Research Article

The Synthetic Effects of Iron with Sulfur and Fluorine on Photoabsorption and Photocatalytic Performance in Codoped TiO$_2$

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The structural and electronic properties of iron-fluorine (Fe-F) and iron-sulfur (Fe-S) codoped anatase TiO$_2$ are investigated by first-principles based on density functional theory. Our results show that the formation energy of codoped system is lower than that of single-element doping, which indicates the synergic effect of codoping on the stability of the structure. Codopants introduced impurity gap states resulting in the electron transition energy reduction and thus the visible light absorption observed in the samples. It is concluded that Fe-S should be a better codoping pair because Fe-S codoping introduces extended impurity states resulting in stronger visible light absorption than that of Fe-F codoped compounds. This work gives understanding to the recent experiment and provides the evidence of choosing the more effective co-dopants in TiO$_2$.

1. Introduction

Titanium dioxide has been extensively studied as a promising photocatalyst due to its cheap, stable, and nontoxic characteristics. However, the use of TiO$_2$ is limited by its wide band gap (∼3.0 eV) which absorbs only ultraviolet light and accounts for just 5% of solar energy. Thus, modification of the electronic structure of TiO$_2$ to enable the visible light absorption is of great importance [1–3]. An efficient way is doping pure TiO$_2$ with metal [4–7] or nonmetal elements [8–12]. Metal elements diffused in the titanium lattice greatly enhance the visible light absorption because the impurity states introduced by the dopants lead to the visible light response of TiO$_2$. However, localized states appearing in the band gap of the host semiconductor often result in the recombination of photogenerated carriers and consequently result in lower photocatalytic activity. A possible way to improve the photocatalytic performance of doped TiO$_2$ is to explore the cooperative effect by introducing more than one species of foreign elements to the host [13–16]. Appropriate choice of the codoping pair is the key factor. Recent experiment has reported that iron-sulfur (Fe-S) codoped TiO$_2$ exhibits quite high photoactivity under visible light illumination and is stable for long-term applications [17]. It is proposed that the doped Fe$^{3+}$ ions can act as electron acceptor and efficiently prevent electron-hole recombination. In addition, Liu et al. [18] found that iron-fluorine (Fe-F) codoped TiO$_2$ displays excellent photocatalytic activity under visible light irradiation. In the experiment, they speculated that the as-prepared TiO$_2$ samples match the anatase type, with no trace of rutile or brookite impurity being observed, and they also demonstrated that F could substitute for O and Fe could substitute for Ti in Fe-F codoped anatase TiO$_2$. Fluorine atom has one more valence electron than oxygen, and sulfur has the same outer-shell electron as oxygen atom; therefore, it is interesting to explore the origin of the high photocatalytic activity under visible light concerning these two kinds of codoped anatase TiO$_2$.

We should have comprehensive knowledge of single-element-doped TiO$_2$ before exploiting the cooperative effects of the codoped systems. For Fe-doped TiO$_2$, a number of studies have been reported experimentally and theoretically. Liu et al. [19] demonstrated that Fe-doped TiO$_2$ shows visible light responses and diminished recombination rates
of the photoexcited carriers. Fe at the 0.5 at.% level can significantly improve the photocatalytic activity of TiO$_2$ for both oxidation and reduction reactions [20]. As for the F-doped TiO$_2$, recent experimental studies suggested that F-doping neither causes any change in the adsorption edge nor affects the optical absorption of TiO$_2$ but is beneficial to the crystalline anatase phase [21–27]. Umebayashi et al. [28] suggested that S-doping causes the absorption edge of TiO$_2$ to be shifted into lower-energy region. The mixing of the S 3$p$ states with VB increases the width of the VB itself and results in a decrease in the band gap due to S-doping [29].

In this work, we examine the microscopic electronic structures of Fe-S and Fe-F codoped anatase TiO$_2$ to explore the synthetic effects of the dopants by means of the first-principles density function theory (DFT) calculations. The defect formation energies are calculated to determine which configuration may be realized more easily in experiment. The corresponding related properties of Fe-S and Fe-F are compared to identify a better codoping pair. To obtain detailed insight, Fe, F, and S monodoped anatase TiO$_2$ structures are also studied systematically. Our theoretical calculations may provide a comprehensive explanation for experimentally observed visible-light photocatalytic activity in the metal and nonmetal codoped TiO$_2$ and may offer some helpful theoretical information for exploiting new effective photocatalysts.

