First Principles Study on the Electronic Structure and Optical Property of Nd-C Codoped Anatase TiO₂

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ABSTRACT

Band structures, density of states, and absorption spectra of pure, Nd doped, C doped, and Nd-C codoped TiO₂ are calculated using first-principles based on density functional theory. Calculation results show that Nd 4f state forms empty impurity energy levels below conduction band, and C 2p state together with Nd 2f state forms occupied impurity energy levels with higher density than that of single doped TiO₂ above valence band. Consequently, more electrons in occupied energy levels can be excited by visible light to empty Nd 4f states rather than Ti 3d states, resulting in further enhancement of visible light absorption and absorption edge red shift. In addition, the impurity energy levels act as carriers trap centers, thus decreasing the recombination rate of carriers.

Keywords: Nd-C co-doping; Anatase TiO₂; first-principles

1. INTRODUCTION

It’s well known that anatase TiO₂ is an excellent photocatalyst due to its nontoxicity, physical and chemical stability, low cost and high photocatalytic activity. However, anatase TiO₂ has a relatively wide band gap (E₉=3.23eV), and only the ultraviolet light whose photon energy exceeds the band gap of TiO₂ can excite photogenerated electron-hole pairs.

Furthermore, TiO₂ has a high carriers recombination rate, leading to photogenerated carriers can not be made full use of. These two problems limit the wide applications of TiO₂. To solve these problems, researchers made great efforts and found that doping appropriate impurities into TiO₂ is an effective and practical approach to cause visible light response and reduce carriers recombination rate.

Through years of development, the dopants change from metal ions[1-7] to nonmetal ions[8-10], and the doping method develop from single doping to codoping[11-14]. Carbon is one of the most adopted nonmetal dopants both in single doping and codoping. For instance, SAKTHIVEL et al.[15] accidentally achieved C doped anatase TiO₂ during their work on N doped TiO₂, and found that it was much more active than N doped TiO₂ in degradation of 4-chlorophenol with visible light irradiation. IRIE et al.[16] fabricated carbon-doped anatase TiO₂ by oxidative annealing of TiC, in which carbon atoms were at substitutional sites of oxygen atoms. Experimental results indicated that the as-prepared carbon-doped TiO₂ had a smaller band gap, its absorption edge had a red shift, and showed visible light photocatalytic activity. Rare earth metal ions doped TiO₂ is also one of the research focus[7,17,18]. LI et al.[19] synthesized Nd³⁺ doped anatase TiO₂ nanoparticles, and found it being superior to undoped TiO₂ nanoparticles in degrading 2-chlorophenol with visible light irradiation.

By theoretical calculations, they considered that the band gap of Nd³⁺ doped TiO₂ was narrowed by introducing Nd 4f state below the conduction band, consequently, the absorption edge shifted to visible light region. Given the important roles of C and Nd ions on the improvement of photocatalytic activity of TiO₂, WU et al.[20] synthetized Nd-C codoped anatase TiO₂ (C at O, and Nd at Ti), expecting for reaching some synergetic effects between codoped ions. Their experimental results indeed indicated that Nd-C codoped TiO₂ gained further enhancement of visible light absorption compared with C or Nd alone doped TiO₂, and the photogenerated carriers recombination was effectively inhibited by introduced Nd 4f energy levels and...
oxygen vacancies. Therefore, the photocatalytic activity of Nd-C codoped TiO₂ was superior to single doped TiO₂. By far as we know, there have no reports concentrate on the theoretical calculations of the Nd-C codoped TiO₂.

So in this paper, using first principles based on density functional theory (DFT), we firstly calculated the band structures, density of states and optical absorption spectra of Nd-C codoped TiO₂. In addition, the related properties of Nd doped TiO₂, C doped TiO₂ and pure TiO₂[21] were also calculated. By comparing the electronic structures differences between Nd-C codoped TiO₂ and the pure and single doped TiO₂, we investigate the mechanism of further improvement as mentioned above from the electronic structure point of view.

2. MATERIALS AND METHODS
In this study, Nd-C codoped anatase TiO₂ is modeled using a 3×3×1 anatase TiO₂ supercell, in which one O atom is replaced by C atom, and one Nd atom substitutes for one Ti atom, as shown in Figure 1. Our calculations are performed using CASTEP program[22]. The interaction between ion core and valence electrons is described by ultrasoft pseudopotential, and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) is employed to describe the exchange-correlation energy for valence electrons. The electron wave functions are expanded in plane wave basis set with a cutoff energy of 360 eV.

The k-points for Brillouin zone sampling is set as 2×2×2. The band structure, density of states, and optical absorption spectra are calculated based on geometry optimized crystal structure. The calculations of corresponding properties of pure and single doped TiO₂ are performed using the same method as that of Nd-C codoped TiO₂.

3. RESULTS AND DISCUSSION
The band structures and density of states (DOS) near Fermi level for pure, Nd doped, C doped, and Nd-C codoped TiO₂ are shown in Figure 2. Fermi level is chosen at zero. It can be seen from Figure 2 that doping does not change band gap significantly, just gives rise to a slight band gap broadening. Therefore, the band gap is not the dominant factor which influences optical absorption. However, the dopants introduce impurity energy levels in the band gap, these gap levels can cause remarkable influence on optical absorption.

