

First-principles calculations of Ca/F co-doped anatase TiO₂

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Abstract

In order to understand the improved photocatalytic activity of Ca/F co-doped TiO₂, the lattice parameters, energy band structures, density of states and absorption spectra of pure, Ca doped, F doped and Ca/F co-doped anatase TiO₂ were calculated by first principles based on the density functional theory. It was found that the doping can result in lattice distortion of TiO₂, especially the biggest lattice distortion was generated by the Ca/F co-doping. The forbidden energy band width of anatase TiO₂ was broadened by Ca or F doping, while it was reduced by Ca/F co-doping. The calculated electronic density of states indicated that Ca doping provided contribution to the valence band of TiO₂, and F doping resulted in the highest energy level occupied by electrons appeared in the conduction band. The energy band of TiO₂ almost kept unchanged after Ca/F co-doping except the reduction of forbidden band width. Therefore, the experimentally obtained photocatalytic activity improvement of TiO₂ co-doped with Ca and F may have resulted from the reduction of forbidden band width of TiO₂.

Keywords: Anatase TiO₂; Ca/F codoping; electronic structure; first-principles; photocatalytic activity

1. Introduction

TiO₂ has become one of the most used materials in the field of environmental protection due to its unique physical and chemical properties. Under the irradiation of photons with suitable energy, the electrons in the valence band of TiO₂ can be excited to the conduction band. In this process, electron-hole pairs are generated and complex chemical reactions occur, which will eventually degrade the pollutants into non-toxic substances (Xiong *et al.*, 2015; Hu *et al.*, 2015). But TiO₂ has a 3.2 eV band gap for anatase phase and a 3.0 eV band gap for rutile phase, which is a serious limitation to the expression of photocatalytic activity of TiO₂. In order to enhance the photocatalytic activity of TiO₂, doping (Rakhshani *et al.*, 2014) is an effective strategy often used in the practical operation process. For example, C and N doped nano-sized TiO₂ particles

were prepared by solution combustion method. The photocatalytic degradation of methyl orange under visible light irradiation was studied and the results indicated that the doping can improve the photocatalytic activity of TiO₂ (Daya *et al.*, 2015). Mn doped TiO₂ nanocomposites were synthesized by adopting modified Sol-Gel method (Oseghe *et al.*, 2015). The photocatalytic activities of the samples were assessed by the degradation of methylene blue under visible light irradiation. It was found that an optimal dose of Mn doped TiO₂ showed 100% decolouration of methylene blue in the presence of O₃ after 100min. Fe/F co-doped TiO₂ was prepared by peroxidation at low temperature (Zhang *et al.*, 2011). It was found that the photocatalytic activity of the Fe/F co-doped TiO₂ was significantly improved than the pure, Fe doped and F doped TiO₂.

Theoretical calculation methods were adopted to have a profound illustration on the origin of the improved photocatalytic activity of TiO₂. In order to clarify the doping effects of P element, P atom at different sites in the anatase TiO₂ lattice was calculated using first-principles based on the density functional theory (Zheng *et al.*, 2013). The calculated results provided basic proof that P atom in the interstitial site of TiO₂ would play an important role in the improvement of photocatalytic activity. By replacing a Ti atom using a transition metal atom in an anatase supercell, the electronic structure and related properties were calculated based on the density functional theory (Wang *et al.*, 2014). The results indicate that most transition metal doping can narrow the band gap of TiO₂, which lead to improvement in the photoreactivity of TiO₂, and simultaneously maintain its strong redox potential.

Recently, Fu *et al.* (2014) reported the Ca/F co-doped TiO₂ nanocrystals with enhanced photocatalytic activity. By employing the photocatalytic degradation of Rhodamine B as a test reaction, it was found that Ca/F co-doped TiO₂ exhibited a higher Rhodamine B photodegradation capacity under both visible and UV light. Based on the characterization using modern physical and chemical instruments, the authors speculated the reasons for the enhanced photocatalytic activity of Ca/F co-doped TiO₂ without any theoretical calculations. Therefore, as a supplementation, we calculated the electronic structures and related properties of pure, Ca doped, F doped, Ca/F co-doped TiO₂ by first-principles based on the density functional theory, aiming at obtaining a profound understanding of the enhanced photocatalytic activity of Ca/F co-doped TiO₂.

