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

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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.

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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.

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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 $2 \times 2 \times 2$.

In the process of calculation, a $2 \times 2 \times 2$ 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 ($2 \times 2 \times 2$ 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 ($2 \times 2 \times 2$ 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 ($2 \times 2 \times 2$ 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.

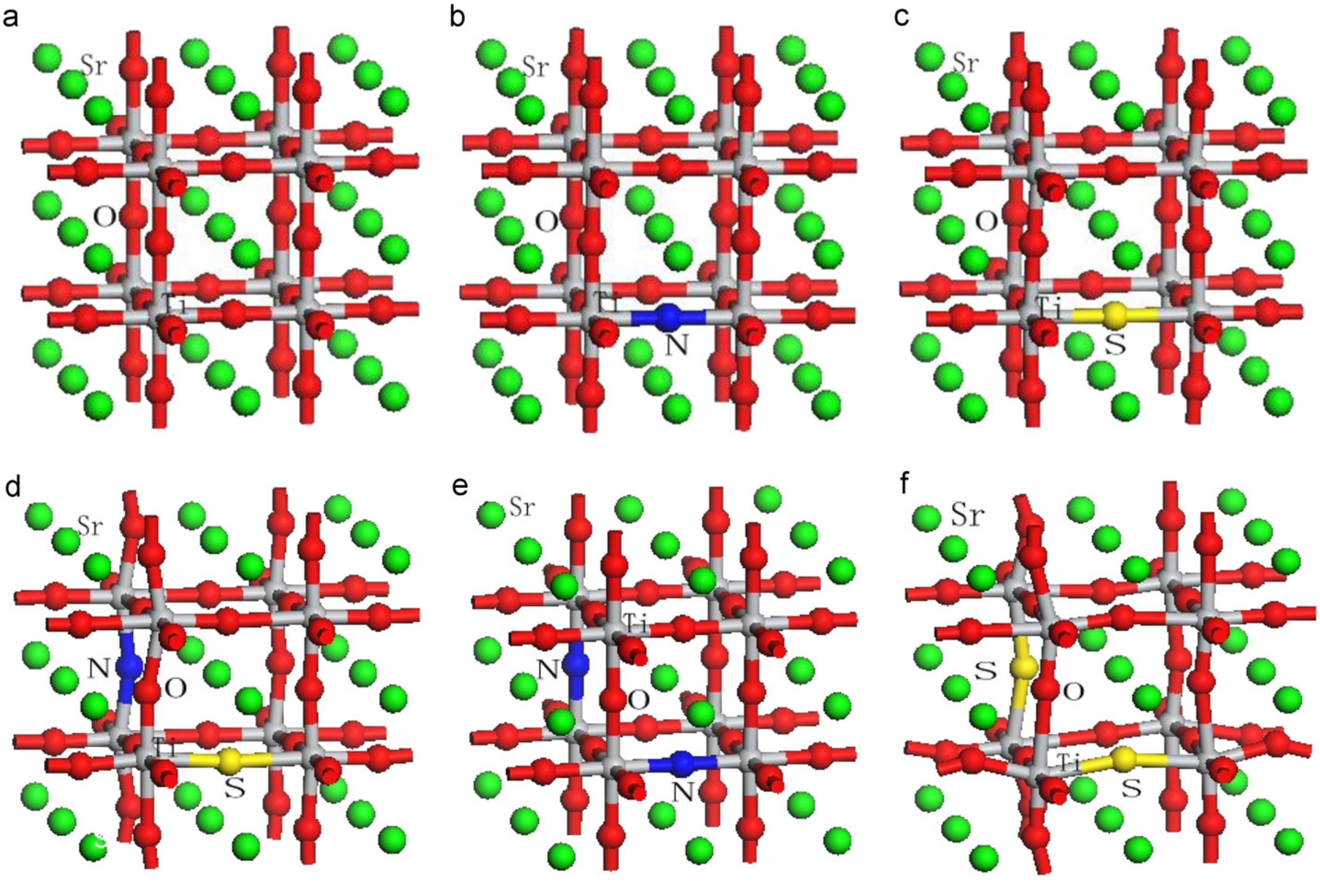

Fig. 1. $SrTiO_3$ super-cell models (a) un-doped $SrTiO_3$, (b) one N atom doped $2 \times 2 \times 2$ $SrTiO_3$ super-cell, (c) one S atom doped $2 \times 2 \times 2$ $SrTiO_3$ super-cell, (d) N/S co-doped $2 \times 2 \times 2$ $SrTiO_3$ super-cell, (e) two N atoms doped $2 \times 2 \times 2$ $SrTiO_3$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

