Physics Letters A 380 (2016) 1462–1468

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Discussion

Investigation on the electronic structures and optical performances of Si–S codoped anatase TiO_2 by first-principles calculation

S.W. Zhou [a,b], P. Peng [a,*], J. Liu [a,c], Y.H. Tang [a], B. Meng [d], Y.X. Peng [b]

[a] School of Materials Science and Engineering, Hunan University, Changsha 410082, China
[b] College of Materials and Chemical Engineering, Hainan University, Haikou, 570228, China
[c] College of Electrical and Information Engineering, Hunan Institute of Engineering, Xiangtan 411105, Hunan, China
[d] College of Physics and Electronic Engineering, Kaili University, Kaili 556011, China

ARTICLE INFO

Article history:
Received 4 October 2015
Received in revised form 20 January 2016
Accepted 8 February 2016
Available online 15 February 2016
Communicated by R. Wu

Keywords:
Anatase TiO_2
Electronic structure
Optical properties
First-principles

ABSTRACT

The electronic and optical properties of Si and/or S (co)doped anatase TiO_2 are investigated by density function theory plus U calculations. Results show that the synergistic effects of Si and S codoping result in higher visible-light absorption compared with pure and Si or S monodoped TiO_2. Moreover, with increasing S doping concentration, the band gap of Si/S-codoping system becomes narrower, and simultaneously the band edge positions may be suitable for water splitting. Additionally, the defect formation energy calculations indicate that Si doping can enhance the thermal stability of TiO_2 under O-rich condition.

1. Introduction

As a versatile wide-gap oxide semiconductor, titanium dioxide (TiO_2) has received intense attention for applications in the field of photocatalysts, water splitting, renewable energy and solar cells because of its excellent properties, such as low cost, nontoxic, high oxidizing power, and long-term stability [1–3]. However, its wide intrinsic band gap of TiO_2 (3.2 eV for anatase phase and 3.0 eV for rutile phase) only allows it to absorb the ultraviolet (UV) light, which accounts for only a small portion of solar energy (approximately 5%), in contrast to visible light for a major part of solar energy (approximately 45%). Therefore, to effectively utilize the cheaper visible light, a great deal of efforts have been devoted to extending the spectra response of TiO_2 to visible light by various strategies, such as dye sensitizing [4], heterostructure [5], impurity doping [6,7], semiconductor compounding [8], etc. In these methods, monodoping with metal (Bi, Fe, Ce, Cr, Al, etc.) [9–13] and nonmetal (B, C, N, Si, S, etc.) [14–18] atoms into TiO_2 were proved to be one of the effective means to improve the visible light absorption of photocatalyst. However, there still are some drawbacks by monodoping. For instance, noble metal doping has little effect on extending the light absorption into visible region [11]; transition-metal-doping leads to a high recombination rate of electron–hole pairs [19]; and nonmetal doping is vulnerable to its thermal stability [16].

Recently, many attempts were commonly used for the metal–nonmetal codoping approach to overcome the above-mentioned disadvantages of monodoped TiO_2. For instance, Lin et al. [19] reported the synergistic effects of Si and Fe codoping can lead to higher visible-light photocatalytic activity than that of pure and monodoped TiO_2. On the other hand, the nonmetal–nonmetal codoping strategy has also been evoking the interest of researchers. For example, very recently, Ju et al. [20] have succeeded in synthesizing (N,S)-codoped TiO_2 by hydrothermal method, showing high visible light absorption. Shi and co-workers [21] discovered that (Si,N)-codoped anatase TiO_2 exhibits high photocatalytic activity under visible light irradiation, and they attributed this phenomenon to the effect of Si and N, which leads to enhanced the lifetime of photo-generated holes and changing the unoccupied N 2p states to occupied states. More interestingly, Long et al. [22] in recent study further indicated that with increasing the N doping concentration, the (Si,N)-codoping system could exhibit a higher visible-light photoactivity, which is strongly correlated to double-hole coupling rather than high doping concentrations and spin effect.

Sulfur and silicon as two effective dopants in modifying the electronic structure of TiO_2 have been extensively studied by both experimental and theoretical methods [17–24]. However, to date, there are few experimental and theoretical studies concerned with Si/S-codoped TiO_2 used as visible-light-activated photocatalysts,

* Corresponding author. Tel.: +86 13873119465.
E-mail address: ppeng@hnu.edu.cn (P. Peng).

http://dx.doi.org/10.1016/j.physleta.2016.02.012
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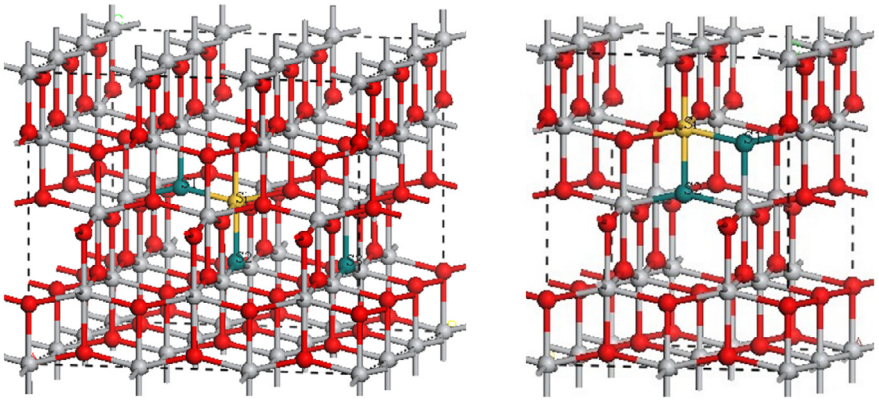

Fig. 1. Perspective view of the $3 \times 3 \times 1$ supercell (a) and $2 \times 2 \times 1$ supercell (b) for Si and S (co)doped anatase TiO_2 showing the location of the dopants. The doping sites of S are marked as blue balls with the symbols of S1, S2 and S3, while the Si doping site is denoted by a yellow ball. The red and grey balls represent O and Ti atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

besides the research of Chen et al. [25]. They suggested that the synthesis of silicon-doped mesoporous anatase SO_4^{2-}/TiO_2 sample has an excellent photocatalytic activity and its thermal stability is improved. In this work, the electronic and optical properties of Si/S-codoped TiO_2 were investigated using the first-principles calculation. We attempt to reveal the mechanism of synergistic effects of Si/S codoping and elucidate the origin of the enhanced visible-light photocatalytic activity.

