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Layered Hg_3AsE_4X as photo catalyst for water splitting under visible light

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Abstract. A systematically study of layered Hg_3AsE_4X (E=S, Se; X= Cl, Br, I) is presented by density functional theory calculations. The family of layered Hg_3AsE_4X shows two types of electronic properties and exhibits a range of bandgaps from 2.22 to 2.53 eV. The calculated band edges of Hg3AsE4X further reveal that ten members of single layer MNX have both suitable band gaps and sufficient over-potentials for thermodynamically feasible water splitting. More fascinatingly, Hg_3AsSe_4X(X=Br, I) are direct band gap semiconductors with relative small band gaps (2.22-2.28eV), and the calculated optical absorption further convinces that such materials own outstanding properties for visible light absorption. Furthermore, by doping Se, the band gaps of Hg_3AsS_4X(X=Cl, Br) are further narrowed and significant improvements of optical absorption in visible light region are revealed by DFT calculation. Such results demonstrate that the single layered Hg_3AsE_4X (E=S, Se; X= Cl, Br, I) own high stability, versatile electronic properties, and high optical absorption, thus such materials have great chances to be high efficient photo catalysts for water-splitting.

1. Introduction

Since the discovery of first photocatalytic water splitting system based on TiO_2 and Pt1, the technology of hydrogen generating by semiconductor-based photocatalytic water splitting has been become an active research field and a promising way to uptake and store energy from the Sun. Hundreds of semiconductors and their derivatives have been examined as catalysts for water splitting2-4. Currently, most of water-splitting photocatalytic devices are based on oxides5. However, since the valence bands (VB) of oxides are mainly made up of the 2p orbital of oxygen atom which is in a very low energy level, the band gaps of oxides are generally very large for visible light absorption. Therefore, it is essential to develop stable and high efficient photo catalysts under visible light for practical and mass hydrogen production. In this case, non-oxides such as nitrides and sulfides are proposed due to their higher VB energy.

In this paper, we propose layered quaternary compounds Hg_3AsE_4X (E = S, Se; X = Cl, Br, I) as photo catalyst candidates and examine whether Hg_3AsE_4X are suitable and efficient for water splitting under visible light. Benefitting from their unique crystal structure, a lot of layered materials have been applied in the field of photo catalysis such as BiOX (X = Cl, Br or I), Bi_2WO_6, $CuMoO_4$. It is considerable to determine whether layered quaternary compounds Hg_3AsE_4X are suitable for water splitting under sunshine.

There are two preconditions for a semiconductor to facilitate photocatalytic water splitting. Firstly, the band gap energy of a photo catalyst must exceed 1.23eV to conquer the standard Gibbs free energy

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change during water splitting into H_2 and O_2. Secondly, to facilitate both the reduction and oxidation of H_2O by electrons and holes, the conduction band minimum (CBM) energy of the photo catalyst should be higher than the reduction potential of H^+/H_2, and its valence band maximum (VBM) energy should be lower than the oxidation potential of O_2/H_2O. Furthermore, to efficiently utilize visible light, the optimal band gap of the semiconductor should be around 2eV and be much smaller than 3.0eV (>415nm).

In this work, we concentrate on the experiment of layered quaternary compounds Hg_3AsE_4X as photo catalysts for water splitting to generate hydrogen by first principle calculation. Firstly, the electronic structures of layered Hg_3AsE_4X are studied by density functional theory calculations with PBE and HSE06 functionals. And then, we align the band edges of layered Hg_3AsE_4X with the redox potentials of water to analyze the water splitting abilities of Hg_3AsE_4X. At last, we discuss the methods of modifying the band gap of a semiconductor to increase optical absorption efficiency of solar energy conversion.

