

Microwave-Assisted Fabrication of Visible-Light Activated BiOBr-Nanoplate Photocatalyst

Meichen Lee, Michael K. H. Leung

Abstract—In recent years, visible-light activated photocatalysis has become a major field of intense researches for the higher efficiency of solar energy utilizations. Many attempts have been made on the modification of wide band gap semiconductors, while more and more efforts emphasize on cost-effective synthesis of visible-light activated catalysts. In this work, BiOBr nanoplates with band gap of visible-light range are synthesized through a promising microwave solvothermal method. The treatment time period and temperature dependent BiOBr nanosheets of various particle sizes are investigated through SEM. BiOBr synthesized under the condition of 160°C for 60 mins shows the most uniform particle sizes around 311 nm and the highest surface-to-volume ratio on account of its smallest average particle sizes compared with others. It exhibits the best photocatalytic behavior among all samples in RhB degradation.

Keywords—Microwave solvothermal process, nanoplates, solar energy, visible-light photocatalysis.

I. INTRODUCTION

WITH the rapid growth of human activities and industrial development in recent decades, high energy consumption and severe pollution problems have caused serious energy and environmental crisis. Clean energy sources, such as solar energy, wind power, geothermal heat as well as all of innovative renewable energy, have drawn remarkable attention worldwide in order to lower the reliance on nuclear energy of high risks and depleted fossil fuels. Among all possible energy sources, solar energy, geothermal heat and wind are considered to be of the highest potential in Taiwan. However, for the development of geothermal heat, at its initial phase, it still takes long term evaluations and tests while the further development of wind power is limited to the locations and concerns of noise pollution. On the other hand, with sufficient sunlight, solar photovoltaics, despite its rather low electricity generation has been of the most interests. Solar cell systems of different scales have already been widely set up on the idle surfaces, such as rooftops of urban areas or farmlands mostly for domestic electricity supply.

Apart from p-n junction photovoltaics, up to more than 100 types of photo-active semiconductors have been found and taken center stages in a variety of fields, mainly environmental remediation and hydrogen production through the process of photocatalysis [1], [2].

Michael K. H. Leung is with the School of Energy and Environment, City University of Hong Kong, Hong Kong (phone: +852 3442-4626; Fax: +852-3442-0688; e-mail: mkh.leung@cityu.edu.hk).

Meichen Lee is with the Department of Chemistry, National Central University, Taiwan (e-mail: mays940328@gmail.com).

II. BiOBr VISIBLE-LIGHT PHOTOCATALYST

BiOX (X= F, Cl, Br, I) candidate of great potential as replacement of common used wide gap photocatalyst. Among all, BiOBr has shown rather superior performance on photolytic activity by the fact that it can form preferable hybridized valence band with Bi 6s and O 2p overlapping to narrow the band gap [3]. Comparing with TiO₂ with direct band gap, this also features BiOBr with the indirect band gap since VB disperse greatly, which favors the mobility of generated holes to oxidize organic dyes. Thus, many researches on its sizes, crystallinity and interesting morphologies have been intensely carried out. Various novel BiOBr structures have been discovered recently, such as nanosheets [4], four-leaf clover-shape BiOBr microstructure [5], hierarchical microspheres [6], and so on.

Several methods have been adopted for the synthesis of BiOBr nanostructures. Traditional methods include vapor reactions, solid state, and the most common hydrothermal or solvothermal method. The effect of solvents on morphologies was studied with solvothermal method [4]. Ethylene Glycol (EG), ethanol, and Glycerol are used. It turned out that in different solvent conditions, morphologies of BiOBr crystals vary due to their varied viscosities and the according formation mechanism. Due to the fact that ethanol has low viscosity, dielectric constant and thermal conductivity, the superior diffusion rate of ions and supersaturating of solution, rendering it to go through the Ostwald ripening process and form well organized nanosheets. As the small crystalline nuclei forms, the anisotropic growth then occurs through ion to ion addition. While EG has larger viscosity, resulting in slower diffusion rates of ions and a flower like hierarchical laminar structures formed by the well assembled alternating Bi₂O₂⁺ layers and Br⁻ layers with the assistance of template reagent, cetyltrimethylammonium bromide (CTAB). glycerol (GR), with much higher viscosity, instead, weakens the effect of template reagent, causing the less assembled hierarchical flower like structure [4].

