

Influence of Ionic Liquids Assisted Synthesis on Morphology and Photocatalytic Properties of $\text{Bi}_4\text{O}_5\text{Br}_2$ [†]

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† Presented at Innovations-Sustainability-Modernity-Openness Conference (ISMO'19), Bialystok, Poland, 22–23 May 2019.

Published: 25 June 2019

Abstract: A series of $\text{Bi}_4\text{O}_5\text{Br}_2$ photocatalysts were prepared via an innovation method of synthesis with ionic liquids (ILs). The crystal structures were investigated by X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). The Field Emission Scanning Electron Microscope (FE-SEM) images illustrated the unique structure of prepared photocatalysts. The photocatalysts were also characterized by N_2 adsorption-desorption analysis, X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectra (UV-vis/DRS) and photoluminescence spectra (PL). The role of ILs in synthesis of $\text{Bi}_4\text{O}_5\text{Br}_2$ on morphology and photocatalytic properties were investigated. Rhodamine B, 5-fluorouracil and chromium (VI) were used as the model micropollutants to evaluate adsorption capacity, photooxidation and photoreduction ability of prepared $\text{Bi}_4\text{O}_5\text{Br}_2$ under artificial solar light. This work provided a new thought for enhanced photocatalytic activity of bismuth oxybromide photocatalysts.

Keywords: photocatalysis; bismuth oxybromide; ionic liquid

1. Introduction

Ionic liquids (ILs) are a very wide group of compounds with unusual properties, which includes: negligible vapor pressure, good thermal stability, high ionic conductivity, broad electrochemical potential windows, good solubility and high synthetic flexibility [1]. Additionally, the interaction occurring in these compounds caused that ILs can be used in the synthesis of micro and nanomaterials [2]. Nowadays, ionic liquids were used as a solvent [3], structure-directing agents [1], templates [2] and reactants [2,4] in the preparation of unique morphology of various catalysts.

Bismuth oxybromides (BiOBr) are crystallized in a tetragonal matlockite structure, they possessed the layered structure that are composed of $[\text{Bi}_2\text{O}_2]$ slabs interleaved with double halogen bromides atom slabs along the (001) direction. The layered structure is beneficial for separation of photogenerated hole-electron pairs. Thus, BiOBr has attracted wide research attention due to its suitable band-structure and high photocatalytic activity under visible light [5]. Density functional theory (DFT) calculation shows that the valence band (VB) of BiOBr is composed of hybrid orbitals of Br 4p and O 2p, and the conduction band (CB) consist of Bi 6p orbitals. More recently, it has been found that bismuth rich oxybromides had lower the semiconductor valence band position, which decreases the band gap and increases utilization of visible light and consequently, higher photocatalytic activity in this range of irradiation [6]. Aim of the research was to evaluate influence of ILs on morphology and photocatalytic activity of $\text{Bi}_4\text{O}_5\text{Br}_2$ toward water micropollutants under

artificial solar irradiation. In this research $\text{Bi}_4\text{O}_5\text{Br}_2$ were prepared via innovative route of synthesis with ionic liquids as a bromide source, dispersing agent and template.

2. Materials and Methods

2.1. Synthesis of $\text{Bi}_4\text{O}_5\text{Br}_2$

Photocatalysts were prepared via solvothermal methods in glycerol as a reaction solvent. Solvothermal reaction conducted in 50 mL Teflon reactor for 16 hours in 160 °C. The obtained precipitate was dried at 80 °C under air atmosphere. Then, the hydrolytic process were carried out. 0.3 g powder was dispersed in 100 mL deionized water and kept continuously stirring for 2 h. The photocatalysts were obtained after centrifugation, washed with deionized water and dried at 80 °C under air atmosphere. Ionic liquids which contains imidazolium (im), pyridinium (py) and pyrrolidinium (pyr) as a cations and bromides as anions were used as a source of Br to prepared series of $\text{Bi}_4\text{O}_5\text{Br}_2$. The reference sample was bismuth oxybromide synthesized from simple inorganic salt KBr without ionic liquid [4].

2.2. Photocatalytic Tests

Photocatalytic activity were evaluated by photoreduction of Cr (VI), photooxidation of rhodamine B and 5-fluorouracil under artificial solar light. In the experiment, 0.2 gL^{-1} of prepared $\text{Bi}_4\text{O}_5\text{Br}_2$ were suspended in 15 mL of 15 mgL^{-1} Rhodamine B and 5-fluorouracil aqueous solution. Concentration of Cr (VI) was 20 mgL^{-1} and pH was adjust to 3. Before irradiation starts, the solutions mixed with photocatalysts were kept in the dark for 30 min to allow the adsorption-desorption equilibrium to be reach. The irradiation lasted 120 min and the source of light were medium pressure Hg lamp 150 W.

