Research Article

Electronic Structures of S/C-Doped TiO₂ Anatase (101) Surface: First-Principles Calculations

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The electronic structures of sulfur (S) or carbon (C)-doped TiO₂ anatase (101) surfaces have been investigated by density functional theory (DFT) plane-wave pseudopotential method. The general gradient approximation (GGA) + *U* (Hubbard coefficient) method has been adopted to describe the exchange-correlation effects. All the possible doping situations, including S/C dopants at lattice oxygen (O) sites (anion doping), S/C dopants at titanium (Ti) sites (cation doping), and the coexisting of anion and cation doping, were studied. By comparing the formation energies, it was found that the complex of anion and cation doping configuration forms easily in the most range of O chemical potential for both S and C doping. The calculated density of states for various S/C doping systems shows that the synergistic effects of S impurities at lattice O and Ti sites lead a sharp band gap narrowing of 1.35 eV for S-doped system comparing with the pure TiO₂ system.

1. Introduction

Many researchers have paid much attention on titanium dioxide (TiO₂). As a promising photocatalytic semiconductor for environmental treatment, it has excellent functionality, long-term stability, and nanotoxicity [1]. However, TiO₂ is a kind of wide band gap semiconductor (3.2 eV for anatase phase and 3.0 eV for rutile phase [2]). It needs ultraviolet (UV) radiation to excite the electrons from valence band (VB) to conduction band (CB). Unfortunately, the energy of UV light accounts for only small fraction of the sunlight. Then, how to enhance the ability of visible light (VIS) absorption of TiO₂ is critical to enable the utility of TiO₂ photocatalyst materials.

Many efforts have been made to achieve this purpose, including introducing metal or nonmetal species for doping. S and C species are special among nonmetal species. For these two species, both cation and anion doping could be formed in TiO₂. The group of Umebayashi [3, 4] have synthesized S-doped TiO₂ by ion implantation and oxidation annealing

of TiS₂. They found that the S atoms occupied oxygen sites to form Ti-S bonds and lead a decrease in the band-gap energy. Based on the theoretical analyses using *ab initio* band calculations, they thought that mixing of the S 3p states with the valence band contributes to the band gap narrowing. Ohno's group [5] have synthesized S-doped TiO₂ photocatalysts chemically in which S (S⁴⁺) substitute some of the lattice titanium atoms, which showed strong absorption for visible light and high activities for degradation of methylene blue, 2-propanol in aqueous solution, and partial oxidation of adamantane under irradiation at wavelengths longer than 440 nm. Long et al. [6] have discussed the structural and electronic properties of S-doping configurations by substitution and adsorption at the rutile TiO₂ (110) surface with first-principles density functional theory calculations. Their results indicate that S dopants replace surface O atoms or bind to Ti atoms preferentially. S-cation doping led to relatively small reductions of the photon transition energy, while S-anion doping and adsorption on the surface resulted in significant red shifts of the optical absorption edge. For

C-doped TiO_2 , some experimental researches have been done by Nakano et al. [7]. They have prepared C-doped TiO_2 film by oxidative annealing of sputtered TiC films at 550°C in flowing O_2 gas. Deep-level optical spectroscopy measurements revealed three deep levels located at 0.86, 1.30, and 2.34 eV below the CB. They thought the 2.34 eV band introduced by the C-doping contributes to band gap narrowing by mixing with the O 2p valence band. Both anion doping and cation doping have been studied by Kamisaka et al. [8] for C-doped TiO_2 . It was found that neither in-gap impurity states nor visible-light absorbance were observed in the case of cation doping, while a density-of-states analysis revealed three in-gap impurity states for anion doping. Kesong et al. [9] have also discussed the structural and electronic properties of two possible substitutional carbon-doped structures of anatase and rutile TiO_2 . They found that the band gap changes slightly for C-anion doping and the optical absorption energy is reduced by about 0.18 and 0.3 eV for cation C-doped anatase and rutile TiO_2 , respectively. Lee et al. [10] presented first-principles density-functional calculations for the electronic properties anion C-doped TiO_2 . They found that three C 2p bands appear in the band gap; they were located at 0.52, 0.96, and 1.48 eV away from the VB maximum of TiO_2 . The energy gap between the highest O 2p band and the lowest Ti 3d band is 2.42 eV, close to 2.39 eV in undoped TiO_2 .