III. MICROWAVE ASSISTED SYNTHESIS

Hydrothermal process and solvothermal process are popular methods for fabricating nanostructured materials. However, they have also confronted several challenges. As the nucleation and the growth of nanocrystals occur when the solvent is heated up, sharp thermal gradients throughout the bulk solution, slow reaction kinetics and non-uniform reaction conditions are expected, making it rather time consuming, inefficient and insufficient for further research.

Nevertheless, microwave heating has drawn great attention

in recent years for overcoming the limits of nanomaterial fabrication. Microwave irradiation, with frequency ranging from 0.3 to 300 GHz, are widely used in our daily life while the microwave oven and reactors for chemical synthesis only operated at 2.45 GHz to avoid the interference from electronics. The interaction between the dipole moments of polar molecules or ionic aggregates is greatly induced during the microwave irradiation by alternating electronic and magnetic fields. Fast and homogeneous thermal reactions with low thermal gradient allow it to produce high quality and high yields of products. Thermal gradient in microwave heating process is dependent on the choice of solvents and solutes, which loss tangent ($\tan \delta$) provides a measure for the ability of material to convert electromagnetic energy into heat. Generally, different materials can be classified into three categories: high ($\tan \delta > 0.5$), medium ($\tan \delta = 0.1-0.5$), low ($\tan \delta < 0.1$) microwave absorbing. Solvents of high microwave absorbing abilities such as ethylene glycol (1.35), ethanol (0.941), water (0.123) and dimethyl sulfoxide (0.825) are all perfect choices for microwave assisted synthesis of nanomaterials.

Many semi-conductive oxides with various bandgaps of great photocatalytic activities, including TiO_2 (3.0- 3.3eV), ZnO (3.2-3.37eV), or even the Bi-based oxides, Bi_2O_3 (2-3.9eV), BiPO_4 (3.35-4.09eV), and Bi_2WO_6 (2.6-2.8eV) were efficiently synthesized [7]. Among them, the visible light region Bi_2WO_6 has successfully degrade MB (10-5M) under the irradiation of Xe lamp 500W for 100mins, which is much better than the ones prepared by solid state reaction. Still, the promising visible light active BiOBr fabricated through microwave assisted method is rarely seen. Thus, in this work, we adopted microwave assisted solvothermal method using Ethylene Glycol as suitable solvents for the fabrication of BiOBr [7]. CTAB (cetyltrimethylammonium bromide) is also chosen as not only the source of Br but also the perfect template reagents to slow down the diffusion rate of ion species during the nucleation and the growth of nanocrystals. It was also found out that the reaction time and holding temperature has great impact of the morphologies of nanostructures. Thus, a few sets of temperature (T) and time period (t) of the solvothermal processes will be used and further investigated the morphologies of according samples and compare the related photocatalytic behaviors.

IV. SPECIMEN PREPARATION

A. Materials

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, EG and CTAB were purchased from Sigma Aldrich. The model pollutant Rhodamine B (RhB) was purchased from Wako Chemical. All reagents were used as purchased without further purification.

B. Sample Preparation

BiOBr nanostructures were prepared by microwave solvothermal method, in which fast and homogeneous thermal reactions with low thermal gradient facilitate production of high quality and high yields of photocatalysts. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

(0.6063g) was first dissolved in 10ml of Ethylene Glycol and 0.4783g CTAB were dispersed in 20ml of deionized water under 80°C which was added to the previous $\text{Bi}(\text{NO}_3)_3$ solution dropwise. Then, for parametric experimental analysis, BiOBr with different nanostructures were synthesized by alteration of reaction temperature increasing from 140°C to 180°C for 60mins and reaction time from increasing 40 mins to 80 mins at 160°C by the ETHOS One Closed Vessel Microwave Digestion System. Two glasses of samples are prepared each time for balance. The obtained precipitates were later on collected and washed by deionized water and absolute ethanol several times, and dried under 60°C .

