Physica B 407 (2012) 4649–4654

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

DFT study on electronic structure and optical properties of N-doped, S-doped, and N/S co-doped $SrTiO_3$

Chao Zhang [a,b], Yongzhong Jia [b,*], Yan Jing [b], Ying Yao [b], Jun Ma [b], Jinhe Sun [b]

[a] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China
[b] Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, PR China

ARTICLE INFO

Article history:
Received 30 July 2012
Received in revised form
22 August 2012
Accepted 26 August 2012
Available online 30 August 2012

Keywords:
First principles
Electronic structure
Optical properties
N/S co-doping
$SrTiO_3$

ABSTRACT

The electronic structures and optical properties of N-doped, S-doped and N/S co-doped $SrTiO_3$ have been investigated on the basis of density functional theory (DFT) calculations. Through band structure calculation, the top of the valence band is made up of the O 2p states for the pure $SrTiO_3$. When N and S atoms were introduced into $SrTiO_3$ lattice at O site, the electronic structure analysis shows that the doping of N and S atoms could substantially lower the band gap of $SrTiO_3$ by the presence of an impurity state of N 2p on the upper edge of the valence band and S 2p states hybrid with O 2p states, respectively. When the N/S co-doped, the energy gap has further narrowing compared with only N or S doped $SrTiO_3$. The calculations of optical properties also indicate a high photo response for visible light for N/S co-doped $SrTiO_3$. Besides, we find a new impurity state which separates from the O 2p states could improve the photocatalytic efficiency and we also propose a model for light electron-hole transportation which can explain the experiment results well. All these conclusions are in agreement with the recent experimental results.

1. Introduction

Finding effective catalysts for degradation of pollutants and water splitting has become an important issue in recent years. Cubic perovskite structure $SrTiO_3$ has attracted extensive attention due to its excellent photocatalytic performance capable of splitting water into H_2 and O_2 [1] and decomposing organic compounds [2]. Besides, $SrTiO_3$ also has superior physical and chemical properties, such as the chemical nature and structural stability. $SrTiO_3$ has merits like good heat resistance, corrosion resistance anti-light and easy to load other doping substances, which makes it one of the promising photocatalytic candidates for TiO_2 [3].

However, because of its wide band gap (about 3.2 eV), $SrTiO_3$ can only absorb a small part of the solar spectrum [4,5] (about 4%), which greatly restricts its photocatalytic efficiency. Therefore, how to extend $SrTiO_3$ absorption of light to the visible region, becomes the aim for majority of photocatalytic scientists.

Doping foreign elements become one of the primary strategies for gaining visible light-driven photocatalysts. Among them, doping with non-metal elements was found to be an efficient way to improve the visible light activity of $SrTiO_3$, which has attracted much attention of scientists. Among them, doping with N, S and C was found to be an efficient way to improve the visible light activity of $SrTiO_3$ [6,7]. Recently, the different ions co-doped into $SrTiO_3$ have been a hot topic of experiment study. Wang et al. [8] prepared sulfur and nitrogen co-doped $SrTiO_3$ by high energy milling method. They found that sulfur and nitrogen co-doping could greatly improve the photocatalytic activity of $SrTiO_3$ under visible light irradiation and N/S co-doped $SrTiO_3$ exhibited higher visible light photocatalytic activity than sulfur and nitrogen doped $SrTiO_3$.

Nowadays, the non-metal elements co-doping $SrTiO_3$ research mainly through the experimental method, but different experimental conditions and sample preparation methods make it difficult to understand their internal mechanism. Through first principle research, it is helpful to explain the reasons of the photocatalytic activity from microscopic point of view. Mi et al. [9] studied N-doped $SrTiO_3$ thin film by first principles calculation, they find the N-doped $SrTiO_3$ visible light absorption change derived from the localized N 2p narrow band above the O 2p valence band. Liu et al. [10] analyzed the C,S cation-doped $SrTiO_3$ system from geometric and electronic structures, they found that the C,S cation co-doping conducive to O 2p orbitals mixed with C 2s and S 3s orbitals, which contribute to the band gap narrowing. However, few theoretical studies describing explicitly the co-doping effect and concerning the concentration effect of single N- and S-doped $SrTiO_3$ structures have been reported, and the origin of high photocatalytic activity under visible light is not explained definitely.

