

Photodegradation of Rhodamine B by bismuth oxybromide nanosheets synthesized via microwave method

Azadeh Tadjarodi^{a,*}, Keyvan Bijanzad^a, Mohammad Moghaddasi^a, Omid Akhavan^{b,c}

^aResearch Laboratory of Inorganic Materials Synthesis, Department of Chemistry, Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran

(E-mail: tajarodi@iust.ac.ir)

^bDepartment of Physics, Sharif University of Technology, P.O. Box 11155-9161, Tehran, Iran,

^cInstitute for Nanoscience and Nanotechnology, Sharif University of Technology, P.O. Box 14588-89694, Tehran, Iran

Abstract

The original Bi-based oxyhalide is the Sillen family expressed by $[M_2O_2][X_m]$ or $[M_3O_{4+n}][X_m]$ ($m=1-3$, $X=\text{halide}$, $M=\text{Bi}$) where bismuth oxide-based fluorite-like layers, $[M_2O_2]$ or $[M_3O_{4+n}]$, are intergrown with single, double, and triple halide. The band gap of BiOX is strictly dependent on the halide participated in its composition and ranges from 3.19–3.44, 2.64–2.91 and 1.77–1.92 eV, respectively for Cl, Br and I. Bismuth nitrate pentahydrate and potassium bromide were applied to synthesize the product in a domestic microwave instrument. The SEM images showed the microflowers were comprised of nanosheets with the thickness of about 54 nm. From energy dispersive X-ray analysis, its empirical formula was estimated to be $\text{Bi}_{1.75}\text{O}_{13.66}\text{Br}$. Fourier transform infrared spectroscopy showed that the peaks at 565 and 815 cm^{-1} were attributed to the stretching vibration of Bi-O. With a band gap energy of 3.58 eV, it showed a high photocatalytic performance in photodegradation of Rhodamine B.

Keywords: **Microwave synthesis, Bismuth oxybromide, Photocatalyst, Rhodamine B.**

1. Introduction

The original Bi-based oxyhalide is the Sillen family expressed by $[M_2O_2][X_m]$ or $[M_3O_{4+n}][X_m]$ ($m=1-3$, $X=\text{halide}$, $M=\text{Bi}$) where bismuth oxide-based fluorite-like layers, $[M_2O_2]$ or $[M_3O_{4+n}]$, are intergrown with single, double, and triple halide [1]. The band gap of BiOX is strictly dependent on the halide participated in its composition and ranges from 3.19–3.44, 2.64–2.91 and 1.77–1.92 eV, respectively for Cl, B and I [2]. Theoretical studies have shown by increasing Bi content in BiOBr, the conduction band could shift negatively; therefore, compositions such as $\text{Bi}_3\text{O}_4\text{Br}$ are better photocatalysts than BiOBr. It was reported

that, $\text{Bi}_3\text{O}_4\text{Br}$ could remove more than 92% of sodium pentachlorophenate under visible light irradiation [3]. Similarly, $\text{Bi}_3\text{O}_4\text{Cl}$ provided by solid-state method, demonstrated better photocatalytic behavior for methyl orange degradation than that of anatase TiO_2 . Here, the internal electric fields between $[\text{Bi}_3\text{O}_4]$ and $[\text{Cl}]$ slabs and also, the hybrid states at the conduction and valence bands, are regarded to be responsible for the efficient separations of electron-hole pairs upon photoexcitation [1]. There are also other photocatalysts containing bismuth such as: $\text{BiOI}/(\text{BiO})_2\text{CO}_3$ [4], Bi_2S_3 [5], N-Doped $(\text{BiO})_2\text{CO}_3$ [6], BiFeO_3 [7], $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [8], $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped Bi_2MoO_6 [9].

2. Experimental section

Bismuth nitrate pentahydrate (98.0%) was purchased from SAMCHUN CHEMICALS, Korea. All the other reagents were purchased from Merck Company and used without further purification. Rhodamine B (RhB) was used as the model pollutant. Deionized water was used to prepare all the solutions. Bismuth nitrate pentahydrate and potassium bromide were utilized to fabricate the product in a domestic microwave instrument (Samsung GE 280) at 180 Watts for 23 minutes.

3. Result and discussion

Fourier transform infrared spectroscopy showed that the peak at 567 cm^{-1} was attributed to the stretching vibration of Bi-O. Other peaks were related to carboxyl and/or hydroxyl surface functional groups.

