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Band structures of TiO_2 doped with N, C and B*

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Abstract: This study on the band structures and charge densities of nitrogen (N)-, carbon (C)- and boron (B)-doped titanium dioxide (TiO_2) by first-principles simulation with the CASTEP code (Segall *et al.*, 2002) showed that the three 2p bands of impurity atom are located above the valence-band maximum and below the Ti 3d bands, and that along with the decreasing of impurity atomic number, the fluctuations become more intensive. We cannot observe obvious band-gap narrowing in our result. Therefore, the cause of absorption in visible light might be the isolated impurity atom 2p states in band-gap rather than the band-gap narrowing.

Key words: CASTEP code, Titanium dioxide, Band structure, Charge density
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INTRODUCTION

Titanium dioxide (TiO_2) is known as a useful photosensitive material, such as for photoanodes (Byrne *et al.*, 1998) and photocatalysts (Yoneyama and Torimoto, 2000). However, only the ultraviolet part of the solar irradiation (amounting to ~4% of the incoming solar energy on the earth's surface) could be absorbed by TiO_2 due to its high intrinsic band gap (3.2 eV for anatase and 3.0 eV for rutile). For designing highly efficient and low cost photocatalytic systems, many approaches, such as doping with various transition metal cations (Zhu *et al.*, 2000), have been introduced to extend the optical absorption of TiO_2-based systems to the visible-light region. Though that way could more or less extend the optical absorption, the thermal instability and increase of carrier recombination centers greatly limit the performances of transition metal dopants (Choi *et al.*, 1994).

On the other hand, anionic nonmetal dopants, such as nitrogen (N) (Asahi *et al.*, 2001; Irie *et al.*, 2003), carbon (C) (Khan *et al.*, 2002) and boron (B) (Moon *et al.*, 2000) atoms, have also been investigated widely aim at extending photocatalytic activity into the visible-light region. Asahi *et al.*(2001) reported that N-doped TiO_2 showed dramatic improvement over undoped TiO_2 in its optical absorption and photocatalytic activity for visible light. Based on their analysis of the density of states, they concluded that the substitution doping of N for O in the anatase TiO_2 crystal would yield a band-gap narrowing driven by mixing of N 2p states with O 2p states. However, recent experimental data seemed contradict their theoretical. Irie *et al.*(2003) suggested that the visible-light response in N-doped TiO_2 might be due to N 2p states isolated above the valence-band maximum of TiO_2. Similarly, the red-shift in C-doped TiO_2 had been observed by Choi *et al.*(2004), and Moon *et al.*(2000) reported the absorption band shifted towards longer wavelengths in B/TiO_2.

In this article, we calculated the band structures and charge densities of N-, C- and B-doped anatase TiO_2 by first-principles simulation with the CASTEP code, which is a state of the art quantum mechanics based program designed specifically for solid state materials science (Segall *et al.*, 2002). Based on the

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results, we explained the photocatalytic activity of three kinds of anionic nonmetal doping in visible-light region.

METHODS

Our first-principles quantum mechanics calculations were performed using the local-density approximation (LDA) with local functional CA-PZ (Ceperley and Alder, 1980; Perdew and Zunger, 1981) in energy calculations and the generalized gradient approximation (GGA) with gradient corrected functional PBE (Perdew *et al.*, 1996) in geometry optimizations. The pseudopotential representation is in the reciprocal space, because it has several advantages both in efficiency and veracity. K-point mesh is set to 5×5×2. The N (C, B)-doped TiO_2 system's calculations are carried on by using the super-cell geometry with four unit cells of anatase TiO_2, where one O atom is replaced by one N, C or B atom. Thus the x in $TiO_{2-x}N_x$, $TiO_{2-x}C_x$ and $TiO_{2-x}B_x$ is 0.0625 (Fig.1). The basic structure of the undoped anatase TiO_2 crystal is picked from the Materials Studio Structures Library, which shows good agreement with the experiment and theory. The structural parameters such as the bond lengths and bond angles (Fig.1) are given in Table 1 together with some previous calculations and experiment (Asahi *et al.*, 2000; Lee *et al.*, 2005; Burdett *et al.*, 1987). Brillouin zone for tetragonal lattice which is used in the calculations is shown in Fig.2.

