Origin of the photoactivity in boron-doped anatase and rutile TiO₂ calculated from first principles

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The electronic and optical properties of several possible B-doped models in both anatase and rutile polymorphs of TiO_2 have been investigated systematically using spin-polarized density functional theory calculations. Our calculated results indicate that the experimentally observed reverse shift of the absorption edge in the B-doped TiO_2 originates from the different chemical environments of B ion. The transition of excited electrons from the valence band to the empty gap states above the Fermi level may be responsible for the redshift of the absorption edge in substitutional B- to O-doped anatase, and the redshift of absorption edge may also be expected in substitutional B- to Ti-doped anatase TiO_2 due to the reduction of electron transition energy, resulting from the decline of conduction band. On contrary, the electron transition energy has a little increase in interstitial B-doped anatase due to the well-known "band-filling mechanism," thus resulting in the blueshift of absorption spectra. Similar doping effects also appear in B-doped rutile TiO_2 .

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I. INTRODUCTION

Titanium dioxide (TiO_2) has received a lot of attention as one of the most promising photocatalyst because of its exceptional properties such as nontoxicity, low cost, and longterm stability against chemical corrosion; thus, it has been widely used in the environmental world. However, the practical effective application of TiO₂ was heavily limited because only a small portion of the solar spectrum is absorbed in the ultraviolet (UV) light region ($\lambda < 380$ nm) due to a high band gap [3.0-3.2 eV (Ref. 1)], and the undesired recombination of photoexcited carriers depresses the efficiency of optical absorption heavily. Therefore, many efforts have been made to modify the electronic properties of TiO₂ in order to extend its optical absorption edge into visible light and enhance its photocatalytic activity. In particular, nonmetal-doped TiO₂ seems to be more effective, and Asahi et al. showed that substituting oxygen with nitrogen is an effectual approach to achieve a band-gap narrowing.² After that, a large number of works have been done to study the photoelectrochemical properties of nitrogen-doped TiO₂.^{3–9} Recent experimental and theoretical studies also showed that localized N 2p states located close to the valence band maximum lead to the absorption of visible light rather than a band-gap narrowing.^{10–15} Furthermore, other nonmetal ions (C, S, P, B, F, etc.) have also received a lot of attention as doping impurities. For example, Umebayashi et al. have reported that S doping into the lattice of TiO₂ will lead to the band-gap narrowing, and later theoretical studies showed that impurity states of S 3p on the upper edge of the valence band lead to the redshift of the absorption edge.¹⁶⁻¹⁹ C-doped titanium dioxide has been synthesized and corresponding theories have also been reported.^{20–22} A redshift in the optical absorption edge was also observed in F- and P-doped TiO₂.^{23,24} Recently, the photocatalytic activity of B-doped TiO₂ has been widely investigated.^{25–29} For example, Zhao et al. reported that B-doped TiO₂ shows a substantial redshift of the spectra absorption and the photocatalytic activity is greatly enhanced as it is further loaded with Ni₂O₃.²⁵ Experiments done by Wei et al. indicated that the UV-visible absorption band wavelength of boron- and cerium-codoped TiO_2 showed an obvious shift toward the visible range.²⁶ Bettinelli et al. also reported that the photocatalytic activity of boron- and vanadium-codoped TiO₂ was improved, and the addition of B favored the transition of anatase to rutile.²⁷ The experimental results of Chen et al. revealed that doped boron ion was situated in the interstitial TiO₂ structure, forming a possible chemical environment such as Ti-O-B, and an unexpected blueshift of absorption edge compared with undoped TiO₂ was observed in the interstitial B-doped TiO₂.²⁸ Jung et al. also reported a blueshift of the light absorption in B-doped TiO₂ when the boron content is less than 5%, and paramagnetic species such as O⁻ and Ti³⁻ defects were detected by the electron paramagnetic resonance (EPR) measurements.²⁹ However, to the best of our knowledge, there has been few reports regarding the origin of photoactivity of B-doped TiO_2 (Ref. 30) and some basic questions about the character of boron impurities, such as the boron doping effects on the crystal size of TiO₂ and what kinds of chemical environment of B ion determining the redshift and blueshift are still open.