C. Material Characterization

The morphologies and microstructures of samples were investigated by Field Emission Scanning electron microscopy (FZSEM, Hitachi S4800 at 0.5kV).

V. PHOTOCATALYTIC EFFECT

The photocatalytic activity of the synthesized BiOBr was evaluated by the degradation of Rh. B at room temperature with 300 W tungsten (W) lamp equipped with as visible light source. The photocatalytic experiment was carried out with 80mg BiOBr samples suspended in RhB solution (30mg/L) and constantly stirred. Prior to illumination, the suspension was first stirred in the darkness for 30 mins to reach the adsorption/desorption equilibrium. 4ml of sample was taken and centrifuged 10 mins per time. The concentration of dye left in the solution was then determined by UV-Vis Spectrometer (SHIMADZU UV-1800).

VI. RESULTS AND DISCUSSION

A. Morphologies of BiOBr

BiOBr samples prepared are in a form of light yellow powder (Fig. 1). The general morphologies of BiOBr time-dependent samples were investigated by SEM (Table I). When the reaction temperature was set at 160°C , quadrilateral nanoplates of various particle sizes were formed (Fig. 2) with different reaction times. As shown in Fig. 3, BiOBr-1 sample has the least uniform nanostructures with particle sizes varied greatly from 100nm-900nm and its average size around 365nm. When adding up the reaction time to 60 mins, BiOBr-2 nanoplates are revealed to have the most uniform nanostructures and the smallest average diameter (d) around 311nm among the three samples, rendering it to own the larger surface-to-volume ratio. As reaction time further extended to 80mins, we can see that the unity of nanostructures decreases with the increase average particle sizes.

B. Visible-Light Photocatalytic Activity of BiOBr

The visible light photocatalytic behavior of BiOBr samples were tested by degradation of RhB. The major absorption peak of RhB is at 553 nm, which shifts to lower wavelength as time goes by. In the process of degradation of RhB under visible light, dye deethylation (from N,N,N',N' -tetra ethylated rhodamine to rhodamine) causes the shift of the major peak

from 553 to 498 nm.

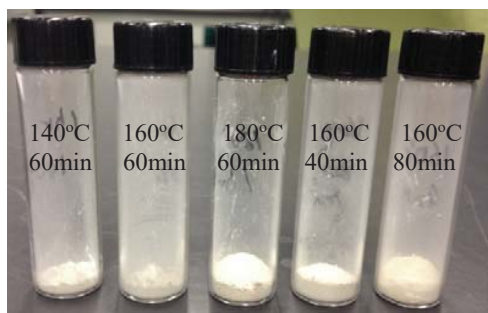


Fig. 1 BiOBr samples with different temperature and time period of fabrication process

TABLE I
PREPARATION CONDITION OF DIFFERENT BIOBR SAMPLES

Sample	Reaction Time (min)	Reaction Temp. (°C)	Morphology	Average Particle Size (nm)
BiOBr-1	40	160	Nanoplates	365
BiOBr -2	60	160	Nanoplates	311
BiOBr -3	80	160	Nanoplates	323

