Lead Bismuth Oxyhalides $PbBiO_2X$ (X = Cl, Br) as Photocatalysts for Water Oxidation Under Visible Light

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Abstract: We show that layered oxyhalides $PbBiO_2X$ (X = Cl, Br, I) with a Sillén-type structure possess band levels appropriate for visible light-induced water splitting. Under visible light, $PbBiO_2Cl$ and $PbBiO_2Br$ with bandgap (BG) of 2.51 and 2.48 eV, respectively, stably oxidized water to O_2 in the presence of an Fe^{3+} electron acceptor. A comparison with structurally related $SrBiO_2Cl$ and $BaBiO_2Cl$ (BG = 3.55 and 3.54 eV) combined with DFT calculations revealed a significant interaction between O 2p and Pb 6s orbitals leading to the upward shift of the valence band maximum in $PbBiO_2X$ as compared with $(Sr,Ba)BiO_2Cl$.

Keywords: Z-scheme, Water splitting, Oxyhalide.

1. Introduction

We have recently demonstrated that Bi_4NbO_8Cl can oxidize water to O_2 efficiently and stably without observing any self-decomposition.[1] The stability against water oxidation is accounted for by the predominant occupation of O 2p orbitals in VBM, instead of Cl 3p orbitals. Madelung site potential analysis revealed that the upward shift of valence band maximum (VBM) in Bi_4NbO_8X (X = Cl, Br) originates from the electrostatic destabilization of the oxide anions in the fluorite layer.[2] Furthermore, we found a significant interaction between Bi 6s and O 2p orbitals derived from the revised lone pair (RLP) model,[3] which also leads to the upward shift of VBM.[4] Unfortunately, it is difficult to elaborate on the contribution of these two factors largely due to the complex crystal structure with coherent octahedral rotations that generate eight inequivalent oxygen sites. In this study, we investigated structurally simpler lead bismuth oxyhalides $PbBiO_2X$ (X = Cl, Br, I), as potential materials for visible light induced water splitting. In addition to the simplicity of the crystal structure (vs. Bi_4NbO_8X), the presence of structurally related *AE*BiO_2Cl (*AE* = Sr, Ba) offers an opportunity to clarify the role of the stereoactive lone-pairs of Pb^{2+} 6s orbitals in the valence band structure.

2. Experimental

All the five compounds in powder form were prepared by a solid-state reaction. $PbBiO_2Cl$ and $PbBiO_2Br$ were prepared by calcining a stoichiometric mixture of PbO and BiOX (X = Cl and Br) at 973 K for 10 h in air. As for $PbBiO_2I$, a 1:1 mixture of PbO and BiOI was pelletized and heated in the same condition, but in an evacuated silica tube. $SrBiO_2Cl$ ($BaBiO_2Cl$) were prepared by the calcination of a stoichiometric mixture of BiOCl and $SrCO_3$ ($BaCO_3$) in air at 1073 K for 20 h.

3. Results and discussion

Figure 1 shows the band levels of $PbBiO_2X$ (X = Cl, Br, I) and *AE*BiO_2Cl (*AE* = Sr, Ba), which were determined by these diffuse reflectance spectra and Mott-Schottky plots. As for oxychlorides, the bandgaps of $SrBiO_2Cl$ and $BaBiO_2Cl$ were similar (~3.55 eV), but that of $PbBiO_2Cl$ was red-shifted (up to 2.50 eV). For Pb, $PbBiO_2Cl$ and $PbBiO_2Br$ have similar bandgaps of ~2.5 eV, but $PbBiO_2I$ has a red-shifted value of 2.35 eV. Clearly, the VBM of $PbBiO_2Cl$ is much more negative compared to *AE*BiO_2Cl. DFT calculations revealed that the significant interaction between O 2p and Pb 6s orbitals provided the elevated VBM (Figure 2). The conduction band minimums (CBMs) are also affected by the divalent cations; the substitution of the alkali earth metals by Pb induces a positive shift of the CBM. Consequently, $PbBiO_2X$ have much smaller bandgaps than *AE*BiO_2Cl. The VBM level of $PbBiO_2Br$ is similar to $PbBiO_2Cl$, implying that the DOS around the VBM in $PbBiO_2Cl$ and $PbBiO_2Br$ are predominantly formed by O 2p orbitals, not halide p orbitals. The VBM of $PbBiO_2I$ is appreciably more negative than that of $PbBiO_2Cl$ and $PbBiO_2Br$ (by ~0.15 V), suggesting an occupation of I 5p orbitals at VBM. These were confirmed by DFT calculations shown in Figure 2.