For one N-doped $2\times2\times2$ $SrTiO_3$ super-cell, the concentration of the doped N is 4.17atom%. The calculated results show that the top of the value band consist of N 2p electronic which is higher than O 2p electronic, resulting in a energy gap between N 2p and O 2p by about 0.41 eV (see in Fig. 2(b)). The position of conduction band edge shows a little moving to the lower energy. The two together make the N doping of the $SrTiO_3$ band gap become lower and the calculated band gap is 1.44 eV.

For one S-doped $2\times2\times2$ $SrTiO_3$ super-cell, the concentration of the doped S is 4.17 atom%. The calculated results show that the top of the value band consist of S 3p electronic and O 2p electronic and the two atoms orbits well mixed with each other (see in Fig. 2(c)). The position of conduction band edge also shows a little moving to the lower energy. The two together make the S doping of the $SrTiO_3$ band gap become lower. The calculated band gap of S-doped $SrTiO_3$ is 1.44 eV.

Table 1
Band gap energy (eV) (scissor operator 1.0 eV) of N-doped, S-doped, and N/S co-doped $SrTiO_3$ super-cells and the lowering value of band gap corresponding to the band gap of pure $SrTiO_3$ Δ, with various atoms and concentrations (C_x).

	C_x (atom%)	Band gap (eV)	Scissor operator (1.0 eV)	Δ (eV)
Pure $SrTiO_3$	0.0	2.2	3.2	0
One N doped $SrTiO_3$	4.17	1.44	2.44	0.76
One S doped $SrTiO_3$	4.17	1.44	2.44	0.76
N/S co-doped $SrTiO_3$	8.33	1.159	2.159	1.041
Two N atoms doped $SrTiO_3$	8.33	1.44	2.44	0.76
Two S atoms doped $SrTiO_3$	8.33	1.44	2.44	0.76

For N/S co-doped $2\times2\times2$ $SrTiO_3$ super-cell, the concentration of the doped N and S atoms are 8.33 atom%. The calculated results show that the top of the value band consist of N 2p electronic which is higher than O 2p electronic, resulting in a energy gap between N 2p+S 3p and O 2p by about 0.522 eV (see in Fig. 2(d)). The position of conduction band edge also shows some moving to the lower energy which may originate from the mix of high unoccupied N 2p electronic and O 2p electronic. The two together make the N/S co-doping of the $SrTiO_3$ band gap become lower. The calculated band gap of N/S co-doped $SrTiO_3$ is 1.159 eV.

Through above calculation and analysis, we found that the band gap of N/S co-doped $SrTiO_3$ was much narrower than that of only N atom doped or S atom doped $SrTiO_3$. The N 2p electronic was separate from O 2p electronic in N-doped and N/S co-doped $SrTiO_3$, resulting in a small gap between N 2p electronic and O 2p electronic. The existed small gap may be conducive to the transmission of light electrons and holes separation which could improve the photocatalytic activity of the doped $SrTiO_3$. The conclusion was in agreement with the experimental results reported by Wang et al. [8].

As the doped concentration of N-doped and S-doped atoms were different from that of N/S co-doped $SrTiO_3$, we also did another two doped models calculation to further explain the relationship of the band gap narrower mechanism between atoms species and atom concentration. We chose two N atoms doped $2\times2\times2$ $SrTiO_3$ super-cell model and two S atoms doped $2\times2\times2$ $SrTiO_3$ super-cell model calculation to fully explain the band gap