2. Computational details

The matrix of TiO₂ is anatase phase in the Ref. (Fu *et al.*, 2014), so a 3×3×1 anatase supercell containing 108 atoms is selected as the model, as shown in Figure 1. For constructing the doped structures, the Ti atom marked as “X” was substituted by one Ca atom and formed Ca-doped anatase TiO₂ (Ca-TiO₂), or the O atom marked as

“Y” was substituted by one F atom and formed F doped anatase TiO_2 (F- TiO_2). If the marked Ti and O atoms were substituted simultaneously by one Ca and F atoms, respectively, then Ca/F co-doped anatase TiO_2 (Ca/F- TiO_2) was obtained. In addition, it is possible that Ca and/or F atom can exist as interstitial dopant in the experimental researches, but the interstitial proportion is very small to the substitutional proportion. Therefore, only the perfect substitutions are considered in this paper.

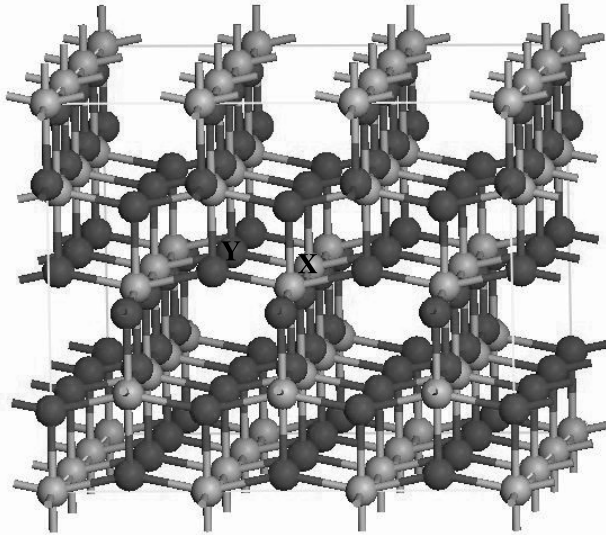


Fig. 1. Structural model of the anatase TiO_2

All calculations were performed using the generalized gradient approximation with Perdew-Burke-Ernzerh of exchange correlation potential. The ion-electron interaction is modeled by the ultrasoft pseudopotential in the Vanderbilt form. The code is implemented in the CASTEP (Clark *et al.*, 2005). The energy cutoff for the plane wave basis set is 300eV, and a k -mesh of $2 \times 2 \times 2$ is used. The valence atomic configurations are $3s^2 3p^6 3d^2 4s^2$ for Ti, $2s^2 2p^4$ for O, $3s^2 3p^6 4s^2$ for Ca, and $2s^2 2p^5$ for F. The crystal structure and the atomic coordinates are fully relaxed without any restriction until the force on each atom converges to less than $0.05 \text{ eV}/\text{\AA}$, with the total energy converged to lower than $2 \times 10^{-5} \text{ eV/atom}$. The maximum stress and maximum atomic displacement are set as 0.1GPa and 0.002\AA , respectively.