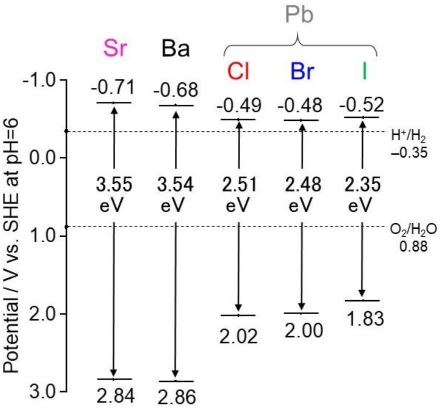

Figure 1. Proposed band edge positions of $ABiO_2Cl$ (A = Sr and Ba) and $PbBiO_2X$ (X = Cl, Br and I) at pH = 6.

Both $PbBiO_2Cl$ and $PbBiO_2Br$ generated O_2 at steady rates in an aqueous $Fe(NO_3)_3$ solution under visible light irradiation, with a higher O_2 evolution rate observed in the chloride system. As for $PbBiO_2I$, no O_2 generation was observed, despite sufficient VBM/CBM levels. XPS analysis showed that $PbBiO_2I$ are subject to self-oxidation by photo-generated holes, which is reasonably explained by the dominant occupation of I 5p orbitals around the VBM. The photo-generated holes will be localized on the I^- anions after energy relaxation, thus preferentially oxidizing I^- in the $PbBiO_2I$ instead of water. On the other hand, $PbBiO_2Cl$ and $PbBiO_2Br$ were more stable against photo-induced self-oxidation, probably as a result of the VBM of $PbBiO_2Cl$ and $PbBiO_2Br$ being predominantly formed by the O 2p orbitals.

Finally, visible-light-driven Z-scheme water splitting was accomplished by combining the RuO_2-loaded $PbBiO_2Cl$ photocatalyst with $SrTiO_3$ doped with rhodium as a H_2-evolving photocatalyst in the presence of the Fe^{3+}/Fe^{2+} redox couple.

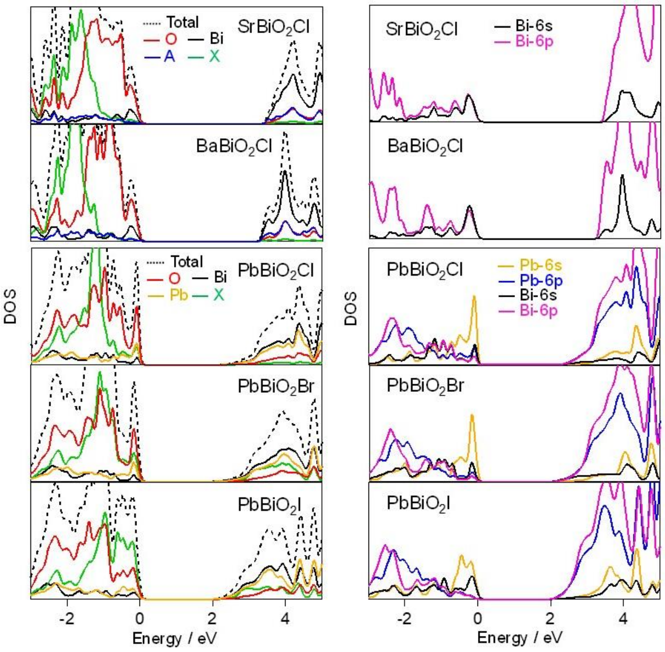

Figure 2. DOS and the partial DOS (PDOS) of *AE*BiO_2Cl (*AE* = Sr and Ba) and $PbBiO_2X$ (X = Cl, Br, and I) for 6s and 6p orbitals of Bi and Pb.

4. Conclusions

$PbBiO_2X$ (X = Cl, Br) were demonstrated to stably oxidize water to O_2 under visible light in the presence of an Fe^{3+} electron acceptor. A comparison with structurally related $SrBiO_2Cl$ and $BaBiO_2Cl$ and DFT calculations revealed that the significant interaction between O 2p and Pb 6s orbitals provided unusually elevated valence band maximum compared to conventional oxides, affording $PbBiO_2X$ materials to have both the visible light absorption and the sufficient stability for water oxidation. Z-scheme water splitting was achieved under visible light using $PbBiO_2X$ as an O_2-evolving photocatalyst.

References

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