Computational Materials Science 93 (2014) 1–5

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Density functional study of X monodoped and codoped (X = C, N, S, F) anatase TiO_2

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ARTICLE INFO

Article history:
Received 3 October 2013
Received in revised form 15 May 2014
Accepted 21 June 2014

Keywords:
DFT
Oxygen vacancy
Valence state
Visible light

ABSTRACT

Using density-functional theory (DFT) calculations within the generalized gradient corrected approximation, the models that nonmetallic impurities X (X = C, N, S, F) substituted for O or Ti sites in anatase TiO_2 were investigated. By calculating the formation energy of X-monodoped TiO_2 with X substituted for O, we suggested that X dopants existed as C^{4-}, N^{3-}, S^{2-} and F^{-} ions, respectively. Meanwhile, the X dopants existed as C^{4+}, N^{3+}, and S^{6+} for X-monodoped (X = C, N, S) TiO_2 with X substituted for Ti. The conclusion of the valence states of nonmetallic impurities X substituted for O or Ti sites in TiO_2 is also supported by the results of optimized cell parameters and the local structures. Furthermore, an effective nonmetallic passivated codoping approach to modify the band edges of TiO_2 is proposed. Based on the first-principle calculations, we suggested that nonmetallic passivated groups such as (S^{2-} + C^{4+}) and (C^{4-} + S^{6+}) could reduce the band gap largely and make less perturbation in conduction band minima (CBM), thus lead to an ideal visible-light absorption region without affecting the reducing power. This work provides some new results and is anticipated to give some inspiration and guidance for design visible-light-driven TiO_2 photocatalyst with high efficiency.

1. Introduction

Among various semiconductors, TiO_2 has been widely employed to promote photocatalytic degradation of harmful organic compounds [1]. However, due to the wide band-gap, pure anatase TiO_2 photocatalyst mainly absorbs ultraviolet (UV) photons, which amounts for 4–5% of the incoming solar energy on the earth's surface. To utilize solar energy effectively, much effort has been directed toward the shift of the optical response of TiO_2 from UV to the visible spectral range. One approach is the doping of various transition metal [2,3] and nonmetal elements [4,5]. However, it is noted that the doping of transition metal elements could act as carrier recombination centers [2].

The pioneering work of nonmetal-doped TiO_2 was made by Asahi et al. in 2001 [6], who reported nitrogen-doped TiO_2 and suggested N 2p level could mix with O 2p states. The mixture states resulted in the narrowing of band gap and photocatalytic activity in visible light. Since then, nonmetallic anion doping has become the most attractive subject. Anionic nonmetal dopants such as nitrogen [7,8], carbon [9–11], fluorine [12], and sulfur [13] atoms have been widely investigated for the extension of photocatalytic activity into the visible-light region. However, the nature of the nonmetallic anion-induced modifications of TiO_2 electronic band structure is also controversial. Band gap narrowing [6,13] or formation of localized midgap states [9,14,15] has been alternatively proposed. To obtain insight into this issue, we have performed a careful and systematic analysis of the nonmetallic anion impurity states as well as their influence on the TiO_2 band structure.

Compared to anion doping, some experimental works demonstrated that the nonmetal cation doped-TiO_2 also exhibited photocatalytic activity under visible light irradiation [16–19]. In particular, Ohno et al. synthesized chemically modified TiO_2 photocatalyst in which S (S^{4+}) and C (C^{4+}) substituted for some of the lattice Ti atoms from X-ray photoelectron spectra (XPS) spectra, and they also found that both S^{4+}-doped and C^{4+}-doped TiO_2 showed excellent photocatalytic activity under visible light irradiation [17–19]. It needs to carry out the theoretical calculation of nonmetal elements X into Ti site to verify the experimental results. Additionally, the valence state of S atom substituting for Ti atom in TiO_2 is uncertain (S^{4+} or S^{6+}) in the experimental works.

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http://dx.doi.org/10.1016/j.commatsci.2014.06.035
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Generally, the nonmetal substituting for a Ti site could lead to a significantly X—O bond, and the valence states would become complex and uncertain due to the similar electronegativity between O and X. Therefore, it is necessary to make certain of the valence states of nonmetal cation substituting for Ti atom in TiO_2.

In addition, Gai et al. proposed a passivated codoping approach to shift the TiO_2 absorption edge into visible light range and improve its photocatalytic efficiency for hydrogen production [20]. They suggested (C^{4-} + Mo^{6+})-codoped TiO_2 with both C anions and Mo cations could reduce the recombination centers and then enhance the photocatalytic activity. This is because the electrons on the donor levels could passivate the same amount of holes on the acceptor levels in the (C^{4-} + Mo^{6+})-codoped TiO_2 system. The next experimental works according to the above theoretical calculation were completed by Zhang et al. [21] and our group [22], respectively. However, their experimental results showed that the transition metal (Mo^{6+}) doped into TiO_2 often acts as the carrier recombination center and decreases the photocatalytic activity. Therefore, it seems that the most anticipated approach is the cooperation of anion and cation nonmetal-codoping, which would result in stronger visible light absorption and prevent the formation of recombination centers.