3. Results and discussions

3.1 Structural optimizations

The lattice parameters calculated for the series of doped anatase TiO_2 were listed in Table 1. From Table 1 it can be seen that the three kinds of doping all result in the lattice distortion of anatase TiO_2 . The biggest lattice distortion was arisen from the

Ca/F codoping. As we know, the negative and positive charge centers are overlapped completely in the pure anatase TiO₂. So, if there are electrons transiting from valence band to conduction band under photons irradiation, the lifetime of such generated electron-hole pairs would eventually depend on the intrinsic nature of anatase TiO₂, which is very important to the photocatalytic activity of TiO₂. When TiO₂ is doped with Ca, F or Ca/F, the lattice distortion can make the separation of the negative and positive charge centers. Then an additional electronic field will set up. This additional electronic field will facilitate the separation of electrons and holes, and prolong the lifetime of electron-hole pairs. This is one of the reasons why the experimental researches can obtain higher performance of Ca-TiO₂ (Moaed *et al.*, 2013), F-TiO₂ (Lin *et al.*, 2013), and Ca/F-TiO₂ (Fu *et al.*, 2014).

Table 1. Structural parameters for different TiO₂ system

	a (Å)	b (Å)	c (Å)	Volume (Å³)
Pure TiO ₂	3.8073	3.8073	9.8232	1281.55
Ca-TiO ₂	3.8175	3.8237	9.9246	1303.81
F-TiO ₂	3.8108	3.8153	9.8341	1286.80
Ca/F-TiO ₂	3.8140	3.8429	9.9238	1309.03

3.2 Band structures

The calculated band structures of the pure TiO₂ (Zheng *et al.*, 2013), Ca-TiO₂, F-TiO₂, Ca/F-TiO₂ are shown in Figure 2(a-d). The energy zero point is set as the highest energy level that the electron occupied. From Figure 2 (a) we know that the calculated band gap of pure anatase TiO₂ is 2.20eV, which is smaller than the experimental value of 3.20eV, but is very similar to the Ref. (Wang *et al.*, 2014) where the calculated result is 2.21eV. This underestimation is a well-known limitation of the density functional theory, but will not affect the results' relative accuracy (Perdew & Levy, 1983).

From Figure 2 (a) it can be seen that the anatase TiO₂ is a direct band gap semiconductor. After Ca is introduced into the lattice of anatase TiO₂, the band gap of Ca-TiO₂ becomes 0.08eV larger than that of the pure one, as shown in Figure 2 (b). This tendency is similar to Cr, Mn and Ni dopings. These elements also result in bigger band gaps of anatase TiO₂ (Wang *et al.*, 2014). The Ca-TiO₂ remains as a direct band gap semiconductor. The larger band gap of Ca-TiO₂ is detrimental to the expansion of the light response during the photocatalytic process. But, when we consider the stronger redox potential generated in the Ca-TiO₂ during the irradiation process, it can be anticipated that the Ca-TiO₂ should have a higher photocatalytic activity than the pure TiO₂ under UV light irradiation with photons energy than their band gaps.

Actually, the experimental results indicate that when Ca is incorporated into TiO_2 , the energy conversion efficiency of the dye-sensitized solar cells is increased greatly (Moaed *et al.*, 2013; Pan *et al.*, 2015).

