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Research paper

Doping bismuth oxyhalides with Indium: A DFT calculations on tuning electronic and optical properties

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ABSTRACT

Doping strategy has demonstrated to be one effective approach to modify the band structure of oxide semiconductors, which usually introduce the discrete mid-gap states to extend the light absorption range. However, the localized mid-gap states have limited benefit to photocatalytic activity. In the present work, the density functional theory (DFT) calculations indicate that indium (In) doping in bismuth oxyhalides (BiOXs, X = F, Cl, Br and I) could overcome this issues through increasing the light absorption and improving the potential for water reduction. Substitutional In (SubIn) doping in BiOXs (X = F, Br and I) leads to band gap narrowing through shifting the conduction band edge to lower energies, which can improve the light absorption without creating the mid-gap states. Specifically, the SubIn-doped BiOCl increases band gap due to the increased energy levels of the In 5s states. Although SubIn-doped BiOCl cannot extend the light absorption of the photocatalyst into the visible light spectrum, it indeed improved the necessary redox potentials for splitting water and preventing from trapping charge carrier. We believe that the DFT calculation results on SubIn-doping BiOXs will guide the further development of highly efficient semiconductor photocatalysts.

1. Introduction

Nowadays, semiconductor-based photocatalysis as a green technology has been used to remove harmful pollutants from the environment or to convert solar energy to chemical energy stored in fuels [1–8]. TiO_2, a typical semiconductor photocatalyst, remained as the benchmark photocatalyst for environmental remediation and water splitting ever since it was discovered for water photolysis in 1972 [9]. However, the wide band gap as well as the highly-selective absorption into ultraviolet light (less than 5% of incident solar radiation) impede its real practice [10]. Therefore, it is rather critical to modify conventional photocatalysts and/or develop novel photocatalysts to realize the efficient use of solar energy.

Bismuth oxyhalides (BiOXs, X = F, Cl, Br and I) photocatalysts have been reported with superior photocatalytic performance in comparison with TiO_2 under ultraviolet and visible light excitation [11–21]. BiOX, a typical layered semiconductor material, is composed of strong interlayer interactions within $[Bi_2O_2]^{2+}$ slabs and weak van der Waals interlayer interactions between adjacent X^- slabs along the $\langle 0\,0\,1 \rangle$ direction. The interleaved $[Bi_2O_2]^{2+}$ and X^- slabs along the *c*-axis direction generate an internal electric field, which remarkably accelerates the transfer electron-hole pairs and reduces the recombination rate of photogenerated carries. Unfortunately, BiOX photocatalysts have the inherit characteristic of wide band gaps similar to TiO_2. A crucial prerequisite for enhancing solar energy conversion efficiency is to enable BiOX to absorb the more abundant visible light by reducing its band gap. Introducing metal [22–26] or nonmetal [27–32] elementals into the crystal lattice has been demonstrated to be one of the most effective approaches to adjust the band structure so as to improve the visible photocatalytic ability of wide bandgap semiconductors. As such, many research efforts have been concentrated on metallic [33–39] or nonmetallic [18,40–46] doping into BiOX to narrow the band gap energy and to improve the light response into the UV–visible region with enhanced photocatalytic activity. This report has demonstrated that the In-doping into BiOXs (X = F, Br, and I) can narrow the band gap, and increase reductive strength towards hydrogen of BiOCl. These results are in stark contrast to mono-doping in BiOXs, where an increase in visible light absorption is only gained by the introduction of the discrete mid-gap states [34–38]. The localized mid-gap states in BiOXs act as the trap states, reducing the carrier mobility and consequently degrading the photocatalytic performance [38].

The electronic configurations of Bi^{3+} and In^{3+} are similar in their absence of d electron participation in photoexcitation [47,48]. And

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In atom in BiOXs form strong hybridization of the Bi and In electronic orbitals in conduction band. Accordingly, the In-doping results in both a continuum of states to form at the edge of the conduction band and a shift in energy of the dopant density of states (DOS). The combination of DOS resulted in the narrowness of the band gap of BiOF, BiOBr and BiOI without introducing deep or shallow trap states. As pointed out in the literature [27,49], introduction of discrete mid-gap states in the band structure has limited benefit to photocatalytic activity although it extends the light absorption of wide band gap semiconductors to longer wavelength. To enhance the photocatalysis efficiency of semiconductors, the desirable engineering of band structure is to narrow the band gap by broadening the valence band and/or the conduction band or by shifting the edges of the valence band and/or the conduction band. In this work, the density functional theory (DFT) calculations demonstrate that SubIn-doping (substitutional In doping) into BiOF, BiOBr and BiOI can achieve a narrowed band gap and the enhanced absorption coefficient in the visible light region; in contrast, In-doping into BiOCl can increase the band gap and reductive strength towards hydrogen.

2. Computational details

The calculations were carried out using the CASTEP code [50], based on density function theory (DFT) within the generalized gradient approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) for exchange correction. The interaction between core electrons and valence electrons was treated by ultrasoft pseudopotential (USP) plane-wave method. The valence configurations of the pseudopotentials are $6s^2 6p^3$ for Bi, $2s^2 2p^4$ for O, $2s^2 2p^5$ for F, $3s^2 3p^5$ for Cl, $4s^2 4p^5$ for Br, $5s^2 5p^5$ for I. The cut-off energy for the plane wave expansion was 340 eV and the Monkhorst-Pack k-point mesh of $2 \times 3 \times 2$ was used. The DFT + U or DFT hybrid methods [27,51], as the improvement of standard DFT, can overcome underestimation of band gap in a standard DFT calculation. However, the DFT is still sufficiently satisfying to investigate the relative changes of band gap after doping. Structural relaxations were performed until all the residual forces on atoms were less than 0.01 eV/Å, and the self-consistent convergence accuracy was set at 1×10^{-6} eV/atom. On the basis of the optimized crystal structure, the electronic structure and the optical properties were calculated.

