



A DFT study on the modification mechanism of (Cr, C) co-doping for the electronic and optical properties of anatase TiO₂



Xuechao Li^a, Jianhao Shi^a, Hao Chen^a, Rundong Wan^{a,*}, Chongyan Leng^a, Song Chen^b, Ying Lei^c

^a Department of Materials Physics and Chemistry, Kunming University of Science & Technology, Kunming, Yunnan 650093, PR China

^b Kunming Institute of Precious Metals, Kunming, Yunnan 650106, PR China

^c Department of Metallurgical Engineering, Anhui University of Technology, Maanshan, Anhui 243002, PR China

ARTICLE INFO

Article history:

Received 15 July 2016

Received in revised form 1 December 2016

Accepted 22 December 2016

Keywords:

anatase TiO₂

Co-doping

Impurity states

Photocatalytic activity

ABSTRACT

To explore an effective doping configuration for TiO₂, thus further improving the photocatalytic performances of anatase TiO₂, we systematically study the electronic structures and optical properties for the pure, Cr-doped, C-doped and Cr/C co-doped TiO₂, using density functional calculations. We find that three doped systems show higher stability under reduction conditions with relatively lower impurity formation energies. For Cr or C mono-doping, the isolated impurity states appear in the band gap region, thus changing the electronic structures and lowering the excitation energy for electron transition, which would result in response to visible light. The Cr/C co-doped TiO₂ shows much bigger red-shift of absorption edge than the mono-doping systems, due to the greater band gap narrowing of the co-doped system. Furthermore, for the co-doped systems, there are more impurity states appearing between the top of the valence band and the bottom of the conduction band. This not only enhances the visible light absorption, but also promotes the separation of photo-excited electron-hole pairs. We also find the doping effect on the electronic structures is localized. The calculated absorption spectra indicate that Cr/C co-doped TiO₂ possesses much higher photocatalytic activity under visible light region.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Extensive studies have been performed to improve the photochemical activity of TiO₂, a promising photo-catalyst material, in recent years, due to its excellent physical and chemical performances. As well-known, the anatase phase of TiO₂ can only show response to the UV light, because of its wide band gap of about 3.23 eV, whereas it cannot show photocatalytic activity under visible light region, thus resulting in huge waste of solar energy resources [1]. Besides, the photo-excited electron-hole pairs tend to recombine easily, which leads to the low photo-quantum efficiency. Researchers have utilized many effective methods to address these issues. They have achieved some partially satisfactory results, such as noble metal loading [2–5], dye-sensitizing [6–9], semiconductor mixing [10–13] and ions doping [14–16].

The ions doping by metal or nonmetal, as one of the most effective modification methods, has attracted extensive attention from scientific researchers. Nonmetal ions are generally incorporated into the lattice by occupying the lattice O sites, such as B-doping

[17–21], C-doping [22–27] and N-doping [28–34]. The valence bands of TiO₂ are mainly composed of O 2p states, whose p orbitals would couple with the p orbitals of the nonmetal dopants, thus introducing the impurity electronic states above the top of valence bands, resulting in the narrowing of band gap and remarkable visible light absorption. For the B mono-doping, Finazzi et al. [20] reported that the B substitution to oxygen leads to a paramagnetic defect, thus introducing new states in the gap region of TiO₂. In addition, they also considered the doping at interstitial sites, and found the electronic characteristics of interstitial B are rather independent of the doping sites. The influence of C mono-doping on the electronic structures of TiO₂ was also studied [22–27]. Researchers found the incorporation of C dopants significantly changes the electronic structures of TiO₂. The impurity states appear above the top of valence bands, which mainly consist of the mixing of C 2p states and O 2p states. They reported that these impurity states also influence the optical absorption spectra of TiO₂. Because the impurity states can accept electrons from the valence bands and then transfer them to the conduction bands, the excitation energy of electrons are significantly reduced, which leads to great red-shift of absorption edge of TiO₂. Russo et al. [35] investigated N-doped TiO₂ by N substitution to Ti sites. Their electronic structure calcu-

* Corresponding author.

E-mail address: rdwan@kmust.edu.cn (R. Wan).

lations showed that the N 2p states at Ti site mix with O 2p states at the top of the valence bands as well as the Ti 3d states at the bottom of conduction bands. They also observed the small amount of band gap narrowing for N doping.

Metal ions doping, especially the transition metal ions, can also improve the electronic and photocatalytic performances of TiO₂ [15,36–38,16]. The conduction bands of TiO₂ mainly consist of Ti 3d states, which would couple with the d orbitals of the transition metal ions, thus resulting in new electronic structure features. Choi et al. [39] reported that the presence of metal ions dopants significantly improves the photocatalytic activity, effectively suppresses the charge carriers' recombination. The photoactivity of doped TiO₂ depends on the doping concentration and the energy level of dopants. Due to the excitation of electrons from the valence band of O 2p to the V 3d orbitals, Tian et al. found V doping can enhance the photocatalytic activity under both the UV and visible light regions [40]. Karakitsou et al. [41] reported the enhancement or reduction of photocatalytic activity is related to the valence and concentration of the doping cations. Although some metal or non-metal ions doping can cause the visible light response, the impurity states induced by the dopants may act as the recombination centers, enhancing the recombination of photo-excited carriers. Therefore, preventing the recombination of carriers is a crucial challenge to improve the photocatalytic activity under visible light region.

