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Effect of non-metal elements (B, C, N, F, P, S) mono-doping as anions on electronic structure of SrTiO₃



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ABSTRACT

We present first-principles density-functional calculation for the electric properties of boron (B)-, carbon (C)-, nitrogen (N)-, fluorine (F)-, phosphorus (P)-, and sulfur (S)-doped SrTiO₃. The obtained results indicate that the bands originating from B (C, N, F) 2p or P 3p states appear in the band gap of SrTiO₃, but the mixing of B (C, N, F) 2p or P 3p states with O 2p states is too weak to produce a significant band gap narrowing. Only in S-doped SrTiO₃ case, the S 3p states mix well with the O 2p states and increase the width of valence-band (VB) of SrTiO₃ which can produce the really band gap narrowing. Our results fully explain the absorption of visible light is due to the B (C, N, F) 2p or P 3p isolate states above the VB maximum of SrTiO₃, while for S-doped SrTiO₃ the visible light absorbance originating from the mixing of S 3p states with O 2p states which causing the band gap narrowing. We also propose that N (S)-doped SriO₃ would be the best choice for single anion doping SrTiO₃, while the B (C, P) elements may be the better candidates for co-doping.

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1. Introduction

Finding new types of photocatalysts which can efficiently split water into hydrogen and oxygen under sunlight irradiation has become a crucial subject for energy source and environment science and technology. An ideal photocatalyst for water splitting should have proper band positions which means that the hydrogen evolution potentials (HEPs) and oxygen evolution potentials (OEPs) must lie between the valence band maximum (VBM) and conduction band minimum (CBM) [1]. It is reported that SrTiO₃ (STO), whose CBM is slightly higher than the HEP and whose VBM is far below the OEP [2], can split water into hydrogen and oxygen when illuminated by photons with energy of the band gap [3–5]. Besides, SrTiO₃ also has superior physical and chemical properties, such as the chemical nature and structural stability, good heat resistance, corrosion resistance anti-light and easy to load other doping substances. These merits make it become one of the promising photocatalytic candidates for TiO₂ [6].

However, because of its wide band gap (about 3.2 eV), SrTiO₃ can only absorb a small part of the solar spectrum [7,8] (about 4%), which greatly restricts its photocatalytic efficiency. Therefore, how to extend SrTiO₃ absorption of light to the visible region, become the aim of majority photocatalytic scientists. Doping foreign elements become the main primary strategies for gaining visible

light-driven photocatalysts. One of the primary strategies is the doping of foreign elements, such as the doping of transition metals [9,10] and non-metals [11,12]. Recently, the different non-metals doping into TiO₂ has been extensively studied by both experiment and theory calculation. Anionic non-metal dopants, such as boron (B) [13–15], carbon (C) [16–19], nitrogen (N) [20–25], sulfur (S) [26,27], and fluorine (F) [28,29] atoms, have been investigated for extension of photocatalytic activity into the visible light region. The visible-light absorption of TiO₂ have different degrees of improvement through non-metal doping [13–29]. As a result, non-metal-doped SrTiO₃ is expected to show similar visible-light absorption phenomenon.

Cubic perovskite structure $SrTiO_3$ as one of the promising photocatalytic candidates for TiO_2 and the drawback is similar to that of TiO_2 . By density functional theory calculation, the original changes of the electric structure could be seen and the visible light absorption changes could be explained. This kind of method can be used well in the TiO_2 band gap engineering design in non-metals doping into TiO_2 . So, by non-metals elements doping, we may also expected that the fully filled gap levels which are higher than the VBM but lower than the OEP could be introduced, and to keep the CBM unchanged. In this way, the light absorption edge could be shifted into visible light region while the reduction potential could be retained.

Nowadays, the non-metal elements doping SrTiO₃ research mainly through experimental method, but different experimental conditions and sample preparation methods make it difficult to



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understand their internal mechanism. Through first principle research, it's helpful to explain the reasons of the photocatalytic activity from microscopic point of view. Mi et al. [30] studied Ndoped SrTiO₃ thin film by first principles calculation, he finds the N-doped SrTiO₃ visible light absorption change derived from the localized N 2p narrow band above the O 2p valence band. Liu et al. [31] analyzed the C,S cation-doped SrTiO₃ system from geometric and electronic structures, he found that the C,S cation codoping conducive to O 2p orbitals mix with C 2p and S 3p orbitals, which contribute to the band gap narrowing. However, few theoretical studies have done explicitly and systematic research on anionic non-metal elements mono-doping of SrTiO₃.

In this article, we present the first principles calculations of the $SrTiO_3$ crystal with the substitution of B (C, N, F, P, or S) for O. Through band structure, density of state and absorbing spectrum calculation, we can systematically study the anionic non-metal elements mono-doping effect and provide some helpful theoretical information for exploiting effective photocatalysts.