In Nd doped TiO₂, Nd 4f states have two density of states peaks, forming a series of intensive impurity energy levels below conduction band and an isolated energy level at Fermi level, respectively. The impurity energy levels below conduction band are above Fermi level, so they are not occupied by electrons. Electrons in valence band can absorb photons whose energy are smaller than band gap energy, and transit to the empty Nd 4f state, therefore, visible light absorption of Nd doped TiO₂ is enhanced by the introduction of Nd 4f state.

Moreover, the impurity energy levels below conduction band also act as electron trap centers. Electron
trap centers have a strong ability to capture electrons, but poor for holes. When electrons are captured by electron trap centers, holes can hardly recombine with the trapped electrons, and it takes a long time to release trapped electrons by visible light irradiation to conduction band, thus decreasing carriers recombination rate and prolonging carriers lifetime. For C doped TiO$_2$, C 2$p$ state hybridizes with O 2$p$ and Ti 3$d$ states, forming three impurity energy levels in band gap, one is below conduction band, one is above valence band, and the other at Fermi level.

Our calculated band structure is in agreement with that of Li et al.\cite{23} in general. The impurity energy level below conduction band lies above Fermi level, so it is lack of electrons, and the one above valence band is blow Fermi level, then is occupied by electrons. Hence, the electrons of valence band and occupied impurity energy level can be excited to conduction band and empty impurity energy level, extending optical absorption range to visible light region.

As with Nd doped TiO$_2$, impurity energy levels below conduction band and above valence band play a role of electrons trap centers and holes trap centers, respectively, consequently inhibit carriers recombination and increase carriers lifetime. Nevertheless, the impurity energy level located at Fermi level is deep in band gap, and when C doping concentration is high enough it may become an effective carriers recombination center, this may be one reason for the existence of optimal C doping concentration\cite{24}.

As for Nd-C codoped TiO$_2$, Nd 4$f$ state remains two density of state peaks, the higher one is below conduction band and forms several impurity energy levels as Nd doped TiO$_2$, the lower one is above valence band, together with C 2$p$ state forms an impurity energy band rather than an isolated energy level as Nd doped TiO$_2$. Because the density of state peak above valence band is much bigger than that of Nd and C single doped TiO$_2$, electrons of corresponding impurity energy levels have a larger probability to be excited to empty Nd 4$f$ and Ti 3$d$ states by visible light. In addition, electrons and holes trap centers can capture more carriers due to increased impurity energy levels concentration, decreasing carrier recombination rate and prolonging carriers lifetime in further. As a consequence, visible light absorption and quantum efficiency of Nd-C codoped TiO$_2$ is enhanced compared with Nd and C single doped TiO$_2$. 

*Figures (a) and (b) show the band structure and density of states (DOS) of TiO$_2$ with and without Nd doping, respectively.*
The polycrystalline model of TiO$_2$ was used to calculate the absorption spectra of the different systems. Because GGA method has the disadvantage of band gap underestimation, we used a “scissor operation” of 1.0 eV to move the absorption edge of pure anatase TiO$_2$ to 3.2 eV. The optical calculations were based on the ground state of the electrons. The calculated absorption spectra for pure, Nd doped, C doped, and Nd-C codoped TiO$_2$ are shown in Figure 3. From Figure 3 it can be seen that the absorption edge of all the doped TiO$_2$ shifts to visible light region with respect to pure TiO$_2$, and Nd-C codoped TiO$_2$ has a greatest red shift extent. As all the doped TiO$_2$ have a wider band gap than pure TiO$_2$, the red shift should be caused by impurity energy levels. The empty impurity energy levels below conduction band form a new conduction band minimum (CBM), and the occupied impurity energy levels above valence band act as new valence band maximum (VBM), it seems like the band gap is narrowed, so the absorption edge shifts to visible light region [19]. Figure 2 also shows that Nd-C codoped TiO$_2$ has a more intense visible light absorption than pure and single doped TiO$_2$, which is in agreement with experimental result [20].

**Figure 2:** Structural mode Band structures and density of states for (a) pure$^{[21]}$ TiO$_2$ (b) Nd doped TiO$_2$ (c) C doped TiO$_2$ (d) Nd-C codoped TiO$_2$
Figure 3: Absorption spectra for pure, Nd doped, C doped, and Nd-C codoped TiO$_2$

4. CONCLUSIONS

We have calculated the band structures, density of states, and absorption spectra of pure, Nd doped, C doped, and Nd-C codoped TiO$_2$ using first-principles based on density functional theory. Nd 4f state forms empty impurity energy levels below conduction band, and C 2p state together with Nd 4f state forms occupied impurity energy levels with higher density than single doped TiO$_2$ above valence band.

Consequently, more electrons in the occupied energy levels can be excited by visible light to empty Nd 4f state rather than Ti 3d state, resulting in further enhancement of visible light absorption and absorption edge red shift. Also, the impurity energy levels act as carriers trap centers, decreasing carriers recombination rate.

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6. BIBLIOGRAPHY


