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The Stabilities and Electronic Structures of Single-layer Bismuth Oxyhalides for Photocatalytic Water Splitting

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Abstract The stabilities and electronic/band structures of single-layer bismuth oxyhalides have been investigated employing the first-principles calculations. The results indicate that the single-layer bismuth oxyhalide materials, except for BiOF, have robust energetic and dynamical stability because of their low formation energies and the absence of imaginary frequencies within the entire Brillouin Zone. Furthermore, the calculations of the electronic structures and optical absorption indicate that single-layer BiOI possesses a providential band gap, suitable band edge positions, different orbital characteristics and different effective masses at the valence band maximum (VBM) and conduction band minimum (CBM), presenting excellent photocatalytic activity for water splitting. Moreover, the resulted compressive strains can shift band edge positions of the single-layer materials to more suitable places to enhance their photocatalytic activities.

Keywords: photocatalyst, Bismuth oxyhalides, first-principles, single-layer, band structures

1. Introduction

As a promising way to generate hydrogen - a clean and renewable energy carrier, photocatalytic water splitting has attracted a great deal of attention because of the increasing energy crisis and environmental problems. Bismuth oxyhalides (BiOX, X=F, Cl, Br and I) have been extensively studied recently, because of their hierarchical structures and promising applications as photocatalyst for water splitting and decompose toxic pollutants into harmless inorganic substance upon solar light irradiation.¹⁻⁶ The mechanism of photocatalytic water-splitting is illustrated in Fig. 1(a). The electrons are excited from valence bands to conduction bands by the incident sunlight, leading to the formation of electron-hole pairs. Subsequently, the photo-generated electrons and holes can participate in the hydrogen and oxygen generation reaction according to the two chemical reactions--H₂: $2\text{H}^+ + 2\text{e}^- = \text{H}_2$, O₂: $\text{H}_2\text{O} + 2\text{h}^+ = 1/2\text{O}_2 + 2\text{H}^+$, respectively. Two conditions must be satisfied for a promising photocatalyst. First, the width of band gap of a candidate has to exceed the free energy of water splitting of 1.23 eV.⁷ Second, the conduction band minimum (CBM) must be higher than the reduction potential of H⁺/H₂ (-4.44 eV at pH=0), and the valence band maximum (VBM) must be lower than the oxidation potential of O₂/H₂O (-5.67 eV at pH=0).^{8,9}

The lamellar structures of BiOX with interleaved atomic-layered [Bi₂O₂]²⁺ and halogen X atom slabs along c direction are constructed by the strong intra-layer electrical fields within BiOX slabs and weak van der Waals bonds between the two closely adjacent halogen X slabs.^{4, 5} The internal electric fields formed between [Bi₂O₂]²⁺ and halogen atom layers can remarkably accelerate the transport and reduce the recombination rate of the electron-hole pair, leading to the high photocatalytic activity^{3, 10} As promoted by the novel mechanical and electronic properties of 2D materials, a great deal of studies have been performed to explore the synthetic methodologies and the potential applications of BiOX nanosheets or nanoplates.^{1, 11} For instance, it has been also demonstrated that all of BiOCl, BiOBr and BiOI nanoplates exhibit more superior activity than commercial TiO₂ (P25, Degussa) towards methyl orange (MO) dye degradation under UV-visible light irradiation, and

BiOI is the best photocatalyst with the degradation efficiency reaching 80% in 3 hour under visible light illumination.¹² The experiments performed by Yu *et al.* have evidenced that BiOI possesses higher photocatalytic activity than Bi₅O₇I and Bi₂O₃ under visible light irradiation.¹³ The higher photocatalytic activity of BiOI is attributed to its narrower band gap. Moreover, heterostructure BiOI/BiOBr¹⁴ and solid solution xBiOBr-(1-x)BiOI¹⁵ have been synthesized to enhance the photocatalytic performances. Indeed, those composite materials showed higher activity than that of the individual component for the degradation of MO under the visible light. A new bismuth-base material, Bi₂₄O₃₁Br₁₀ is thought of an important photocatalyst with remarkable reduction activity to generate hydrogen from water under visible-light irradiation.¹⁶ BiOCl with wide band gap has attracted extremely considerable attention, because of its high activity and high stability. Zhao and co-workers³ revealed that the photocatalytic activity of BiOCl single-crystalline nanosheets is surface-dependent. BiOCl (001) surface has higher activity in direct semiconductor photoexcitation pollutant degradation under UV light, while (010) surface exhibited higher activity in indirect dye photosensitization degradation under visible light. The photocatalytic activities of noble metal decorated BiOX investigated by Yu *et al.* have showed that the deposition of noble metal can enhance the visible light absorption and improve the photocatalytic performance.¹⁷