To address these questions, in the present work, we studied the electronic and optical properties of several possible B-doped models of anatase and rutile TiO_2 systematically using spin-polarized density functional theory (DFT) calculations. The theoretical analysis provided a possible explanation for experimentally observed redshift and blueshift in B-doped TiO_2 .

II. COMPUTATIONAL DETAILS

The DFT calculations were performed by the PWSCF code³¹ based on the plane-wave method. Exchange-correlation effects were treated with the generalized gradient approximation (GGA), and the interaction between the valence electrons and the ionic core is described by the



FIG. 1. Partial geometries of B-doped anatase model for (a) one substitutional B atom to O, (b) one interstitial B atom in the supercell, and (c) one substitutional B atom to Ti. The big light spheres represent Ti atoms, the small gray spheres represent O atoms, and the dark spheres represent B atoms. The unit of bond length is Å.

Perdew-Wang91 gradient-corrected functional³² and ultrasoft pseudopotentials.³³ We simulated the B-doped TiO₂ (48atom supercell) using a $2 \times 2 \times 1$ repetition of the unit bulk anatase and $2 \times 2 \times 2$ rutile supercell. The *k* space integration was done with the Monkhorst-Pack³⁴ grid with $2 \times 2 \times 2$ *k* points in the Brillouin zone of the supercell, and the wave functions were expanded with kinetic energy cutoffs of 25 Ry. The convergence threshold for the self-consistent energy error was set to 10^{-6} Ry, and atomic relaxations were carried out until all components of the residual forces were less than 10^{-3} Ry/bohr.

III. RESULTS AND DISCUSSION

A. Model structures of B-doped anatase and rutile

We considered three possible ways to introduce B atoms into the anatase and rutile lattices of TiO₂. The first one is an oxygen atom replaced with a boron atom; the second one is a boron atom sited at an interstitial position, and the last possibility is a titanium atom substituted by a boron atom. For the anatase phase of TiO₂, the calculated crystal parameters are a=3.776 Å and c/a=2.512, which are consistent with the experimental data.³⁵ The three partial geometries taken from the structural optimized B-doped anatase supercell are shown in Fig. 1. For the substitutional B to O model [see Fig. 1(a)] two of Ti-B bond lengths, 2.031 Å, are slightly longer than the original Ti-O bond length (1.930 Å), while the distance of the B and the third Ti atom is 2.256 Å. much longer than the corresponding Ti-O bond lengths (1.973 A). Hence, it is difficult to form the third Ti-B bond. In the interstitial B-doped anatase model, after structural optimization, the B ion is bounded by adjacent two O ions and forms the Ti-O-B bond. The distances between the interstitial B atom and adjacent two O atoms are 1.333 and 1.451 Å [see Fig. 1(b)]. For the structure of the substitutional B to Ti model [see Fig. 1(c)], the B ion forms six B-O bonds with surrounding O ions and the B-O bond lengths are 1.604 and 1.890 Å, respectively, much shorter than original Ti-O ones (1.973 and 1.930 Å).

For the rutile phase of TiO₂, the calculated parameters of the rutile unit cell are a=4.594 Å and c=2.959 Å, which agree with the experimental values.³⁶ Figure 2 gives the three partial geometries of a structural optimized B-doped rutile supercell. For the substitutional B- to O-doped model, two of



FIG. 2. Partial geometries of B-doped rutile model for (a) one substitutional B atom to O, (b) one interstitial B atom in the supercell, and (c) one substitutional B atom to Ti.

the B-Ti bonds are 1.988 Å and the third B-Ti bond is 1.966 Å [see Fig. 2(a)]. This substitution does not lead to significant structure modifications with respect to the original Ti-O bonds (1.949 and 1.980 Å). In the interstitial B-doped rutile model, as in the case of the doped anatase, the B ion is bounded by two O ions and forms the Ti-O-B bond. The two B-O bonds are 1.518 and 1.813 Å [Fig. 2(b)]. For the substitutional B- to Ti-doped rutile model, the replacement of one lattice Ti ion by B ion causes some constriction of local structure (four of the B-O bonds are 1.754 Å and the other two bonds are 1.940 Å, whereas the corresponding original Ti-O bonds are 1.949 and 1.980 Å).

