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Theoretical study on the electronic and optical properties of (N, Fe)-codoped anatase TiO_2 photocatalyst

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ABSTRACT

Electronic and optical properties of pure, N-doped, Fe-doped and (N, Fe)-codoped anatase TiO_2 were evaluated, respectively, by using the density functional theory. The results indicate that the elemental doping narrows the band gap of TiO_2 and realize its visible-light response activity; and incorporation of Fe into N-doped TiO_2 further increases the photocatalytic activity under visible-light irradiation compared with that of the N-doped TiO_2.

1. Introduction

Titania has been widely studied as a promising material for photochemical applications due to its excellent properties, such as chemical stability, non-toxicity, low cost, etc. [1–4] However, anatase TiO_2 shows photocatalytic activity only under ultraviolet light irradiation ($\lambda < 385$ nm) because of its wide band gap (~3.20 eV), which leads to a low solar energy utilization with pure anatase TiO_2 [5]. Great efforts have been made to modify the electronic property of TiO_2 in order to extend its optical absorption edge into visible-light region and enhance its visible-light photocatalytic activity. An effective approach is doping the TiO_2 with metal or non-metal elements [6–10].

Since Sato reported for the first time that N-doped TiO_2 showed visible-light photocatalytic activity [11], many studies have been conducted to investigate the doping effect of TiO_2 theoretically and experimentally [12–17]. Most of these studies concentrated on mono-doping of the TiO_2 with metal or non-metal ions. Doping by non-metal ions can extend the optical absorption edge [18] of the TiO_2 by means of narrowing its band gap; however, the narrowed band gap results in an increased recombination rate of photo-excited carriers, reducing the photo-excited current or photocatalytic efficiency [19,20]. And the transition metal doping promotes the photocatalytic efficiency, with the existence of carrier recombination centers and strongly localized d states in the band gap, which reduces the carrier mobility significantly [21]. Recent studies suggested that introducing metal ions into nonmetal doped TiO_2 can make the metal ions as a mediator for interfacial charge transfer, and prevent the recombination of electron–hole pairs. Therefore, the synergistic effect of codoping with nonmetal and metal ions into the TiO_2 can extend the absorption edge into visible-light range and noticeably promote the efficiency of photocatalysis [22–27].

It has been reported recently that adding Fe to N-doped TiO_2 significantly increases the photocatalytic activity under visible-light irradiation [28]. The doping of N into TiO_2 can enhance the photo-response in visible-light region and that of Fe can reduce the recombination of electrons and holes. Both of these two effects are beneficial to the improving the performance of (Fe, N)-codoped TiO_2 photocatalyst. However, the mechanism of such enhancement has not been studied in detail. In the present work, the electronic and absorption properties of (N, Fe)-codoped TiO_2 have been investigated by using the density functional theory (DFT) to reveal the microscopic mechanism for band gap narrowing and the origin of the enhanced photocatalytic activity. For comparison, the corresponding calculation and theoretic

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analysis were also conducted for pure, N-doped and Fe-doped anatase.

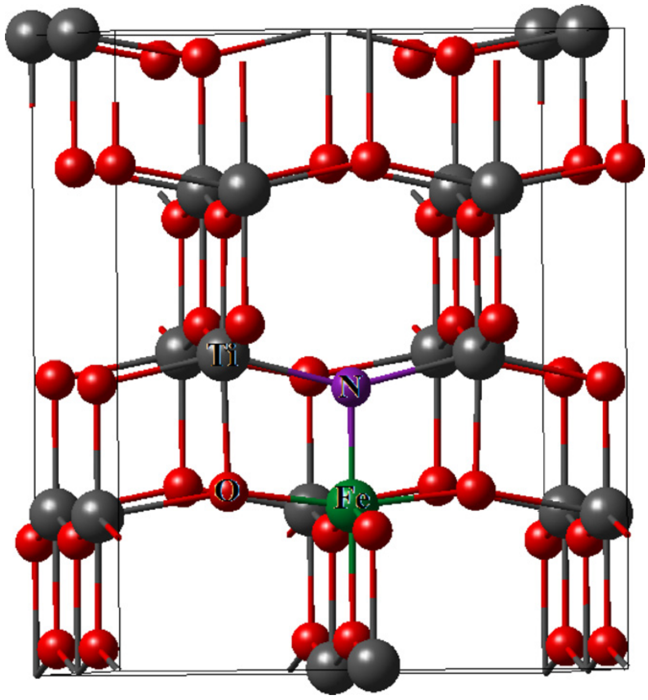

Fig. 1. Supercell model for defective anatase TiO_2 showing the location of the dopants. The ion doping sites are marked with N and Fe. The large grey spheres and the small red spheres represent Ti and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Calculation details