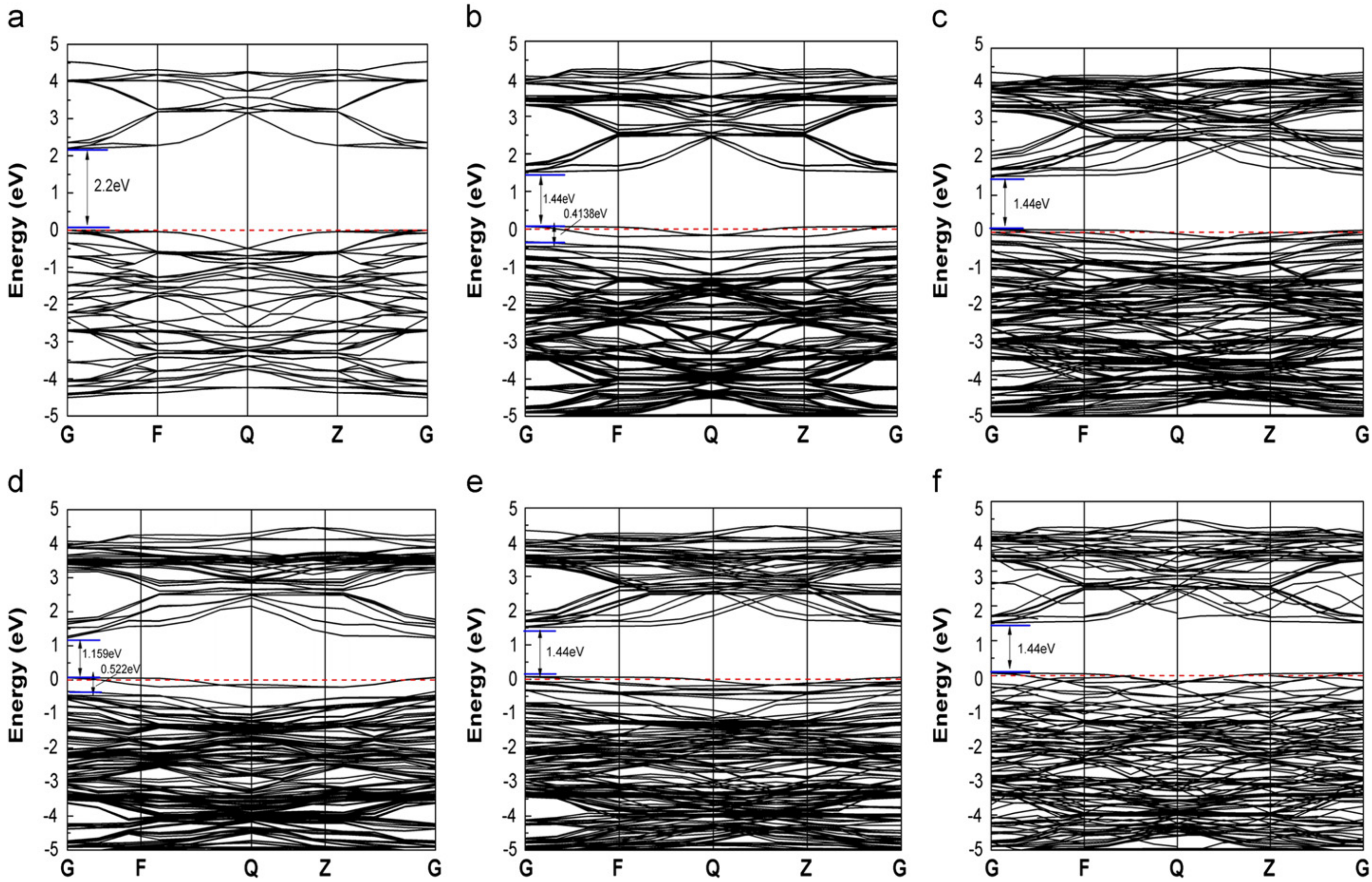

Fig. 2. Band structure plots of (a) un-doped $SrTiO_3$, (b) one N atom doped $SrTiO_3$ at 4.17 atom%, (c) one S atom doped $SrTiO_3$ at 4.17 atom%, (d) N/S co-doped $SrTiO_3$ at 8.33 atom%, (e) two N atoms doped $SrTiO_3$ at 8.33 atom%, and (f) two S atoms doped $SrTiO_3$ at 8.33 atom%.

narrower mechanism. In Fig. 2(e)–(f) it can be observed that with the concentration of doped N or S atoms increases, the band gap nearly keep the same as that of single N or S atom doped $SrTiO_3$. These N 2p localized states electronic above the valence band shift little when the number of doped N atoms increases, which explains why they have little contribution to the further energy band gap narrowing with an increase of the nitrogen concentration in N-doped $SrTiO_3$. The same phenomenon can be seen in two S atoms doped $SrTiO_3$. By comparing the two N atoms doped, two S atoms doped, and N/S co-doped $SrTiO_3$, we could conclude that the synergistic effects of co-doped N/S atoms are the main reason which causes the N/S co-doped $SrTiO_3$ energy band gap narrowing.