To understand the charge redistribution and spin properties induced by different types of B impurity, we also calculated the electron density and spin density of the three B-doped models for anatase and rutile TiO_2 , shown in Figs. 3 and 4, respectively. The left plane of Fig. 3 shows a twodimensional profile of the electron density of the B-doped anatase supercell while the right plane shows the spin density of the corresponding section. In the substitutional B- to O-doped anatase model, the B ion forms two Ti-B bonds by capturing electrons from adjacent two Ti ions, and the relatively long distance (2.256 Å) between the B ion and the third Ti ion oversteps the bonding range, resulting in the decrease of electron cloud and weak interaction between the B ion and the O ion [see Figs. 1(a) and 3(a)]. Furthermore, according to the Mulliken population analysis, the charge on the B ion is about -0.37, and the spin density is largely localized on the B ion, and relatively less spin states are localized on the adjacent Ti and O ions. In the interstitial B-doped model [see Fig. 3(b)], after the electron redistribution, the calculated charge on the B ion is 0.41 and the B ion forms a Ti-O-B structure. The optimized geometry structure and chemical bonding analysis favored the experimental observations that interstitial B ion forms a chemical environment such as Ti-O-B.²⁸ In addition, it is also observed that the spin density is mainly localized on the B ion and the adjacent Ti ions. For the substitutional B to Ti model, the calculated charge on the B ion is 0.73 and small spin density states are localized on the adjacent O atoms, shown in Fig. 3(c'). The calculations of spin density for the three B-doped anatase models support the experimental EPR measurements that the paramagnetic species of O^{-1} and Ti^{3+} defects are produced by the addition of boron.²⁹

For the B-doped rutile phase of TiO_2 , in the substitutional B- to O-doped rutile model [see Fig. 4(a)], three B-Ti bonds are formed by a common electron cloud after electron redis-



FIG. 3. The electron density maps (left) and spin density maps (right) of B-doped anatase supercells. (a) (010) cross section of the substitutional B- to O-doped model, (b) the section containing B impurity in the interstitial B-doped model, (c) (010) cross section of the substitutional B- to Ti-doped model.

tribution and negative charge of about -0.41 on the B ion is obtained. For the interstitial B-doped rutile [see Fig. 4(b)], as in the case of anatase, the interstitial B ion also forms the chemical environment of the Ti-O-B bond, and the calculated charge on the B ion is about 0.21, resulting from the transfer of electrons from the B ion to the adjacent O ions. In the substitutional B- to Ti-doped rutile [see Fig. 4(c)], the positive charge of about 0.71 on the B ion is obtained, with the electrons transferring from the B ion to the neighboring O ions, and six B-O bonds are formed. In addition, the spin density is mainly localized on the B ion and neighboring Ti ions in both the substitutional B- to O-doped and interstitial B-doped rutile TiO₂, while less spin density centralizes on the O ions in the substitutional B- to Ti-doped rutile (see the right plane of Fig. 4). Hence, some paramagnetic species (O, Ti, and B ions) are also expected to be detected in the B-doped rutile TiO₂ by EPR measurement as in the case of B-doped anatase.

In order to study boron doping effects on the crystalline size of TiO_2 , we did test calculations with a variable-cell structural optimization for three B-doped anatase models. Compared with the lattice parameters of undoped anatase, the substitutional B- to O-doped model and the interstitial B-doped model increase obviously, and thus the cell volume expands by about 7.7% and 7.0% for the 12-atom anatase cell, respectively. The calculated results support the experiments of Jung *et al.* that the incorporating boron oxides of more than 10% could enlarge the grain size of the anatase



FIG. 4. The electron density maps (left) and spin density maps (right) of B-doped rutile supercells. (a) $(\overline{1}10)$ cross section of substitutional B- to O-doped model, (b) the section containing B impurity in interstitial B-doped model, (c) (110) cross section of substitutional B- to Ti-doped model.

phase and thus decrease the surface area of B_2O_3 -SiO₂/TiO₂ ternary mixed oxides significantly.²⁹ However, the opposite experimental phenomenon was also observed by Chen *et al.*, and their experimental x-ray diffraction results showed that the doping of boron ions inhibited the crystal size and increased the surface area of TiO₂.²⁸ Although the optimized lattice parameters of the substitutional B- to Ti-doped model decreased and the cell volume shrinked to about 5% in our results, the model structure is not consistent with the experiment of Chen *et al.* in which the boron ion is sited in interstitial position; thus it cannot account for the phenomenon. Hence, further studies should be done to reveal the boron doping effects on crystalline size TiO₂.