2. Methods

The calculations are performed using the ab initio simulation package. The exchange-correlation term has been described within the generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) functional[7]. A vacuum region greater than 15 Å perpendicular to the sheets (along the **c** axis) is applied to avoid the interaction between layers caused by the periodic boundary condition (PBC). For the geometry optimization and the optical property calculation, a kinetic-energy cutoff for plane-wave expansion is set to 500eV. All the atoms in the unit cell are fully relaxed until the force on each atom is less than 0.01eV/Å. Electronic minimization was performed with a tolerance of 10^{-6}eV. The Brillouin-zone sampling is carried out with a 10×10×1 Monk horst-Pack grid for 2D sheets and a 10×10×10 Monkhorst-Pack grid for bulk. In order to avoid the disadvantages of DFT-PBE calculation, hybrid functional calculations with HSE06[8] are performed to calculate accurate electronic structures of Hg_3AsE_4X. In this case, the plane wave cutoff of 400eV is used, and the convergence tolerance is 0.01eV/Å for force and 10^{-5}eV for electronic minimization.

To evaluate the band edge of single-layer MNX relative to vacuum, we calculate the VBM and CBM of Hg_3AsE_4X as follows[9]

$$E_{CBM} = E_{VBM} + E_g \tag{1}$$

Where E_g is band gap calculated with HSE06 functional. The VBM position relative to vacuum is calculated with HSE06 functional from the monolayer unit cell to mimic a work function calculation at a surface. The CBM position then calculated by adding the energy gap (calculated with HSE06 functional) to the VBM position. To align the energy levels for the different materials, their vacuum levels are set to zero. The standard reduction potential for H^+/H_2 and the oxidation potential for O_2/H_2O are adopted as -4.44eV and -5.67eV, respectively[10].

3. Results and Discussion

3.1. Crystal structure of layered Hg_3AsE_4X

The structure of layered Hg_3AsE_4X (E = S, Se; X = Cl, Br, I) is built of layers spreading along the *ab* plane. These layers are formed by two different kinds of six-membered rings. One is an Hg_2AsE_3 ring in the boat conformation, the other an Hg_3E_3 ring in the chair conformation. The layers are separated by halide ions. The Hg-X distances indicate only weak metal-halogen interactions, whereas the bond lengths within the layers are in good agreement with the respective sum of the covalent radii. These are 2.48 Å for Hg-S, 2.61 Å for Hg-Se, 2.25 Å for As-S, and 2.38 Å for As-Se bonds. Therefore, the structure can be described as consisting of two-dimensional polyatomic layers with predominant covalent bonds within these layers and discrete halide ions between them.

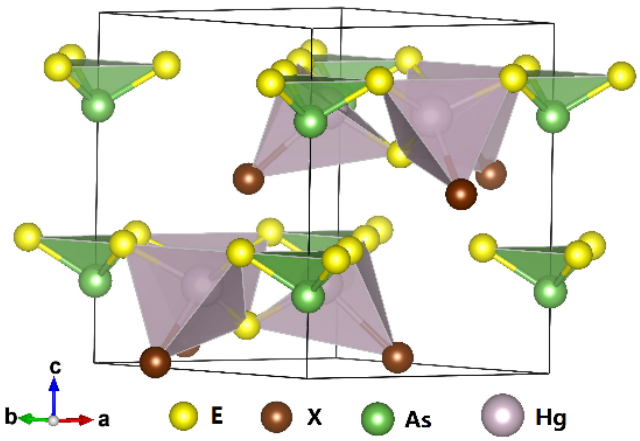


Figure 1. The crystal structures of the layered $Hg_3A_sE_4X$ (E = S, Se; X = Cl, Br, I).

3.2. Electronic Structures of layered Hg_3AsE_4X

The electronic structures of layered Hg_3AsE_4X (E = S, Se; X = Cl, Br, I) are determined by first principle calculations. The electronic structure type of Hg_3AsE_4X has an indirect band gap with CBM locating at Gamma point and CBM locating at K point.

All the results of bandgaps calculated with the HSE06 functional are listed in Table 1. The HSE06 functional results agree well with the experimental ones.