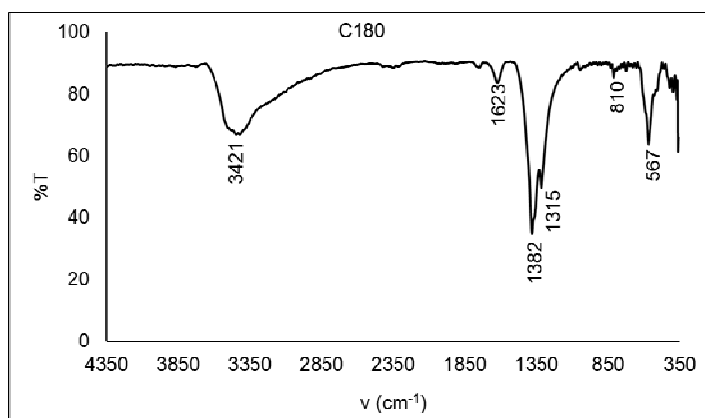


Fig. 1. FT-IR spectrum of the bismuth oxybromide nanostructure.

As it can be seen in Fig. 2, the reflections of the product could be indexed to the tetragonal phase of BiOBr pattern with the space group of P4/nmm and lattice parameters of $a=3.93$, $b=3.93$ and $c=8.10$ Å, $\alpha=\beta=\gamma=90^\circ$ (JCPDS card no. 00-009-0393).

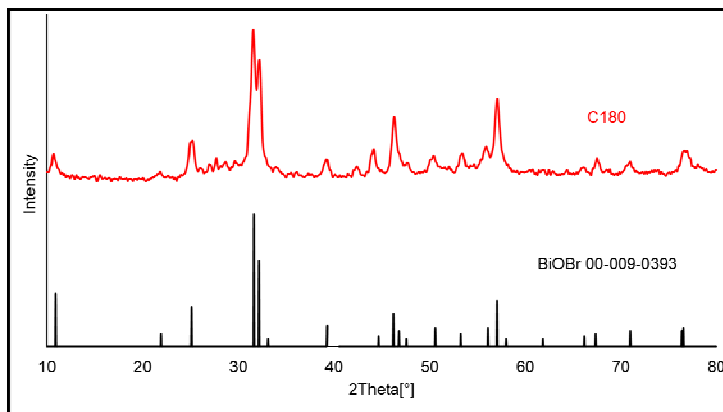


Fig. 2. XRD patterns of bismuth oxybromide nanostructure and BiOBr (JCPDS file no. 00-009-0393).

The SEM images showed the microflowers were comprised of nanosheets with the thickness of about 54 nm. They revealed a distinct rose-like morphology comprising of nanosheets.

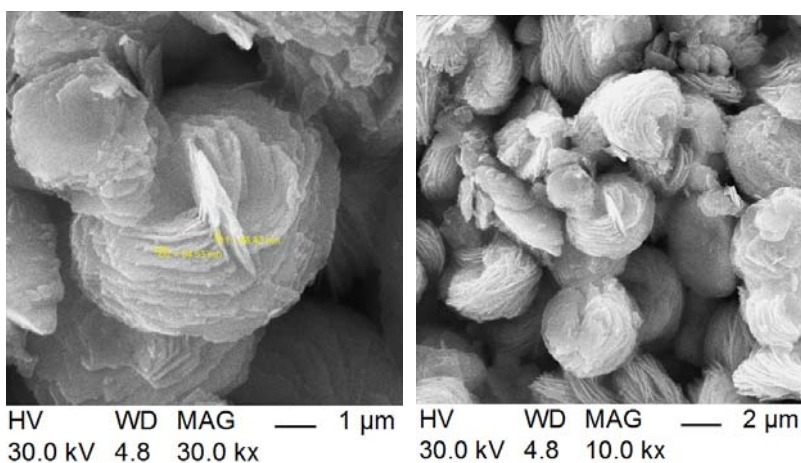


Fig. 3. SEM images of bismuth oxybromide nanostructure

From energy dispersive X-ray analysis, its empirical formula was estimated to be $\text{Bi}_{1.75}\text{O}_{13.66}\text{Br}$.

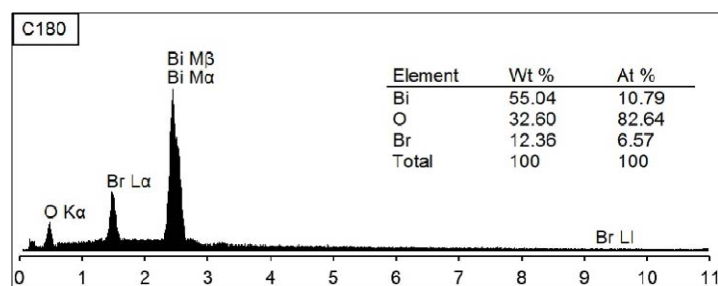


Fig. 4. EDX analysis of bismuth oxybromide nanostructure.