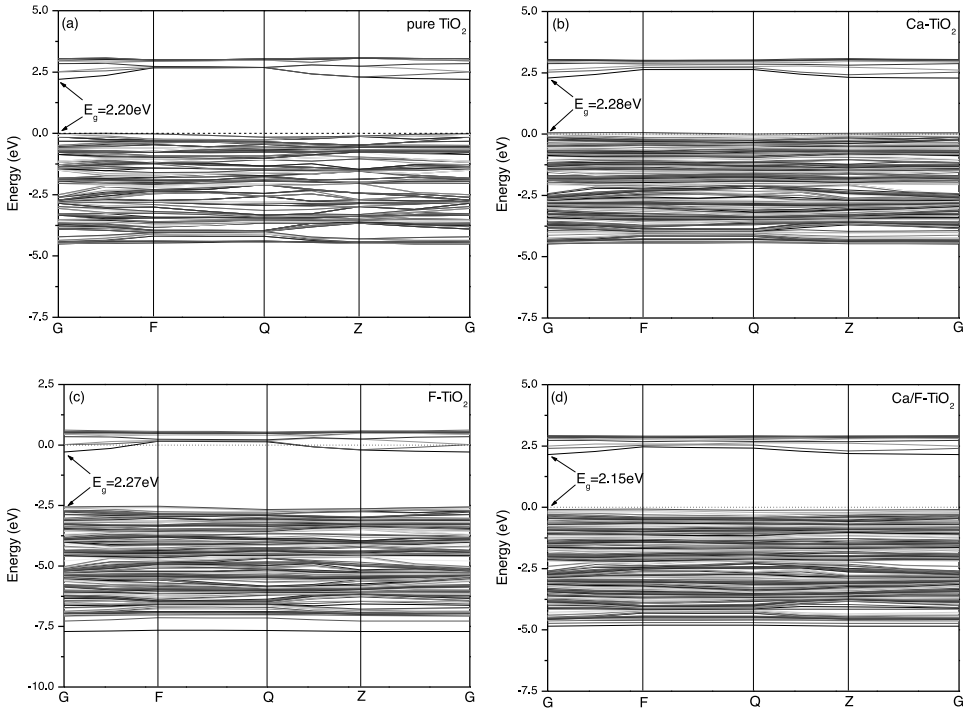


Fig. 2. Band structures of (a) pure TiO_2 , (b) Ca-TiO_2 , (c) F-TiO_2 , (d) Ca/F-TiO_2

When F is incorporated into the anatase TiO_2 lattice, the band gap of F-TiO_2 is 0.07 eV larger than that of the pure one, as shown in Figure 2 (c). The highest energy level occupied by the electrons goes into the conduction band, which indicates the F-TiO_2 is a degenerated semiconductor. This characteristic will result in the fast transport of the electrons in the F-TiO_2 to the particles' surface and the electrons have a high opportunity to participate in the photocatalytic process, which will cause a higher photocatalytic activity in F-TiO_2 . Maybe this is one of the reasons why the experimental researches obtain a higher photocatalytic activity in the F doped TiO_2 (Lin *et al.*, 2013; Wu & Chen, 2008).

It is interesting to look at the band structure of Ca/F co-doped anatase TiO_2 , as shown in Figure 2 (d). Now we know that both Ca and F doped TiO_2 have a larger band gap than pure TiO_2 . On the contrary, the Ca/F codoped TiO_2 shows a 0.05 eV narrower band gap than pure TiO_2 . This result is consistent with Liang's calculated report that Mo-F co-doped anatase TiO_2 shows a little narrower band gap than undoped TiO_2 (Liang *et al.*, 2012). So in the Ca/F-TiO_2 system, the elements Ca and F must have an

interaction with each other and result in the narrower band gap. The interaction can be explained as below: F has more stronger attraction ability for electrons than O, so the electrons of Ca 3p can be attracted tightly to F, thus push the electrons of O 2p to a higher energy, which will result in the reduction of the band gap of Ca/F-TiO₂. That is to say, Ca and F should provide a synergistic effect on the photocatalytic activity of the TiO₂. Ca/F-TiO₂ should show a higher photocatalytic activity than single Ca or F doped TiO₂. Because of the lack of related experiments, only the photocatalytic activity Ca/F-TiO₂ > F-TiO₂ > TiO₂ is supported by the Ref. (Fu *et al.*, 2014).

3.3 Partial density of states

In order to observe the composition of the energy bands, the partial density of states (PDOS) of the four systems were calculated, as shown in Figure 3 (a-d). It is well known that the conduction band of pure TiO₂ is mainly composed of Ti 3d orbits, and the valence band is mainly composed of Ti 3d and O 2p orbits, as shown in Figure 3 (a) (Zheng *et al.*, 2013).

The PDOS of the Ca-TiO₂ is shown in Fig.2 (b). From the Figure 3 (b) it can be seen that the Ca impurity has apparently affected the valence band because the peak shapes of Ti 3d and O 2p in the valence band are different with those of pure TiO₂.