Table 1. Bandgaps calculated with the HSE06 functional, the CBM and VBM positions are calculated by equation (1). The unit is eV.

	E_g	CBM	VBM
Hg_3AsS_4Cl	2.52	-4.35	-6.87
Hg_3AsS_4Br	2.53	-4.33	-6.87
Hg_3AsSe_4Br	2.28	-4.29	-6.57
Hg_3AsSe_4I	2.22	-4.09	-6.31

From the resalts calculated with HSE06 listed in Table 1, we observe that Hg_3AsS_4Cl and Hg_3AsS_4Br have almost equal band gaps and Hg_3AsSe_4I and Hg_3AsS_4Br have almost equal band gaps. Hg_3AsSe_4X have rather smaller bandgaps compared to Hg_3AsS_4X. For Hg_3AsE_4X, the bandgaps decrease as the atom going from S to Se. To better understand the band structure of Hg_3AsE_4X, we perform analyse the projected density of states (PDOS) of selected Hg_3AsE_4X.

3.3. Photocatalytic Water Splitting and band engineering

As shown in Table 1, the calculated band gaps of all Hg_3AsE_4X (E= S, Se; X = Cl, Br, I) with HSE06 functional are in the range of 2.22-2.53eV, which indicates a significant fraction of solar light could harvest by these materials. Beside the reasonable band gap of a semiconductor for photocatalytic water splitting, it also requires that a semiconductor has decent band edge position to fit the reduction and oxidation potential.

The reduction/oxidation ability could be evaluated by aligning the CBM and VBM with respect to the water redox potential levels. The CBM and VBM of all Hg_3AsE_4X (E= S, Se; X = Cl, Br, I) are shown in Figure 2. Both the CBM and VBM of Hg_3AsE_4X lying within reduction and oxidation potentials of water indicates reduction and oxidation reaction can occur simultaneously. It is of interest to note that for Hg_3AsE_4X, the CBM potentials are sufficiently higher than the reduction potential of hydrogen, and the VBM potentials are sufficiently lower than the oxidation potential of O_2/H_2O. This indicates that both water oxidation and reduction reactions are thermodynamically feasible for them.

More fascinatingly, besides sufficient over-potentials for thermodynamically feasible water splitting, Hg_3AsSe_4Br and Hg_3AsSe_4I are also direct band gap semiconductors with relatively small band gaps (2.22ev and 2.2.28eV, respectively) for highly efficient light absorption.

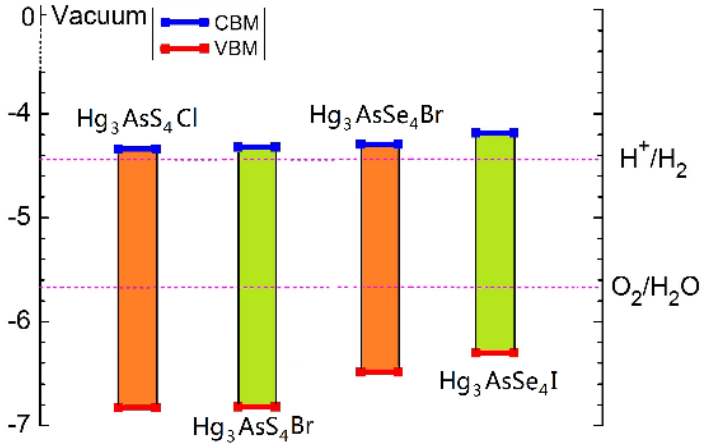


Figure 2. Band edge positions of Hg_3AsE_4X (E= S, Se; X = Cl, Br, I). The energy scale is indicated by the vacuum level (left Y-axis) in electron volts as a reference. The CBM (blue color) and VBM (red color) are presented along with the potentials in electron volts. The redox potentials (green dash line) of water splitting are shown for comparison.