Lots of atomically-thick materials have shown outstanding properties and the tremendous potential in applications. For instance, Wang and co-workers¹⁸ suggested that graphene oxide can be used as an ideal substrate for hydrogen Storage. Small concentration hole-doping into graphene-like MnO single layer leads to switching from antiferromagnetism into half-metallic ferromagnetic configuration.¹⁹ Xiang's group²⁰ predicted a stable 2D boron-carbon compound BC₃ exhibiting semiconductor behavior. Moreover, Liu and co-workers²¹ proposed that single-layer metal phosphorus trichalcogenides are potential photocatalysts for overall water-splitting. As inspired by the progressive achievements, we thus expect that single-layer BiOX could be also obtained through mechanical or chemical exfoliation strategies and exhibit highly efficient photocatalytic performance. Therefore, it is of importance to

perform comprehensive investigation on the stabilities and electronic structures of single-layer BiOX materials. To the best of our knowledge, the study of the properties of single-layer BiOX is rather limited.

In this work, we attempt to study the single-layer BiOX employing first-principles calculations. First, the stabilities of materials were investigated according to the formation energies and the phonon spectrum analysis. Subsequently, the feasibility of the single-layer BiOX used as photocatalysts for water splitting was studied based on the calculated electronic structures. Finally, we explored the efficiency of the mechanical strains adjusting the band gaps and band edge positions of single-layer BiOX to enhance their photocatalytic activity.

2. Computational Methods

First-principles calculations were performed by using the Vienna Ab *initio* Simulation Package (VASP).²² The projector-augmented-wave (PAW) potentials²³ were used for the treatment of the core electrons. The electron exchange correlation interactions were treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.²⁴ To ensure that the interactions between the slabs along the vertical direction are negligible, a vacuum layer with the total thickness of 30 Å was set at the both sides of the respective atomic layer. Soft oxygen pseudopotential with valence configuration $2s^22p^4$ and default cutoff energy of 250 eV was adopted in the calculations. In order to check the accuracy of the calculations, the phonon of BiOCl was also checked with 500 eV, and the results show that the higher energy cutoff gives the same result as that of 320 eV. The energy cutoff was set to 320 eV and the k-points sampling of $7 \times 7 \times 1$ utilized the Monkhorst-Pack²⁵ scheme. The equilibrium geometries were obtained via fully optimizing both the atom positions and lateral lattice vectors to a tolerance of less than 0.02 eV/Å on each atom. To study the stabilities of BiOX, we performed phonon calculations using the supercell approach.²⁶ Force constants and phonon frequencies were calculated using the PHONOPY code.²⁷

The electronic structures of single-layer BiOX were calculated by HSE06²⁸⁻³⁰

methods to overcome the deficiency of standard DFT in describing the exchange-correlation (XC) energy. The exact exchange contribution is represented by a value of 25% HF and 75% PBE contributions. The work functions were calculated, and then the CBM and VBM were placed to the positions referring to the vacuum level, according to^{31, 32}

$$E_{CBM/VBM} = E_{BGC}^{HSE06} \pm \frac{1}{2} E_g^{HSE06} \quad (1)$$

where the band center energy E_{BGC} and band gap were calculated by HSE06 method.

3. Results and Discussion

3.1 Geometric Structure and Stabilities

The structures of single-layer BiOX were illustrated in Fig. 1(b). Upon relaxation by PBE-based DFT calculations, the lateral lattice constants $a=b$ for single-layer BiOX were optimized to be 3.711, 3.889, 3.930, and 4.014 Å, which are very close to the experimental values of 3.748, 3.89, 3.916 and 3.985 Å for BiOF, BiOCl, BiOBr and BiOI unit bulks,³³ respectively. The subtle differences in the lattice parameters indicate that ideally isolated single-layer BiOX slabs can keep the geometric integrity and experience negligible relaxation or construction. The binding interactions of single atom in the halogen X slabs with $[\text{Bi}_2\text{O}_2]^{2+}$ slabs were determined according to

$$E_b = (E_{\text{BiOX}} - E_{\text{BiO}} - E_X) / n \quad (2)$$

where E_{BiOX} , E_{BiO} , E_X are the total energies of BiOX, $[\text{Bi}_2\text{O}_2]^{2+}$, halogen X slabs, respectively, and n is the atom number in the halogen X slabs. The calculated values are -5.77, -4.13, -3.52 and -2.74 eV/atom for BiOF, BiOCl, BiOBr and BiOI, respectively, indicating the typical chemical bonding interactions between halogen X atoms and $[\text{Bi}_2\text{O}_2]^{2+}$ slabs.