2. Computational method and details

In this work, the DFT calculations have been performed by the CASTEP [32] 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 [33] and ultra-soft pseudo-potentials [34]. The kinetic energy cut-off (E_{cut}) was 390 eV; the Monkhorst and Pack [35] *k*-mesh was 2 × 2 × 2.

In the process of calculation, a $2 \times 2 \times 2$ super-cell was used in constructing the pure SrTiO₃ structures. To set the doped model, one O atom is substituted by one B (C, N, F, P, or S) atom ($2 \times 2 \times 2$ super-cell). Therefore, 4.167 atom% of the O site is replaced by one B (C, N, F, P, or S), i.e., SrTiO_{3-x}A_x (A = B, C, N, F, P, or S)

S) where x = 0.125. All the seven models are displayed in Fig. 1a– g, 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, respectively. 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. Electronic structure

We first determine the atomic structure of the un-doped SrTiO₃ crystal. Our optimized structural parameters of the pure SrTiO₃ (a = b = c = 3.935 Å) are in good agreement with the experimental data [36] (a = b = c = 3.905 Å), which implies that the calculation methods are reasonable and the calculated results are reliable. The calculated band gap of pure SrTiO₃ at the Γ point is about 2.2 eV (see Fig. 2a), 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 GGA. However, the character of the band structure and the trend of the energy gap variations as a function of the atoms species from the calculations are expected to be reasonable and reliable.

Next, we optimize the atomic structure of B (C, N, F, P, or S)doped $SrTiO_3$ using the super-cell geometry. The atomic displacement of the B (C, N, F, P, or S) atom in B (C, N, F, P, or S)-doped $SrTiO_3$ relative to the position of the O atom in un-doped $SrTiO_3$ are given in Table 1. We find that the atomic displacement of the



Fig. 1. SrTiO₃ super-cell models (a) un-doped SrTiO₃, (b) one B atom doped 2 × 2 × 2 SrTiO₃ super-cell, (c) one C atom doped 2 × 2 × 2 SrTiO₃ super-cell, (d) one N atom doped 2 × 2 × 2 SrTiO₃ super-cell, (e) one F atom doped 2 × 2 × 2 SrTiO₃ super-cell, (f) one P atom doped 2 × 2 × 2 SrTiO₃ super-cell, (g) one S



Fig. 2. Band structure plots of (a) un-doped SrTiO₃, (b) one B atom doped SrTiO₃ at 4.167 atom%, (c) one C atom doped SrTiO₃ at 4.167 atom%, (d) one N atom doped SrTiO₃ at 4.167 atom%, (e) one F atom doped SrTiO₃ at 4.167 atom%, (f) one P atom doped SrTiO₃ at 4.167 atom%, (g) one S atom doped SrTiO₃ at 4.167 atom%.

Table 1 Atomic displacements of the B (C, N, F, P, or S) atom in B (C, N, F, P, or S)-doped SrTiO3 relative to the position of the O atom in un-doped SrTiO3.

	Δx (Å)	Δy (Å)	Δz (Å)
B-doped SrTiO ₃	0.145432	0.005216	0.004374
C-doped SrTiO ₃	0.08212	0.008302	0.009573
N-doped SrTiO ₃	0.034157	-0.018	0.030684
Un-doped SrTiO ₃	0	0	0
F-doped SrTiO ₃	0.04722	0.001337	0.001337
P-doped SrTiO ₃	0.327216	-0.0014	-0.00298
S-doped SrTiO ₃	0.302366	-0.01465	-0.01465

doped atom increases with decreasing atom number in the same period and with increasing atom number in the same main group. This phenomenon implies that the incorporation of the larger atom in the O sites yields more strains to the neighboring Ti atoms compared with the smaller atom. As the doped atom along the *x*-direction, the strains yielded most to the Δx .

The band structure of B (C, N, F, P, or S)-doped SrTiO₃ has been calculated, the band gap and band structure are displayed in Table 2 and Fig. 2a–g, respectively. First, we investigate the two N and S atoms whose properties are close to O atom doped SrTiO₃. The calculated band structure of N (S)-doped SrTiO₃ is displayed in Fig. 2d and g. We find the bands originating from N 2p and S 3p state appear in the band gap of SrTiO₃. Here, the calculated band structure of N-doped SrTiO₃ shows that the N 2p bands are located a little