However, these theoretical and experimental studies are not enough to give a clear insight of the real mechanism for VIS sensitivity of S/C-doped TiO_2 . In this paper, we demonstrated a relatively more comprehensive investigation on the effects of S/C impurities on the electronic structures of TiO_2 . Firstly, the surface models were adopted to calculate the band structure of S/C-doped TiO_2 anatase. To our opinion, the surface model is more suitable to simulate synthesized powder or film samples than bulk model. Of the anatase single-crystalline surfaces, the (101) surface is the predominant face that is exposed on anatase minerals and polycrystalline powders, and theory calculations also show that it is thermodynamically the low-energy surface [1, 11]. Moreover, besides the isolated anion and cation doping that have been discussed in our calculations, the case of anion and cation codoping with two S/C atoms (lattice O and Ti atoms are replaced by S/C atoms synchronously) has also been studied. Furthermore, because the local density approximation (LDA) and general gradient approximation (GGA) which are generally used to describe the exchange-correlation effects always lead to a severe underestimation of the band gap [12] for transition metal oxides, GGA + U (Hubbard coefficient) was used in this present work to compensate for the limitation for those strongly correlated systems [13] which introduces an additional term based on a simple Hubbard model for electron on-site repulsion.

2. Methods and Models

2.1. Computational Details. The computational calculations have been performed by density-functional theory (DFT) plane-wave pseudopotential method [14], as implemented in the CASTEP 5.0 codes [15]. GGA + U was used for describing

the exchange-correlation effects. Within GGA + U , the Coulomb correlation interaction of Ti 3d electrons has been taken into account. The $U = 8.50$ eV of Ti 3d electrons was adopted in all energy calculations which has been confirmed by our previous works [16–18]. The ultrasoft pseudopotential was used to describe electron-ion interactions. The kinetic energy cutoff for the plane-wave basis was chosen as 380.0 eV. The Brillouin zone sampling was restricted to the point in surface geometry optimization. In energy calculations, it was set to $1 \times 2 \times 4$. Structure optimization was performed by minimizing the total energy and the ionic force, until all the components of the residual forces were less than $0.01 \text{ eV} \cdot \text{\AA}^{-1}$. The energy and the displacement tolerance were set to $5.0 \times 10^{-6} \text{ eV} \cdot \text{atom}^{-1}$ and $5.0 \times 10^{-4} \text{ \AA}$, respectively.

2.2. Models. The TiO_2 (hereafter referring to the anatase structure exclusively) (101) surfaces were modeled by vacuum slabs. According to our previous computational results [19] and some references [20, 21], we have selected a slab of $\text{Ti}_{24}\text{O}_{48}(\text{TO})$ with surface area of $11.15 \times 7.55 \text{ \AA}^2$ and slab thickness of 3 layers (see Figure 1(a)). The surface species, namely, the bridging two-fold coordinated oxygen atom ($\text{O}_{2\text{C}}$), three types of three-fold coordinated oxygen atom ($\text{O}_{3\text{C}}^1$, $\text{O}_{3\text{C}}^2$, and $\text{O}_{3\text{C}}^3$), and five/six-fold coordinated titanium atoms ($\text{Ti}_{5\text{C}}$ and $\text{Ti}_{6\text{C}}$), are denoted in Figure 1(a) as well.