Subsequently, we evaluated the interactions between two adjacent BiOX slabs via the calculations of the formation energy of single-layer BiOX, according to the formula:³¹

$$E_f = E_{2D} / N_{2D} - E_{3D} / N_{3D} \quad (3)$$

where E_{2D} and E_{3D} are the energies of the single-layer and 3D bulk BiOX, N_{2D} and N_{3D} are the numbers of atoms in their unit cells, respectively. In order to ensure the accuracy of the description of the interactions between atomic layers, four different functionals were adopted for the calculations of the formation energies of the single-layer BiOX materials. The results were compared in Fig. 2. We first performed PBE functional based conventional DFT calculations to evaluate the formation energies. The value for single-layer BiOF is calculated to be 0.06 eV/atom, which is significantly smaller than the energy of F atom binding with $[\text{Bi}_2\text{O}_2]^{2+}$ slab, and indicating that single-layer BiOF might be easily exfoliated from the bulk BiOF. Moreover, the negative values of -0.0006 (almost naught), -0.02 and -0.06 eV/atom for the formation energies of single-layer BiOCl, BiOBr and BiOI suggest that the ground states of the three atomically-thick materials could be more stable than their 3D counterparts, and thus may be formed spontaneously. More accurate HSE06 functional were then performed to verify the results got by the PBE functional based calculations. The calculations show that HSE06 method yields slightly positive formation energies of 0.12, 0.004, -0.008 and -0.03 eV/atom for single-layer BiOF, BiOCl, BiOBr and BiOI respectively. Since the values of single-layer BiOBr and BiOI are calculated to be negative by both PBE and HSE06 methods, it is implied that the two materials might be probably stable in 2D morphology. Nevertheless, note that the interactions between two adjacent single-layer BiOX are weak, it's necessary to take the dispersive electrostatic interactions between halogen X atom slabs into consideration. We thus performed PBE+vdW and HSE06+vdW calculations by employing the DFT-D2 method of Grimme³⁴ on the total energies of these structures to determine the feasibility of single-layer BiOX formation. In this way, all of the formation energies are calculated to be slightly positive. The formation energy of BiOF calculated by HSE06+vdW method is still the largest one with the value of 0.16 eV/atom. Similarly, the formation energies of single-layer BiOCl, BiOBr and BiOI calculated by PBE+vdW and HSE06+vdW methods are comparative to the values for single-layer GaS, GaSe, and MoS_2 ,³¹ which have been already successfully obtained by mechanical exfoliation or chemical synthesis.³⁵⁻³⁷ Therefore, we expect that

single-layer BiOX materials can be feasibly obtained by cleaving from their 3D counterparts, except for BiOF because of its relatively high formation energy. Overall, our extensive calculations showed that the intra-layer interactions of X atoms and $[\text{Bi}_2\text{O}_2]^{2+}$ slab within the single-layer BiOX are significantly stronger than the inter-layer interactions between two adjacent BiOX sheets in the 3D bulk structures.

Phonon dispersion spectrum analysis is a reliable method for verification of the stabilities of single-layer BiOX. It's requisite for a stable structure to meet the condition that all of its phonon frequencies on the k-points in the Brillouin Zone should be positive.^{38, 39} As shown in Fig. 3, there is no imaginary vibration frequency appears in the phonon band spectrums for single-layer BiOCl, BiOBr and BiOI, which indicates the structures have high phonon stability. However, the evidenced imaginary frequency on the phonon spectrum of BiOF demonstrates that this material is an unstable sing-layer material (see Fig. 3 (a)), and thus difficult to prepare.

3.2 Electronic Structures

Since single-layer BiOF is not stable, it is not necessary to further investigate its band/electronic structures. The band structures of the rest of single-layer BiOX (henceforth, X=Cl, Br and I) materials calculated by HSE06 functional shown in Fig. 4 indicate that all the BiOX materials exhibit indirect band gaps with CBM located at Z points and VBM located between R and Z points in irreducible Brillouin zone (IBZ). As suggested by Zhang and co-workers,⁴⁰ indirect band gap characteristic helps to reduce the recombination rate of photo-generate carriers, in that the excited electrons must emit phonon during the transition back to the valence band with certain k-space distance travel. But we must note that the indirect band gap also makes the material a poor absorber of light. The itinerancy of electrons increasing as the order of the atomic number of halogen atoms in single-layer BiOX gives reasons to the band gaps decreasing in the order of BiOCl>BiOBr>BiOI with the calculated values of 3.79, 3.41 and 2.3 eV, respectively. Because of the quantum size effect, the band gaps of single-layer BiOX are larger than the values of 3.47, 2.84 and 1.87 eV for BiOCl, BiOBr and BiOI,¹⁷ respectively. The band gaps indicate single-layer BiOCl and BiOBr materials might be only activated under UV light, while BiOI material can