higher to the valence-band maximum (VBM) of SrTiO₃ leaving the direct band gap of N-doped is 1.85 eV and the small band gap between O 2p band and N 2p band is 0.41 eV. However, the calculated results show that the S 3p bands are mixing with the valence-band maximum (VBM) of SrTiO3 and increase the VB width. The calculated band gap of S-doped SrTiO₃ is 1.44 eV between the valence-band maximum (VB) and conduction-band (CB) minimum, smaller to that ($E_g = 2.2 \text{ eV}$) in pure SrTiO₃. The calculated results of the N-doped SrTiO₃ is in agreement well with recent research outcome [30] which conclude that N 2p states are localized at about 0.4 eV above O 2p state, and the mixing of the N 2p with O 2p states is too weak to produce a significant band gap narrowing in SrTiO₃. For N-doped TiO₂ system, recent calculation based on DFT also indicate that localized N 2p states just lie above valence-band maximum, which cannot induce the band gap narrowing [37]. In the S-doped TiO₂ case, Umebayashi et al. [26] find that S 3p states mix with O 2p states leading to the band gap narrowing by the annealing of titanium disulphide (TiS_2) experiment and DFT calculation. Trough above analysis, we conclude that the S 3p states has a strong interaction with the O 2p states, while the N 2p states has the weaker interaction compared with the S 3p states. Both of the two cases could lead to the redshift of the optical absorption.

In order to fully understand other anions except for N (S), we also have done the electronic structure calculation for B (C, F, P)-doped SrTiO₃. However, to the best of our knowledge there has

Table 2

Band gap energy (eV) (scissor operator 1.0 eV) of B (C, N, F, P, S)-doped SrTiO₃ super-cells and the lowering value of band gap corresponding to the band gap of pure SrTiO₃ \triangle , with various atoms and concentrations (C_x).

	C _x (atom%)	Band gap (eV)	Scissor operator (1.0 eV)	⊿ (eV)
Pure SrTiO ₃	0.0	2.2	3.2	0.0
B-doped SrTiO ₃	4.167	2.21	3.21	0.0
C-doped SrTiO ₃	4.167	1.89	2.89	0.31
N-doped SrTiO ₃	4.167	1.85	2.85	0.35
F-doped SrTiO ₃	4.167	2.20	3.2	0.0
P-doped SrTiO ₃	4.167	2.13	3.13	0.07
S-doped SrTiO ₃	4.167	1.44	2.44	0.76

been no detailed investigation of the doping of B (C, F, P) atoms as anions in SrTiO₃ (STO). This may be due to the difficulty of the ptype doping of atoms in STO [38]. The doping of B (C, F, P) atoms in TiO₂, which is another photocatalyst, has been extensively studied [39,40,37,41-43]. By comparison the calculated B (C, F, P)doped SrTiO₃ results of us with that case in TiO₂, we could fully learn the effect of the doping of B (C, F, P) atoms as anions in STO. The calculated band structure of B (C, F, P)-doped SrTiO₃ is displayed in Fig. 2b, c, e and f. We could observe the isolated energy states in the band gap with B-doped, C-doped, F-doped and P-doped SrTiO₃. This kind of phenomenon can also be identified in B-doped [39,40], C-doped [37,41], F-doped [42], and P-doped TiO₂ [43]. The different p orbital energies of the doped anions from that of O may be the main cause of the isolated energy states in the band gap. The detailed orbital energy calculation can be seen in the work of Yin et al. [44]. From Fig. 2b-f and Table 2, we could see that the band gap of B (C, F, P)-doped SrTiO₃ is 2.21 eV. 1.89 eV. 2.20 eV and 2.13 eV, respectively. From the results analysis, we conclude that the band gap could hardly be narrowed by B (F, P)-doped as anions as the no mixing of the doped atoms p orbitals with O 2p orbital bands. The band gap has been small narrowed by C (N)doping, while S-doped SrTiO₃ has the narrowest band gap compared with other anions doped SrTiO₃ discussed above.

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 projected density of states (PDOS), it is can detailed and clearly description of the electronic states of various elements on the contribution to the total density of states.

Fig. 3 shows the density of states of B (C, N, F, P, or S)-doped SrTiO₃. The pure SrTiO₃ total density of states (STO-DOS); B-doped SrTiO₃ total density of states (STO-B₀ DOS); C-doped SrTiO₃ total density of states (STO-C₀ DOS); N-doped SrTiO₃ total density of

states (STO-N₀ DOS); F-doped SrTiO₃ total density of states (STO-F₀ DOS); P-doped SrTiO₃ total density of states (STO-P₀ DOS); Sdoped SrTiO₃ total density of states (STO-S₀ DOS); O partial density of states (O 2p PDOS); B partial density of states (B 2p PDOS); C partial density of states (C 2p PDOS); N partial density of states (N 2p PDOS); F partial density of states (F 2p PDOS); P partial density of states (P 3p PDOS); S partial density of states (S 3p PDOS). For un-doped SrTiO₃, the top of the value band is consisting of O 2p state electronic and the bottom of conduction band is consisting of Ti 3d state electronic (see in Fig. 3a). From the Fig. 3b, we can see that the B 2p state electronic is higher than that of O 2p state electronic and close to the Ti 3d state. From the Fig. 3c and f, we can see that the C 2p state electronic and P 3p state electronic is higher than that of O 2p state electronic. In Fig. 3d and g, we put the density states of N-doped and S-doped SrTiO₃. We could find that the N 2p states lie a little higher than O 2p states, while S 3p states mix well with the O 2p states. For F doped SrTiO₃, F 2p state electronic is much lower than that of O 2p state electronic and has no mix with O 2p state electronic (see in Fig. 3e).