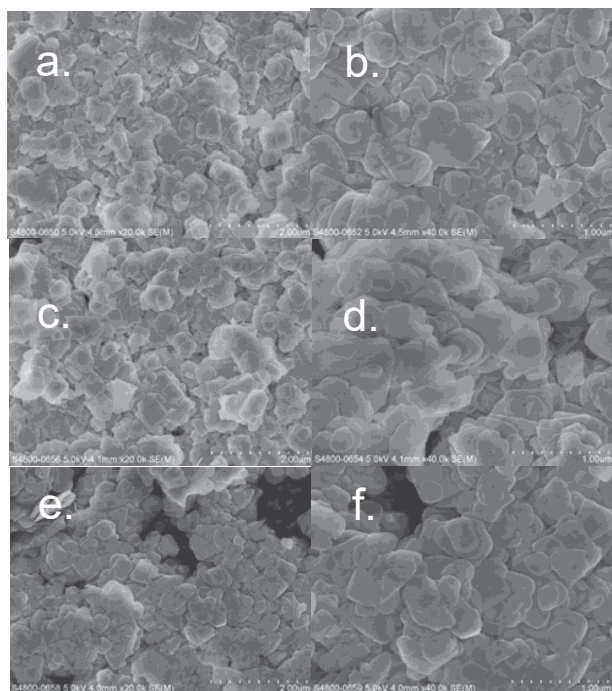


Fig. 2 FZSEM images of BiOBr-1 (a-b), BiOBr-2 (c-d), and BiOBr-3 (e-f)

Each major peak of maximum UV absorptions is picked for analyzing the changes of dye concentrations, shown in Figs. 4 and 5. The results of background tests are also presented. Adsorption test was carried out without the illumination of visible light, which shows that BiOBr samples only adsorb little amount of dyes. Without the presence of catalysts, RhB has also been proven not to be degraded.

Two sets of tests were carried out for obtaining the BiOBr samples with optimal photocatalytic activity. With the

alteration of reaction temperature, it turned out that the BiOBr sample synthesized under 160°C shows the best results (Fig. 4). Thus, all samples were synthesized under 160°C in the second test, with the alteration of reaction time (Fig. 5).

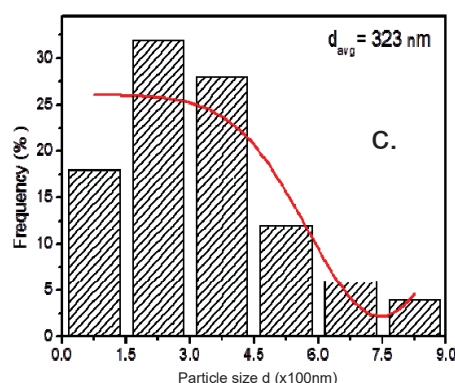
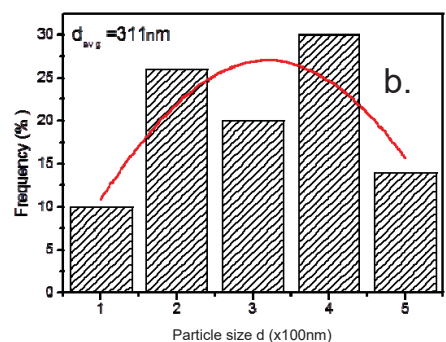
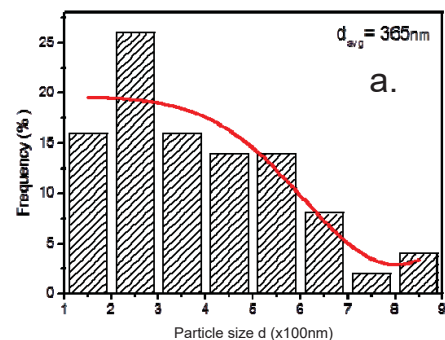


Fig. 3 Particle size distribution of BiOBr-1 (a), BiOBr-2 (b), and BiOBr-3 (c)

We also found out that as the average particle sizes become smaller, the photocatalytic activity of the according samples become higher. In the test with BiOBr-2 sample, it took only 70mins to fully degrade RhB, indicating the optimal performance, which is consistent with the analysis of its morphology. With uniform nanostructures of highest surface-to-volume ratio, the highest density of photo active sites is expected.

VII. CONCLUSION

In attempts of obtaining clean water from wastewater by

utilizing natural solar energy with higher efficiency of solar energy conversion, a cost effective controllable temperature and time dependent visible light photocatalyst BiOBr nanosheets has been obtained via a promising microwave solvothermal method using Ethylene Glycol as solvent. With average particle sizes 311 nm, the predicted sufficient surface-to-volume rate allows BiOBr nanoplates to have plenty active sites for dye degradation. Its high photocatalytic activity is proven by completion of RhB degradation within 70 mins.