absorb visible light of solar spectrum. Therefore, the single-layer BiOI material is expected to be the best photocatalyst candidate for water splitting among these BiOX materials. Single-layer BiOI with band gap of 2.3 eV is appropriate for reaction of photocatalytic water splitting, which requires at least $\sim 1.9\text{-}2.0$ eV.^{41,42} Furthermore, the distinctively dispersive feature at band edges implies that photo-generated carriers should have high carrier mobility. We thus estimate the effective masses of electron and hole by fitting the dependence relationship of energy to wave vector at the VBM and CBM. The effective masses for BiOCl, BiOBr and BiOI at CBM (m_e^*) are calculated to be 0.56, 0.48 and 0.40 m_e along R \rightarrow Z, respectively, presenting the electron has excellent mobility, even better than that in anatase TiO₂ ($m_e^* = 1 m_e$).⁴³ On the other hand, as for photo-generated hole, the diffusion in valence bands is relatively weak, because the hole effective masses for BiOCl, BiOBr and BiOI at VBM (m_h^*) are calculated to be 1.10, 1.05 and 2.75 m_e along R \rightarrow Z, respectively, are much larger than those values of electron at CBM. The significant difference between m_e^* and m_h^* indicates the great difference in the mobility of carriers and the resulting lower recombination rate of the electron-hole pairs.⁴⁴ Note that, high diffusion rate and long lifetime of carriers are distinctly important for high-efficiency photocatalysts.

In order to catalyze the water splitting reaction, the positions of CBM and VBM must straddle the redox potential of water. We first performed work function calculations upon these single-layer BiOX with HSE06 functional, and then placed the positions of the CBM and VBM with respect to the vacuum level to determine the photocatalytic capability, as suggested by Zhuang.³¹ For BiOCl, BiOBr and BiOI, the work functions are calculated to be 7.94, 7.83, 6.65 eV, respectively. Taking single-layer BiOI for instance, as shown in Fig. 5, the CBM lies higher in energy than the reduction potential of H⁺/H₂ and its VBM energy is lower than the oxidation potential of O₂/H₂O, which indicates that single-layer BiOI is appropriate for the reaction of photocatalytic water splitting. In addition, the results indicate that it's unfeasible to catalyze the reduction reactions of CO₂ to produce methane, methanol and formic acid, because the CBM of BiOI is lower than the reduction potentials of CO₂.

The comparison of the CBM and VBM energy levels with the redox potentials of water splitting in Fig. 6 shows that all of single-layer BiOX have band edges situated in energetically favorable positions for water splitting. The results indicate that the three single-layer BiOX materials are appropriate for catalyzing the overall water splitting.

The density of states (DOS) of BiOI was taken for instance to understand the bonding characteristics of single-layer BiOX, as shown in Fig. 7. The valence band (VB) top of -0.5~0 eV is occupied by I-5p states, within the energy of -2.0~-0.5 eV the orbits mainly consist of I-5p and O-2p with a small amount of Bi-6s, and the bonding states locating between -6.0 and -2.0 eV significantly formed by Bi-5p and O-2p with a little bit of I-5p. Nevertheless, the conduction band (CB) bottom mainly derives from Bi-6p states with minor contribution from I and O atoms. It is thus reasonable to expect that the conduction and valence band edges with different characteristics can help to substantially reduce the photo-generated electron-hole recombination rates. Bader charge analysis⁴⁵ shows each Bi atom donates 2.95 electrons, while each I and O obtain 0.59 and 2.36 electrons, respectively, representing the strong chemical bonding interactions within the atomic BiOX layers.