* Corresponding author. Tel.: +86 0971 6304561; fax: +86 0971 6321767.
E-mail address: zhangchaoqhu@126.com (Y. Jia).

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.08.038

In the present work, we have performed first principle calculations on N-doped, S-doped and N/S co-doped $SrTiO_3$. Through the band structure and absorbing spectrum calculation, we can systematically study N/S co-doping effect and provide some helpful theoretical information for exploiting effective photocatalysts.

2. Computational details

In this work, the DFT calculations have been performed by the CASTEP [11] within the MS 4.4 package and the generalized gradient approximation (GGA) was adopted. The interaction between the valence electrons and the ionic core is described by the Perdew-Wang 91 gradient-corrected functional [12] and ultra-soft pseudo-potentials [13]. The kinetic energy cut-off (E_{cut}) was 390 eV; the Monkhorst-Pack [14] k-mesh was $2\times2\times2$.

In the process of calculation, a $2\times2\times2$ super-cell was used in constructing the pure $SrTiO_3$ structures. To set the doped model, an O atom is substituted by one N or S atom ($2\times2\times2$ super-cell); the stoichiometry of the doped model is $SrTiO_{3-x}N_x$ or $SrTiO_{3-x}S_x$ with $x=0.0417$, the atom concentration of impurity is about 4.17 atom%. For the co-doping model, two O atoms are replaced by one N and one S atom ($2\times2\times2$ super-cell); the stoichiometry of the doped model is $SrTiO_{3-2x}N_xS_x$ with $x=0.0417$, the atom concentration of impurity is about 8.33 atom%. In order to further explain the relationship between co-doping effect and doped element concentration, we construct another two models. Two O atoms are substituted by two N or two S atoms ($2\times2\times2$ super-cell); the stoichiometry of the doped model is $SrTiO_{3-2x}N_{2x}$ or $SrTiO_{3-2x}S_{2x}$ with $x=0.0417$, the atom concentration of impurity is about 8.33 atom%. All the six models are displayed in Fig. 1(a)–(f), respectively.

Geometry optimization was carried out before single point energy calculations, and the self-consistent convergence accuracy was set at 5×10^{-5} eV/atom. The convergence and criterion of the largest force on atoms was 0.1 eV/Å, the stress was no more than 0.2 GPa, and the maximum displacement was 5×10^{-4} nm. Electronic structures and optical properties were calculated on the corresponding optimized crystal geometries and all the calculation were carried in reciprocal space.

3. Results and discussion

3.1. Band structure

The band structure of N-doped, S-doped and N/S co-doped $SrTiO_3$ has been calculated, the band gap and band structure are displayed in Table 1 and Fig. 2, respectively.

The calculated band gap of pure $SrTiO_3$ at the Γ point is about 2.2 eV (see Fig. 2(a)), which is underestimated by about 30% compared with the experimental value of 3.2 eV. The underestimation always exists in the band gap calculations due to the well-known limitation of the DFT theory. However, the character of the band structure and the trend of the energy gap variations as a function of the atom species and concentration from the calculations are expected to be reasonable and reliable.

