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Density functional theory of Ca/F co-doped anatase TiO$_2$

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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: DFT; Doping; TiO2.

1. INTRODUCTION

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 [1]. 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 [2]. 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.

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 [3,4]. 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 [5] 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 [6]. Mn doped TiO2 nanocomposites were synthesized by adopting modified Sol-Gel method [7]. 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 [8]. 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 [9]. 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 [10]. 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. [11] 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

We employed the FP-LAPW method to solve the Kohn Sham equations as implemented in the wien2k code [12]. The exchange-correlation contribution was described within the generalized gradient approximation (GGA) proposed by Perdew et al. [13] to calculate the total energy, while for the electronic properties, in addition to the GGA correction Engel- Vosko's (EVGGA) formalism [14] was also applied. The core states of Pb, Ca, S, Se and Te atoms were treated self-consistently and fully relativistically relaxed in a spherical approximation, while the valence states were treated self-consistently within the semi-relativistic approximation (no spin-orbit effects included). Wave functions, charge density and potential were expanded inside muffin-tin spheres of radius RMT by using spherical harmonies expansions, while in the remaining space of the unit cell a plane wave basis set was chosen. The plane wave cutoff of Kmax = 8.0/R_{MT} (R_{MT} is the smallest muffin-tin radius) was used for the expansion of the wave function in the interstitial region for all three alloys and the six binary compounds CaS, CaSe, CaTe, PbS, PbSe and PbTe. Values of R_{MT} were assumed to be 1.9, 2.0, 2.1, 2.2 and 2.4 a.u. for Ca, S, Se, Pb and Te atoms, respectively. The charge density was Fourier expanded up to Gmax = 14 $(Ry)^{1-2}$. The maximum l value for the wave function expansions inside the spheres was confined to l_{max}=10. Meshes of 47 k-points for binary compounds and 125 k-points for alloys were used in the irreducible wedge of the Brillouin zone. Both the plane wave cutoff and the number of k-points were varied to ensure total energy convergence.

3. RESULTS AND DISCUSSION

In the present work we analyze the structural properties of the binary compounds PbS, PbSe, PbTe, CaS, CaSe, CaTe and their alloys. A rocksalt structure was assumed. The alloys were modeled at some selected compositions with ordered structures described in terms of periodically repeated supercells with eight atoms per unit cell, for the compositions x = 0.25, x = 0.5, x = 0.75. For the structures considered, the calculated total energies at many different volumes around equilibrium were fitted by the Murna-ghan equation of state [15] in order to obtain the equilibrium lattice constant and the bulk modulus for the binary compounds and their alloys. Our results for the materials of interest are compared with the available experimental and theoretical predictions in Table 1. Considering the general trend that the GGA usually overestimates the lattice parameters, our GGA results for the binary compounds are in reasonable agreement with experimental values and other calculated values. Usually, in the treatment of alloy problems, it is assumed that the atoms are located at ideal lattice sites and the lattice constants of alloys should vary linearly with composition x according to Vegard’s law [16], however, violations of Vegard’s rule have been reported in semiconductor alloys both experimentally [17] and theoretically [18].

The lattice parameters calculated for the series of doped anatase TiO2 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 TiO2. 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 [19-21].

Table 1 Structural parameters for different TiO2 system.

	a (Å)	**b (Å)**	**c (Å)**	**Volume (Å^3)**
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

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 [22].

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 [23]. 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 [24,25].

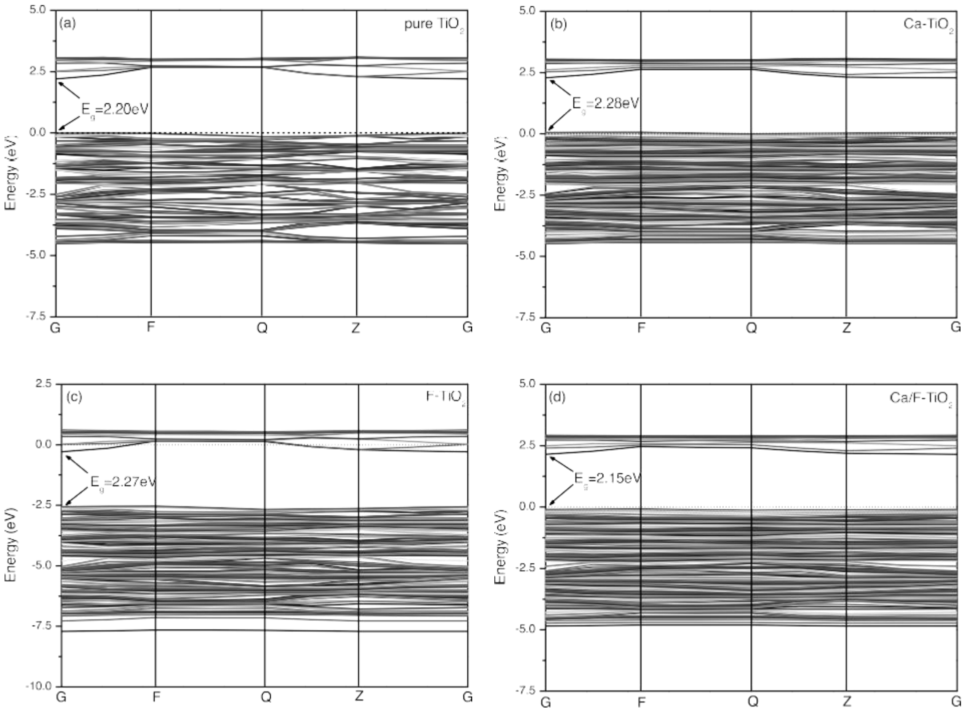

FIGURE 2 Band structures of (a) pure TiO2, (b) Ca-TiO2, (c) F-TiO2, (d) Ca/F-TiO2.

