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A DFT study of the electronic structures and optical properties of (Cr, C) co-doped rutile TiO_2

Hao Chen [a], Xuechao Li [a], Rundong Wan [a,*], Sharon Kao-Walter [b,c], Ying Lei [d]

[a] Department of Materials Physics and Chemistry, Kunming University of Science & Technology, Kunming, Yunnan 650093, PR China
[b] Dept. of Mech. Eng., Blekinge Institute of Technology, SE 37179 Karlskrona, Sweden
[c] Fac. of Mech. & El. Eng., Shanghai Second Polytechnic Univ., 201209 Shanghai, PR China
[d] Department of Metallurgical Engineering, Anhui University of Technology, Maanshan, Anhui 243002, PR China

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ABSTRACT

To get an effective doping model of rutile TiO_2, we systematically study geometrical parameters, density of states, electron densities, dielectric functions, optical absorption spectra for the pure, C mono-doping, Cr mono-doping and (Cr,C) co-doping rutile TiO_2, using density functional calculations. We find that a C doped system presents higher stability under Ti-rich condition, while Cr doped and (Cr,C) co-doped systems are more stable under O-rich condition. For (Cr,C) co-doping situation, the imaginary part of the dielectric function reflects the higher energy absorption efficiency for incident photons. Moreover, co-doping system exhibits much bigger red-shift of optical absorption edge compared with Cr/C single doping systems, because of the great reduction of the direct band gap. The calculated optical absorption spectra show that the (Cr,C) co-doping rutile TiO_2 has higher photocatalytic activity in the visible light region.

1. Introduction

The most urgent task in the current society is to develop new environmental-friendly materials to replace traditional materials. This trend gives the driving force of TiO_2 (rutile and anatase) as photocatalytic materials, since they have great potential to utilize solar energy. Rutile is the most stable phase of titanium dioxide. It is used in photocatalysis, such as hydrogen production by water decomposition, self-cleaning, antimicrobial surfaces, water or air purification [1–5]. However, the intrinsic wide band gap (3.0 eV for rutile [6]) limits these applications. Moreover, the wide band gap restricts rutile to respond only to ultraviolet (UV) irradiation. Since the UV-light region accounts for less than 5% of the total solar spectra, rutile has low efficiency for using sunlight. To overcome these limitations, we have to find a way to reduce the band gap and consequently to enhance the photocatalytic efficiency.

In order to overcome the UV limitation, some scholars use non-metal ions to dope rutile titanium dioxide. He et al. [7] found that band gap narrows by 0.4 eV after iodine doping, which promotes the photocatalytic activity. Dan et al. [8] found that replacing two O atoms with two N atoms can greatly increase the optical absorption in the visible light region. Pan et al. [9] found that the impurity energy level is introduced due to the coupling between O 2p and C 2p states, leading to the red-shift of optical absorption edge obviously. Moreover, the efficiency of light absorption increases after doping. Other scholars put forward the method of metal ions doping. Yu et al. [10] calculated a substitutional Sn doping at the Ti site, leading to reduce the band gap of rutile TiO_2, with a strong red-shift enhancement. Shao et al. [11] performed DFT (density functional theory) on Mn substitutional doping rutile, which can make full use of wide spectral region under solar irradiation.

Recent studies have shown that by using appropriate dopants, rutile TiO_2 can be transformed into a superior photocatalyst. M Fittipaldi et al. [12] concentrated on (B,F) co-doping rutile TiO_2, finding that the interaction between B and F leads to evidently enhanced performances in pollutant degradation. Liu et al. [13] have synthesized (S,N) co-doping rutile TiO_2 photocatalyst, applying a hydrothermal method and subsequent nitridation under NH_3 flow. They found that (S,N) co-doping rutile TiO_2 has a better photocatalytic activity than S mono-doping or N mono-doping for degradation of methylene blue in the visible light region (wavelength is about 400–760 nm). Han et al. [14] found that N + H co-doping induces obvious band gap reduction without introducing any impurity states in the forbidden gap. Meanwhile, metal ions and nonmetal ions co-doping rutile began to attract the attention of scholars. Dan et al. [8] studied the (N,Co) co-doping rutile TiO_2, which extends the optical absorption to the visible light region. Zhu et al. [15] calculated that optical properties of co-dop-

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* Corresponding author.
E-mail address: rwan69@kmust.edu.cn (R. Wan).

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ing rutile TiO_2 with nitrogen and platinum group metals (Ru,Rh, Pd), showing that an improvement of the absorption efficiency of visible light to some extent.

In this work, we calculate geometry structures, electronic structures and optical properties of Cr/C substitutional mono-doping and (Cr,C) substitutional co-doping rutile TiO_2, using density functional theory. According to our previous experience, we first use WC (Wu and Cohen) [16] flavored generalized gradient approximation to optimize the geometrical structures, using the plane-wave ultrasoft pseudopotentials method as executed in CASTEP module. To explore electronic structures, we perform the total density of states and partial density of states for pure TiO_2 and doped TiO_2 models with HSE06 hybrid functional calculation on the frame of Gaussian type of orbital. The HSE06 hybrid functional calculation in Gaussian 09 has the advantages of significant time saving in comparison with HSE06 in CASTEP. Therefore, we can use the HSE06 hybrid functional in Gaussian 09 to calculate band gaps rapidly and accurately [22]. To predict the dielectric function and optical absorption spectra, we treat the band gaps by using HSE06/6-31G hybrid functional calculation in Gaussian 09 program as the experimental values. Then we calculate the band gap values using GGA-WC functional in CASTEP. The difference between two different kinds of band gap values is deemed as a correction value, i.e. 'scissors operator'. Finally, we put the 'scissors operator's back in CASTEP to calculate dielectric functions and UV–Vis absorption spectra, because Gaussian 09 lacks the ability to compute these two properties for extended systems. Thus, we can give a relatively reasonable explanation for the modification mechanism of (Cr,C) co-doped rutile TiO_2.

