Investigation of Band Offsets of Interface BiOCl:Bi$_2$WO$_6$: A First-Principles Study

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Investigation of band offsets of interface BiOCl:Bi₂WO₆: a first-principles study

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Received 9th October 2011, Accepted 7th December 2011
DOI: 10.1039/c2cp23186g

Density functional theory calculations are performed to study the band offsets at the interface of two photocatalytic materials BiOCl:Bi₂WO₆. It is found that the W–O bonded interface shows the most stability. An intrinsic interface fails to enhance the charge-carrier separation due to the improper band alignment between these two materials. Sulfur (S) is proposed to replace the bulk oxygen (O) site and thus tune the band edges of BiOCl to enhance the photocatalytic performance of the heterojunction. Furthermore, the presence of S provides an extra charge to generate a clean interface with minimal gap states that also benefits carrier migration across the heterojunction.

Photocatalysts have drawn great attention in both industrial and scientific communities due to their potential applications in energy and environmental related fields, such as hydrogen production and water purification. With incident photons’ energies being larger than the band gap of a photocatalyst, electrons are excited to the conduction bands, resulting in the generation of electron–hole pairs. These photo-generated electrons and holes can react with H₂O and cause the evolution of H₂ and O₂ via water splitting reaction. Furthermore, electron transfers to O₂ and from H₂O can form highly reactive superoxide anions (O₂⁻) and hydroxyl radicals (•OH) that are responsible for the decomposition of various organic contaminants. In both cases, alignments between water’s and the photocatalyst’s molecular levels, light absorption capability, and electron–hole recombination rates play an essential role in determining the photocatalytic activity. To minimize electron–hole recombination rates and boost photocatalytic performance, people have attempted different approaches to enhance the carrier separation efficiency, such as the surface decoration of metal nanoparticles as electron traps and the creation of heterojunctions by interfacing two well known catalysts. In recent years, heterojunctions have received great attention in photocatalytic research. For instance, many heterojunctions such as WO₃/TiO₂, MoO₃/TiO₂, ZrO₂/TiO₂, Fe₂O₃/TiO₂ and BiOCl/Bi₂O₃ have been fabricated and shown to provide different levels of performance boost, with many more other hetero-pairs still being under investigation. Nonetheless, formation of a heterojunction would improve the catalytic performance only if the band offsets (BOs) at the interface facilitate charge carrier separation, and this condition cannot always be guaranteed. In this article, a heterojunction consisting of Bi₂WO₆ and BiOCl is investigated since both components are popular candidates for the photocatalysis. A first-principles method is used to investigate the interface BOs and thus disclose the interface impact on the overall catalytic performance. Some previous studies have utilized sulfur in engineering the band gap of a photocatalyst. Through our theoretical study, further insights are provided to fine tune the BOs via sulfur (S) doping to enhance charge-carrier separation at the heterojunction.

Our calculations are based on the density functional theory (DFT) with the Perdew–Burke–Ernzerhof version of the generalized gradient approximation (GGA-PBE) for the exchange–correlation potential, as implemented in a plane-wave basis code VASP. The pseudopotential is described by the projector-augmented-wave (PAW) method. An energy cutoff of 400 eV and an 8 × 8 × 1 k-point with a Γ centered k mesh were used in our calculations. The force on each atom was converged to 0.02 eV Å⁻¹ during the atomic structure optimization. For the supercells of our interface models, the atomic positions are relaxed and the interface distance re-optimized with a conjugate gradient (CG) method.
We consider a model interface between an orthogonal BiOCl (Pca21) and an orthogonal Bi2WO6 (Pca21). The unit cell of BiOCl is derived from the fluorite (CaF2) structure [ref. 12]. It is a known tetragonal structure with lattice constants \(a = b = 3.890\ \text{Å}\) and \(c = 7.890\ \text{Å}\). For Bi2WO6, the lattice constants are \(a = 5.437\ \text{Å}, b = 16.433\ \text{Å}, c = 5.4587\ \text{Å}\) [ref. 21]. To accommodate the lattice constant difference, the (010)-oriented Bi2WO6 surface is stretched by \(\sim 1.0\%\) and BiOCl is rotated counter-clockwise by 45° to match each other’s surface (see Fig. 1a). At the interface, it could form either Bi–O, Bi–Cl or W–O bonds. Due to the stronger dissociation energy of W–O bonds (7.20 eV) than Bi–O (3.37 eV) and Bi–Cl (3.00 eV), an interface model with W–O bonding is energetically more favorable. In order to systematically study the impacts of various interfacial bonding configurations on the BOs, Bi–O bonding interfaces with varying interfacial oxygen content are also considered. A 10 Å vacuum region is used to prevent the interactions between top and bottom atoms in the periodic slab images. Half the amount of oxygen atoms are removed from top and bottom surfaces to mimic Bi–O bulk bonds and thus electronically passivate both surfaces. We carefully tested different passivation schemes and the passivations of the top (Bi2WO6) and bottom (BiOCl) surfaces by removing oxygen atoms are shown to be most effective. Such passivation ensures that surface states are removed from top and bottom surfaces and all the calculated electronic states of interest originate from the interface. The whole slab is 40.26 Å thick with 80 atoms. The BiOCl slab consists of 4 layers of Bi, 4 layers of Cl and 3 layers of O, while the Bi2WO6 slab has 6 layers of Bi, 3 layers of W and 13 layers of O.