Through above electric structure analysis, we conclude that the S-doped SrTiO₃ has the narrowest energy band gap compared with that of N doped or S doped SrTiO₃. For B (F, P)-doped SrTiO₃, the band gap could hardly be changed as the no mixing of the doped atom p orbital bands with O 2p orbital bands. The band gap has small change for C (N)-doped SrTiO₃, as the low mixing of the doped atom p orbital bands with O 2p orbital bands. The band gap has small change for C (N)-doped SrTiO₃, as the low mixing of the doped atom p orbital bands with O 2p orbital bands. The band structure calculation is consistent with the result of the density of states calculation.

To evaluate the influence of the non-metal ions doping on the photocatalytic activity of $SrTiO_3$, the CBM and VBM of the non-metal-doped $SrTiO_3$ at the O site as compared to the undoped $SrTiO_3$ are depicted in Fig. 4. The VBM and CBM values of pure $SrTiO_3$ with respect to the NHE potential are taken from the experimental values [45]. Based on our calculation results, we conclude that the effects of the doped atoms on the band gap could be classified into four categories according to the relative difference impurity level



Fig. 3. Density of states (DOS) for the (a) un-doped SrTiO₃, (b) one B atom doped SrTiO₃ at 4.167 atom%, (c) one C atom doped SrTiO₃ at 4.167 atom%, (d) one N atom doped SrTiO₃ at 4.167 atom%, (e) one F atom doped SrTiO₃ at 4.167 atom%, (f) one P atom doped SrTiO₃ at 4.167 atom%, (g) one S atom doped SrTiO₃ at 4.167 atom%.



Fig. 4. Calculated VBM and CBM positions of metal-doped SrTiO₃ as compared with those of the corresponding experimental values of pure SrTiO₃. The VBM and CBM values are given with respect to the NHE potential (V) and energy with respect to vacuum (eV). (a) Un-doped SrTiO₃, (b) one B atom doped SrTiO₃ at 4.167 atom%, (c) one C atom doped SrTiO₃ at 4.167 atom%, (d) one N atom doped SrTiO₃ at 4.167 atom%, (e) one F atom doped SrTiO₃ at 4.167 atom%, (f) one P atom doped SrTiO₃ at 4.167 atom%, (g) one S atom doped SrTiO₃ at 4.167 atom%.

position: (i) the impurity level located just above the VB like Ndoped SrTiO₃; (ii) the impurity level located in the center of the VB like C (P)-doped SrTiO₃; (iii) the impurity level located in the just below the CB like B (F)-doped SrTiO₃; (iv) the impurity level mixing with the VB and increase the width of the VB like S-doped SrTiO₃. All over the six doped models, we propose that N (S) elements would be the best choice for single anion doping SrTiO₃, while the B (C, P)-doped SrTiO₃ may cause the original impurity level between the VB and CB which may be better candidates for codoping. The C atom was found to be a good candidate for co-doping in TiO₂ [44,46].

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 B (C, N, F, P, S)-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 B (C, N, F, P, S)-doped $SrTiO_3$ are showed in Fig. 5. We found that the optical absorbance curves of B (C, N, F, P, S)-doped $SrTiO_3$ show some red shifts toward the visible light region. However, the visible-light absorbance mainly origins from the isolated band levels for B (C, N, F, P)-doped $SrTiO_3$ rather than band gap narrowing, while for S-doped $SrTiO_3$ the visible-light absorbance results from the band gap narrowing.



Fig. 5. DFT calculation absorption spectra of SrTiO₃ with B (C, N, F, P, S)-doped.

4. Conclusion

In summary, we carry out first principles calculations on the B (C, N, F, P, S)-doped SrTiO₃ by means of DFT method within the GGA scheme. Our results reveal that the band gap of SrTiO₃ remains almost unchanged for B (F, P)-doped SrTiO₃, while the band gap has small changed by C (N)-doped. The S-doping results in a significant band gap narrowing among the six doping models. The different band gap narrowing effects arise from the different mixing states between the doped atom p orbital bands with the O 2p orbital bands. Our results provide a full explanation for the observed visible-light photocatalysis data of B (C, N, F, P)-doped in terms of the presence of isolated band gap states rather than a band gap narrowing, while in the S-doped case the visible-light photocatalysis really comes from the band gap narrowing. We also propose that N (S) elements would be the best choice for single anion doping SrTiO₃, while the B (C, P) elements may be the better candidates for co-doping.

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