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First-principles study on strontium titanate for visible light photocatalysis

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ABSTRACT

Density functional calculations have been performed on the electronic structure of donor–acceptor (V–N, Nb–N, Cr–C and Mo–C) co-doped $SrTiO_3$ to improve their photocatalytic activity in visible light region. By analyzing the electronic structure of pure and co-doped $SrTiO_3$, we propose that the Mo–C co-doped system is promising materials for the visible light photocatalyst. It is found that the doping of Mo–C complex may shift the valence band edge up significantly, while keeping the conduction band edge almost unchanged. The calculated defect binding energies indicate that the co-doped systems are energetically favorable than their respective mono-doped systems.

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1. Introduction

Strontium titanate ($SrTiO_3$), apart from its wide application in ferroelectric and electronic ceramic materials, is also a good photocatalyst for the photogeneration of hydrogen from water using solar energy [1–4]. However, the energy conversion efficiency of $SrTiO_3$ is low. This is mainly because its large band gap ($\sim$3.2 eV) [5] only allows it to absorb the ultraviolet (UV) light. To improve the photocatalytic efficiency of $SrTiO_3$ for hydrogen production through water splitting, the band structure should be modified to match with visible light absorption and the redox potential of water [6,7]. A common method for band gap reduction is to dope $SrTiO_3$ with foreign elements [8–10]. For example, it is reported that $SrTiO_3$ doped with N showed high visible light photocatalytic activity due to acceptor levels above the valence band maximum (VBM) introduced by the impurities [8]. Ohno et al. [10] reported that, compared with pure $SrTiO_3$, the absorption edge of S and C doped $SrTiO_3$ was greatly shifted from 400 to 700 nm. Moreover, the photocatalytic activity of the S and C doped $SrTiO_3$ was also improved.

Mono-doping with transitional metal ions (TMs) has also been investigated for expanding the light absorption edge of $SrTiO_3$ into the visible region [11–14]. Liu et al. [12] found that Cr-doped $SrTiO_3$ can absorb not only UV light but also the visible light, and its photocatalytic activity is increased with increasing amounts of Cr impurities. Konta et al. [13] reported that Rh doped $SrTiO_3$ is a novel photocatalyst for hydrogen production under visible light irradiation. They indicated that the visible light response of Rh doped $SrTiO_3$ is attributed to the discontinuous gap levels introduced by the impurities. Nevertheless, the effect of mono-doping in wide band gap semiconductors is limited by several reasons [15–17], such as solid solubility of impurities and the spontaneous formation of compensating defects. To overcome these limitations, donor–acceptor co-doping in these materials has been proposed [18–20]. In this Letter, we present the first-principles calculation of $SrTiO_3$ with donor–acceptor co-doping. The effect of co-doping on electronic structure of $SrTiO_3$ has been investigated to search effective dopant complex for band gap reduction. From the analysis of the total and partial density of states (DOS), we suggest that Mo–C co-doped $SrTiO_3$ may be a good candidate photocatalyst for hydrogen production with the illumination of visible light. The Mo–C complex may shift the valence band edge up significantly, while keeping the conduction band edge almost unchanged. So, the band edges of co-doped $SrTiO_3$ system straddle the water redox potential level, which is a necessary condition for the water-splitting reaction. The calculation of defect binding energy indicates that the co-doped systems are energetically favorable than their respective mono-doped systems.

2. Commotional method

Our first-principles calculations are performed within the framework of density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [21]. The core–valence interaction is described by the frozen-core projector augmented wave (PAW) method [22,23]. The exchange and correlation potential are treated in the framework of generalized gradient approximation (GGA) of Perdew–Burke–Ernzerbof (PBE) [24]. For doping cases, a $2 \times 2 \times 2$ repetition of bulk $SrTiO_3$ unit cell is used (see Figure 1). A larger $3 \times 3 \times 2$ supercell with 90 atoms has also been used to test the calculated results, and we found that our conclusion is not affected by the supercell size. Structural relaxations are performed until all the components of residual