Fig. 1b shows the interface configuration with irrelevant atoms removed for clarity in visualization. The W–O bond length at the interface is 1.912 Å which is slightly smaller than that of the W–O bond in bulk Bi2WO6. Parts of interfacial oxygen atoms are removed from the interface to check the variation of the interface stability with respect to oxygen content. It is found that the O fully-terminated (four O atoms) interface shows the most stability for both Bi–O and W–O bonded interfaces. As a result, we focus on these two most stable interfaces for electronic analysis in this study. In order to compare the stabilities of Bi–O and W–O bonded interfaces, interface formation energies are calculated that are defined as the energy difference between the total system and individual components (BiOCl and Bi2WO6). To calculate the individual component energy of BiOCl, Bi2WO6 are removed from the interface; similarly, Bi2WO6 energy is calculated with BiOCl removed from the interface. The interface formation energy is then obtained by subtracting the individual component’s energy from the total system energy. Compared with Bi–O bonded interface, the W–O-bonded interface is 1.66 eV Å−2 more stable. Resulting from the strong W–O bond and the small planar strain (~1%), the corresponding interface (Fig. 1b) model is a realistic reflection of interfacial bonding situations and is adopted in all subsequent BO calculations, unless otherwise noted. Our charge difference plot also indicates that interfacial charge transfer takes place within a few atomic layers from the interface (~13 Å on the Bi2WO6 side and ~7 Å on the BiOCl side). Fig. 1c displays the
interface with one O site replaced by a sulfur atom in the bulk region of the BiOCl. Considering the atomic radius difference between O (48 pm) and S (88 pm), a full structural relaxation including a unit cell volume change with the CG method [ref. 18] is performed here. After the structure optimization, xy-plane lattice length increases 0.04 Å compared to that of an ideal interface. S bonds to three Bi atoms with an average bond length of 2.59 Å compared to the experimental value of 2.54 Å. Compared an ideal interface, a 0.6% strain is introduced into the system. It is possible that doping of S could potentially influence the thermal stabilities of the interfaces. However, with regard to the only slightly bonding energy difference between Bi–O (3.37 eV [ref. 22]) and Bi–S (3.15 eV [ref. 22]), S-doping is not expected to significantly alter the structural stability. In fact, based on our calculations, the interface formation energy changes only slightly by around 0.05 eV Å⁻² when S dopes the interface.

The BO between BiOCl and Bi₂WO₆ is a key quantity in determining electron–hole separation and photocatalytic performance. In our study, BO is determined by the local density of states (LDOS) scheme. Another method for calculating BO, namely the reference method, is also performed to double check the accuracy of the BO and yields essentially the same result. To be consistent, we adopt the LDOS method throughout the present work. For a general slab model with asymmetric top and bottom surfaces, the vacuum level might not be flat due to the difference of the surface dipole moments. Here, top and bottom surfaces share the same amount of the oxygen atoms, specifically two, and thus dipole correction is negligible in the present calculation. We calculate the LDOS of atoms in the BiOCl and Bi₂WO₆ far away from the interface and extract the energy difference between their valence band maximums (VBMs). Due to the inaccuracy involved in the GGA in predicting the bandgap, the conduction band minimum (CBM) offsets are derived from the experimental values for the band gaps of BiOCl and Bi₂WO₆ (BiOCl: 3.46 eV, Bi₂WO₆: 2.75 eV). It is worth noting that the BOs between BiOCl and Bi₂WO₆ depend on detailed atomic geometries and charge transfers across the interface, in particular on interfacial oxygen terminations. Similar phenomenon, i.e., deviation of band alignment from the “Schottky-Mott” model, has also been observed in other metal/semiconductor, metal/organic, and semiconductor/semiconductor interfaces.

