Design of stable mixed-anion semiconductors for photocatalytic water splitting under visible light

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Abstract: Oxyhalides Bi_4MO_8X (M = Nb, Ta; X = Cl, Br) are revealed to function as stable O_2-evolving photocatalysts under visible light without suffering from self-oxidative deactivation, related to their unique valence bands with O-2p orbitals located at unusually high potential compared with conventional oxides. DFT calculations revealed a fairly strong hybridization between the Bi-6s and O-2p orbitals, which is interpreted in terms of a revised lone pair model, thus explaining partly why the O-2p orbitals are elevated in energy.
Keywords: photocatalyst, water splitting, visible light.

1. Introduction

Photo-induced water splitting using semiconductor photocatalysts has attracted considerable attention for producing H_2 as a clean energy carrier. Especially, the effective utilization of visible light is imperative to achieve the desired efficiency for practical applications. However, it is essentially difficult to develop metal oxides that possess a bandgap below 3.0 eV for visible light absorption while placing a conduction band minimum (CBM) more negative than the water reduction potential, because the valence band maximum (VBM) of conventional metal oxides are fairly positive due to the dominant contribution of O-2p orbitals. Although mixed-anion compounds such as oxynitrides have been intensively studied as promising candidates, most of them are subject to facile self-oxidation by photogenerated holes. Here, we show that a series of oxyhalides with a Sillén–Aurivillius type perovskite structure (Fig. 1), possess appropriate band levels for water splitting and indeed work as a stable O_2-evolving photocatalyst under visible light without suffering from self-oxidative deactivation.[1, 2]

2. Experimental

The Bi_4MO_8X samples were prepared by solid state reactions. A stoichiometric mixture of Bi_2O_3, BiOCl (or BiOBr), and Nb_2O_5 (or Ta_2O_5) was pelletized and heated in an evacuated silica tube at 1073 K for 20 h. Ionization energies of particulate sample were directly measured by photoelectron yield spectroscopy (PYS; BIP-KV201, Bunkoukeiki) in a vacuum. Mott–Schottky (MS) analysis was also carried out for the electrodes to estimate the flat-band potentials (FBP). The electronic structures of the materials were calculated by using the Cambridge Serial Total Energy Package. The photocatalytic reactions were carried out in a Pyrex glass reactor connected to a closed gas circulation system.

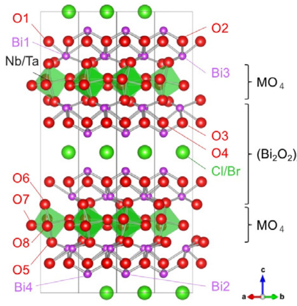

Figure 1. Crystal structure of Bi_4MO_8X.

3. Results and discussion

Shown in Fig. 2 are the UV-vis diffuse reflectance spectra of Bi_4MO_8X. We determined their FBP *via* MS analysis, and also applied a PYS, by which ionization energy can be directly measured from particle specimen, to estimate the VBM values independently of uncertain factors such as feature of electrodes; the obtained values are also summarized in Table 1. Importantly, the VBMs of Bi_4MO_8X are