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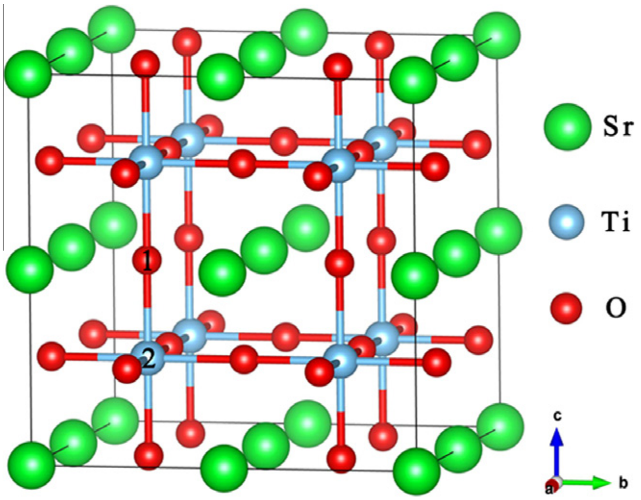

Figure 1. The $2 \times 2 \times 2$ supercell of $SrTiO_3$. N and C are doped at site 1 and TMs are doped at site 2. Green, light blue, and red balls represent Sr, Ti, and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

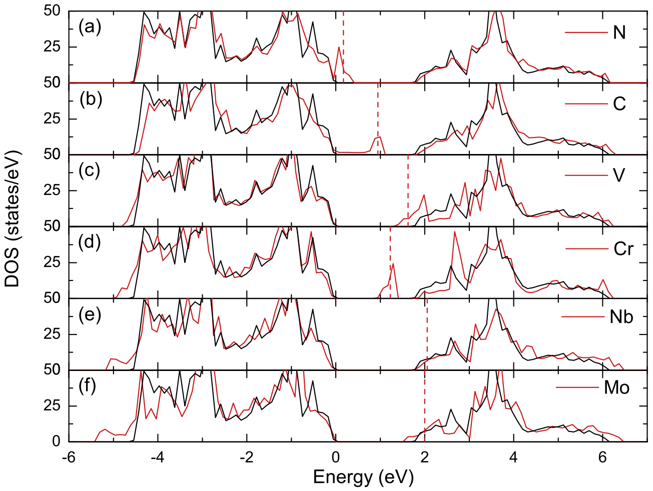

Figure 2. The GGA-calculated total DOS for mono-doped $SrTiO_3$ (red) compared with the DOS of pure $SrTiO_3$ (black). The VBM of pure $SrTiO_3$ is set as energy zero. The dashed lines indicate the highest occupied levels in the doped systems. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

forces on atoms are smaller than 0.01 eV/Å. The cutoff energy for the plane-wave basis set is 500 eV and the convergence criterion for the total energy is set to 10^{-5} eV. Reciprocal space integrations are carried out at $7 \times 7 \times 7$ Monkhorst–Pack k-grids.

3. Results and discussion

$SrTiO_3$ has a typical cubic perovskite structure with *Pm*3*m* space group and the experimental lattice parameter is 3.905 Å. Our calculated lattice parameter for the unit cell of $SrTiO_3$ is 3.944 Å, which is in excellent agreement with experimental value and previous theoretical results [25]. The calculated band gap using GGA-PBE method is 1.8 eV, which is smaller than the experimental value of 3.2 eV [26]. The reason for such a disagreement is the well-known shortcoming of the GGA for semiconductors and insulators. Because we mainly focus on the changing of the band gap, the absolute value of the band gap is not a significant concern.