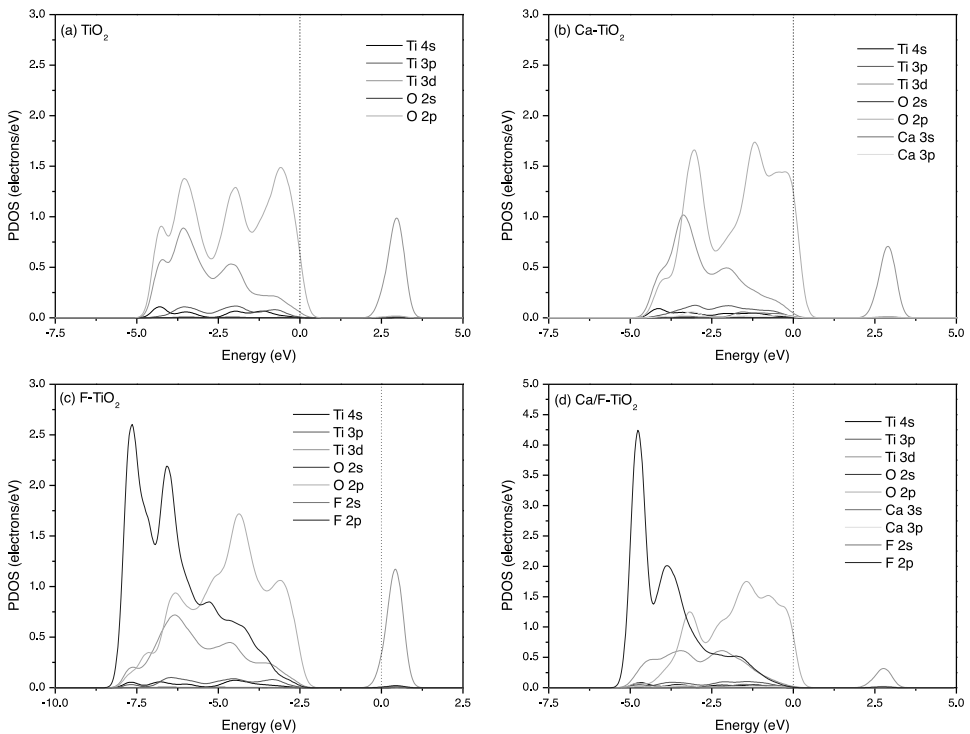


Fig. 3. PDOS of (a) pure TiO₂, (b) Ca-TiO₂, (c) F-TiO₂, (d) Ca/F-TiO₂

F 2p orbitals have an important contribution to the valence band of F-TiO₂, as shown in Figure 3 (c). It is clear that F 2p orbitals are mainly contributed to the lower energy part of the valence band. The peak at 7.64 eV of F 2p orbitals corresponds to the energy level below the valence band which is shown in Figure 2 (c).

Ca/F co-doping influences both the valence band and the conduction band of TiO₂, as shown in Figure 3 (d). It is obviously observed that the peak intensity of Ti 3d in the conduction band is reduced when comparing with those of Ca-TiO₂ and F-TiO₂. All of the F 2p orbitals are going into the valence band of Ca/F-TiO₂. So it is confirmed that the dopants of Ca and F must be interacted with each other, and this will lead to a synergistic effect on the photocatalytic property of TiO₂.

3.4 Absorption spectra

Due to underestimation of the band gap, it is difficult to obtain the exact optical band gap. But for calculating the absorption spectra of the four systems, we only focus on the relative changes of the absorption spectra. The underestimation of the band gap does not affect the qualitative analysis of the results. It is clearly observed that Ca-doped, F-doped and Ca/F-co-doped TiO₂ all show a blue shift in the absorption edges. The degree of blue shift is Ca/F-TiO₂ > F-TiO₂ > Ca-TiO₂. But for Ca-TiO₂ and Ca/F-TiO₂, the absorption ability in the visible region is stronger than pure TiO₂, while F-TiO₂ shows similar absorption ability to the pure TiO₂. So the experimental results of improved photocatalytic activity of Ca/F-co-doped anatase TiO₂ (Fu *et al.*, 2014) can be explained as follows: 1) under the irradiation of light with wavelength >420nm, the higher photocatalytic activity of Ca/F-TiO₂ can be ascribed to the stronger visible light absorption ability; 2) under UV light irradiation, the higher photocatalytic activity of Ca/F-TiO₂ can be due to the stronger redox ability generated by the electron-hole pairs. 3) the lattice distortion also play an important role on the photocatalytic activity of Ca/F-TiO₂.