3. Results and discussions

3.1. Structural properties and formation energy

The doped systems were constructed from a relaxed 72-atom supercell ($3 \times 2 \times 2$) of BiOXs. Fig. 1 illustrates the optimized structures of pure and In-doped BiOXs. There are two kinds of doping modes, interstitial and substitutional, for doped metal ions in oxides. For substitutional doping systems (SubIn) is created by substitution of one Bi atom by one In atom (Fig. 1**b**). For interstitial doping systems (IntIn), one In atom is inserted into two Bi atom (Fig. 1**c**). The lattice parameters and angles of a relaxed cell for pure and In-doped BiOXs are listed in Table 1. The optimized lattice parameters of BiOX are calculated: $a = b = 3.768$ Å and $c = 6.299$ Å for BiOF, $a = b = 3.882$ Å and $c = 8.031$ Å for BiOCl, $a = b = 3.916$ Å and $c = 9.832$ Å for BiOBr, and $a = b = 4.008$ Å and $c = 10.531$ Å for BiOI, which are in excellent agreement with other theoretical results [19]. In experiment, the lattice parameters (a and c) for BiOF are 3.7592 Å and 6.2354 Å [52], while the corresponding values are 3.898 Å and 7.424 Å for BiOCl, 3.929 Å and 8.132 Å for BiOBr, 3.992 Å and 9.15 Å for BiOI [53]. However, c lattice parameter exists a small difference between calculated results and experimental values, which could be attributed to the essential characteristic and unique layered structure of BiOXs. For the SubIn-doped BiOX structure, the doping does not cause significant change of the lattice constant, benefiting from the optimized size match. For interstitial doping systems, the lattice constant expands a small along the c axis compared to the substitutional doping structure. It is well known that impurities usually induce the atomic structural relaxation in the host lattice, resulting in modifying the electronic structures of the doped system. Therefore, it is necessary to perform a detailed investigation on the band structures and electronic DOS for In-doped BiOXs, so that our obtained results provide theoretical and foundational guidance for further understanding the experimental phenomena and facilitating actual application of In-doped BiOX photocatalytic system.

The formation energy is an important criterion to evaluate the stability for dopant in the host lattice. We calculate the dopant formation energy according to the equation below:

$$E(\mathrm{BiOX})_{\mathrm{form}} = E(\mathrm{SubIn\ doped\ BiOX}) - E(\mathrm{pure}) - \mu_{\mathrm{In}} + \mu_{\mathrm{Bi}}, \tag{1}$$

$$E(\mathrm{BiOX})_{\mathrm{form}} = E(\mathrm{IntIn\ doped\ BiOX}) - E(\mathrm{pure}) - \mu_{\mathrm{In}}, \tag{2}$$

where E(doped) is the total energy of BiOX with dopant, and E(pure) is the total energy of the supercell of pure BiOX. μ_{Bi} or μ_{In} is calculated from the bulk mono Bi or In crystal. The calculated formation energies are summarized in Table 1. The formation energy values increased with the packing order of BiOF < BiOCl < BiOBr < BiOI for SubIn doping systems. Furthermore, the impurity formation energy of In is negative for all BiOX, indicating that the process of In atom incorporating into the host crystal lattice is energetically favorable. Thus, the preparation In-doped BiOX sample is not relatively problematic in experiments. The formation energy of IntIn doped BiOX is larger than that of substitutional In atom doped BiOX. It should also be noted that the SubIn doped BiOX is more energetically favorable in comparison with the IntIn doping systems. Herein, we consider the most stable position (SubIn doped BiOX) in electronic structure calculation.

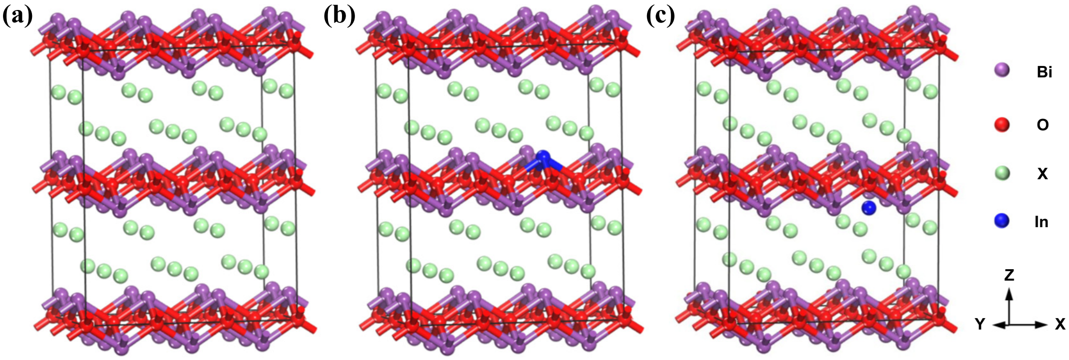

Fig. 1. The optimized structures for (a) pure, (b) SubIn-doped BiOXs (X = F, Cl, Br, and I), (c) IntIn-doped BiOXs (X = F, Cl, Br, and I).