The models of anion doping surfaces $\text{Ti}_{24}\text{O}_{47}\text{S}(\text{A-STO})$ and $\text{Ti}_{24}\text{O}_{47}\text{C}(\text{A-CTO})$ were built by replacing a surface oxygen atom with a sulfur or carbon atom in the slab of TO (the configuration of an S or C atom substituting an O atom is denoted S_O or C_O). There are four types of surface oxygen site, namely, the $\text{O}_{2\text{C}}$, $\text{O}_{3\text{C}}^1$, $\text{O}_{3\text{C}}^2$, and $\text{O}_{3\text{C}}^3$ site (as shown in Figure 1(a)), for a sulfur or carbon atom to substitute. For the models of cation doping surfaces $\text{Ti}_{23}\text{SO}_{48}(\text{C-STO})$ and $\text{Ti}_{23}\text{CO}_{48}(\text{C-CTO})$, there are two possible surface sites, $\text{Ti}_{5\text{C}}$ and $\text{Ti}_{6\text{C}}$ site, for a sulfur or carbon atom to substitute (the configuration of a S or C atom substituting a Ti atom is denoted S_{Ti} or C_{Ti}). By comparing the total energy of the optimized slabs for S/C doping (the values are shown in Table 1), it was clear that the $\text{O}_{2\text{C}}$ site and $\text{Ti}_{5\text{C}}$ site are energetically favored for anion and cation doping, respectively. Long's results also show that S dopants replace surface O atoms preferentially [6].

Figures 2(a), 2(b), 2(d) and 2(e) exhibit the relaxed configurations of S_O , C_O and S_{Ti} , C_{Ti} . It can be seen from the structures that S atom substituting Ti atom at $\text{Ti}_{5\text{C}}$ site (see Figure 2(d)) and C substituting O atom at $\text{O}_{2\text{C}}$ site (see Figure 2(b)) do not lead significant lattice distortion, while substitutional S atom at $\text{O}_{2\text{C}}$ site extends upwards and tends to leave the surface (see Figure 2(a)) and substitutional C atom at $\text{Ti}_{5\text{C}}$ site seems to be attracted by O atoms at $\text{O}_{2\text{C}}$ and $\text{O}_{3\text{C}}^3$ site strongly (see Figure 2(e)), forming two short C–O bond with distance of 1.360 and 1.387 $\text{\AA}$, which is consistent with [6].

According to the above discussions, the model of anion and cation codoping surface with two S atoms, $\text{Ti}_{23}\text{SO}_{47}\text{S}(\text{AC-STO})$, or that with two C atoms, $\text{Ti}_{23}\text{CO}_{47}\text{C}(\text{AC-CTO})$, was created by one S or C atom substituting an O atom at $\text{O}_{2\text{C}}$ site and the other S or C atom substituting a Ti atom

FIGURE 1: (a) Relaxed structure of $\text{Ti}_{24}\text{O}_{48}$ surface cell (TO) with surface area of $11.15 \times 7.55 \text{ \AA}^2$, the first layer is in the dashed line. (b) Relaxed structure of the first layer of TO, the bond length of $\text{Ti}_{5\text{C}}$ with its neighboring O atoms and $\text{O}_{2\text{C}}$ with its neighboring Ti atoms are labeled. Ti and O atoms are represented by grey and red spheres, respectively.

TABLE 1: Energy differences for S and C dopant at different substitutional doping site on TiO_2 anatase (101) surface. A-STO and A-CTO denote anion doping surfaces $\text{Ti}_{24}\text{O}_{47}\text{S}$ and $\text{Ti}_{24}\text{O}_{47}\text{C}$; C-STO and C-CTO denote cation doping surfaces $\text{Ti}_{23}\text{SO}_{48}$ and $\text{Ti}_{23}\text{CO}_{48}$, respectively.

	Substitutional doping site					
	$\text{O}_{2\text{C}}$	$\text{O}_{3\text{C}}^1$	$\text{O}_{3\text{C}}^2$	$\text{O}_{3\text{C}}^3$	$\text{Ti}_{5\text{C}}$	$\text{Ti}_{6\text{C}}$
A-STO	0.00	0.45	1.51	2.47	—	—
A-CTO	0.00	0.06	0.17	0.21	—	—
C-STO	—	—	—	—	0.00	1.16
C-CTO	—	—	—	—	0.00	1.13

Unit: eV.