2. Computational Method

We carry out the spin-polarized density functional calculations of Fe-S codoped, Fe-F codoped, and single-element-doped anatase TiO$_2$ using the Vienna ab initio simulation package (VASP) [30, 31]. The Perdew-Wang 91 of generalized gradient approximation (GGA) is implemented to describe the exchange correlation function. The projector-augmented wave (PAW) potential is used to represent the electron-ion interaction. The crystal lattice parameters are taken from previous calculations ($a = 3.776$, $c = 9.486$), which are in agreement with the experimental values ($a = 3.785$, $c = 9.514$) [32]. We use a $2 \times 2 \times 1$ supercell containing 32 O atoms and 16 Ti atoms to model the bulk anatase TiO$_2$. In the codoped calculation models, one oxygen atom is replaced by a S (or F) atom and titanium atom by iron. In the mono-doped TiO$_2$, we have just one O atom substituted by S (or F). The Monkhorst-Pack k-point is set as $4 \times 4 \times 4$ in the Brillouin zone of the supercell, and we choose the plane-wave cutoff energy of 400 eV. All the atoms are fully optimized until the force on each atom is less than 0.1 meV.

3. Results and Discussion

3.1. Optimized Structure and Stability of Doped TiO$_2$

To investigate the relative stability of Fe-F and Fe-S codoped TiO$_2$, we calculate the defect formation energies. For comparison, the energies of F, Fe, and S monodoped TiO$_2$ are also studied. The formation energies $E_f$ are calculated according to the following formulas:

$$E_f = E_{\text{Fe-doped}} - E_{\text{pure}} - \mu_{\text{Fe}} + \mu_{\text{Ti}}$$

$$E_f = E_{\text{F(S)-doped}} - E_{\text{pure}} - \mu_{\text{F(S)}} + \mu_{\text{O}}$$

$$E_f = E_{\text{Fe/F(S)-codoped}} - E_{\text{pure}} - \mu_{\text{F(S)}} - \mu_{\text{Fe}} + \mu_{\text{O}} + \mu_{\text{Ti}}$$

in which $E_{\text{Fe-doped}}$, $E_{\text{F(S)-doped}}$, and $E_{\text{Fe/F(S)-codoped}}$ are total energies of Fe, F(or S) monodoped and Fe-F (or Fe-S) codoped TiO$_2$, respectively. $E_{\text{pure}}$ is the total energy of TiO$_2$ without dopants. $\mu_{\text{Fe}}$, $\mu_{\text{Ti}}$, $\mu_{\text{F(S)}}$, and $\mu_{\text{O}}$ are the chemical potential of Fe, Ti, F(or S), and O, respectively. It is commonly known that if the doped systems have smaller formation energies, it means that they are in a relatively stable phase. It should be also mentioned that formation energy is in connection with crystal growth circumstance. We simulate the corresponding Ti-rich and O-rich conditions in our theoretical calculations. Under Ti-rich condition, $\mu_{\text{Ti}}$ is gotten from bulk Ti and $\mu_{\text{O}}$ is calculated according to the following formula:

$$2\mu_{\text{O}} + \mu_{\text{Ti}} = \mu_{\text{TiO}_2}.$$  

Here $\mu_{\text{TiO}_2}$ is energy of one formula unit of TiO$_2$. Under O-rich, $\mu_{\text{O}}$ can be obtained from the ground-state energy of the O$_2$ molecule ($\mu_{\text{O}} = 1/2 \mu(\text{O}_2)$), while $\mu_{\text{Ti}}$ is fixed by condition (2).

In codoped TiO$_2$ crystal lattice, dopants may substitute any host atoms however, not all of the configurations are stable. With the aim to find out the most stable configuration, different substitution sites according to the different distances between the two dopants are tested. Formation energy calculations imply that the structure with one Fe substituting for a Ti atom and simultaneously with one F (or S) at the first nearest neighboring (denoted as 1NN) O atom site is the most energetically favorable. We find that, in general, when the distances between the two dopants increase, the formation energies increase. This is probably because that the attraction forces between the anion and cation ions decrease when the two elements locate far from each other. Thus, it can be concluded that 1NN substitution is the most viable configuration in experimental process and then is chosen as our computational model hereafter (Figure 1).

The calculated formation energies of different-element-doped TiO$_2$ are summarized in Table 1, which suggests that (1) Fe mono-doped, Fe-F and Fe-S codoped TiO$_2$ are both energetically favorable under O-rich condition, but unfavorable under Ti-rich condition, (2) the formation of F mono-doped TiO$_2$ is thermodynamically favorable under both Ti-rich and O-rich conditions, but S monodoped TiO$_2$ is more stable under Ti-rich condition, which agrees with the former calculations [11], (3) the formation energy of Fe-F codoped TiO$_2$ is much lower than both Fe and F mono-doped TiO$_2$. For Fe-S codoping under O-rich condition, the formation energy is smaller than S mono-doped but larger than Fe mono-doped TiO$_2$. The lower formation energies of codoping systems indicate cooperative effects
viable in experiment. Thus, we can conclude that codoped semiconductor with higher dopants concentration more

Table 1: Formation energies $E_f$ (eV) of single-element-doped and codoped TiO$_2$ in different conditions.