To overcome the shortcomings of single ion mono-doping, multiple ions co-doping has been widely utilized to enhance the performances of TiO₂. One effective method is the introduction of the co-doping with transition metal and nonmetal ions in TiO₂. More importantly, making the two different ions become bonded to each other can enhance the stability of doped systems. The formation energy of co-doping system may become much lower than that of an anion doping system, due to the strong interaction between the nonmetal-metal defect pairs [42]. Because of the synergistic effects between different ions, the recombination of photo-excited carriers can be effectively suppressed, thus enhancing the electron mobility rate and improving the photocatalytic activity under visible light region [43,44,34,45,46]. Yin et al. [47] reported that both the higher visible-light optical absorption and band gap narrowing depend critically on the donor-acceptor concentration. English et al. [44] found that the N/W co-doped titania exhibits higher visible-light photocatalytic efficiency than either N- or W-doping alone.

In our previous study on C mono-doping [50], we found that the impurity states induced by C dopants appear around the top of the valence bands, limiting the band gap narrowing and thus hindering the improvement of photocatalytic activity. What's more, the impurity states in the band gap are easy to become the recombination centers of photo-excited carriers. In this study, to understand more about these issues, we calculate Cr/C co-doping effects on the electronic and photocatalytic performances of TiO₂. To obtain more stable doping configuration, we mainly consider the structure with Cr and C atoms at the adjacent positions, namely the doping cation and anion are bonded together directly. Due to the synergistic effects between cations and anions, the co-doping system may yield more ideal results than the individual C or Cr mono-doping system. The impurity states appear both above the top of valence bands and below the bottom of conduction bands, greatly inhibiting the recombination of photo-excited electron-hole pairs. The band gap becomes significantly narrowed due to the coupling between impurity states and energy bands, resulting in the red-shift of absorption edge. Our calculated results reveal that the Cr/C co-doping can not only enhance the visible light absorption, but also improve the photocatalytic activity under visible light region.

2. Computational details

2.1. Models

In this work, we adopt a $2 \times 2 \times 1$ anatase supercell to simulate the three different doped structures, which contains 48 atoms and possesses the I41/amd symmetry. To build the substitutional mono-doping systems, the dopant C atom occupies the lattice oxygen sites, whereas one host Ti atom is replaced by one Cr atom. The atomic doping concentration for the mono-doping system is about 2.08 at.%. For the Cr/C co-doping system, one host Ti atom and one host oxygen atom are replaced with one Cr atom and one C atom, respectively. The doping concentration for the Cr/C co-doping TiO₂ is about 4.16 at.%. We also ensure that the substitutional Cr and C atoms are bonded together directly. Based on previous study, the bonding of anion to cation could lead to the compensated effect, thus resulting in the lower total energy than other concentrations, which makes it become more energetically favored [48,49]. For the finite-size effects in the supercell, we have taken the influence of size effects into account in our previous work [50]. The calculated results indicate that a different supercell almost has little influence on the formation energies. The electronic structures and optical properties also display the similar features in different supercell models. All of these apparently show that the finite-size effects could almost be ignored, validating the rationality of the doped models we chose here. In the following manuscript, the C mono-doping configuration, the Cr mono-doping configuration and the co-doping configuration are denoted with the label of TiO₂@C, TiO₂@Cr and TiO₂@CrC, respectively. All the three doped models are presented in Fig. 1.

2.2. Computational methods

All the geometry optimization calculations in the present work are carried out in the framework of density functional theory within the generalized gradient approximation (GGA) using the plane-wave ultrasoft pseudopotentials method as implemented in the CASTEP package in Materials Studio program [51]. To simulate the extend nature of these structures, we employ the three-dimensional (3D) periodic conditions. We employ the Wu and Cohen (WC) functional to describe the exchange-correlation [52,53]. Based on our previous test for cutoff energy [50], the energy cutoff for the planewave basis set is 380 eV. We first relax both the atomic positions and cell parameters. Based on the optimized TiO₂ unit cell, we built the supercell models, construct the doped systems and then optimize them. All the optimized calculations are performed in the reciprocal space. The minimization algorithm we adopt is the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme [54]. The valence atomic configurations are set as $3s^2 3p^6 3d^2 4s^2$ for Ti, $2s^2 2p^4$ for O, $3s^2 3p^6 3d^5 4s^1$ for Cr and $2s^2 2p^2$ for C. To realize the accurate and fast calculation, the convergence threshold for geometry relaxations are set as: the maximum atomic interactional forces are below 0.01 eV/nm, the maximum atomic displacement is below 5×10^{-4} nm, the maximum internal atomic stress are less than 0.02 GPa, and the maximum atomic variational energy is less than 5×10^{-6} eV.

In order to calculate the electronic properties accurately based on the optimized geometry, we adopt the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional with the revised 6-31G basis set to calculate the band structure and density of states (DOS) by using Gaussian-type orbitals (GTO) implemented in the Gaussian 09 programs. Our previous experience shows that the plane-wave DFT optimized structures are almost the same as the GTO optimized structures, while the utilization of the former has tremendous time-saving [50]. The conventional density functional

Download English Version:

<https://daneshyari.com/en/article/5453481>

Download Persian Version:

<https://daneshyari.com/article/5453481>

[Daneshyari.com](https://daneshyari.com)