Rhodamine B ($C_{28}H_{31}N_2O_3Cl$), an organic dye, presently used as dye laser material, is part of the triphenylmethane family of dyes that contain four N-ethyl groups at both sides of the xanthene rings. It is stable in aqueous solution, used in the textile, food and cosmetics industry which can cause hazardous pollution in the environment [10]. A possible mechanism for the degradation of RhB is based on deethylation and carboxylation of the organic dye molecules and the intermediates where dye is finally mineralized to CO_2 and H_2O . The gradual blue-shift of the main absorption peak of RhB was related to the step-by-step deethylation of the dye molecules [11].

With a band gap energy of 3.01 eV, $Bi_{1.75}O_{13.66}Br$ showed a good photocatalytic performance in photodegradation of rhodamine B (RhB) and more than 60 % of the dye molecules were degraded in 4 hours.

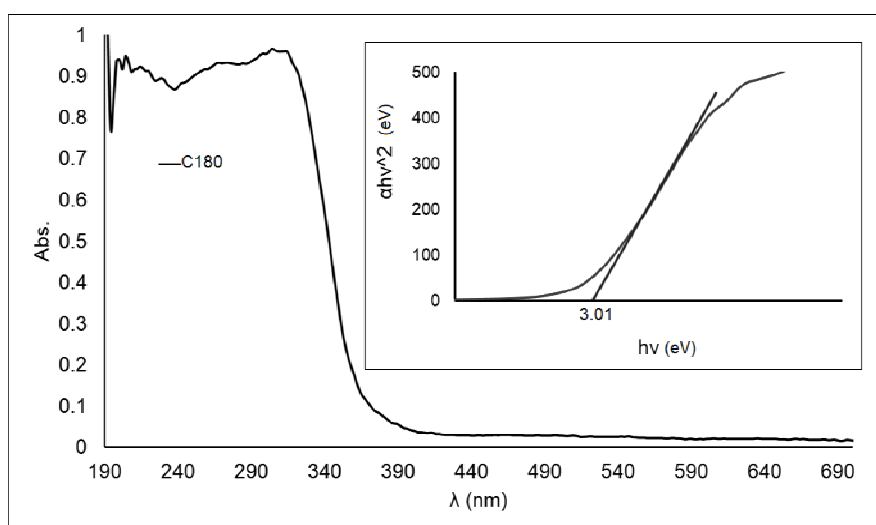


Fig. 5. UV-Vis diffuse reflectance spectrum of bismuth oxybromide (the inset shows plot of $(\alpha hv)^2$ vs. hv for corresponding product).

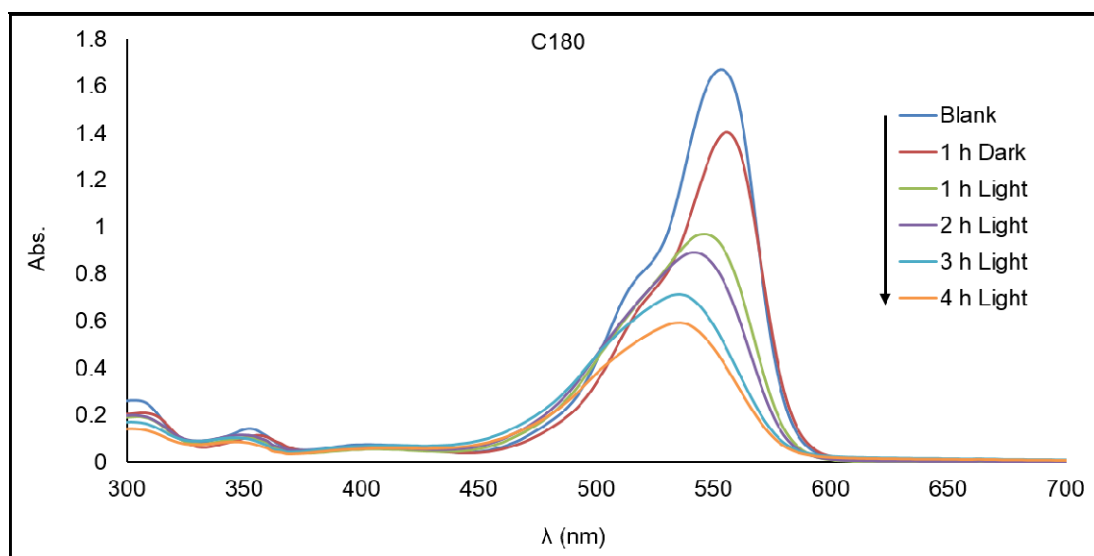


Fig. 6. UV absorption spectra of RhB in presence of 0.05 g of photocatalyst under Mercury lamp for 4h.

4. Conclusion:

Bismuth nitrate pentahydrate and potassium bromide were applied to synthesize $\text{Bi}_{1.75}\text{O}_{13.66}\text{Br}$ microflowers in a domestic microwave instrument. The SEM images showed the microflowers were comprised of nanosheets. With a band gap energy of 3.58 eV, it showed a high photocatalytic performance in photodegradation of Rhodamine B.

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