Interlayer-decoupled BiOX (X=Cl, Br, and I) sheets for photocatalytic water splitting: a computational study*

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In this work, we comprehensively study the electronic and photocatalytic properties of single-layer and multilayer bismuth oxyhalides BiOX (X=Cl, Br, and I) sheets by means of extensive density functional theory, which have been successfully synthesized in the previous experimental studies. Our computational simulations show that single-layer BiOX sheets possess indirect band gap, suitable band edge alignments, and pronounced optical properties, suggesting that they can be utilized as photocatalysts for splitting H_2O into H_2 and O_2 from theoretical aspects. In the case of multilayer BiOX sheets, some primary physical properties determined the photocatalytic performance are rather robust, almost independent of the layer number. According to these calculated results, we are optimistic that BiOX sheets, especially for single-layer BiOI, have great chances to be used for photocatalytic water splitting.

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Since the successful exfoliation of graphene[1], two-dimensional (2D) materials have been a subject of material science owing to the diverse physical and chemical properties. A great deal of efforts are performed to develop their potential applications in various fields, such as electronics and optoelectronics[2]. Over the past decade, many 2D semiconductor materials have been predicted to be efficient water splitting photocatalyst by extensive experimental and theoretical studies because of their intrinsic advantages, including large surface area and small charge migration distances[3,4]. Besides, as shown in Fig.1(b), such semiconductor photocatalysts generally satisfy some crucial requirements: (i) appropriate band gap for effective utilization of the solar energy; (ii) ideal band edge positions; (iii) adequate oxidation/reduction ability[5].

In recent years, bismuth oxyhalides BiOX (X=Cl, Br, and I) with alternating $[Bi_2O_2]$ and $[X_2]$ layers have attracted great interest due to their unique optoelectronic properties, which leads to their utility in photocatalytic applications such as N_2 fixation, pollutant control, and CO_2 reduction[6-8]. However, the photocatalytic performance of water splitting is seriously limited by the fast recombination of photogenerated electrons and holes. Recently, BiOX nanosheets or nanoplates exposed with {001} facets have been synthesized for improving the photocatalytic activity[9-11]. To the best of our knowledge, few theoretical works have been carried out on these single-layer and multilayer BiOX sheets although there are extensive experimental researches. More attention should be paid to explore their electronic structure and photocatalytic properties.

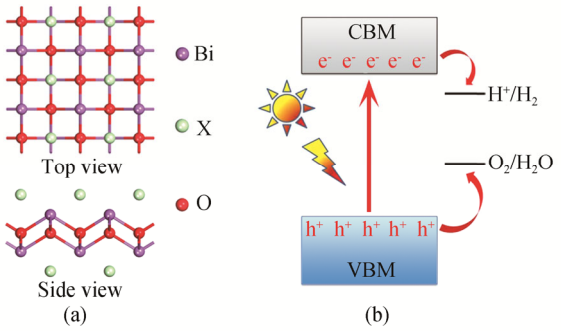

Fig.1 (a) Top and side views of the geometric structure of single-layer BiOX; (b) Illustration of the mechanism of photocatalytic water splitting

In this work, we perform first-principles calculations to unveil whether single-layer and multilayer BiOX are potential water splitting photocatalysts for hydrogen generation. Firstly, we focus on exploring the electronic structures, optical absorbance, and oxidation/reduction abilities of single-layer BiOX sheets. Then, the influence

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of layer thickness on the band gaps and energy level positions of multilayer BiOX sheets are investigated. The obtained calculated results show that single-layer BiOX have ideal band gaps, favorable VBM/CBM alignments, and pronounced optical absorb properties, indicating that they are high-efficiency photocatalysts for water splitting.

First-principles calculations are performed using the Vienna Ab initio Simulation Package. The interaction between the core and valence electrons is described using the frozen-core projector augmented wave approach[12]. Exchange and correlation effects are described by the PBE functional[13]. The energy cutoff energy is set to 500 eV, and the Monkhorst-Pack mesh of k-points 15×15×1 points are used to sample the Brillouin zone[14]. All atomic positions are fully relaxed by using the conjugate gradient algorithm until total energy and atomic forces are converged to 10^{-5} eV and 0.02 eV/Å.

