

BiO(ClBr)_{(1-x)/2}I_x Solid Solutions with Controllable Band Gap Engineering as Efficient Visible-Light Photocatalysts for Wastewater Treatment

Connie Wu

Electrical Engineering and Economics, University of Pennsylvania

NNIN iREU Site: National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan

NNIN iREU Principal Investigator: Prof. Jinhua Ye, International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute of Materials Science (NIMS), Tsukuba, Ibaraki, Japan

NNIN iREU Mentor: Guigao Liu, International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute of Materials Science (NIMS), Tsukuba, Ibaraki, Japan

Contact: wuconnie@seas.upenn.edu, liu.guigao@nims.go.jp, jinhua.ye@nims.go.jp

Abstract:

The objective of this research was to find an efficient photocatalytic material for wastewater treatment. The motivation was the high cost of water treatment by oil refineries, industrial plants, and domestic waste. According to the American Society of Civil Engineers, wastewater infrastructure alone will cost around \$285 billion to build over the next 20 years [1]. As a result, BiO(ClBr)_{(1-x)/2}I_x solid solutions were investigated, because they are promising photocatalysts due to their efficient degradation capability, controllable band gap engineering, and visible light activity. The BiO(ClBr)_{(1-x)/2}I_x solid solutions were tested on water pollution proxies in the form of three dyes: methylene blue (MB), rhodamine B (RhB), and Orange II.

Introduction:

In choosing the particular material to be used, the most important requirement was that the material be visible-light reactive. The current industry standard is titanium dioxide (TiO₂). However, TiO₂ is only UV-light active, which is not ideal in terms of cost-efficiency. Similarly bismuth oxychloride (BiOCl) and bismuth oxybromide (BiOBr) are other bismuth oxyhalides that are only active under UV-light stimulation. Bismuth oxyiodine (BiOI) is visible-light active, however it has a low redox capability, which is detrimental to the degradation process in which the ability to separate electrons and holes is crucial [2]. Finally, the BiO(ClBr)_{(1-x)/2}I_x solid solution is both visible-light active and has a relatively high redox capability, and as such it provided a good basis to start our investigation into its ability to degrade wastewater liquid pollutants. Furthermore from previous research, it was also found that the photocatalyst's band gaps could be altered based on the ratio of halide composition [3]. Consequently, this allows for a method of band gap engineering that can allow for precise control of its visible-light activity.

Experimental Procedure:

The BiO(ClBr)_{(1-x)/2}I_x solutions were prepared using a solvothermal method. First, ethylene glycol was mixed with Bi(NO₃)₃•5H₂O to form a clear solution. Then the appropriate amounts of KCl, KBr, and KI salts were added with molar ratios (1-x)/2:(1-x)/2:x, where x is the percentage of KI. Next the mixture was transferred to a Teflon[®]-lined autoclave, which was then placed into a 160°C oven for 12 hours.

After the solution was removed from the oven, the resultant mixture was washed with water and air-dried at 70°C.

The photocatalyst was tested against the three pollutant proxies. First 100 ml of dye with a concentration of 8 mg/100 ml was mixed with 20 mg of photocatalyst. This was then placed into a liquid chamber cell and sonicated for 30 seconds before being placed under a 300W Xe arc lamp. Below was a L42 glass filter used to exclusively allow visible light and a water filter to disperse heat. Finally, 3 ml samples of the dye mixed with photocatalyst, taken in either 5-minute or 20-minute intervals depending on the characteristic degradation rate, were filtered through a syringe-driven filter unit. The samples' absorption spectra were obtained with a UV-vis spectrophotometer.

Results:

Displayed in Figure 1 are the SEM images of the solid solutions. They formed uniform crystal spheres with larger clusters as the molar ratio of iodine increased. In the UV-vis absorption spectra (Figure 2), there was a continued blue-shift of the absorption edge as x increased. The reason was that the valence band minimum (VBM) had an upward shift as x increased from the increase in orbital potential energy with the substitution of Cl 3p and Br 4p orbitals by I 5p orbitals, creating a higher VBM [4]. This narrowed the band gap. Generally, a wider visible-light absorption would be beneficial to achieving a higher photocatalytic activity.

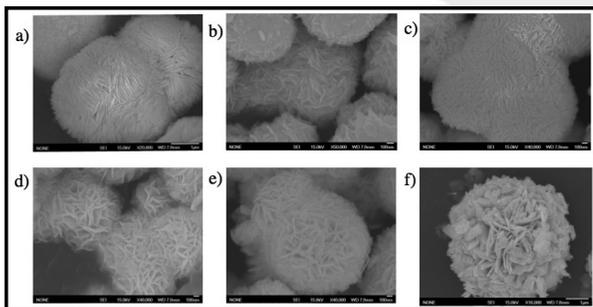


Figure 1: SEM images of the $\text{BiO}(\text{ClBr})_{(1-x)/2}\text{I}_x$ crystals. (a) $\text{BiO}(\text{ClBr})_{0.5}\text{I}$ (b) $\text{BiO}(\text{ClBr})_{0.33}\text{I}_{0.33}$ (c) $\text{BiO}(\text{ClBr})_{0.25}\text{I}_{0.5}$ (d) $\text{BiO}(\text{ClBr})_{0.13}\text{I}_{0.67}$ (e) $\text{BiO}(\text{ClBr})_{0.08}\text{I}_{0.83}$ (f) BiOI .