at $\text{Ti}_{5\text{C}}$ site in the slab of TO. For the case of coexistent S_O and S_{Ti} ($\text{S}_\text{O} + \text{S}_{\text{Ti}}$) or C_O and C_{Ti} ($\text{C}_\text{O} + \text{C}_{\text{Ti}}$) on TO surface, there are four $\text{Ti}_{5\text{C}}$ sites around a $\text{O}_{2\text{C}}$ site, which could be distinguished by distance, namely, the nearest one, the next nearest one, the next next nearest one, and the farthest one. For S doping, the total energy differences are 0.14, 0.08, 0.07, and 0.00 eV of the optimized slabs, for C doping, and the total energy differences are 0.00, 0.04, 0.07, and 0.12 eV of each optimized configuration. It was found that S_O and S_{Ti} tend to be apart, while C_O and C_{Ti} tend to be close; the optimized C–C bond length is only 1.360 Å. Figures 2(c) and 2(f) exhibit the relaxed configuration of $\text{S}_\text{O} + \text{S}_{\text{Ti}}$ and $\text{C}_\text{O} + \text{C}_{\text{Ti}}$.

3. Results and Discussion

3.1. Defect Formation Energy. In order to evaluate the relative stability of various doping configurations under deferent oxygen atmosphere, the defect formation energies (E_f) of each doping configuration as a function of O chemical potential ($\mu(\text{O})$) has been calculated and the results were exhibited in Figure 3. Taking S doping, for example, the calculation scheme was displayed as follows.

Firstly, for the neutral S_O , S_{Ti} defect, and the complex $\text{S}_\text{O} + \text{S}_{\text{Ti}}$ defect, the substitutional formation energies are calculated as the following equations [22]:

$$\begin{aligned}
 E_f(\text{S}_\text{O}) &= E(\text{A-STO}) - E(\text{TO}) - \mu(\text{S}) + \mu(\text{O}) \\
 E_f(\text{S}_{\text{Ti}}) &= E(\text{C-STO}) - E(\text{TO}) - \mu(\text{S}) + \mu(\text{Ti}) \\
 E_f(\text{S}_\text{O} + \text{S}_{\text{Ti}}) &= E(\text{AC-STO}) - E(\text{TO}) \\
 &\quad - 2\mu(\text{S}) + \mu(\text{Ti}) + \mu(\text{O}),
 \end{aligned} \tag{1}$$

where $E(\text{TO})$, $E(\text{A-STO})$, $E(\text{C-STO})$, and $E(\text{AC-STO})$ are the total energies of TO, A-STO, C-STO, and AC-STO, respectively. $\mu(\text{S})$, $\mu(\text{Ti})$, and $\mu(\text{O})$ are the chemical potentials of S, Ti, and O atom, respectively.

Nextly, the atom chemical potentials of Ti and O must satisfy the boundary conditions $\mu(\text{O}) \leq 1/2\mu(\text{O}_2)$ and $\mu(\text{Ti}) \leq \mu(\text{Ti metal})$, where $\mu(\text{O}_2)$ and $\mu(\text{Ti metal})$ are the chemical potentials of oxygen gas and titanium metal, respectively.

FIGURE 2: Relaxed structure of the first layer of S/C-doped surfaces: (a) $\text{Ti}_{24}\text{O}_{47}\text{S}$ (A-STO), (b) $\text{Ti}_{23}\text{SO}_{48}$ (C-STO), (c) $\text{Ti}_{23}\text{SO}_{47}\text{S}$ (AC-STO), (d) $\text{Ti}_{24}\text{O}_{47}\text{C}$ (A-CTO), (e) $\text{Ti}_{23}\text{CO}_{48}$ (C-CTO), and (f) $\text{Ti}_{23}\text{CO}_{47}\text{C}$ (AC-CTO). The bond length of S or C dopants with its neighboring Ti or O atoms is labeled. Ti and O atoms are represented by grey and red black spheres, respectively. Substitutional S and C dopants are represented by yellow and green spheres.

Under the oxygen-rich (metal-poor) condition, $\mu(\text{O})$ is set as $1/2\mu(\text{O}_2)$. While, under the oxygen-poor (metal-rich) condition, $\mu(\text{Ti}) = \mu(\text{Ti metal})$. Correspondingly $\mu(\text{Ti})$ or $\mu(\text{O})$ is derived from the relation $\mu(\text{Ti}) + 2\mu(\text{O}) = \mu(\text{TiO}_2 \text{ bulk})$ [23–25]. $\mu(\text{TiO}_2 \text{ bulk})$ is the chemical potentials of TiO_2 anatase bulk.