<table>
<thead>
<tr>
<th></th>
<th>Ti-rich</th>
<th>O-rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-TiO$_2$</td>
<td>5.51</td>
<td>-4.80</td>
</tr>
<tr>
<td>F-TiO$_2$</td>
<td>-4.97</td>
<td>0.18</td>
</tr>
<tr>
<td>S-TiO$_2$</td>
<td>-2.31</td>
<td>2.85</td>
</tr>
<tr>
<td>F-Fe-TiO$_2$</td>
<td>-0.19</td>
<td>-5.35</td>
</tr>
<tr>
<td>Fe-S-TiO$_2$</td>
<td>4.35</td>
<td>-0.80</td>
</tr>
</tbody>
</table>

of the different dopants and make the high photocatalytic semiconductor with higher dopants concentration more viable in experiment. Thus, we can conclude that codoped TiO$_2$ samples have lower formation energies than mono-element-doped systems, which is due to the charge balance by incorporating both anion and cation ions. This effect is more obvious in Fe-F codoped TiO$_2$ since the charge neutrality is well maintained relative to the undoped system, while the charge neutrality is not maintained so well for the Fe-S codoped TiO$_2$.

We further investigate the optimized structures of different-element-doped TiO$_2$. For Fe mono-doped TiO$_2$, the optimized O-Fe bond lengths (1.873 Å and 1.891 Å) are shorter than O-Ti bond lengths in pure TiO$_2$ (1.930 Å and 1.973 Å). This is because that bond length is determined mainly by radius and electronegativity of bonded atoms. The electronegativity of iron (1.83) is stronger than that of titanium (1.54), and the ionic radius of iron (0.64 Å) is smaller than that of titanium (0.68 Å). In F mono-doped TiO$_2$, the distance between F and Ti (2.000 Å) is longer than O-Ti bond length (1.930 Å). This can be ascribed to the fact that electronegativity of F (3.98) is stronger than that of O (3.44) while the radius of F$^-$ is a little bigger than that of O$^{2-}$ (1.32). In S-doped TiO$_2$, the S-Ti bond lengths are 2.147 and 2.354 Å, which are much longer than the O-Ti bond lengths in pure TiO$_2$ due to the bigger atom radius of S. As for F-Fe codoped TiO$_2$, the optimized F-Fe bond length is 1.966 Å, 1.9% of distortion compared with that of the pure TiO$_2$, which is smaller than the distortions of both F-Ti and Fe-O bond length (3.6% and 2.8%, resp.). S-Fe bond length (1.979 Å) in Fe-S codoped TiO$_2$ is longer than that of F-Fe (1.966 Å), which is due to the bigger atom radius of S than that of F. The distortion of optimized S-Fe band length (2.5%) is smaller than that of both S-Ti and Fe-O bond length (11.2% and 2.8%, resp.) in S and Fe mono-doped TiO$_2$. The smaller distortion of codoped TiO$_2$ is in connection with the smaller formation energy, and this should be ascribed to the synergetic effect of codoping.

3.2. Electronic Structures. To clarify how the dopants modify the electronic structure of TiO$_2$, we calculate the total density of states (DOS) and partial density of states (PDOS) of bulk TiO$_2$ and doped TiO$_2$ shown in Figure 2. For pure TiO$_2$ (Figure 2(a)), the calculated band gap is 1.90 eV, which is consistent with the previous theoretical studies [33]. Although the theoretical band gap is smaller than the experimental value (3.2 eV) due to the well-known shortcoming of GGA, it is reasonable to analyze the relative variations of the electronic structure without considering the exact band gap value. We can see from Figure 2(a) that the top of the valence band (VBM) of pure TiO$_2$ consists mainly of O 2p states, while the bottom of the conduction band (CBM) is dominated by Ti 3d states.

After substitution of fluorine for oxygen atom (Figure 2(b)), the Fermi level is pinned at the bottom of the conduction band which shows a donor character because of one more electron of F than that of host O. The PDOS (Figure 2(b’)) shows that most of F 2p states are delocalized in the lower-energy range of VB and do not contribute to the band edge and may not lead to the absorption of visible light. Figure 2(c) shows that incorporation of iron into the lattice results in localized gap states. The Fermi level is pinned at the down-spin orbit of the gap states, which shows half-metallic character. Further projected density of states (PDOS) as shown in Figure 2(c’) predicates that the minority- and majority-spin states within the gap are mainly attributed to Fe 3d. The impurity states induced above the VBM, below the CBM, and in the forbidden gap are beneficial to the visible light absorption. Figure 2(d) is the DOS of S-doped TiO$_2$, and the VBM has a little shift. From the calculated PDOS of Figure 2(d’), the valence band is composed mainly of O 2p, and the conduction band is mainly Ti 3d. The localized states are generated by S 3p about 0.7 eV above the VBM relative to the undoped one. The excitation from these occupied S 3p states to conduction band might lead to a decrease of the photon excitation energy and induce more significant red shift of absorption, which is consistent with experimental absorption spectra measurements. However, the localized gap states in the middle of the forbidden band in Fe-doped TiO$_2$ provide recombination center of photogenerated electron-hole pair, which is detrimental to the photocatalytic activity. The improvement of photocatalytic activity originating from visible light absorption is weakened by the increase of
recombination of the carriers and eventually limits the great enhancement of photocatalytic activity.