The typical crystal structures of the single-layer bismuth oxyhalides, BiOX, are shown in Fig.1(a). After geometry optimization, the lattice parameters of single-layer BiOCl, BiOBr and BiOI are calculated to be 3.89 Å, 3.94 Å, and 4.03 Å, respectively. Meanwhile, their respective thicknesses are 5.16 Å, 5.68 Å and 5.80 Å, respectively. These results agree well with previous theoretical and experimental values, implying that our chosen calculation methods are reasonable[15].

Subsequently, we investigate the electronic properties of the single-layer BiOX materials by employing the HSE06 method. Their band structures are displayed in Fig.2. We find that all of these single-layer BiOX materials are indirect-bandgap semiconductors with their CBMs located at the Γ point and the VBMs lied at the middle region along the X-Γ line in the irreducible Brillouin zone. The band gaps of single-layer BiOCl, BiOBr, and BiOI are predicted to be 3.76 eV, 3.37 eV and 2.28 eV, respectively. The decrease of band gap observed in the single-layer BiOX (X=Cl, Br, I) is ascribed to the decrease in ionicity of halogen atom. As shown in Fig.2, both the valence and conduction bands of these single-layer BiOX materials are well dispersive. Moreover, there are no localized states in their respective forbidden band gap. Hence, the recombination possibility of the photogenerated electrons and holes can be substantially reduced, and these single-layer BiOX materials are expected to have better photocatalytic performance. Besides, our results indicate that these single-layer materials meet the requirement of minimum band gap value (1.23 eV) for spontaneous water-splitting. Therefore, single-layer BiOX are promising candidates as photocatalysts.

To gain more insight into the bonding characteristics, we analyse the total density of states (DOSs) and projected density of states (PDOSs) of single-layer BiOX. As shown in bottom panel of Fig.2, the CBMs of three single-layer BiOX sheets are dominated by the Bi-6*p* states, While their VBMs comprise of the states of X-*p*, O-2*p*, and Bi-6*s*, indicating different characteristics near the band edges, which is beneficial to reduce the possibility of electron-hole recombination. Besides, our calculate results demonstrate that the X-*p* states make greater contribution to the VBM with the halide atom X changing from Cl to I. For example, the VBM in single-layer BiOI is mostly contribute by the p states of the I atom. It is therefore clear that different kinds of halogen in single-layer BiOX can significantly tune their valence band composition, resulting in the band gap reduction in the order of BiOCl>BiOBr>BiOI.

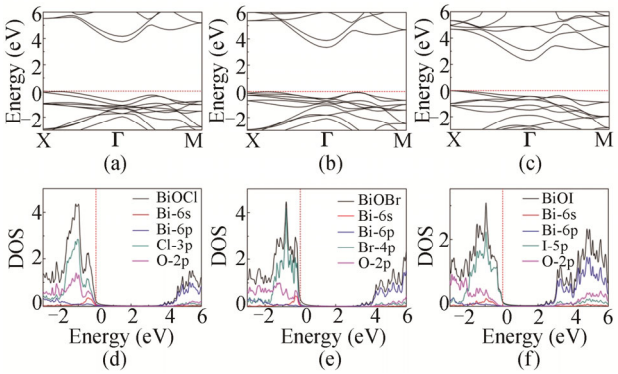

Fig.2 Band structures of single-layer BiOX, (a) BiOCl, (b) BiOBr and (c) BiOI at the HSE06 functional level; Total and projected densities of states of single-layer BiOX: (d) BiOCl, (e) BiOBr and (f) BiOI

Besides a desirable band gap for harvesting solar light, it also requires that the semiconductor photocatalyst possesses decent band edge positions for water splitting[16]. Consequently, the band edge alignments of single-layer BiOX are further calculated and shown in Fig.3. Clearly, the VBM and CBM positions of these three single-layer BiOX materials straddle water oxidation and reduction potentials, suggesting that they are promising photocatalysts for water splitting. Moreover, the CBM energies of single-layer BiOCl, BiOBr and BiOI are higher than the reduction potential of H^+/H_2 by 0.37 eV, 0.18 eV and 0.26 eV, respectively, whereas their corresponding VBM energies are lower than the oxidation potential of O_2/H_2O by 2.16 eV, 1.96 eV and 0.79 eV, respectively. These results indicate that single-layer BiOX not only satisfy the thermodynamic requirements for solar water splitting, but also have adequate driving force for both water redox reactions.