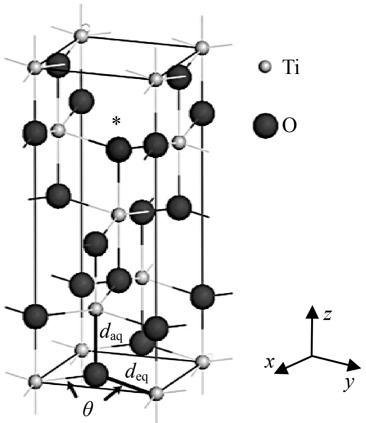


Fig.1 Primitive unit cell of the anatase TiO_2 crystal, the substitution atom is marked with "*"

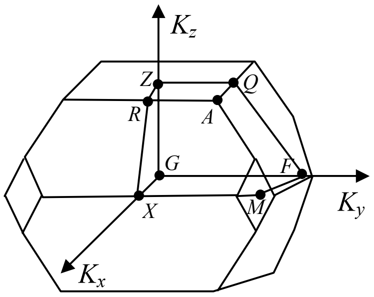


Fig.2 Brillouin zone for tetragonal structure of anatase TiO_2

Table 1 Structural parameters of the anatase TiO_2 crystal comparing with other researches

	This work	Lee's work	FLAPW	Experiment
a (Å)	3.776	3.845	3.692	3.782
c (Å)	9.486	9.537	9.471	9.502
c/a	2.512	2.481	2.566	2.512
d_{eq} (Å)	1.930	1.960	1.893	1.932
d_{aq} (Å)	1.973	2.002	1.948	1.979
θ (degree)	156.1	157.6	154.4	156.3

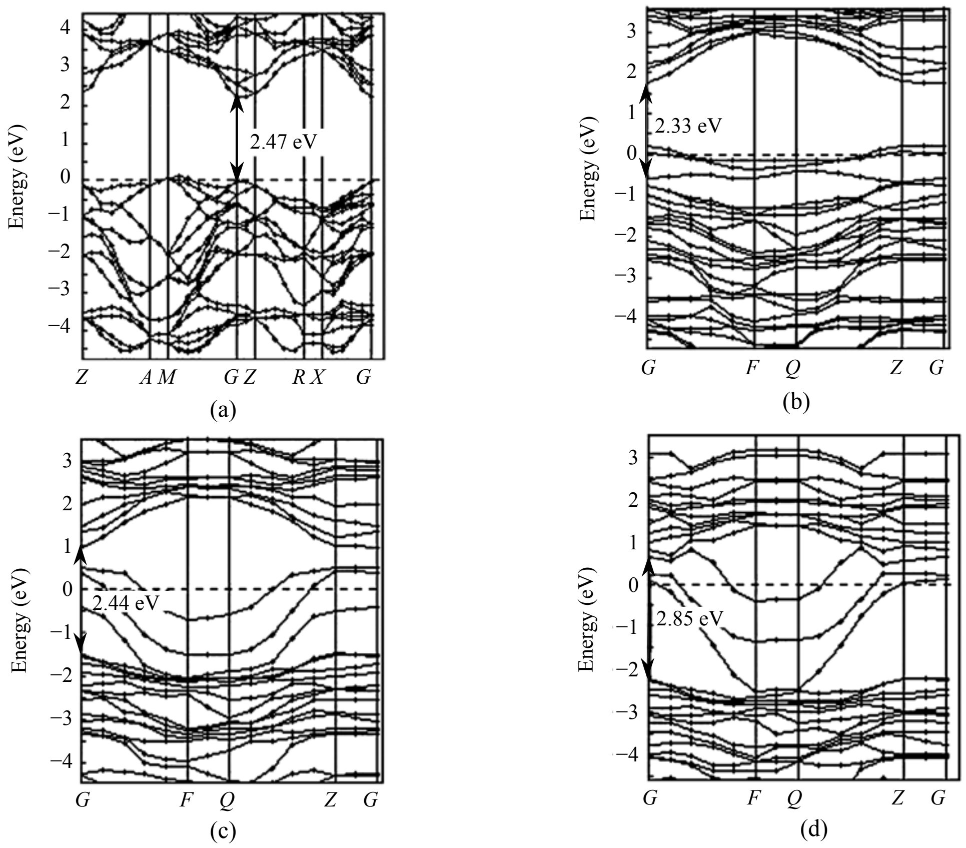
RESULTS AND DISCUSSION

The band structure of undoped anatase TiO_2 calculated by our method is shown in Fig.3a. The energy zero represents the valence-band maximum. The minimum band gap at the G point is 2.47 eV, less than the experimental value (E_g=3.2 eV), and is due to the well-known underestimate of the LDA (Perdew, 1983).