Figure 3(a) exhibits the formation energies of S_O , S_Ti and the complex $\text{S}_\text{O} + \text{S}_\text{Ti}$, as a function of $\mu(\text{O})$, with the zero of the vertical scale corresponding to the formation energy of S_Ti . $E_f(\text{S}_\text{O} + \text{S}_\text{Ti})$ is always lower than $E_f(\text{S}_\text{Ti})$, only under the sufficient O-poor (Ti-rich) growth condition; $E_f(\text{S}_\text{O} + \text{S}_\text{Ti})$ is larger than $E_f(\text{S}_\text{O})$, which indicates that in the most range of $\mu(\text{O})$, the complex $\text{S}_\text{O} + \text{S}_\text{Ti}$ forms much more easily. Thus, S_O and S_Ti could be created synchronously in S-doped TiO_2 samples.

For the case of C doping, the defect formation energies are calculated in the same way. Figure 3(b) shows the formation energies of C_O , C_Ti and the complex $\text{C}_\text{O} + \text{C}_\text{Ti}$, as a function of $\mu(\text{O})$, with the zero of the vertical scale corresponding to the formation energy of C_Ti . Namely, in the most range of $\mu(\text{O})$, $E_f(\text{C}_\text{Ti})$ is lower than $E_f(\text{C}_\text{O})$ and $E_f(\text{C}_\text{O} + \text{C}_\text{Ti})$ is always the lowest in all the range of $\mu(\text{O})$, which shows that isolated C_Ti

forms more easily than isolated C_O and $\text{C}_\text{O} + \text{C}_\text{Ti}$ has the most possibility to be on the C-doped TiO_2 surfaces.

3.2. Electronic Structures of Substitutional S/C-Doped Surfaces.

The density of the states (DOS) for TO is shown in Figure 4, with the Fermi level being 0 eV on the energy axis. For the pure surface TO, the calculated band gap energy is about 2.64 eV which is smaller than 3.2 eV calculated for bulk structure. The valence band (VB) consists of Ti 3d and O 2p orbits with the width of 5.40 eV, and the conductive band (CB) consists of Ti 3d states mainly.

The calculated partial density of the states (PDOS) of S-doped surfaces is shown in Figure 5. In the PDOS of A-STO (Figure 5(a)), S 3p states are localized; a part of them are lying at the Fermi level and adjacent to the TiO_2 VB maximum, which leads an expansion of VB from 5.40 to 5.80 eV. The electron excitation energy from the occupied VB states to the CB minimum shortens to 2.00 eV. However, in the PDOS of C-STO (see Figure 5(b)), the majority of S 3p states locates far away from the Fermi level; only a few of them disperse and mix with O 2p and Ti 3d VB states. There is a slight change for

FIGURE 3: (a) The formation energies of the S_{Ti} , S_O , and $S_{Ti} + S_O$ complexes as a function of O chemical potential. The zero in the vertical axis corresponds to the formation energy of S_{Ti} . (b) The formation energies of the C_{Ti} , C_O , and $C_{Ti} + C_O$ complexes as a function of O chemical potential. The zero in the vertical axis corresponds to the formation energy of C_{Ti} .

FIGURE 4: Density of the states (DOS) calculated for the pure surface $Ti_{24}O_{48}(TO)$. Fermi level is at 0 eV and U is 8.50 eV for Ti 3d electrons.

the band gap energy from 2.64 eV to 2.45 eV. The conclusion accords with [6] that S-anion doping leads significant red shifts of the optical absorption edge.

For the AC-STO, the PDOS (Figure 5(c)) shows that the localized S 3p states introduced by S dopant at O_{2C} site still appear at the top of VB, and S dopant at Ti_{5C} site provides some localized 3p states at the bottom of CB; thus the width of VB states expands to 6.10 eV and the band gap energy decreases to 1.45 eV, which indicates a great decrease of excited energy for electronic transition

and a red shift of the optical absorption for S-doped TiO_2 . Obviously, the electronic properties of codoped systems are not a mechanical mixture of those of both single-doped systems, but the coupling contribution of surface S impurities at O_{2C} and Ti_{5C} sites, which is consistent with [26, 27].

