

Photocatalytic degradation of organic pollutants using surfactant-free hydrothermally prepared flower-like BiOBr hierarchical structures under visible light irradiation

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Abstract. Flower-like BiOBr hierarchical structures were successfully prepared via a facile hydrothermal route in the absence of any surfactants. Various characterization tests were carried out to analyze the as-prepared BiOBr samples. By utilizing the flower-like BiOBr as photocatalysts, enhanced photocatalytic performance on the sunset yellow degradation was observed in comparison with the BiOBr nanosheets and commercial TiO₂. The photocatalytic enhancement was ascribed to the unique hierarchical porous surface structure with good crystallinity and optical properties, which could improve the electron-hole pairs separation and led to high yield of reactive oxygen species for photocatalytic reaction. Other organic pollutants such as bisphenol A and methylparaben were also successfully degraded over flower-like BiOBr under similar experimental conditions.

1. Introduction

Bismuth oxybromide (BiOBr), as an important V-VI-VII ternary semiconductor with exceptional physical and chemical properties has recently drawn much attention for their great potential applications [1] [2]. BiOBr has a tetragonal structure consisting of [Bi₂O₂] positively charged slabs and interleaved by double slabs of Br atoms to form [Br-Bi-O-Bi-Br], which enable the formation of internal static electric field. Moreover, the highly dispersive band structure of BiOBr also led to high mobility of the photogenerated charge carriers. BiOBr has exhibited exceptional performance in view of its application in the field of biosensors, dye-sensitized solar cells, pigments and heterogeneous catalysis [1]-[5]. It has been demonstrated that the ultimate performance and application of BiOBr materials are considerably dependent on the morphology and dimensionality in micro- and nano-scale systems [6] [7]. Compounds with the same chemical compositions but different morphologies and dimensionalities can lead to substantial variations in performance [7]. Hitherto, BiOBr crystals with various morphologies have been developed including nanobelts, nanoparticles, nanoplates, flower shaped, hierarchical and complex BiOBr microarchitectures [1],[7]-[10]. In particular, three-dimensional hierarchical structures combined the features of low-dimensional nanoscale building blocks not only showed unique properties different from those of the mono-morphological structures, but also provided large number of surface activation sites to realize region-dependent surface reactivity [11].



The increasing environmental deterioration and the continuing energy crisis have stimulated intense interest on the heterogeneous photocatalytic technologies. As a versatile semiconductor, BiOBr has recently received enormous scientific attention as significant photocatalytic material for its excellent performance for the environmental pollutants degradation under visible light irradiation [1],[12]. For example, Mera et al. [12] reported the exceptional photocatalytic activity of hierarchical BiOBr microspheres on the anion dye degradation under solar irradiation. A study of Li et al. [1] also showed the efficient degradation of rhodamine B and methylene blue over belt-like BiOBr hierarchical nanostructures irradiated under visible light. In this study, 3D BiOBr hierarchical structure with flower-like morphology was synthesized via a simple and surfactant-free hydrothermal route. The as-prepared samples were characterized by different techniques and used for sunset yellow (SSY), bisphenol A (BPA) as well as methylparaben (MP) degradation under visible light irradiation. An improvement of photocatalytic activity was observed when as-prepared samples were used as photocatalysts compared to two-dimensional (2D) BiOBr nanosheets and commercial TiO₂ photocatalysts.

2. Experimental

The flower-like BiOBr hierarchical structures were prepared by a facile hydrothermal method. In a typical experiment, Bi(NO₃)₃•5H₂O (4 mmol) was first dissolved in 80 mL acetic acid under magnetic stirring. Then, 40 mL KBr solution (4 mmol) was added with constant stirring. The resulting reaction mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 120°C for 12 h. After cooling the autoclave naturally, the as-formed precipitates were collected by filtration and repeated washing with deionized water and ethanol for several times. The resulting products were dried in oven at 80°C, ground into fine powder and finally calcined at 400°C for 3 h.

The obtained samples were characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM-6701F), energy dispersion X-ray (EDX, Oxford X-max), X-ray diffraction (XRD, Philips PW1820 diffractometer), fourier transform infrared spectroscopy (FTIR, Spectrum RX 1) and UV-vis diffuse reflectance spectroscopy (UV-vis DRS, Perkin Elmer Lambda 35).

The photocatalytic experiment was as follows: the photocatalyst (200 mg) was suspended in the organics aqueous solution (10 mg/L, 200 mL) and stirred in the dark for 30 min to establish the adsorption-desorption equilibrium. The degradation was carried out at room temperature under irradiation of a 55 W compact fluorescent lamp with average light intensity of 14,500 lx. Air bubbling at a flow rate of 2 mL/min was added during the reaction process. 4 mL of sample suspensions were withdrawn at given time intervals and centrifuged. The SSY concentration was analyzed by UV-vis spectrophotometer at a wavelength of 480 nm while the concentrations variation of BPA and methylparaben were obtained using a high performance liquid chromatography. The HPLC separations were performed with a mobile phase mixture of acetonitrile and water at wavelength of 225 and 254 nm for bisphenol A and methylparaben, respectively. The organic pollutants degradation was expressed as C/C_0 versus irradiation time, where C_0 is the equilibrium concentration of organic pollutants and C is the concentration at time t . Meanwhile, the comparison studies with commercial TiO₂-P25 and 2D BiOBr nanosheets prepared by the solvothermal method according to Jiang et al. [13] were also conducted.