The unit cell of anatase TiO_2 (Ti_4O_8) has a symmetry of space group $D_{4h}^{19} - I_{41}/\text{amd}$. The doped systems were constructed from a relaxed ($2 \times 2 \times 1$) 48-atom anatase supercell, as shown in Fig. 1. In N- or Fe-doped TiO_2 model, an O atom is substituted by an N atom or a Ti atom is substituted by an Fe atom. (N, Fe)-codoped TiO_2 is modeled by single substitution of an N atom for an O atom, and one of its adjacent Ti atoms is replaced by an Fe atom in the supercell. Although it is assumed that there are no oxygen vacancies in the doped systems, neglecting the effects of oxygen vacancies on the properties of the (N, Fe)-codoped anatase TiO_2 in calculations, the oxygen vacancies may be formed in the structure caused by doping in practice, due to the requirement of charge balance. Iijima et al. [29] studied the influence of oxygen vacancies on optical properties of anatase TiO_2 thin films, and it was found that the oxygen vacancy states were widely distributed in the region below 2.5 eV, in which a broad absorption peak was observed.

All the spin-polarized calculations were performed using the projector augmented wave (PAW) pseudopotentials as implemented in the Vienna ab-initio simulation package (VASP) [30,31]. The exchange correlation function was treated within the Generalized Gradient Approximation (GGA) and parameterized by Perdew–Burke–Ernzerhofer (PBE) formula [32]. The Brillouin-zone integrations were approximated by using the special k-point sampling of the Monhkorst-Pack scheme [33]. A cutoff energy of 400 eV and a mesh size of $4 \times 4 \times 4$ were used for geometry optimization and electronic property calculations. Using the block Davidson scheme, both the atomic positions and cell parameters were optimized until the residual force was below 0.01 eV/Å. It is well known that the GGA method underestimates the band gap of the TiO_2 significantly in comparison with the experimental result (2.0 eV vs. 3.2 eV). In order to obtain the band gap that is consistent with the experimental result, the so-called GGA + U method [34] was employed to amend the difference. The Coulombic interaction *U* and exchange energy *J* were set to be 6.3 eV and 1 eV, respectively. Accordingly, the calculated band gap of pure anatase TiO_2 was 3.08 eV, which is in good agreement with the experimental value of 3.20 eV [35].

Table 1
Average bond lengths of the doped TiO_2 after geometry optimization.

Bond length (Å)	Pure TiO_2	N-doped	Fe-doped	Codoped
Ti–O	1.976	1.980	1.978	1.962
Ti–N		2.008		2.001
Fe–O			1.915	1.889
Fe–N				1.776

For optical properties the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$, the imaginary part ($\varepsilon_2$) and the real part ($\varepsilon_1$)were calculated theoretically based on the DFT. The corresponding absorption spectrum was estimated using the following equation:

$$I(\omega) = 2\omega \left(\frac{\left[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right]^{1/2} - \varepsilon_1(\omega)}{2} \right)^{1/2}$$

The valence electron configurations considered in this study included Ti ($3d^2 4s^2$), O ($2s^2 2p^4$),N ($2s^2 2p^3$) and Fe ($3d^6 4s^2$).

3. Result and discussion

3.1. Geometry analysis

After structure optimization of the pure anatase TiO_2 supercell, the lattice parameters were obtained as follows: $a = b = 3.8176$ Å, $c = 9.4801$ Å. These data are in good agreement with the measured results [36], which implies that the calculation methods are reasonable and the calculated results are considered to be reliable.

The average bond lengths of the doped TiO_2 after geometry optimization are summarized in Table 1. For pure TiO_2, the average Ti–O bond length is 1.976 Å; there is no significant change compared with that of the N or Fe doped one. However, the average Ti–O bond length in the supercell is shorter in the N and Fe codoped TiO_2. The average Ti–N bond length in N-doped and (N, Fe)-codoped systems are longer than the Ti–O bond length as the radius of N ion is slightly larger than that of O ion. Due to the smaller radius of Fe, the average Fe–O bond length of Fe-doped and the codoped TiO_2 is shorter than that of the Ti–O bond. In the case of codoped TiO_2, the length of all these bonds is decreased. The results indicate that N and Fe codoping leads to an obvious lattice distortion, which in turn changes the dipole and moments, makes the separation of photo-excited electron–hole pairs easier.

3.2. Electronic structure

The band structure of the four various TiO_2 based materials was obtained by the GGA + U calculations, as shown in Fig. 2. The Fermi level is set to 0 eV on the energy axis; the red lines refer to the up-spin states, while the blue ones refer to the down-spin states. It can be seen from Fig. 2a, the calculated band gap of pure anatase TiO_2 is 3.08 eV, which is consistent with previous experimental and calculation results [27,35]. Only red lines can be observed because of the overlap of the up-spin and down-spin states. And the valence band and conduction band moves to low energy states with doping. The calculated band gap of the N-doped, Fe-doped and (N, Fe)-codoped TiO_2 is 2.77, 2.76 and 2.73 eV, respectively, regardless of the impure states. In the case of the N-doped TiO_2 (Fig. 2b), an impure state is