3. Results

The morphology of synthesized series of photocatalysts was different and ionic liquids had significant influence on the shapes and structures of the samples. Specific surfaces area of $\text{Bi}_4\text{O}_5\text{Br}_2$ _ils were higher than the reference $\text{Bi}_4\text{O}_5\text{Br}_2$ obtained from KBr. XRD analysis confirmed pure $\text{Bi}_4\text{O}_5\text{Br}_2$ phase in all samples. XPS revealed that $\text{Bi}_4\text{O}_5\text{Br}_2$ photocatalysts were composed with Bi, O and Br. Obtained energy binding suggested trivalent oxidation state of bismuth and monovalent state of bromide. FT-IR analysis confirmed absence of ionic liquids on photocatalysts surface. No characteristic absorption peaks (N-C band vibrations from IIs) were observed. Obtained results were in accordance with XPS analysis.

3.1. Photocatalytic Activity

The photocatalytic activities of $\text{Bi}_4\text{O}_5\text{Br}_2$ samples were measured in degradation of Rhodamine B, 5-fluorouracil and chromium (VI) in acidic solution under artificial solar irradiation. The obtained results were shown in Figure 1.

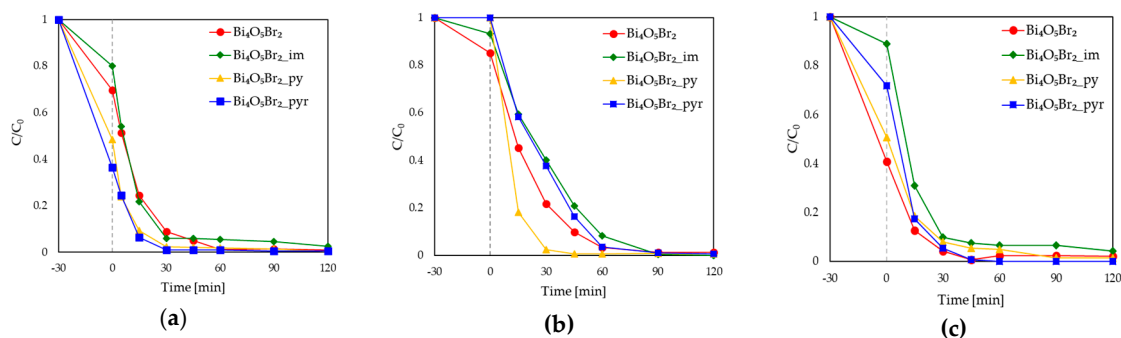


Figure 1. Photocatalytic activity of prepared photocatalysts toward (a) Rhodamine B, (b) 5-fluorouracil and (c) chromium (VI) under artificial solar irradiation.

A blank experiment without prepared photocatalysts indicated that 5-fluorouracil and Cr (VI) were not degraded while Rhodamine B decomposed in no more than 20% after 120 min of irradiation. The photocatalytic degradation kinetics of Cr (VI), rhodamine B and 5-fluorouracil was pseudo-first order. For rhodamine B, the most active photocatalysts were Bi₄O₅Br₂_py and Bi₄O₅Br₂_pyr which were characterized the high sorption capacity. The 5-fluorouracil degradation rate under Bi₄O₅Br₂_py was the fastest. Efficiency of Cr (VI) photoreduction was similar for all prepared photocatalysts.

4. Conclusions

The beneficial influence of ionic liquids used in the solvothermal synthesis on the morphology, structure and optical properties of the bismuth semiconductors was improved. The ILs caused loosening of the structure and increasing the particle size of semiconductors which had favorable impact on specific surface area and pore volume. The results indicate that ionic liquids applied as a halogen source can increase the photocatalytic activity of bismuth oxyhalides in micropollutants degradation.

Author Contributions: A.B.-G. and E.M.S. conceived and designed the experiments; P.W. and A.F.B. performed the experiments; A.B.-G. and P.W. analyzed the data; A.B.-G., A.P., E.M.S. contributed reagents/materials/analysis tools; A.B.-G. and P.W. wrote the paper.

Acknowledgments: This work was supported by the National Science Center within program MINIATURA 1 (DEC-2017/01/X/ST5/01136), Sonata 10 (2015/19/D/ST5/00710) and DS530-8626-D596-18.

Conflicts of Interest: The authors declare no conflict of interest.

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