B. Electronic structures

To understand the effects of boron doping on the photocatalytic activity and optical absorption properties of anatase and rutile TiO₂, the electronic structures are calculated. As shown in the earlier calculations employing both GGA and local spin density approximation,^{12,37,38} our spin-polarized DFT calculations at the GGA level also give band gaps of about 2.2 and 1.9 eV at the Γ point for anatase and rutile, respectively, smaller than the experimental value (3.0–3.2 eV), which shows the typical underestimation characteristic of the band gap due to the well-known shortcoming in DFT. There are several ways of correcting the deficiency, the most effective one of which is to use the hybrid func-



FIG. 5. (A) The total density of states (DOS) and (B) projected density of states (PDOS) for the 48-atom anatase supercell. (a) Undoped anatase model, (b) substitutional B- to O-doped model, (c) interstitial B-doped model, and (d) substitutional B- to Ti-doped model. The energy is measured from the valence band maximum of pure anatase TiO_2 , and the dot lines represent the Fermi level.

tional, i.e., introducing an appropriate Hartree-Fock (HF) exchange in the DFT calculation such as the well-known Becke's three-parameter hybrid functional (B3LYP),^{39,40} in which the ratio of the HF exchange is fixed to 20%. Recent DFT calculations for TiO₂ indicated that the hybrid functional could significantly improve the description of the band gap and correct the position of the localized defect states.^{41–44} We also calculated the electronic structure of pure anatase and rutile TiO₂ using hybrid functional with 13% HF exchange by the CRYSTAL06 code.⁴⁵ The calculated values of band gap are 3.58 eV for anatase and 3.07 eV for rutile, which are consistent with the previous studies and experimental values.^{42,44}

The density of states (DOS) and projected density of states (PDOS) of three B-doped anatase models are displayed in Figs. 5(A) and 5(B), respectively. For comparison, the DOS and PDOS of pure anatase are also calculated [see Figs. 5(a) and 5(a'), which indicate that the valence band mainly consist of the O 2p orbital with a large bandwidth of about 5.0 eV, showing strong delocalization and bonding characteristic among the O 2p electrons. For substitutional B- to O-doped anatase model [see Fig. 5(b)], the calculated DOS shows that the top of the valence band has a little shift and the conduction bandwidth has a little increase compared with the pure anatase. In addition, some gap states are located close to and mix with the conduction band edge, and further PDOS calculations based on the Mulliken population analysis show that the gap states mostly consist of the B 2p orbital and adjacent Ti 3d and O 2p orbitals, and the Fermi level is pinned in the gap states of about 0.3 eV down the bottom of the conduction band. Hence, the electron excitations from the valence band to the unoccupied gap states above the Fermi level may induce a redshift of the absorption edge with a maximum of about 0.3 eV, which is consistent with

the experimental measurements that the incorporation of boron in anatase TiO₂ resulted in a redshift of absorption of about 0.25 eV.²⁵ It should be noted here that the calculated location of gap states is different from a previous calculation,³⁰ which probably results from the difference of the geometrical structure of the substitutional B- to O-doped model induced by the spin-polarized effects. For example, two B-O bonds and two B-Ti bonds were formed in previous calculations, but only two Ti-B bonds are formed in our calculation for the model. For the interstitial B-doped model [see Figs. 3(c) and 3(c')], compared with the pure anatase, the valence band maximum has a little rise of about 0.2 eV and the conduction bandwidth expands to about 0.5 eV, resulting from the increase of electrons introduced by boron. However, the bottom of the conduction band has little shift and most of B 2p states are centralized in the conduction band. Furthermore, the Fermi level is pinned above the bottom of the conduction band of about 0.4 eV, showing a typical *n*-type metallic character. As a consequence, some of the states within the conduction band below the Fermi level are then filled, and electrons excited by a UV-visible photon from the valence band must go into higher levels in order to enter empty states of the conduction band, thus resulting in a blueshift in optical absorption of about 0.2 eV. The calculated result is in agreement with the blueshift in interstitial B-doped TiO₂ observed by Chen et al., in which the light absorption energy increased by about 0.12 eV (see Fig. 8 in Ref. 28). This is the well-known "band-filling mechanism" associated with the optical properties in an *n*-type semiconductor.⁴⁶ Hence, the calculated results give another possible explanation for an experimentally observed blueshift in interstitial B-doped TiO₂.^{28,29} For the substitutional B- to Ti-doped model [see Figs 5(d) and 5(d')], there is a relatively larger decline of the conduction band about 0.4 eV