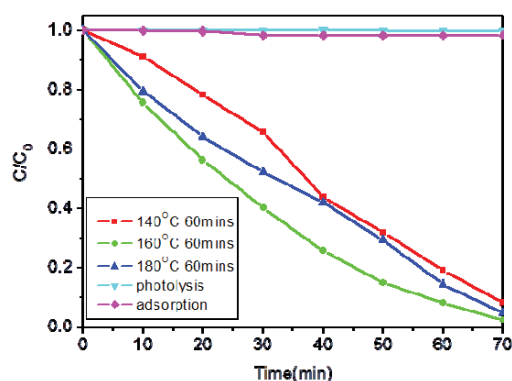


Fig. 4 UV absorption spectra of BiOBr synthesized under 140°C (a), 160°C (b), and 180°C (c); and concentration changes of RhB in the presence of different catalyst under visible light

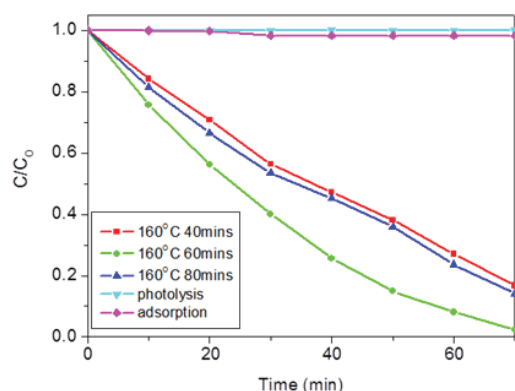


Fig. 5 Concentration changes of RhB in the presence of different catalyst under visible light. UV absorption spectra of BiOBr samples, BiOBr-1(a), BiOBr-2 (b) and BiOBr-3 (c)

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support by GRF Project CityU 11207414.

REFERENCES

- [1] Leung M.K.H., Tang S.M., Lam R.C.W., Leung D.Y.C., Yam W.C., Ng S.P., Vrijmoed L.L.P., Parallel-plate Solar Photocatalytic reactor for air purification: semi-empirical correlation, modeling, and optimization," Solar Energy, 2006, 80: 949-955.
- [2] Ni M., Leung M.K.H., Leung D.Y.C., Sumathy K., A Review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production, Renewable and Sustainable Energy Reviews, 2007; 11(3): 401-425.
- [3] Shang J., Hao W. C., Lv X. J., Wang T. M., Wang X. L., Du Y., Dou S. X., Xie T. F., Wang D. J., Wang J., Bismuth oxybromide with reasonable photocatalytic reduction activity under visible light, ACS Catalysis 2014.
- [4] Liu Z. S., Wu B. T., Xiang D. H., Zhu Y. B., Effect of solvents on morphology and photocatalytic activity of BiOBr synthesized by solvothermal method, Materials Research Bulletin 2012; 47: 3753-3757.
- [5] Wang X. L., Yang J., Chen Y. Y., Zhang Y. M., Tang Y., EDTA-modified hydrothermal synthesis of a novel four-leaf clover-shape BiOBr microstructure, Materials Letters 2014; 116: 171-174.
- [6] Zhang L., Cao X.F., Chen X. T., Xue Z. L., BiOBr hierarchical microspheres: Microwave-assisted solvothermal synthesis, strong adsorption and excellent photocatalytic properties, Journal of Colloid and Interface Science 2011;354: 630-636.
- [7] Pan L. K., Liu X.J., Zhuo S. and Chang Q.S., Nanophotocatalysts via microwave-assisted solution-phase synthesis for efficient photocatalysis, Journal of Materials Chemistry A 2013, 1, 8299-8326.

Michael K.H. Leung is the Associate Dean (Undergraduate Studies) and Associate Professor in the School of Energy and Environment at the City University of Hong Kong.

Meichen Lee is an Undergraduate Student in the Department of Chemistry at the National Central University in Taiwan. Meichen participated in an Exchange Programme at the City University of Hong Kong in summer 2014, under the supervision by Dr. Michael Leung.