In conclusion, the band gap of N-doped, S-doped and N/S co-doped $SrTiO_3$ has varying degrees of narrowing and the N/S co-doped $SrTiO_3$ has the narrowest energy band gap. Through comparing and analysis, we conclude that the synergistic effects of co-doped N/S atoms are the main reason which causes the N/S co-doped $SrTiO_3$ energy band gap narrowing. Besides, we also find that the N 2p electronic is separate from that of O 2p electronic when N-doped and S 3p electronic is mixed with O 2p electronic S-doped $SrTiO_3$. The difference of electronic structure between N-doped and S-doped $SrTiO_3$ may be the main reason which cause the different photocatalytic activity.

3.2. Density of states

Through band structure calculation, we can have an intuitive description of the band gap change after doping. From the calculation of the total density of states (DOS) and partial DOS (PDOS), it is detailed and clearly described of the electronic states of various elements on the contribution to the total density of states.

Fig. 3 shows the density of states of N-doped, S-doped, and N/S co-doped $SrTiO_3$. The pure $SrTiO_3$ total density of states(STO-DOS);N-doped $SrTiO_3$ total density of states(STO-N_O DOS); S-doped $SrTiO_3$ total density of states(STO-S_O DOS);N/S co-doped $SrTiO_3$ total density of states(STO-NS_O DOS);two N atoms doped $SrTiO_3$ total density of states(STO-NN DOS);two S atoms doped $SrTiO_3$ total density of states(STO-SS DOS);O partial density of states (O 2p PDOS); N partial density of states (N 2p PDOS); S partial density of states (S 3p PDOS). For un-doped $SrTiO_3$, the top of the value band is consisting of O 2p state electronic and the bottom of conduction band consist of Ti 3d state electronic (see in Fig. 3(a)). From the Fig. 3(b), we can see that the N 2p state electronic is higher than that of O 2p state electronic. For S doped $SrTiO_3$, S 3p state electronic is lower than that of O 2p state electronic and mix with each other (see in Fig. 3(c)). Through the band structure calculation, we conclude that there is a small gap between N 2p state electronic and O 2p state electronic. From Fig. 3(d), we can also see that the N 2p state electronic is higher than that of O 2p and S 3d states electronic. This could explain the different properties between N-doped, S-doped $SrTiO_3$ and N/S co-doped $SrTiO_3$.

We also plot the density state of two N atoms doped and two S atoms doped $SrTiO_3$. In Fig. 3(e)–(f) it can be observed that with the concentration of doped N or S atoms increases, the density state of N and S atom also increased. With increasing concentration of doped N atom, N 2p state electronic begins to mix with O 2p state. But the band gap nearly keeps the same as that of the lower concentration N doped $SrTiO_3$ and the result is in agreement with the band structure calculation.

