Research Article

Sensitization of Perovskite Strontium Stannate SrSnO_3 towards Visible-Light Absorption by Doping

Hungru Chen¹ and Naoto Umezawa^{1,2,3}

¹ Environmental Remediation Materials Unit, National Institute for Materials Sciences, Ibaraki Prefecture 305-0044, Japan

² PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama Prefecture 332-0012, Japan

³ TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, China

Correspondence should be addressed to Naoto Umezawa; umezawa.naoto@nims.go.jp

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Perovskite strontium stannate SrSnO_3 is a promising photocatalyst. However, its band gap is too large for efficient solar energy conversion. In order to sensitize SrSnO_3 toward visible-light activities, the effects of doping with various selected cations and anions are investigated by using hybrid density functional calculations. Results show that doping can result in dopant level to conduction band transitions which lie lower in energy compared to the original band gap transition. Therefore, it is expected that doping SrSnO_3 can induce visible-light absorption.

1. Introduction

Photocatalysis is an important technology for fuel production and environmental remediation from solar energy conversion [1–4]. Perovskite strontium stannate SrSnO_3 has been reported to be a promising photocatalyst [5–7]. Due to its suitable valence band and conduction band edge positions, it is able to split water into hydrogen and oxygen. The main drawback of SrSnO_3 is the large band gap of 4.1 eV [7] and therefore it can only absorb light in the ultraviolet region. A material for efficient solar energy conversion should be able to absorb the majority of the sunlight, namely, visible light. In order to sensitize wide gap materials to visible light, doping has been a common approach [8–10]. In this study, hybrid density functional theory calculations are carried out to investigate the effect of doping in SrSnO_3 . Cations Cr^{3+} , Fe^{3+} , and Rh^{3+} and anions N^{3-} , N^{2-} , and S^{2-} , which have been reported to be effective dopants for sensitizing titanates to visible light, are considered [10, 11].

2. Computational Methods

All calculations are carried out based on density functional theory [12] with the range separated HSE06 hybrid functional

[13]. Valence electrons are described by a plane wave basis set with the energy cutoff of 500 eV. The interactions between core and valence electrons are treated with the projector augmented wave (PAW) method [14]. The k-space is sampled with k-point spacing less than $0.03 \text{ \AA}^{-1}$. The lattice vectors and atomic positions in all cells are optimized until the force is converged to less than $0.03 \text{ eV-\AA}^{-1}$ at each atomic position. Vienna ab initio simulation package (VASP) [15] is used for all calculations.

SrSnO_3 adopts the orthorhombic perovskite structure with space group symmetry $Pbnm$ [16], as shown in Figure 1. To model doped SrSnO_3 , a $2 \times 1 \times 2$ SrSnO_3 supercell, which contains 16 formula units (80 atoms), is constructed. Cation doping is simulated by substituting a dopant, Cr^{3+} , Fe^{3+} , or Rh^{3+} , for one Sn^{4+} , which corresponds to 6.25% of B-site cation impurity. To ensure the correct trivalent charge states of cation dopants, in each of the above cases La^{3+} is simultaneously substituted for Sr^{2+} . Anion doping is modeled by substituting a dopant, N^{3-} , N^{2-} , or S^{2-} , for one O^{2-} , which corresponds to 2.08% of anion impurity. In the N^{3-} case La^{3+} is simultaneously substituted for Sr^{2+} .

FIGURE 1: The orthorhombic perovskite structure of SrSnO_3 . The green and red spheres denote strontium and oxygen, respectively. The gray octahedra denote SnO_6 units.

3. Results and Discussions

The calculated lattice parameters for the orthorhombic perovskite SrSnO_3 are $a = 5.717 \text{ \AA}$, $b = 5.729 \text{ \AA}$, and $c = 8.084 \text{ \AA}$, which are in good agreement with experimental values $a = 5.709 \text{ \AA}$, $b = 5.703 \text{ \AA}$, and $c = 8.065 \text{ \AA}$ [17]. Figure 2 shows the density of states and band structure from our calculations. The calculated band gap of pristine SrSnO_3 is 3.52 eV, smaller than experimentally reported optical gap 4.1 eV. The origin of this 0.5 eV discrepancy is not clear at the moment. It could be an underestimation from the functional used in calculations. It could be that the transition from the highest occupied state to the lowest occupied state is forbidden [18]. More detailed analysis is necessary to clarify this. The bottom of the conduction band is a mixture of Sn 5s states and O 2p states. Different from d state conduction bands, it is very dispersive and therefore electrons in this band should possess lower effective mass than in d bands. The top of valence band is comprised mainly of oxygen 2p states.

Figure 3 shows the calculated density of states of cation and anion doped SrSnO_3 . It is assumed that dopants do not influence the position of the SrSnO_3 O 2p valence band and the top of O 2p valence band in each cell is aligned at 0 eV. In each case, dopant produces occupied states above the SrSnO_3 valence band maximum (VBM). This indicates the

FIGURE 2: Calculated density of states and band structure of the pristine SrSnO_3 .

emergence of dopant to conduction band minimum (CBM) transitions. However, in the cases of Cr^{3+} , Fe^{3+} , and Rh^{3+} doping, the position of CBM is also shifted up by about 0.3 eV compared to pristine SrSnO_3 . This is probably due to the s state interaction between Sn^{4+} ions, which form the lowest part of conduction band, being disturbed by the presence of cation impurity. Overall, the $\text{Cr}^{3+} \rightarrow \text{CBM}$ and $\text{Rh}^{3+} \rightarrow \text{CBM}$ transitions are 3.21 eV and 2.63 eV, respectively. The position of Fe^{3+} states above VBM is relatively shallow and therefore the $\text{Fe}^{3+} \rightarrow \text{CBM}$ transition 3.53 eV is even higher in energy than the pristine SrSnO_3 band gap. In anion doping cases, the position of CBM is less affected. In the S^{2-} doping case, the CBM is actually downshifted by about 0.1 eV. Overall, the transitions from N^{2-} , N^{3-} , and S^{2-} to CBM are 2.94 eV, 2.45 eV, and 3.09 eV, respectively.

4. Conclusions

Through hybrid density functional calculations, it is shown that the doping of various cations and anions introduces occupied dopant states above the SrSnO_3 O 2p valence band. Transitions from these dopant states to the SrSnO_3 conduction band cost lower energies than the original band gap transition, apart from the Fe^{3+} case, and are hoped to contribute more towards visible-light photocatalytic activities. Among all considered cation dopants, Rh^{3+} gives rise to the deepest in gap states. The transition from Rh^{3+} to SrSnO_3 conduction band is 0.89 eV lower than the band gap. Among all considered anion dopants, N^{3-} appears to show the best result. The transition from N^{3-} to SrSnO_3 conduction band is 1.07 eV lower than the SrSnO_3 band gap. Nevertheless, one should be cautioned that whether or not dopant associated

FIGURE 3: The calculated density of states in the pristine and doped cases. The shaded areas denote total density of states and the red lines denote the dopant states. The positions of the highest occupied state and the edge of conduction band minimum are marked by green lines. The magnitudes of the dopant to conduction band minimum transitions in each case are listed.

localized states can really contribute to steady-state activities is a question [8, 19].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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