Another promising route toward the production of photoactive semiconductors is through bandgap engineering by doping14-19. As discussed previously, the CBM of Hg_3AsE_4X is dominated by Hg d state. To improve the optical absorption, we can narrow the band gap of Hg_3AsE_4X by doping metal atoms with lower energy level of d state than that of Hg d state. As examples, we dope Ti atom to Hg_3AsE_4I. We create a 22 supercell of Hg_3AsE_4I(X= Cl, Br) and substitute one Ti atom for one Hg atom, then we obtain a 12.5% Ti-doped Hg_3AsE_4I(X= Cl, Br). The band gaps and band edge positions of Ti-doped Hg_3AsE_4I(X= Cl, Br) compared with Hg_3AsE_4I(X= Cl, Br). As expected, the band gaps of Ti-doped Hg_3AsE_4I(X= Cl, Br) have distinct decreases (0.29eV for Hg_3AsS_4I and 0.45eV for Hg_3AsSe_4I, respectively) with Ti doping. However, the decreases happen with the sacrifice of the CBM over-potentials. It needs to find the balance of the band gaps narrowing and the over-potentials decreases. The CBM over-potential (0.56eV) of 12.5% Ti-doped Hg_3AsS_4I is adequate for H_2 production from water while it (0.21eV) is not very enough for Hg_3AsS_4I with 12.5% Ti-doped. The decreases of the CBM positions are mainly because of the CBM of Hg_3AsSe_4I dominates by metal atom d obital and Ti 3d state has a lower energy than that of Hg 4d state.

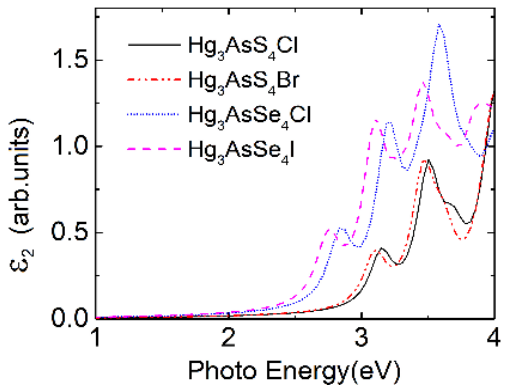


Figure 3. Imaginary part of the dielectric function, ε_2, as a function of photon energy $\hbar\omega$ calculated with PBE functional for Hg_3AsE_4X.

To evaluate the effect of band gap narrowing, we perform optic absorption calculation with PBE functional. As demonstrated in Figure 3, significant improvements of optical absorption in visible light region are apparently observed. More efficient optical absorption can be achieved by a smaller band gap narrowing by doping. In the meanwhile, sufficient over-potentials for both reduction and oxidation reactions should be guaranteed.

4. Conclusion

We performed a systematic study of the family of Hg_3AsE_4X (E= S, Se; X = Cl, Br, I) with layer structured polymorphs. And the formation energies, electronic structures, optical absorptions, band edge positions for all Hg_3AsE_4X (E= S, Se; X = Cl, Br, I) materials have been examined by DFT calculations. Hg_3AsE_4X (E= S, Se; X = Cl, Br, I) show two types of electronic properties for the different forms of Hg_3AsS_4X (X = Cl, Br, I) and Hg_3AsSe_4X (X = Cl, Br, I), and the calculated band gaps are in the range of 2.22-2.53 eV. The further examination of band edges shows that some of Hg_3AsE_4X (E= S, Se; X = Cl, Br, I) are excellent candidates for photocatalytic water-splitting. Especially, Hg_3AsSe_4I has a direct band gap of 2.22eV for visible-light driving and sufficient over-potentials (0.45eV for CBM and 0.54 for VBM, respectively) for thermodynamically feasible water splitting. By doping Ti, the band gaps of Hg_3AsSe_4I are further narrowed and significant improvements of optical absorption in visible light region are observed by DFT calculation.

Acknowledgments

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