For Fe-F codoped TiO$_2$ (Figure 3(a)), localized impurity states are introduced between VBM and CBM. The PDOS in Figure 3(a') demonstrates that three gap states mainly stem from Fe 3$d$ orbital. The energies needed for electrons excitation from two occupied up-spin states to the CBM are 1.6 and 0.9 eV, respectively, while the energy from down-spin state to CBM is 0.5 eV. Hence, the electron transition from these impurity energy levels to the conduction band would lead to an obvious reduction of absorption energy. Our results give a good explanation for the experimentally observed red shift of absorption edge of the Fe-F codoped anatase TiO$_2$ [18]. However, as the Fe mono-doped structure, localized states introduced in the middle of the forbidden band can lead to the recombination of electro-hole pair and thus do harm to the photocatalytic activity. Therefore, even though codoping with Fe and F may promote the incorporation of dopants into the TiO$_2$ host lattice, it will not have pronounced enhancement in the photocatalytic activity compared with Fe-doped TiO$_2$.

When Fe and S are introduced into TiO$_2$ simultaneously, more obvious spin polarization can be observed in the band edge compared with mono-doped TiO$_2$ and localized gap states appear about 0.2 eV above the valence band with width of 0.4 eV and 0.2 eV below the conduction band with width of 0.6 eV (Figure 3(b)). The bandwidth decreases to 1.7 eV, 0.2 eV smaller than that of pure TiO$_2$, and the Fermi level is pinned in the gap states located below the conduction band due to the slight break of the charge neutrality by Fe-S codoping. Electron excitation from VBM to the gap states and CBM could lead to the visible light absorption as observed in experiment [17]. The PDOS shown in Figure 3(b') indicates that the gap states above the valence band are the mixing of Fe 3$d$, O 2$p$, and S 3$p$ orbitals while the states below the CBM are mainly hybridization of Fe 3$d$ and O 2$p$. The formation energy reduction is found in both Fe-F and Fe-S codoped TiO$_2$ which could enhance the solubility of dopants in the host lattice. Furthermore, the codoping of Fe and S produces extended states near the band edge and does not induce localized states in the center of the gap that often act as recombination centers. This electronic structure could enhance the visible light absorption and reduce the recombination of photogenerated electron-hole pairs. Moreover, the impurity states near the band edge are more extended than those of mono-doped and Fe-F-doped structures, which
means that electron excitation between the valence band (conduction band) and impurity states can be more intense, and consequently the intensity of visible light absorption can be stronger. It should be mentioned that the mobility of the photocarriers in the impurity states is lower than that in the valence band of pure TiO$_2$; however, the impurity states near the band edge can also act as electron/hole traps, which reduces the recombination of photocarriers. Additionally, since the oxidation (reduction) power of photogenerated holes (electrons) in the gap states is reduced relative to that in the VB (CB) of pure TiO$_2$, one should accommodate a balance between the oxidation (reduction) power and visible light absorption of the photocatalysts.

Based on these analyses, we conclude that the Fe-S codoped TiO$_2$ could possess the best photocatalytic activity under visible light irradiation among the Fe mono-doped and Fe-F, Fe-S codoped structures.

4. Conclusions

We have examined the crystal structures and electronic and optical properties of Fe-F and Fe-S codoped anatase TiO$_2$ based on DFT calculations. For comparison, Fe, S, and F single-doped TiO$_2$ are also studied. Formation energy of the codoped system is much lower than that of the mono-element doping indicating the synergic effects of codopants on the stability of the doped structure. The calculated results indicate that the codoped atoms introduce impurity energy levels in the band gap mainly composed of Fe 3d states. Due to the less energy needed for an electron transition from the impurity energy levels to the conduction band bottom, codoped anatase TiO$_2$ may show higher photocatalytic activity than the mono-doped one under visible light, which may account for the experimentally observed phenomenon. However, Fe-F codoping introduced localized gap states which may result in visible light absorption but decline the photocatalytic activity. Compared with Fe-F codoping, Fe-S codoped TiO$_2$ produces gap states near the band edge that are extended and may greatly enhance the visible light absorption and reduce the carrier recombination. Consequently, the photocatalytic performance under visible light of Fe-S codoped TiO$_2$ is better than that of Fe-F codoped one, and Fe-S should be a better codoping pair.

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