The calculated PDOSs of C-doped surfaces are shown in Figure 6. Figure 6(a) exhibits the PDOS of A-CTO. A part of localized C 2p states locate at the TiO_2 VB maximum, which leads a slight expansion of VB from 5.40 to 5.50 eV, the band gap energy has a very small shortness of 0.14 eV. Additionally, another part of localized C 2p is lying in the gap and 1.70 eV away from the Fermi level. In the PDOS of C-CTO (Figure 5(b)), C dopants do not introduce any states around the Fermi level, and the calculated band gap energy is almost equal to that of TO. These conclusions are similar with [8].

For the AC-CTO, the PDOS (Figure 6(c)) shows that the C dopant at O_{2C} site still provides two parts of localized 2p states: one is at the bottom of VB and the other is in the gap, 1.23 eV away from the Fermi level. The band gap energy decreases from 2.64 eV to 2.23 eV, and the VIS absorption of C-doped TiO_2 could be improved by the decrease of intrinsic absorption energy. On the other hand, extrinsic absorption from VB states to unoccupied gap states contributes to the VIS sensitivity of C-doped TiO_2 , either. However, the gap states may also act as the electron-cavity recombination centers, thus reducing the photocatalytic efficiency.

4. Conclusions

In this present work, all spin-polarized density-functional theory plane-wave pseudopotential method has been adopted to investigate the electronic properties of TiO_2 anatase (101) surfaces with S and C doping. GGA + U (Hubbard

FIGURE 5: Density of the states (DOS) calculated for S-doped surfaces: (a) $\text{Ti}_{24}\text{O}_{47}\text{S}$ (A-STO), (b) $\text{Ti}_{23}\text{SO}_{48}$ (C-STO), and (c) $\text{Ti}_{23}\text{SO}_{47}\text{S}$ (AC-STO). Fermi level is at 0 eV and U is 8.50 eV for Ti 3d electrons. The 3p states of S dopant at $\text{O}_{2\text{C}}$ site and that of S dopant at $\text{Ti}_{5\text{C}}$ site are represented by dark grey and black area, respectively.

FIGURE 6: Density of the states (DOS) calculated for C-doped surfaces: (a) $\text{Ti}_{24}\text{O}_{47}\text{C}$ (A-CTO), (b) $\text{Ti}_{23}\text{CO}_{48}$ (C-CTO), and (c) $\text{Ti}_{23}\text{CO}_{47}\text{C}$ (AC-CTO). Fermi level is at 0 eV and U is 8.50 eV for Ti 3d electrons. The 2p states of C dopant at $\text{O}_{2\text{C}}$ site and that of C dopant at $\text{Ti}_{5\text{C}}$ site are represented by dark grey and black area, respectively.

coefficient) method has been used to describe exchange-correlation effects. For the case of S doping, our calculations demonstrated that the formation energy of the complex $\text{S}_{\text{O}} + \text{S}_{\text{Ti}}$ is lower than that of the isolated S_{Ti} or S_{O} in the most range of chemical potentials of O, which indicates that the complex $\text{S}_{\text{O}} + \text{S}_{\text{Ti}}$ may form more easily under most of conditions for S-doped TiO_2 . The calculated density of the states of anion and cation codoping surface AC-STO shows that there is a sharp decrease for the band gap energy from 2.64 to 1.45 eV due to

the synergistic effect of S_{O} and S_{Ti} defects. Thus, the ability of VIS absorption for S-doped TiO_2 could be improved greatly. For the case of C doping, the formation energy of the complex $\text{C}_{\text{O}} + \text{C}_{\text{Ti}}$ is the lowest in all the range of chemical potentials of O. The calculated density of the states of anion and cation codoping surface AC-CTO also shows a decrease for the band gap energy from 2.64 to 2.23 eV and the VIS absorption could be improved by the decrease of intrinsic absorption energy appreciably, but the gap states induced by C_{O} defect may act

as the electron-cavity recombination centers, thus reducing the photocatalytic efficiency.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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