FIG. 6. (A) The DOS and (B) PDOS for the 48-atom rutile supercell. (a) Pure rutile model, (b) substitutional B- to O-doped model, (c) interstitial B-doped model, and (d) substitutional B- to Ti-doped model. The energy is measured from the valence band maximum of pure rutile TiO₂, and the dot lines represent the Fermi level.

with a spread of the valence band to lower energy, and most of B 2p states are located in the valence band. The origin is that the reduction of the electrons from the supercell, resulting from the replacement of one Ti with B atom, leads to a reduction of the Coulomb repulsion and the shift of the energy band edges. However, the top of the valence band has no obvious shift compared with the pure anatase, and the Fermi level is pinned in the valence band at about 0.1 eV below the valence band maximum of pure anatase. Hence, the transition energy of excitations from occupied O 2pstates below the Fermi level to empty Ti 3d states may have a relatively larger decrease of about 0.3 eV and may thus induce a redshift of absorption spectrum in the substitutional B- to Ti-doped anatase. Furthermore, we also discover that O 2p spin-up frontier orbital levels have a little decline while the spin-down frontier orbital rises slightly in contrast with that of the pure anatase, and the potential differences between the spin-up states and spin-down states near the Fermi level result from the unpaired electrons of O ions near the B ion and then lead to the small spin density polarization and localization on the O ions [see Fig. 3(c')].

As in the case of doped anatase, the electronic structures of three possible B-doped rutile models were also calculated in order to investigate the boron doping effects on the optical absorption of rutile TiO₂. The DOS and PDOS of three B-doped rutile models are displayed in Figs. 6(A) and 6(B), respectively. Similar to the case of boron impurities in anatase TiO₂, B doping induces similar modifications of electronic structures in rutile TiO₂. In the substitutional B- to O-doped model [see Figs 6(b) and 6(b')], the valence band maximum has little shift compared with that in pure rutile, and substitutional B replacing an O atom introduces some gap states bordering the conduction band, which are mostly composed of B 2*p* states and adjacent Ti 3*d* states. Furthermore, the Fermi level is pinned in the gap states at about 0.2 eV below the conduction bottom of pure rutile, and thus the transition energy of excited electrons from the valence band to the empty states above the Fermi level may induce a redshift of optical absorption. For interstitial B-doped rutile TiO₂, Fermi level is positioned within the conduction band and a blueshift of optical absorption at about 0.3 eV is also expected in interstitial B-doped rutile TiO₂ due to the bandfilling mechanism [see Fig. 6(c)]. In the substitutional B- to Ti-doped rutile TiO₂, substitutional B replacing a Ti atom causes a decline of conduction band at about 0.4 eV because of the reduction of total electrons, but does not introduce new states in the gap and a large part of B 2p states located in the valence band. In addition, the Fermi level is pinned in the valence band below the valence maximum of pure rutile at about 0.3 eV, and thus the electronic transition energy from the valence band to the conduction band has a reduction of about 0.1 eV. A redshift of absorption spectra may also occur in substitutional B- to Ti-doped rutile TiO₂.

IV. CONCLUSIONS

We have studied several possible B-doped anatase and rutile models by spin-polarized density functional theory calculations based on the plane-wave method. The calculated results show that substitutional B replacing an O atom induces some gap states close to the bottom of the conduction band, and the excitation from the valence band to the empty impurity states above the Fermi level may account for the experimental redshift of the absorption edge in anatase; the lower photon absorption energy than pure anatase may also be expected in substitutional B- to Ti-doped anatase TiO₂ due to the decline of the conduction band. In addition, we also put forward a possible explanation for the experimentally observed blueshift of absorption spectra in interstitial B-doped anatase TiO_2 due to the well-known band-filling mechanism. Consequently, the observed reverse shift of the absorption edge in the B-doped TiO_2 may be due to the different kinds of B doping. Similar doping effects also occur in B-doped rutile TiO_2 .

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