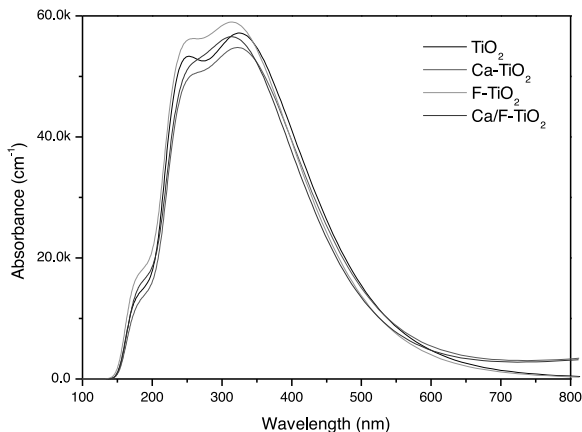


Fig. 4. Absorption spectra of the series TiO₂

4. Conclusions

The lattice parameters, band structures, density of states and absorption spectra of TiO₂, single Ca-doped or F-doped, and Ca/F co-doped anatase TiO₂ were calculated using the first-principles method based on density functional theory. The results indicate that single Ca-doping or F-doping, and Ca/F-codoping all induce lattice distortion in TiO₂. The degree of lattice distortion is Ca/F-TiO₂ > Ca-TiO₂ > F-TiO₂. The forbidden band widths of Ca-TiO₂ and F-TiO₂ are larger than that of pure TiO₂, while the Ca/F-TiO₂ has a 0.05 eV narrower band gap than TiO₂. Ca-doping has influences to the valence band of TiO₂. F-doping provides an energy level below the valence band and make the TiO₂ become a degenerated semiconductor. Ca/F-codoping decreases the peak intensity of Ti 3d in the conduction band. All the dopings result in blue shift in the absorption edges. The calculation results could provide some insight for understanding the higher photocatalytic activity of Ca/F-codoped TiO₂.

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حساب المبادئ الأولية للمنتشط تشاركيا أنتاز TiO₂

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خلاصة

لأجل فهم زيادة نشاط التحفيز الضوئي Ca/F المنشط تشاركيا TiO₂، و فهم عوامل الوسط وبنى شريط الطاقة و كذا كثافة الحالات و طيف الإمتصاص الضوئي Ca المنشط F المنشط Ca/F، مخدر التيتانيوم TiO₂ مشترك من المبادئ الأولى على أساس الكثافة النظرية الوظيفية. وأيضا بروز Ca/F عرض شريط القوة في حالة TiO₂ بينما يتسبب النشاط التشاركي في نقص عرض ..بينما يظهر الحساب الإلكتروني لكثافة الحالات أن ال Ca المنشط يساهم في تقوية الشريط التكافئي ل F، و أن ال Ca/F المنشط الناتج في الطاقة الاكبر المشغولة بالالكترونات التي تظهر في الشريط الناقلي. كما أن شريط القوة ل TiO₂ يبقى دائما بدون تغيير بعد التنشيط التشاركي ب Ca/F بإستثناء خفض عرض الشريط (الممنوع). لذلك فان تحسن نشاط التحفيز الضوئي ل TiO₂ المنشط تشاركيا مع ال Ca و F قد يكون ناتج أساسا عن نقصان عرض شريط TiO₂ (الممنوع).