2. Computation

2.1. Models

Rutile TiO_2 belongs to the tetragonal crystal system [17], and the space group is *P*42/*mnm* (D144h). Each lattice contains six atoms (two Ti atoms and four O atoms). One Ti^{4+} ion is surrounded by 6 O^{2-} ions, and its coordination number is 6; one O^{2-} ion is surrounded by 3 Ti^{4+} ions, and its coordination number is 3. We use a 2 × 2 × 3 rutile supercell ($Ti_{24}O_{48}$) as a computational model, containing twelve primitive unit cells of rutile TiO_2. To build the mono-doping models, we substitute the single C and Cr atoms for single O and Ti atoms, respectively. Hence the obtained configuration is $Ti_{24}CO_{47}/Ti_{23}CrO_{48}$. For the (Cr,C) co-doping rutile TiO_2, we replace O and Ti atoms with C and Cr atoms, as shown in Fig. 1. Thus, the configuration of $Ti_{23}CCrO_{47}$ with 2.08 at% C and 4.17 at% Cr is formed. The three doping concentrations chosen are relatively reasonable compared with experimental execution [18].

2.2. Computing methods

To optimize geometric structure, we do all the calculations with the WC (Wu and Cohen) flavor of GGA, using the plane-wave ultrasoft pseudopotentials method in CASTEP [16,19]. We first use the Visualizer in Materials Studio to realize the model building. Based on the optimized rutile TiO_2 unit cell, we build a 2 × 2 × 3 supercell, in which Cr and C atoms replaces Ti atom and O atom, respectively. After atomic substitution, we optimize the doped models. We have performed the optimization calculation with the minimization algorithm using the Broyden-Fletcher-Goldfarb-Shanno scheme [20]. The valence electronic configurations are considered 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, $2s^2 2p^2$ for C. To achieve accurate calculation and fast convergence, the 2 × 2 × 2 Monkorst-park Special K point is used to calculate the integral calculation of the irreducible Brillouin zone [21]. The convergence criteria for geometry relaxations in computational progress are set as: the cutoff energy for the plane wave basis set is 340 eV, the atomic maximal interaction forces are less than 0.3 eV/nm, the maximum displacement distance is less than 1×10^{-4} nm, atomic maximum internal pressure is less than 0.05 GPa, and the maximum atomic variational energy is less than 1×10^{-5} eV. In addition, we calculate the TiO_6 dipole moments according to the dipole moment formula: $\mu = qd$, where q denotes the net charge between Ti and O atoms, and d indicates the central distance between Ti and O atoms [22].

To accurately calculate the electronic properties after optimizing geometric structure, we use the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional with the modified 6-31G basis sets under the framework of the Gaussian-type orbital to calculate the density of states (DOS) in Gaussian 09 program. According our previous experience, the GGA-WC optimized geometric structures are very close to the optimized geometric structures in Gaussian 09 [23]. Therefore, we can use the former to save a lot of time. Gaussian 09 is a comprehensive computational quantum program for quantum chemistry, but now it has begun to be applied in solid state physics. For the modified 6-31G basis sets, we can remove the diffuse functions with an exponent less than 0.12, because good-quality molecular basis sets normally include diffuse functions to model tails of wave functions that do not exist in solids [24]. Therefore, the revised Ti and Cr basis sets can be used for TiO_2 solid calculation. To get the most satisfactory integration, we choose the ultrafine precision (int = ultrafine) in the energy calculation progress. Gaussian 09 provides a single point energy calculation for each system, and we use 8 × 8 × 8 k-mesh and corresponding 256k-points, which is quite different from plane-wave scheme to adopt much fewer irreducible k-points. This is enough to produce necessary features in the density of states analyses for 2 × 2 × 3 rutile supercells. By completing the settings for these parameters, HSE06 hybrid functional in Gaussian 09 has full ability to predict electronic structures of doped models closest to experimental values.

Because Gaussian 09 is unable to calculate some optical absorption spectra for three-dimensional periodic solid systems, we take the band gaps of the doped systems in Gaussian 09 as the experimental values. After calculating band gaps for the same systems using GGA-WC functional, we treat the difference between two different band gap values as a 'scissors operator'. Then we calculate the dielectric functions and UV–Vis optical spectra by using 'scissors operator's in CASTEP.

3. Results and discussion

3.1. Geometrical parameters

To analyze geometrical changes after the dopant entering the lattice, we calculate the optimized cell parameters for the pure and different doped models, as shown in Table 1. The optimized bulk cell parameters for pure TiO_2 (a = b = 4.593 Å, c = 2.940 Å) are in good agreement with experimental values (a = b = 4.594 Å, c = 2.959 Å) [25,26] and other theoretical values (a = b = 4.614 Å, c = 2.976 Å) [7]. Clearly, our calculated a and b by GGA-WC are very close to experimental values. The value of c is different from ours. Our result is 0.64 percent less than experimental value, showing the reliability of our method. After doping, we find that the volumes for three doping samples have increased. This indicates that the introduction of dopant causes the volume expansion of supercells. Besides, we also calculate the average bond lengths, total energies, defect formation energies, average net charges, and