Bismuth Tantalum Oxyhalogen: A Promising Candidate Photocatalyst for Solar Water Splitting

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Abstract: Exploring new semiconductor-based materials is crucial for photocatalytic water splitting. In this work, a series of photocatalysts, bismuth tantalum oxyhalide, Bi_4TaO_8X (X=Cl, Br), with valence band and conduction band positions at ~-0.70 eV and ~1.80 eV (vs NHE), respectively, are founded to be capable for both water oxidation and reduction under visible light irradiation. The photocatalyst based on these materials shows an apparent quantum efficiency as high as 20% at 420 nm for water oxidation. In addition, a Z-scheme system coupling Bi_4TaO_8Br with Ru/$SrTiO_3$:Rh is successfully achieved for overall water splitting with a stoichiometric ratio of H_2 and O_2 evolutions.

Keywords: Photocatalysis, Solar energy conversion, Water splitting.

1. Introduction

As wide range of light absorption and suitable redox potentials are prerequisites for photocatalytic water splitting, exploring new semiconductor-based materials with proper band structures for water splitting still calls for longstanding efforts. [1, 2] In recent studies, bismuth-based oxides were revealed to be of the most fabulous photo(electro)catalysts. Generally, bismuth-based oxides possess strong hybridizations of Bi 6s and O 2p orbitals both in the valence band and conduction band, which not only decrease the effective masses of holes and electrons to favor a longer traveling distance for excited carriers, but also render the valence band raise to a more negative level. In addition, the common layered structure in many bismuth-based oxides materials well-behaved in photocatalytic reactions possess an internal electric fields among the layers which are supposed to promote charge separation and subsequently facilitate the photocatalytic efficiency. Intrigued by the merits of layered structure and hybridized energy band, it is of great significance to develop new bismuth-based, especially layered structure compounds for solar energy utilization.

2. Experimental

Bi_4TaO_8X (X=Cl, Br) was synthesized through a solid state reaction. Stoichiometric quantities of Bi_2O_3, BiOX (X=Cl, Br) and Ta_2O_5 were mixed, grinded and heated in an evacuated silica tube at 973 K for 14h. The flux-treated Bi_4TaO_8X (X=Cl, Br) was prepared by mixing stoichiometric quantities of Bi_2O_3, BiOX (X=Cl, Br) and Ta_2O_5 with NaCl and KCl (molar ratio of NaCl / KCl is 1:1), acting as flux agents, followed with heating in air at 973 K for 14h. The cooled mixture was washed with deionized water for several times and dried at 353 K for 5 h.

3. Results and discussion

The XRD patterns of the obtained Bi_4TaO_8X (X=Cl, Br) as well as the halogen-free sample Bi_3TaO_7 were shown in Figure 1a, in which all the peaks are well matched with standard cards. Results of spectra show an obvious absorption edge at ~500 nm for Bi_4TaO_8X (X=Cl, Br), and the band gaps were estimated to be 2.53 eV and 2.48 eV for Bi_4TaO_8Cl and Bi_4TaO_8Br, respectively (Figure 1b). Figure 1c shows the morphology of the as-prepared samples. Mott-Schottky plots and XPS valence band spectra were performed to study the electronic band structure of Bi_4TaO_8X (X=Cl, Br) experimentally. The valence band and conduction band position is located at -0.66 eV and 1.82 eV (vs NHE) for Bi_4TaO_8Cl. In the same way, the VBM and CBM of Bi_4TaO_8Br is estimated to be -0.79 eV and 1.74 eV (vs. NHE), respectively.

The DFT calculationswere adopted to investigate the band gap structure of Bi_4TaO_8X (X=Cl, Br) theoretically in Figure 1e which is in accordance with the results of experiments.