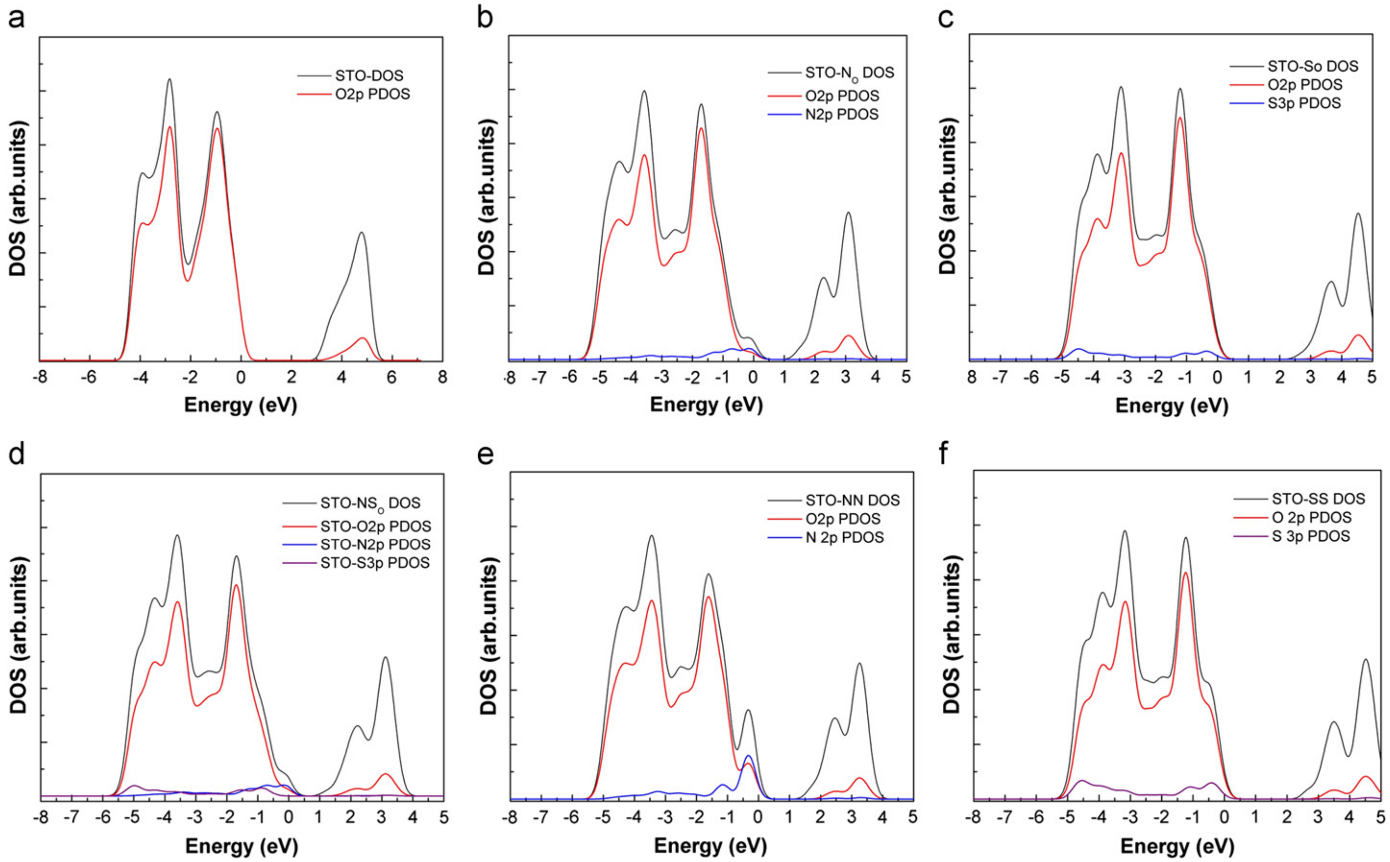

Fig. 3. Density of states (DOS) for the (a) un-doped $SrTiO_3$, (b) one N atom doped $SrTiO_3$ at 4.17 atom%, (c) one S atom doped $SrTiO_3$ at 4.17 atom%, (d) N/S co-doped $SrTiO_3$ at 8.33 atom%, (e) two N atoms doped $SrTiO_3$ at 8.33 atom%, and (f) two S atoms doped $SrTiO_3$ at 8.33 atom%.

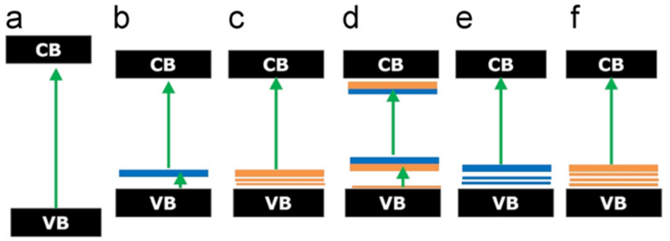

Fig. 4. Model of light electron-hole transportation for the (a) un-doped $SrTiO_3$, (b) one N atom doped $SrTiO_3$ at 4.17 atom%, (c) one S atom doped $SrTiO_3$ at 4.17 atom%, (d) N/S co-doped $SrTiO_3$ at 8.33 atom%, (e) two N atoms doped $SrTiO_3$ at 8.33 atom%, and (f) two S atoms doped $SrTiO_3$ at 8.33 atom%.

Through the above electric structure analysis, we conclude that the N/S co-doped $SrTiO_3$ has the narrowest energy band gap compared with that of N doped or S doped $SrTiO_3$. The band structure calculation is consistent with the result of the density state calculation. The conclusion could well explain the experimental results reported by Wang et al. [8]. Based on our calculations results, we propose a model for light electron-hole transportation (see in Fig. 4). When N doped, the impurity energy level is higher than valence band and leaving a small gap between N 2p states electric and O 2p states electric which may promote the visible light absorption and light electron-hole separation (see in Fig. 4(b)). In Fig. 4(d), we can see the small gap also existed in N/S so-doped $SrTiO_3$. But, there is no obvious small gap between S 3p state electric and O 2p states electric in S-doped $SrTiO_3$ (see in Fig. 4(c)). With the increasing concentration of doped N or S, the N 2p states electric and S 3p states electric mix with the O 2p states electric and the band gap hardly has any further narrowing (see in Fig. 4(e)–(f)). So we think that the stable existence of the impurity level near the valence band could promote the light electron-hole transportation and separation which could improve the photocatalytic activity. Through this model analysis, we could get the order of photocatalytic activity as N/S co-doped $SrTiO_3 >$ N doped $SrTiO_3 >$ S doped $SrTiO_3$, which is consistent with the experiment results reported by Wang et al. [8].