First, we have investigated the effect of mono-doping on the electronic structure of $SrTiO_3$. In this study, we choose N and C substituting on the O site as the p-type dopants and 3d TMs V and Cr, and 4d TMs Nb and Mo substituting on the Ti site as the n-type dopants. The calculated total DOS for pure and mono-doped $SrTiO_3$ are displayed in Figure 2. In the case of N or C doped $SrTiO_3$, the substitution of N or C for O induces partial occupied gap states above the VBM of $SrTiO_3$ (Figure 2a and b), which has mostly O p character. The 2p orbital energy of carbon and nitrogen are 3.8 and 2.0 eV higher, respectively, than O 2p orbital energy. Thus, the acceptor levels induced by C are deep inside the gap of $SrTiO_3$, whereas the N acceptor level appearing at the valence band edge of $SrTiO_3$. Moreover, there is no significant shift of the conduction band minimum (CBM) in both N doped and C doped cases. As N has one less valence electron than O, the substitution of N on the O site acts as a single acceptor, while the substitution of C on the O site acts as a double acceptor.

In case of TMs doped $SrTiO_3$, the dopants mostly affect the CBM of $SrTiO_3$ which has Ti d character. The substitution of V or Cr for Ti induces partial occupied gap levels below the CBM, as shown in Figure 2c and d. The Fermi levels (E_F) are pinned in the gap levels for both cases. Also, our results show that the VBM has no significant changes. In contrast, the Nb and Mo dopants do not introduce gap levels and only affect the VB and CB edges (Figure 2e and f). We can see that the VBM of Mo doped system is shifted downwards, while the VBM of Nb doped system is shifted upwards slightly. This is because the Mo 4d orbital energy is lower, whereas the Nb 4d orbital energy is higher than Ti 3d orbital energy [19]. The E_F is lifted up to the conduction band, which correspond to the n-type doping. For these dopants, both V and Nb have one more valence electron than Ti, so the substitution of V or Nb on the O site acts as single donors. Similarly, the substitution of Cr or Mo on the O site acts as double donors.

For mono-doped $SrTiO_3$, the gap levels introduced by impurities will reduce the band gap as expected. However, these partially occupied subbands themselves can also facilitate the formation of recombination centers [20], which suppress the photocatalytic activity of $SrTiO_3$. To overcome shortages of the mono-doping, we propose to dope $SrTiO_3$ using donor–acceptor pairs such as V–N, Nb–N, Cr–C and Mo–C. In these cases, the electrons on the donor levels passivate the same amount of holes on the acceptor levels, so these co-doping systems will maintain the semiconductor character. The optimized atomic structures of donor–acceptor co-doped $SrTiO_3$ are shown in Figure 3. For pure $SrTiO_3$, Ti atom is coordinated to six O atoms to form a TiO_6 octahedron and the Ti–O bond length is 1.972 Å. In the co-doped model, after the structural relaxation, the distance between the donor and acceptor atom is much shorter, and the adjacent structure has a relatively large distortion, as shown in Figure 3a–d. For example, the length of Mo–C bond is 1.776 Å. Moreover, the length of Mo–O bond along *c* axis is 2.368 Å, while the Mo–O bond is 2.006 Å along the *b* axis. So, the *c* axis of Mo–C co-doped system is lengthened (4.1 Å), while the lattice constant is shortened in ab plane (3.927 Å). Similar results are also obtained for other three co-doped $SrTiO_3$ systems.

The total DOS of V–N, Nb–N, Cr–C and Mo–C co-doped $SrTiO_3$ are shown in Figure 4. We can see that the VBM increased more or less compared with the pure $SrTiO_3$, whereas the change of CBM is small. Because both the acceptor levels induced by N and the donor levels induced by V are relatively shallow, V–N co-doping in $SrTiO_3$ reduces the band gap slightly, as shown in Figure 4a. Similar results are also obtained for Nb–N co-doped $SrTiO_3$ (Figure 4b). In contrast, the VBM of Cr–C and Mo–C co-doped $SrTiO_3$ is lifted largely due to the relatively deep acceptor levels introduced by C impurity (Figure 4c and d).

To further investigate the electronic structure of co-doped $SrTiO_3$, we calculate the partial DOS of these systems, as shown in Figure 5a–d. We can see that, compared with pure $SrTiO_3$, the

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