In Fig. 2a, LDOSs of Bi₂WO₆ and BiOCl in the bulk region (far from interface) show that the VBM of Bi₂WO₆ leads by 0.46 eV. As it is well known that DFT is limited to produce right band gaps and describe the excited states, we take the practical approach of calculating CB offsets utilizing the VB offsets and the experimental band gaps of individual materials. Using this approach, the deduced CBM offset is 0.25 eV. As a result, the band edges of Bi₂WO₆ nest into the band gap region of BiOCl, as schematically shown in Fig. 3(a). In photocatalysis, such band alignment is not beneficial for the separation of electron–hole pairs. As the incident light sheds on the BiOCl, electrons are excited to the conduction band and subsequently transferred to the CBM of Bi₂WO₆. Meanwhile, the created holes transfer to Bi₂WO₆ as well due to the lower VBM of BiOCl (see Fig. 3(a)). Consequently, carriers do not separate at the heterojunction and recombination readily happens on the Bi₂WO₆ side. Moreover, slightly above the VBM of Bi₂WO₆, the existence of interfacial gap states (see Fig. 2a) might act as recombination centers and further degrade photocatalytic activities. To act as an ideal charge-carrier separator, the VBM of BiOCl...
offset of these two materials should be flipped to facilitate charge carrier separation.

To better engineer the BO of this specific interface, it is insightful to further investigate the interface electronic structure. For both BiOCl and Bi₂WO₆ bulk materials, the VBMs are dominated by O p-orbitals. In bulk Bi₂WO₆ with a band gap of 2.50 eV, conduction band minimum is mainly dominated by W 5d orbitals which is consistent with previous work [ref. 13]. For bulk BiOCl, valence band maximum is mainly composed of Cl p and O p orbitals while Bi 6p orbitals dominate the CBM region [ref. 12]. To achieve the right VB offset, the leading edge locations of O p-orbitals must change accordingly. One possible solution to push up the BiOCl VB is to increase the O p-orbital energy. From the theoretical point of view, introducing S to replace O sites could increase the O p-orbital energy (∼3.2 eV difference) [ref. 22]. From our simulation results, S-doped interface calculation (Fig. 2b) indeed provides the strong theoretical evidence, i.e., the VB edge of BiOCl leads by 1.5 eV of Bi₂WO₆. From this analysis, we could obtain a general picture of tuning the band edge alignments at the interface. In fact, the VBOs are controlled by the highest occupied orbitals (O p-orbital) in the bulk region of the interface. Consequently, modifying this specific orbital energy results in an effective tuning of the band offsets. To further confirm the role of S, we plot the partial charge distribution (see Fig. 2c) within the energy range of ±0.2 eV in the valence bands of BiOCl, as marked with a dash box in Fig. 2b. It is clearly shown that the partial charge distributes around the S atom with a π-like behavior.

Besides band offset issues, large amounts of interfacial states might also act as carrier traps and degrade heterojunction performance. From Fig. 2a, certain states within the band gap region arise from the planar strain at the interface and could be removed by replacing the right amount of O at the interface by materials with less electro-negativity than O, such as S. In the case of the S-doped interface, it shows a clean band gap based on local density of states analysis (Fig. 2b), which confirms the superiority of S in facilitating charge carrier separation. Based on the same argument, Se might also act as carrier traps and degrade heterojunction performance.

In conclusion, the first-principles method has been used to study the band offsets of the BiOCl:Bi₂WO₆ interface. We find that the intrinsic stable interface fails to provide advantages of carrier separation due to improper band alignments. This can be overcome by the incorporation of S into O sites in the BiOCl bulk to reverse the valence band offsets and enhance photocatalytic performance.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (11004068) and PCSIRT (Program for Changjiang Scholars and Innovative Research Team in University) and Program for New Century Excellent Talents in University (NCET). D.W. Zeng would like to acknowledge the support from the National Basic Research Program of China (Grant No. 2009CB939705 and 2009CB939702). The authors acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin (http://www.tacc.utexas.edu) and the High Performance Computing Center experimental testbed in SCTS/GGCL (http://grid.hust.edu.cn/hpcc) for providing grid resources that have contributed to the research results reported within this paper.

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