalysts with $[\text{TiO}_8]$ cubes in surfaces were proposed to be visible-light active, which were theoretically confirmed in this study. Thus, surface engineering of TiO_2 is a doable approach to achieve their visible-light activity without any doping.

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- 40