As mentioned in the Introduction, accurate control the layer number is extremely difficulty in experiments. In general, the synthesized BiOX sheets are nanometer-scale thickness, which comprise of a few atomic layers. To ascertain the effect of layer thickness on the electronic properties, the band structures of *N*-layer BiOX with *N*=2—5 are calculated with the HSE06 functional. Taking BiOI as an example, the band plots for *N*-layer BiOI are shown in Fig.4. We observe that multilayer BiOI sheets are indirect-bandgap semiconductors as before.

More interestingly, For 2- to 5-layer BiOI, their band structures exhibit hardly any change relative to the case of the single-layer. As shown in Fig.5(a), the band gaps of multilayer BiOX sheets decrease as the layer thicknesses increases, but the magnitudes are quite small. According to our HS06 calculations, the obtained band gaps are 3.66 eV, 3.17 eV and 2.23 eV for 5-layer BiOCl, BiOBr and BiOI, respectively, which are only 0.1 eV, 0.2 eV and 0.05 eV decrease in compare with that of each single-layer. Therefore, the electronic structures of multilayer BiOX sheets are almost independent of their layer thickness, which is different from most other 2D semiconductor materials[17].

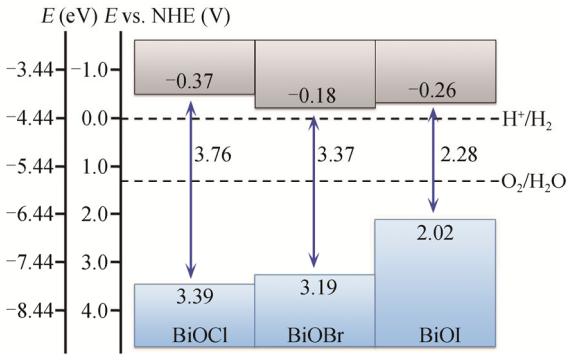

Fig.3 Band edge alignments of single-layer BiOX relative to the vacuum level

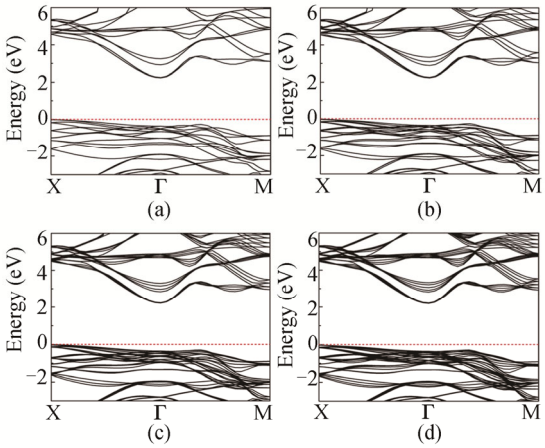

Fig.4 HSE06 calculated band structures of (a) bilayer, (b) three-layer, (c) four-layer and (d) five-layer BiOI

Having affirmed the robustness of the band gap, one would wonder whether *N*-layer BiOX sheets with *N*=2—5 are still appropriate for direct overall water splitting when their atomic layers grow. Accordingly, we give the band edge alignments of multilayer BiOX sheets with respect to the oxidation/reduction potentials of water splitting, as illustrated in Fig.5(b). Comparing with the single-layer systems, the band edge energy positions of multilayer BiOX sheets keep almost unchanged. In the case of 5-layer BiOX sheets, their CBMs are approximately 0.33 eV, 0.17 eV and 0.21 eV above the reduction potential of H^+/H_2, while the corresponding VBMs are approximately 2.11 eV, 1.79 eV and 0.81 eV below the oxidation potential of O_2/H_2O, which are very close to those of single-layer BiOX. Furthermore, the VBM and CBM positions of all multilayer BiOX sheets are energetically favorable for both water oxidation/reduction reactions, demonstrating that they are still potential photocatalysts for water splitting. According to these observations, we find that BiOX sheets have thickness-independent electronic structures and band edge alignments, which would be highly desirable for practical application as photocatalysts.