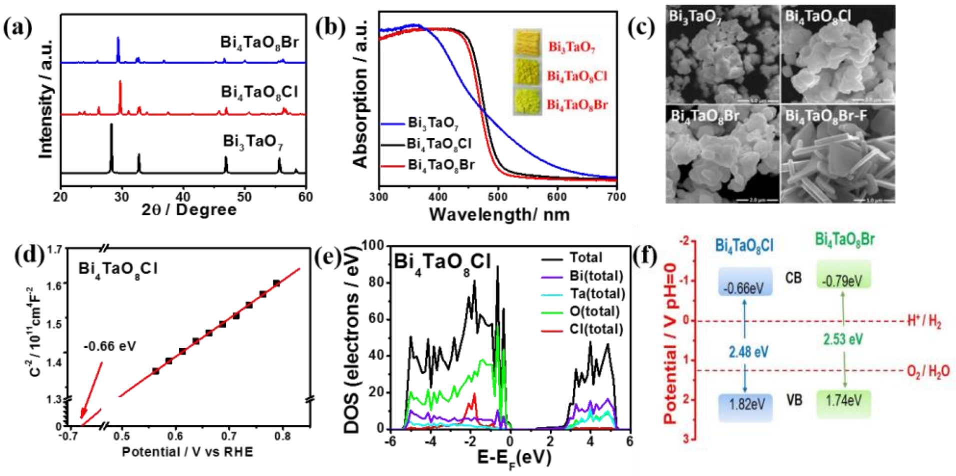

Figure 1. Crystal and electronic structures of Bi_4TaO_8X (X=Cl, Br)

Inspired by the energy band structure of Bi_4TaO_8X (X=Cl, Br), photocatalytic water splitting were conducted to evaluate the photocatalytic performance. Efficient water oxidation could be achieved for both Bi_4TaO_8Cl and Bi_4TaO_8Br in the presence of aqueous solution of $Fe(NO_3)_3$ and $AgNO_3$ under the irradiation of visible light and the photocatalytic H_2 production from water catalyzed by Bi_4TaO_8Cl and Bi_4TaO_8Br decorated with Pt as a cocatalyst was demonstrated in Figure 2a and 2b. As shown in Figure 2c, the AQE was measured to be 22.3% at 420 nm towards water oxidation. In addition, a Z-scheme overall water splitting system coupling Bi_4TaO_8Br with Ru/$SrTiO_3$:Rh was constructed. As shown in Figure 2d, simultaneous evolution of H_2 and O_2 with a stoichiometric ratio was successfully detected under visible light.

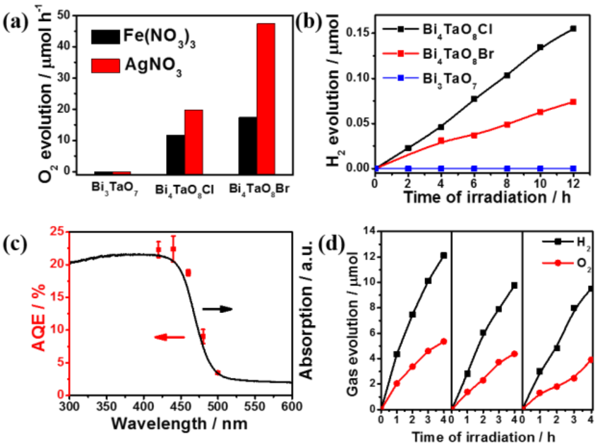

Figure 2. Photocatalytic performance of Bi_4TaO_8X (X=Cl, Br)

4. Conclusions

In summary, we report a series of bismuth tantalum oxyhalide materials with Sillen-Aurivillius layered perovskite structure, which is capable for both water oxidation and proton reduction under visible light irradiation. Photocatalyst based on these materials show a high water oxidation activity and give an apparent quantum efficiency higher than 20% at 420 nm. In addition, a Z-scheme overall water splitting system coupling Bi_4TaO_8Br with Ru/$SrTiO_3$:Rh was successfully achieved with a stoichiometric ratio of H_2 and O_2 evolutions. Our work not only developed a serious of promising photocatalysts but also present an approach to rational design of photocatalysts through adjusting both the band structure and the redox power, thereby leading to the efficient and sustainable solar fuels production.

References

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