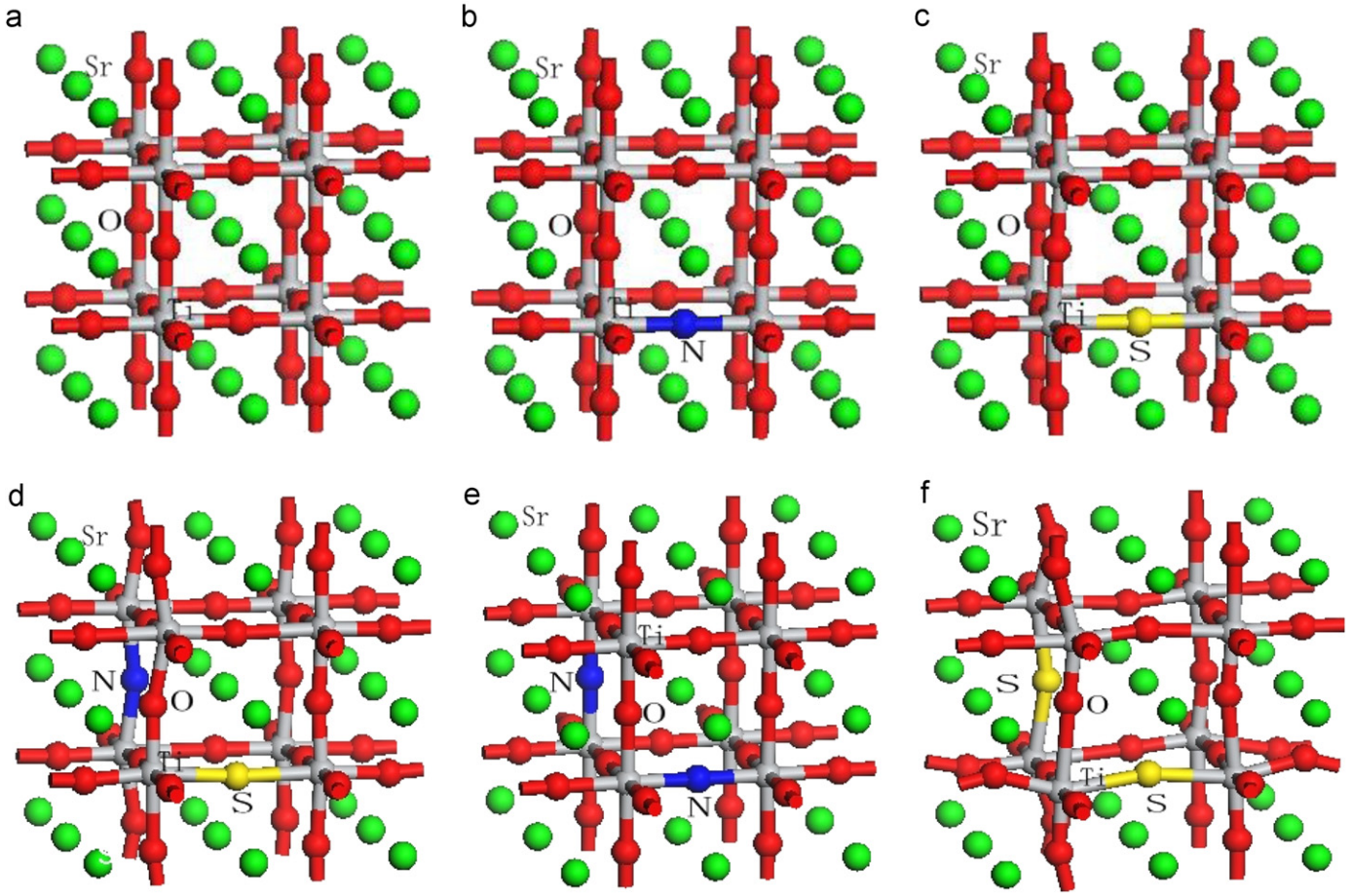

Fig. 1. $SrTiO_3$ super-cell models (a) un-doped $SrTiO_3$, (b) one N atom doped $2\times2\times2$ $SrTiO_3$ super-cell, (c) one S atom doped $2\times2\times2$ $SrTiO_3$ super-cell, (d) N/S co-doped $2\times2\times2$ $SrTiO_3$ super-cell, (e) two N atoms doped $2\times2\times2$ $SrTiO_3$ super-cell, and (f) two S atoms doped $2\times2\times2$ $SrTiO_3$ super-cell.