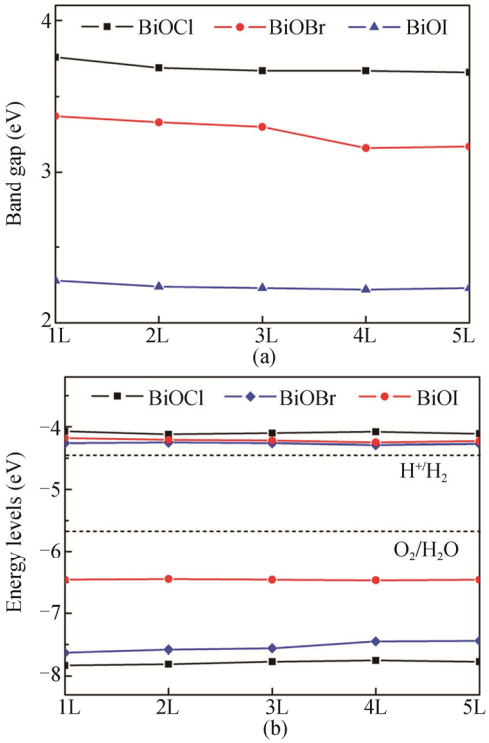

Fig.5 (a) Band gap values of BiOX with different layer thicknesses; (b) Band edge positions of multilayer BiOX relative to the vacuum level

To assess the photocatalytic water splitting ability using solar energy, the optical absorption spectra of single-layer BiOX and multilayer BiOI (from 1- to 5-layers) are further simulated based on the HSE06 functional. As shown in Fig.6(a), single-layer BiOI has a better optical absorption in the visible light region (about 400 nm—500 nm in wavelength) than the other two single-layer sheets (BiOCl and BiOBr). This is expected because single-layer BiOI has smaller band gap (2.28 eV). Noted that these single-layer BiOX materials exhibit the weak absorption of the incoming light represented by the gentle edge of the spectrum because of their indirect band gaps. Fig.6(b) displays the optical spectra of multilayer BiOI sheets as the function of light wavelength. It can be seen that all multilayer BiOI sheets show substantial adsorption under visible light irradiation. Interestingly, as the layer thickness grows, the ab-

sorption edges are almost intact, but the absorption intensity obviously increases in both the ultraviolet and visible light area. We assume that this characteristic of absorption is as a result of the weak interlayer interaction. These results suggest that BiOI sheets could be highly promising solar water splitting materials despite the layer thickness.

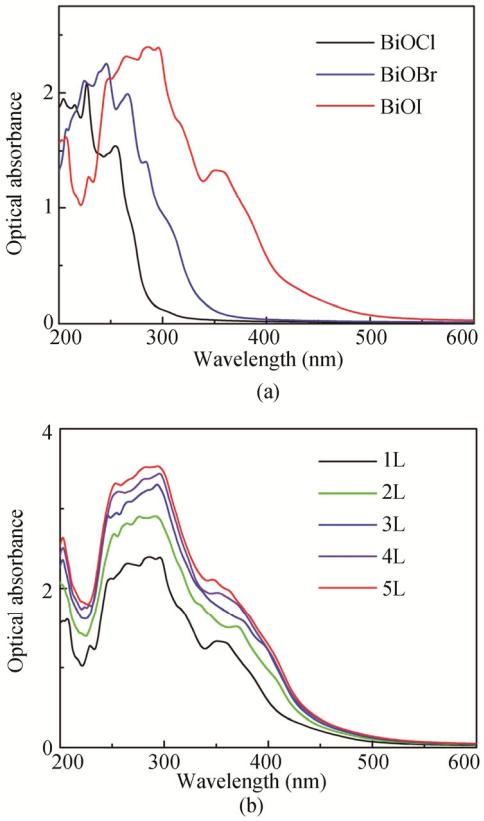

Fig.6 (a) The HSE06 calculated optical absorbance spectrum of (a) single-layer BiOX and (b) multilayer BiOI

In conclusion, based on the first-principles calculations, we perform a systematic investigation of the BiOX sheets for potential application as water splitting mate rials. The single-layer BiOX sheets are predicted to be indirect semiconductors with band gaps of 3.76 eV, 3.37 eV and 2.28 eV, respectively. Moreover, we find that all the single-layer BiOX have great possibility to be used as photocatalysts for hydrogen production because of their ideal VBM and CBM positions. Most interestingly, multilayer BiOX sheets are shown to possess thickness-independent electronic structures, band edge alignments, and optical properties. Our these theoretical results indicate that BiOX sheets, especially for single-layer BiOI, could be efficient photocatalysts for water splitting.

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