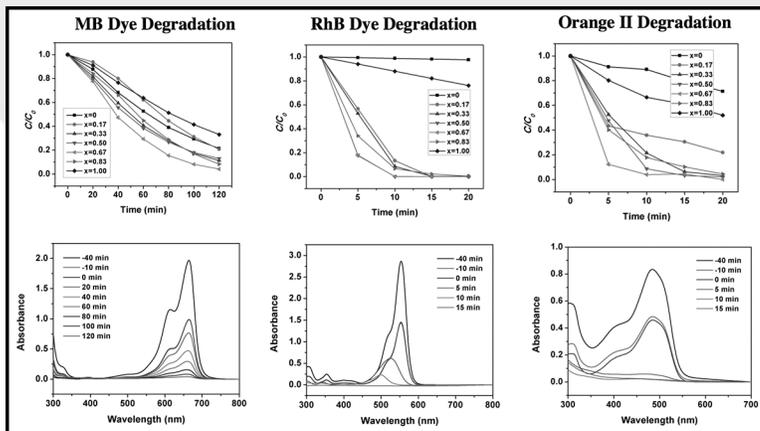


Figure 3: Degradation results.

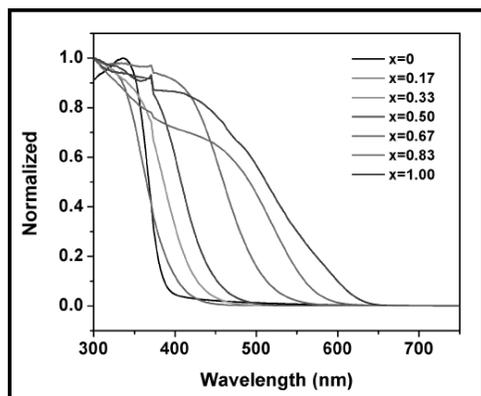


Figure 2: UV-vis absorption spectra of $\text{BiO}(\text{ClBr})_{(1-x)/2}\text{I}_x$. (See full color version on page xxxvi.)

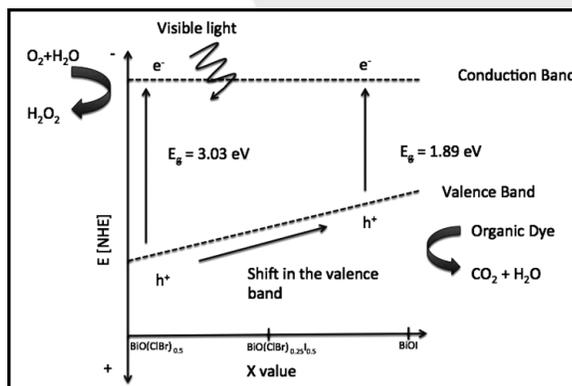


Figure 4: Band gap narrowing from shift in valence band.

Summarized in Figure 3 are the sample degradation results of the three dyes. It was found that an x value of 0.67 had the fastest degradation across all dyes. MB achieved the quickest degradation rate at 120 min, RhB at 5 min, and Orange II at 20 min.

The degradation is achieved through two differing mechanisms. When the photocatalyst was exposed to visible light, there was an excitation of electrons from the valence band to the conduction band, causing a separation of electrons and holes. Some holes reacted with water to form $\bullet\text{OH}$. The dye then reacted with either holes or $\bullet\text{OH}$ to form water and carbon dioxide, completing the degradation process.

RhB, however, degraded faster than the other two dyes due to an additional mechanism. Typically for RhB degradation there is an added mechanism in which the RhB molecules form 2-3 unstable states, which will emit an electron to form RhB^+ . This ion will then interact with holes or $\bullet\text{OH}$ to simultaneously degrade the RhB dye.

Conclusions:

$\text{BiO}(\text{ClBr})_{0.17}\text{I}_{0.67}$ exhibited the best photocatalytic properties across the dye pollutants. This is due to the tradeoff between

the increased absorption spectra inherent in the materials and the decrease in the redox capability as shown in the band gap diagram.

Future Work:

In the future, we would like to quantify hole and $\bullet\text{OH}$ generation in the photocatalytic process to confirm and characterize the reactions taking place.

Acknowledgments:

I would like to thank my principal investigator, Jinhua Ye, and my mentor, Guigao Liu, for providing the inspiration for this project. I am also thankful to the NNIN iREU Program and NSF for providing the support and funding for this research.

References:

- [1] "2013 Report Card for America's Infrastructure." American Society of Civil Engineers, n.d. Web. 30 July 2014.
- [2] Zhang, W.; Ind. Eng. Chem. Res. 2013, 52, 6740.
- [3] Zhang H. Phys. Chem. Chem. Phys. 2012, 14, 1286.
- [4] Shannon, R. Acta. Cryst. A 1976, 32, 751.