When F is incorporated into the anatase TiO2 lattice, the band gap of F-TiO2 is 0.07eV 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-TiO2 is a degenerated semiconductor. This characteristic will result in the fast transport of the electrons in the F-TiO2 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-TiO2. Maybe this is one of the reasons why the experimental researches obtain a higher photocatalytic activity in the F doped TiO2 [26,27].

It is interesting to look at the band structure of Ca/F co-doped anatase TiO2, as shown in Figure 2 (d). Now we know that both Ca and F doped TiO2 have a larger band gap than pure TiO2. On the contrary, the Ca/F codoped TiO2 shows a 0.05eV narrower band gap than pure TiO2. This result is consistent with Liang's calculated report that Mo-F co-doped anatase TiO2 shows a little narrower band gap than undoped TiO2 [22]. So, in the Ca/F-TiO2 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 elctrons 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-TiO$_2$. That is to say, Ca and F should provide a synergistic effect on the photocatalytic activity of the TiO$_2$. Ca/F-TiO$_2$ should show a higher photocatalytic activity than single Ca or F doped TiO$_2$. Because of the lack of related experiments, only the photocatalytic activity Ca/F-TiO$_2$ > F-TiO$_2$ > TiO$_2$ is supported by [19].

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) [20].

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.

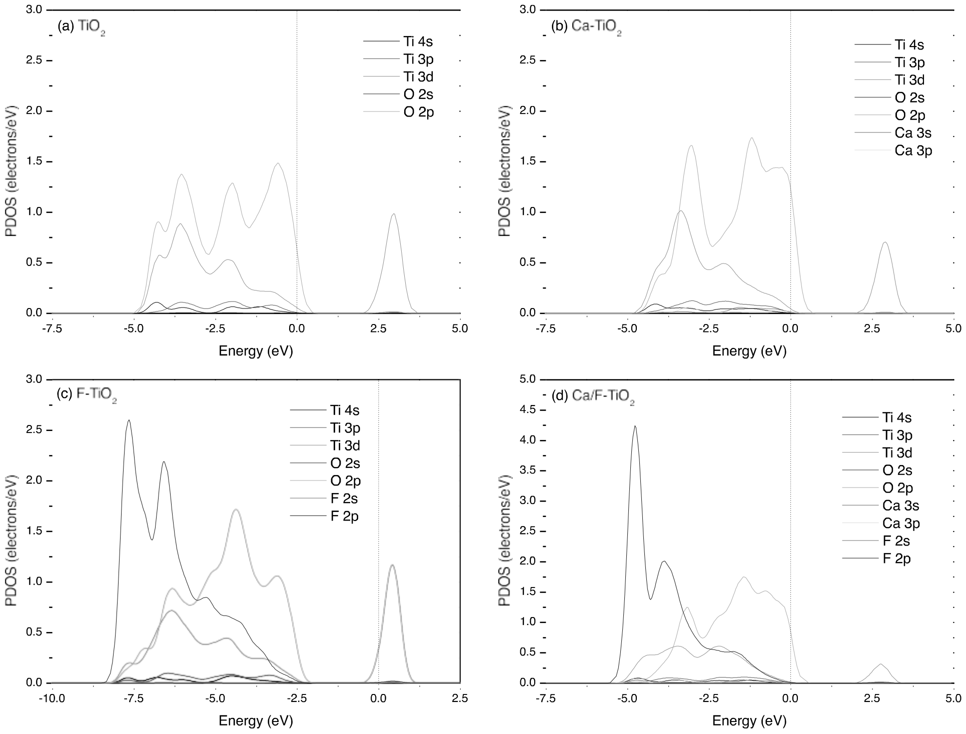

FIGURE 3 PDOS of (a) pure TiO2, (b) Ca-TiO2, (c) F-TiO2, (d) Ca/F-TiO2.

F 2p orbits have an important contribution to the valence band of F-TiO2, as shown in Figure3 (c). It is clear that F 2p orbits are mainly contributed to the lower energy part of the valence band. The peak at 7.64 eV of F 2p orbits 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 orbits 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.

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 [18] 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 plays an important role on the photocatalytic activity of Ca/F-TiO2.

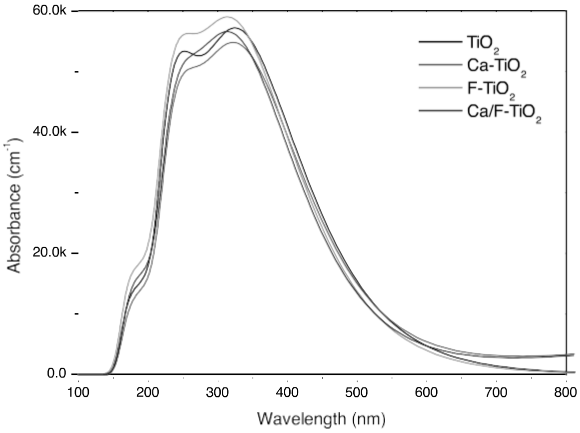

FIGURE 4 Absorption spectra of the series TiO2.

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-doping 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 0.05eV narrower band gap than TiO2. Ca-doping has influnces 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 doping result in blue shif in the absorption edges. The calculation results could provide some insight for understanding the higher photocatalytic activity of Ca/F-doped TiO2.

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