2. Calculation models and computational details

The crystal of anatase TiO_2 has a tetragonal structure with $I4_1/amd$ space group and D_{4h}^{19} symmetry. Its primitive unit cell includes 12 atoms, four Ti atoms and eight O atoms. We simulated the various doping systems by using a 108-atom anatase supercell with a $3 \times 3 \times 1$ repetition, which were modeled by substitution of one Si atom at Ti lattice and/or single or double S atoms at O lattice sites. As demonstrated in Fig. 1(a), we considered several possible configurations of Si/S-codoped TiO_2, which are denoted by (Si,S1)–TiO_2, (Si,S2)–TiO_2, (Si,S3)–TiO_2, (Si,S1S2)–TiO_2, (Si,S1S3)–TiO_2 and (Si,S2S3)–TiO_2. After the geometry optimization and energy calculations, the calculated results show that the sequence of the total energy values for the above-named configurations are −87675.150, −87674.885, −87674.892, −87514.1597, −87514.459, −87514.266 eV, respectively. The lowest energy configuration, i.e. (Si,S1)–TiO_2, imply that Si and S atoms by setting in the nearest lattice sites in TiO_2 crystals lead to more favorable energetics, which is similar with the reports of several groups [21,22]. Compared with the configurations of (Si,S1S2)–TiO_2 and (Si,S2S3)–TiO_2, (Si,S1S3)–TiO_2 manifests more stable, which may be ascribed to the fact that the distance between the two doping S atoms is slightly longer than that of the other configurations. Herein, in the process of electronic structure and optical performances calculations, we only take into account of the configurations of (Si,S1)–TiO_2 and (Si,S1S3)–TiO_2. For comparison, the monodoping models of S1–TiO_2 and Si–TiO_2 were also considered. To study the size effect, we further employed a $2 \times 2 \times 1$ supercell to simulate the codoping system, which was named as (Si,S1S2)*–TiO_2, shown in Fig. 1(b).

In this work, the density functional theory (DFT) calculations were performed using the Cambridge serial total energy package (CASTEP) program code [26], in which a plane-wave basis set was used. The Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation (GGA) was used for the exchange-correlation functional [27]. In order to obtain accurate electronic structures and optical properties, the GGA + U approach has been used for the treatment of strong on-site Coulomb repulsion among the localized Ti 3d electrons. On the basis of some literatures [11,19] and our test results, the U value was set to be 8.0 eV for the 3d orbital of Ti atoms. Electron–ion interactions were described by ultrasoft pseudopotentials with valence electron configurations of $3s^23p^63d^24s^2$ for Ti atom, $2s^22p^4$ for O atom, $3s^23p^2$ for Si atom, and $3s^23p^4$ for S atom. The plane-wave expansion was truncated by the cutoff energy of 380 eV and the Monkhorst–Pack k-points samplings were set as $3 \times 3 \times 3$. In the calculation of self-consistent field (SCF), the Pulay scheme of density mixing [28] was utilized. All atoms of the structures were fully relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [29]. Geometry optimization was carried out before single point energy calculations, and the energy change, maximum force, maximum stress, and maximum displacement tolerances were set as 5.0×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 0.0005 Å, respectively. Electronic structures and total energies were calculated on the basis of the optimized crystal geometries. In order to obtain comparable results with the experiment, unpolarized polycrystalline models and the scissors operator [30] of 0.049 eV were carried out in computations of optical properties.

3. Results and discussions

3.1. Crystal structure

By optimizing the pure anatase TiO_2 supercell, we attained the lattice parameters of the unit cell as follows: $a = b = 3.789$ Å, $c = 9.797$ Å (listed in Table 1), and $u = 0.206$ ($u = d_{ap}/c$, d_{ap} is the apical Ti–O bond length, which is equaled to 2.017 Å). These optimized lattice parameters are in good with theoretical and experimental research results [13,31]. These results indicate that our calculation methods are reasonable and the calculated results should be authentic.

From Table 1, it can be seen that the values of V shrink obviously after Si doping in TiO_2, which is may be attributed to the fact that the ionic radius of Si^{4+} (0.40 Å) is smaller than that of Ti^{4+} (0.61 Å). On the contrary, because the ionic radius of S^{2-} (1.84 Å) is larger than that of O^{2-} (1.40 Å), the lattice parameters of S1–TiO_2, (Si,S1)–TiO_2, (Si, S1S2)–TiO_2 and (Si,S1S2)*–TiO_2 systems are increased. These apparent lattice distortions imply that Si and/or S doping into TiO_2 can not only change the symmetry of TiO_2 crystals, but also effect on the redistribution of the charge. As a result, the crystal dipole moment maybe produced. In these Si and/or S (co)doping models, the octahedral dipole moments of SiO_6, TiO_5S, SiO_5S, and SiO_4S2 in TiO_2 crystals are obviously larger