3.3 Optical Absorption

It is well-known that the interactions between a photon and electrons system can be interpreted in terms of the time-dependent perturbations of the ground-state electronic states. The optical spectra caused by the interband transitions of excitations from occupied to unoccupied states can be described as a joint density of states between valence and conduction bands. Dielectric function, $\epsilon(\omega)$ is an important aspect of the optical properties. Considering the appropriate transition momentum matrix elements, the imaginary part of the dielectric function, $\epsilon_2(\omega)$ is calculated by summing all possible transition from unoccupied to occupied wave functions within the selection rules.⁴⁶ The real part of the dielectric function, $\epsilon_1(\omega)$ can be derived from $\epsilon_2(\omega)$ using the Kramer-Kronig relationship. Therefore, the absorption coefficient $\alpha(\omega)$ can be calculated from the dielectric components $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ using the following expression:

$$\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2} \quad (4)$$

The calculated optical adsorption spectrum of single-layered BiOX using HSE06 functional was shown in Fig. 8. The absorption is activated by the irradiation with energy larger than 3.82, 3.41 and 2.43 eV for BiOCl, BiOBr and BiOI, respectively, which are very close to the values of the indirect band gaps. The transition of electrons from R point at VBM to Z point at CBM needs the assistance of phonon, resulting in the weak adsorption of the visible light represented by the gentle edge of the spectrum. The first peaks around 3.8 eV and 2.7 eV on the respective absorption spectrum of BiOBr and BiOI can be attributed to the direct transition of electrons at Z point of Brillouin-zone. There is no remarkable peak around 4.2 eV on the absorption spectrum of BiOCl, which is corresponding to the energy difference between its valence and conduction band edges at Z point. On the contrary, the absorption coefficient rises rapidly to the order of 10^6 cm^{-1} at about 5.0 eV. We assume that the representing characteristic of absorption for BiOCl is a result of the collective contribution from the direct and/or indirect interband transition at high-symmetry points and/or axes in the Brillouin zone, caused by the incident photon with appropriate energy. The noise in the absorption spectrums could be result from the anisotropy band structures and a small smearing in the calculations in order to achieve high precise.

3.4 Strain effects

As mentioned above, suitable width of band gap and appropriate band edge positions are two critical factors to efficiently harvest solar energy. However, the band gaps of BiOCl and BiOBr are too large, leading to low photocatalytic efficiency to absorb sun light. In addition, the positions of CBM for the three single-layer BiOX are just slightly over the reduction potential level of water splitting, leading to the reduction potential of photo-generated electrons might be not easy to produce hydrogen from water. A valid method to solve these problems is through band gap engineering by applying strains.⁴⁷ The epitaxial growth on suitable substrates, in practice, is an effective way to realize these strains.³¹

Biaxial strains in the range from -4% to +4% were applied on the single-layer BiOX to explore the effects of strain on the band gaps and band edge positions. HSE06 functional was employed to relax atomic coordinates to the equilibrium positions at each biaxial strain and then calculate the corresponding band structures. The variation of CBM and VBM of single-layer BiOX with strains, as shown in Fig. 9, provides an important guidance for tuning the CBM and VBM levels of single-layer BiOX to maximize the efficiency of photocatalysis. There is little change for the band gaps upon the applied strains, while the position adjustment of CBM and VBM levels is depending linearly on strain. Specifically, the band edge positions of all single-layer BiOX are shifted upwards to higher positions with respect to the redox potential level of water at compressive strains. The positions of CBM were elevated much faster than that of VBM during the compression process. Thus, the photo-generated electrons could be endowed stronger reduction capability to generate hydrogen from water. Conversely, tensile strains make the band edge positions of all these three materials unfavorable for water splitting, due to the positions of CBM are enforced below the reduction potential of H^+/H_2 .

4. Conclusion

We have comprehensively investigated the stabilities and electronic structures of single-layer BiOX and explored the potential of the materials for photocatalytic water splitting. Negative or low positive formation energies obtained by different approaches indicate that single-layer BiOCl, BiOBr, BiOI can be feasibly obtained by mechanical exfoliation. Furthermore, the phonon dispersion spectrums analysis verified the stabilities of single-layer BiOCl, BiOBr and BiOI, except BiOF. The calculations of band structures performed with HSE06 functional suggest that the single-layer BiOX (X=Cl, Br, I) materials are promising photocatalysts for water splitting. Especially the band gap of single-layer BiOI is 2.3 eV, indicating the atomically-thick material can be responded to visible light. The different orbital characteristics and different effective masses at the valence band maximum (VBM) and conduction band minimum (CBM) are important factors for a high-efficiency

photocatalyst. However, the optical properties calculations indicated that the absorption of visible light is relatively weak because of the indirect band gaps of the single-layer BiOX. In addition, we explored the effects of mechanical strains on the adjustment of the band gaps and band edge positions. Our calculations show that compressive strains on BiOCl, BiOBr and BiOI can increase band gaps slightly but render the band edge positions to be more favorable for hydrogen production, and thus enhance the efficiency of photocatalytic activities of BiOCl, BiOBr and BiOI.

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