In this work, the band structures of nonmetallic impurities X-doped (X = C, N, S, F) anatase TiO_2 with X substituted for O or Ti sites are systematically investigated using DFT calculations, and the valence states of X dopants are clarified. Moreover, a nonmetal passivated codoping approach to modify the band edges of TiO_2 is proposed.

2. Calculation method

The calculations presented in this work were performed by using the WIEN2k package, which is an implementation of the full-potential linear-augmented-plane-wave (FLAPW) method, while the generalized gradient approximation (GGA) is employed for the exchange–correlation potential. The scalar-relativistic effects are included for the band states, while the core-level states treated fully relativistically. The muffin-tin (MT) sphere radii RMT are chosen as 1.86 a.u. for Ti, and 1.65 a.u. for O, respectively. The cutoff parameter RMTKmax for limiting the number of the plane waves is 7.0 and the largest vector Gmax is 12.0. We simulated the X doping effects using 2 × 2 × 2 (96-atom) repetition of the unit bulk anatase TiO_2 and the stable structure was assumed when the atomic force is less than 1 mRy/a.u. For the Brillouin zone integration, we used 50 sampling *K* points to calculate density of state (DOS) and partial density states (PDOS). The calculated band gap is 1.96 eV, much smaller than the experimental band gap of 3.20 eV [23]. The band gap underestimation of DFT calculations always exists due to the well-known limitation of predicting accurate excited states properties. The charge transfer of X dopants is investigated quantitatively by using Bader's quantum theory.

3. Results and discussion

3.1. Electronic structures and valence states in monodoped TiO_2

3.1.1. The substitution for oxygen (anion monodoped TiO_2)

The electronic structures of X-doped TiO_2 with X replaced an O site are examined. Fig. 1 shows the calculated DOS and PDOS for anion monodoped anatase TiO_2. The relative positions of DOS are adjusted by referencing to the core levels of the atom farthest from the impurity. The substitution of X on oxygen lattice site induces the isolated states in the band, which indicated that the anion dopants induced the formation of localized midgap states instead of band gap narrowing. The electronegativity of X increases in the order C < S < N < F (i.e., 2.48, 2.69, 2.90 and 3.91, respectively), while that of O is 3.41. The position of dopants' level induced by C, N, S and F decreases in the order C > S > N > F, which is corresponding to the electronegativity. Moreover, the highest localized states of C 2p, N 2p and S 3p orbitals in the PDOS are isolated inside the gap of TiO_2 (i.e., 1.05, 0.89, 0.14 eV above the VBM, respectively), which result in the photocatalytic activity in visible light region. The peak in the PDOS located at −8 to −6 eV belongs to the 2p orbitals of F atoms is lower than O 2p states, which did not contribute to the reduction of the optical band gap. Furthermore, it should be noted that the C 2s and N 2s states are located at much lower energies (at about −8 and −12 eV, respectively), which is impossible to participate in bonding with O or Ti.

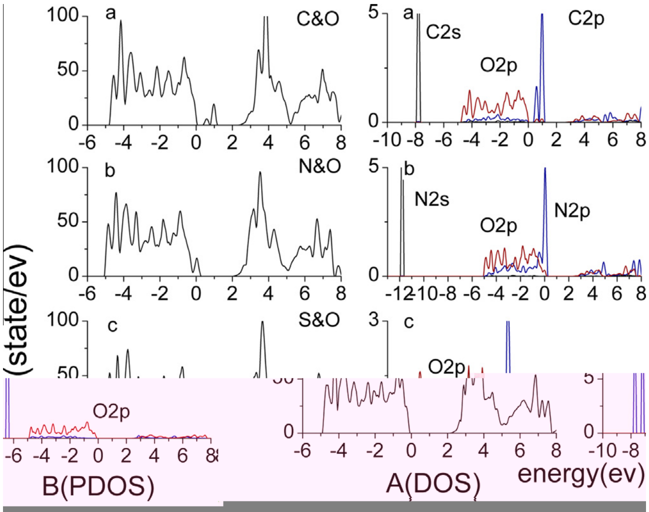

Fig. 1. DOS (A) and PDOS (B) for 96-atom anatase supercell with X replaced O: (a) C-doped, (b) N-doped, (c) S-doped, and (d) F-doped. The energy is measured from the top of the valence band of TiO_2.

In principle, the substitution with an element of different charge can induce a charge imbalance, resulting in the formation of a crystallographic point defect such as oxygen or titanium vacancy. Recently, DFT calculation of N-doped TiO_2 [24] gave a successful explanation for the relative relationship between nitrogen and oxygen vacancy. The formation energies of oxygen vacancy in pure anatase (Eq. (1)) and the doped TiO_2 (Eq. (2)) were calculated in this work to find out the relationship and clarify the valence states of impurities, as shown in Table 1.

$$TiO_2 \rightarrow TiO_{2-x} + xV_o + 1/2xO_2 \tag{1}$$

$$TiO_{2-y}X_y \rightarrow TiO_{2-x-y}X_y + xV_o + 1/2xO_2 \tag{2}$$

Table 1
Oxygen vacancy formation energy (*eV) of pure anatase and X anion-doped anatase TiO_2 and atomic charges (Q_x) of X dopants.

	Pure	C and O	N and O	S and O	F and O
*(eV)	4.09	0.78	1.21	4.18	8.81
Q_x	–	−3.763	−2.855	−1.741	−0.882