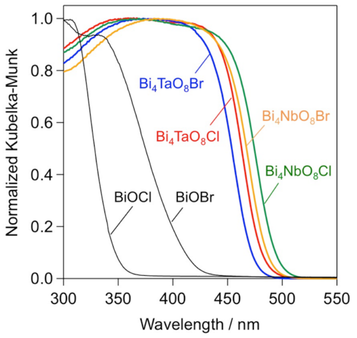

Figure 2. UV-vis diffuse reflectance spectra of Bi_4MO_8X

estimated to locate at +2.3 ~ 2.4 V (vs. SHE at pH 0) from MS or +2.0 ~ +2.1 V (vs. SHE at pH 0) from PYS), much negative than typical oxides and oxychlorides with VBMs of *ca.* + 3.0 V (vs. SHE at pH 0). The estimated CBMs, more negative than water reduction potential, are indeed supported by the appreciable activity of these materials for H_2 production from water in the presence of methanol as an electron donor (not shown). The DFT calculation results indicated that the CBMs of Bi_4MO_8X are mainly composed of Bi-6p orbitals, whereas Nb-4d or Ta-5d orbitals are positioned at higher levels. As for the DOS near VBM, we found a sizable contribution of Bi orbitals in addition to O-2p orbitals. Although the Bi $6s^2$ electrons have been often regarded as chemically "inert" (*i.e.*, lone pair), it has been theoretically proposed that there is a s-p interaction between $5s^2$ or $6s^2$ electrons of post-transition metals (e.g., Sn, Sb, Pb, and Bi) and O-2p electrons in oxides such as Bi_2O_3 and $BiVO_4$.[3] According to this theory, called the Revised Lone Pair (RLP) model, bonding and anti-bonding orbitals are formed from Bi-6s and O-2p orbitals, a situation that is unstable as it is. However, the resultant anti-bonding orbital of $(Bi\text{-}6s + O\text{-}2p)^*$ is concurrently stabilized through the interaction with the unoccupied Bi-6p orbital, leading to the elevated energy level (red line) relative to the original O-2p orbital, as illustrated in Fig. 3. We also found that Madelung site potentials of anions can reproduce the essential features of the valence band structures in Bi_4MO_8X.[4] Fig. 4 shows the time courses of O_2 evolution on Bi_4MO_8X in 5 mM aqueous $FeCl_3$ solution under visible light, along with that on BiOBr for comparison. All the Bi_4MO_8X samples generated O_2 at steady rates, with the chloride system having slightly higher O_2 evolution rates than the bromide system. No evidence of halogen exchange or other reactions was observed in the XRD patterns after the reaction, implying their high durability. On the other hand, the O_2 evolution rate on BiOBr gradually decreased and became almost negligible after 4 h. Weak but apparent peaks corresponding to BiOCl were emerged after the reaction, indicating the occurrence of self-oxidation of Br^- by holes. These observations demonstrate that all the Bi_4MO_8X materials have a high degree of stability against the self-oxidative deactivation during the water oxidation, supporting our hypothesis that the unusual stability is ascribed to the predominant occupation of O-2p orbitals at the VBM. Since O^- anions are known to be relatively stable, photogenerated holes populated at the O-2p orbitals will not lead to self-decomposition but to oxidize water.

		Mott-Schottky analysis		PYS measurement	
Compounds	Band gap[a] / eV	FBP(CBM)[b] / V_{SHE}	VBM[c] / V_{SHE}	CBM[d] / V_{SHE}	VBM[e] / V_{SHE}
Bi_4TaO_8Cl	2.50	–0.10	2.40	–0.47	2.03
Bi_4TaO_8Br	2.55	–0.09	2.46	–0.53	2.02
Bi_4NbO_8Cl	2.43	–0.13	2.30	–0.35	2.08
Bi_4NbO_8Br	2.48	–0.10	2.38	–0.41	2.07

Table 1. Estimated band potentials for Bi_4MO_8X.

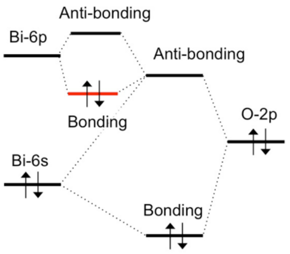

Figure 3. Schematic interactions among Bi-6s, Bi-6p, and O-2p.

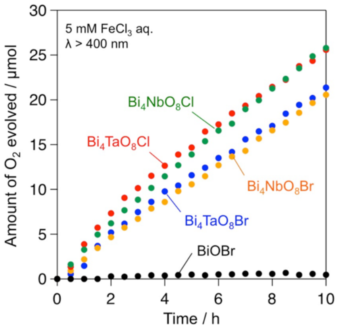

Figure 4. O_2 evolution over Bi_4MO_8X and BiOBr

4. Conclusions

We revealed that the VBMs of Bi_4MO_8X are located at very negative potentials compared to conventional metal oxides, even though they are predominantly formed by O-2p. These results could provide new strategies for developing durable photocatalysts for water splitting under visible light, by manipulating the interaction between post-transition metal *s* orbitals (*e.g.*, Pb-6s, Bi-6s) and O-2p orbitals.

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