3.3. Optical properties

The absorption spectra of visual description of the light absorption of the doped system, provides a good analytical tool to describe the light sensitivity of the photocatalytic material. Further insights into the effects of N doping, S doping, and N/S co doping on the electronic structure of $SrTiO_3$ can be obtained from the calculation of optical properties.

A rigid scissor operator correction of 1.0 eV, was applied in the absorption spectra. The calculated optical absorption curves of pure and N-doped, S-doped, and N/S co-doped $SrTiO_3$ are shown in Fig. 5. We found that the optical absorbance curves of N-doped, S-doped, and N/S co-doped $SrTiO_3$ show some red shifts toward the visible light region. The N/S co-doped $SrTiO_3$ shows the highest visible light absorption compared with the other two one atom doped models. The absorption edge for N/S co-doped $SrTiO_3$ is 542 nm which is calculated from the band gap energy. N/S co-doped $SrTiO_3$ sample was prepared by Wang et al. [8], and also the photocatalytic had been tested with pure $SrTiO_3$. They found that the photocatalytic activity of nitrogen and sulfur co-doped $SrTiO_3$ was 10.9 times greater than that of pure $SrTiO_3$ under the irradiation of light with wavelength larger than 510 nm. So, our conclusion is well consistent with the experiment result. Through comparing and analysis, we conclude that the synergistic effects of co-doped N/S atoms are the main reasons which cause the N/S co-doped $SrTiO_3$ energy band gap narrowing and improving the visible light photocatalytic. We also find other research papers concerning on co-doping effects and think co-doping may be the best way to improve the visible light photocatalytic, as shown in the literature [15–19].

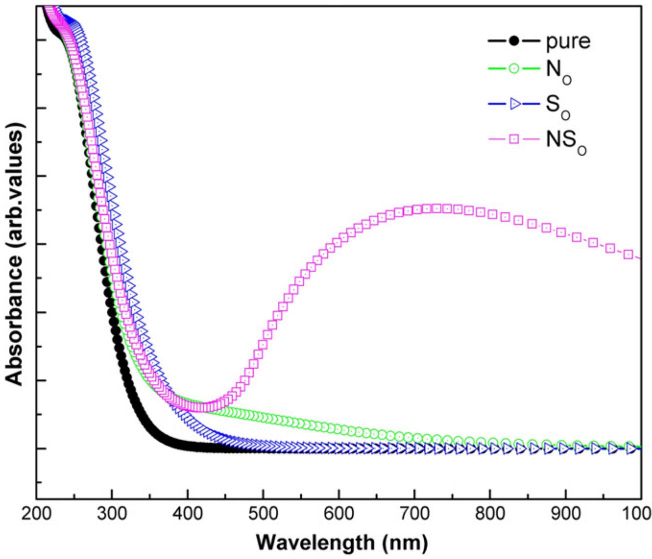

Fig. 5. DFT calculation absorption spectra of $SrTiO_3$ with N-doped, S-doped, and N/S co-doped. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

4. Conclusion

The electronic and optical properties of N-doped, S-doped, N/S co-doped $SrTiO_3$ have been studied by means of first principles DFT calculations. Through our calculation we find that the N/S co-doped $SrTiO_3$ has the narrowest band gap and can absorb visible light well. The band gap narrower may come from the synergistic effects of co-doped N/S atoms which are the main reason, which causes the N/S co-doped $SrTiO_3$ energy band gap narrowing. We also find a small gap between N 2p electric and O 2p electric in N-doped and N/S co-doped $SrTiO_3$. We think the existed small gap could promote the visible light absorption and light electron-hole separation. Then we propose a model for light electron-hole transportation based on our calculations results, which can explain the experiment results well. Besides, we consider that the co-doping may be the best way to improve the visible light photocatalytic.

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