Before calculating the band structures of other doped TiO_2, we optimize the crystal geometry with GGA method. The changes of the crystal after geometry optimization are shown in Table 2. We found that the doped atom displacement increases with decreasing atomic number. This phenomenon could be explained by the incorporation of the doped atoms. The larger the atom is, the more is the strain on the neighboring Ti atoms.

Next, we use LDA method in the N (C, B)-doped TiO_2 band structure calculations, and the results are given in the Figs.3b~3d. The energy zero point has the same meaning with Fig.3a. The energy gaps between the lowest Ti 3d band and the highest O 2p band are denoted in each figure, and values are also listed in Table 3 for comparison. Moreover, we draw the charge density of each crystal in (1/2, 0, 0) plane. They are shown in Fig.4.

Fig.3 shows that the energy gap of N-doped TiO_2 (E_g=2.33 eV) is a little bit smaller than that of undoped TiO_2 (E_g=2.47 eV), and that three N 2p bands are located around the Fermi level and above the valence-band maximum of TiO_2. Comparing Fig.4a with Fig.4b, we found that the doped N atom has very weak influence on the TiO_2 energy structure. This finding negated previous explanation that N atom doping would narrow the band gap, because it can only be produced by the strong mixing of the N 2p states with O 2p states. Therefore, we could draw the conclusion that the isolated N 2p bands should be the cause of the photocatalytic activity for visible-light. This result is consistent with the work of Di Valentin *et al.*(2004).



(a) (b) (c) (d)

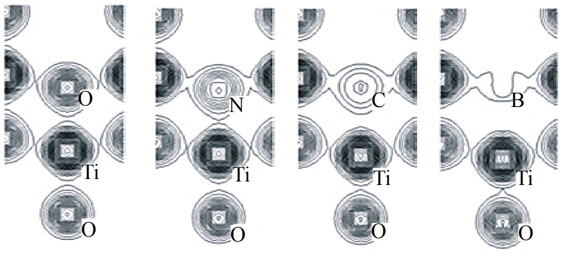
Fig.3 Band structure of (a) anatase TiO_2; (b) N-doped TiO_2; (c) C-doped TiO_2; (d) B-doped TiO_2

Table 2 Atomic displacements of impurity atoms after geometry optimizations

	Δx (Å)	Δy (Å)	Δz (Å)
N-doped TiO_2	0	0	0.03
C-doped TiO_2	0	0	0.12
B-doped TiO_2	0	0	0.23

Table 3 Energy gaps of doped TiO_2

	TiO_2	N-doped TiO_2	C-doped TiO_2	B-doped TiO_2
E_g (eV)	2.47	2.33	2.44	2.85



(a) (b) (c) (d)

Fig.4 Charge density of (a) undoped anatase TiO_2, (b) N-doped TiO_2, (c) C-doped TiO_2, (d) B-doped TiO_2
The plots are drawn in (1/2, 0, 0) crystal plane. Contour spacings are 50 e/bohr^3

Due to the relatively lower electronegativity, C and B atom can intensively affect TiO_2 charge distribution. This result is shown in Fig.4c and Fig.4d. However, in Fig.3b and Fig.3c, we cannot observe the band-gap narrowing either. C-doped TiO_2 E_g is 2.44 eV while the B-doped TiO_2 E_g is 2.85 eV, even larger than that of TiO_2. We contribute this phenomenon to the low or no mixing of the C or B atom 2p bands with O 2p bands, because the matching of p bands decreases along with the difference in electronegativity. On the other hand, we found that the impurity atom's three 2p bands were still in the band gap and along with the decreasing of impurity atomic number, the fluctuations become more intensive. It can greatly reduce the energy for electron transition between the O 2p states and Ti 3d states, and make the transition easier. At the same time, these kinds of 2p states can act as recombination centers of carriers, and make doped TiO_2 not suitable as photocatalytic or photoelectrochemical material. Hence, the red-shift of optical absorption can be explained by the isolated C 2p or B 2p states in the band gap of TiO_2 rather than the band-gap narrowing theory.

CONCLUSION

The energy structures and charge density of N-doped, C-doped, and B-doped anatase TiO_2 were calculated by LDA method. The results revealed that band-gaps of those three kinds of doped TiO_2 are not narrowing actually, and that the absorption of visible light is due to the isolated impurity states in the band gap.

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