The photoluminescence (PL) technique using terephthalic acid as a probe molecule was performed to detect the hydroxyl radicals (•OH). Experimental procedure was similar to that of photocatalytic process. 5×10^{-4} M terephthalic acid aqueous solution in 2×10^{-3} M NaOH solution replaced the organics aqueous solution. The PL spectra of generated 2-hydroxyterephthalic acid at 425 nm were measured on a Perkin-Elmer Lambda S55 spectrofluorometer using excitation wavelength of 315 nm. The PL intensity of 2-hydroxyterephthalic acid was proportional to the amount of •OH produced in the degradation system.

3. Results and Discussion

The general morphologies of the as-prepared BiOBr samples were characterized by FESEM which indicated the synthesis of flower-shaped BiOBr. The flower-like BiOBr were synthesized in large quantity with diameters ranging from several hundred nanometers to micrometers (Figure 1a). The microflowers also exhibited hierarchical structure composed of many nanosheets, which were interlaced with each other and have formed porous flowery BiOBr through oriented aggregation

(Figure 1b). The flower-like assemblies of nanosheets were made of Bi, O and Br elements as confirmed via EDX analysis. A signal of C was also detected, which attributed to the adhesive carbon tape used in the EDX analysis (Figure 1c). No other crystalline phase related to impurity was identified in the XRD spectrum which further verified the formation of pure BiOBr. The XRD diffraction peaks can be corresponded to the tetragonal structure of BiOBr (JCPDS no. 09-0393) (Figure 1d). In addition, the intense and sharp diffraction peaks indicated the high crystallinity of the as-prepared BiOBr samples.

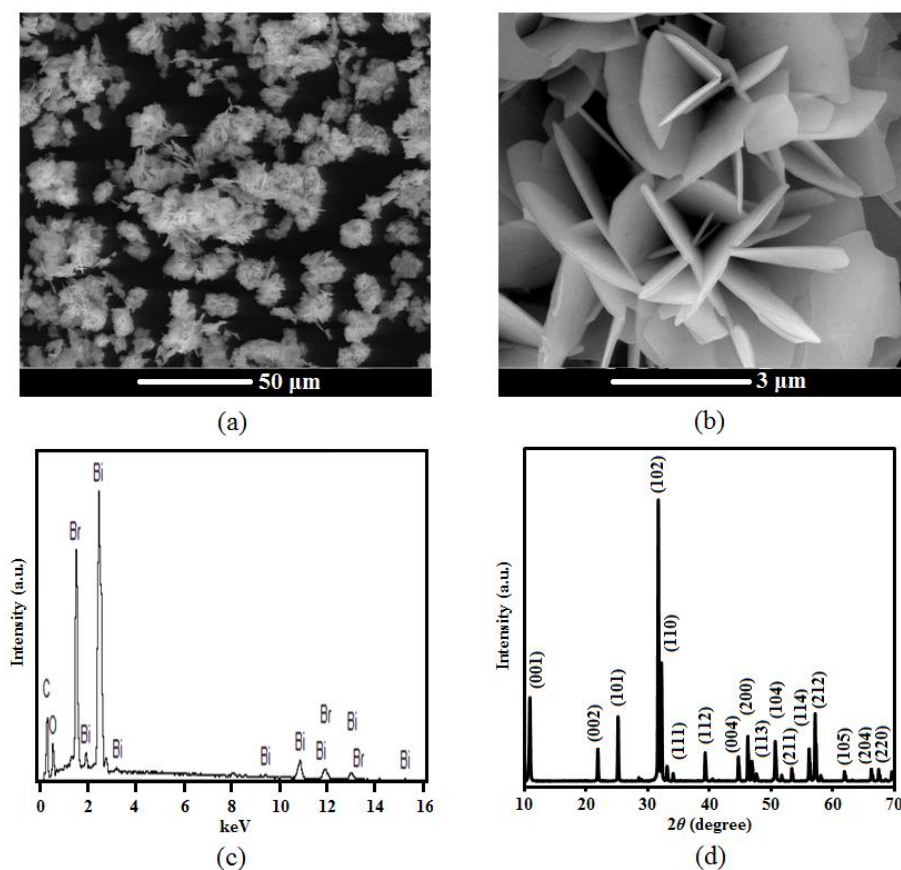


Figure 1. (a) Low and (b) High magnification FESEM images, (c) EDX spectrum and (d) XRD pattern of as-prepared flower-like BiOBr hierarchical structures.

The FTIR spectrum was recorded in the range 4000–400 cm^{-1} (Figure 2a). The main absorption bands at 500–1200 cm^{-1} were ascribed to stretching vibrations of Bi–O bonds. Particularly, the peak at 520 cm^{-1} was assigned to the stretching vibration bonds in crystal tetragonal BiOBr [14]. A strong absorption at wavelengths lower than 430 nm was observed in UV-vis DRS spectrum, implying that the as-prepared samples can be promising in solar photocatalysis (Figure 2b). The band gap energy was determined using $E_g (\text{eV}) = 1240/\lambda (\text{nm})$, where E_g is the band gap energy and λ is the wavelength (nm) of absorption onset. The E_g of the samples was measured to be 2.88 eV, which was close to the values reported in literatures [12],[13].

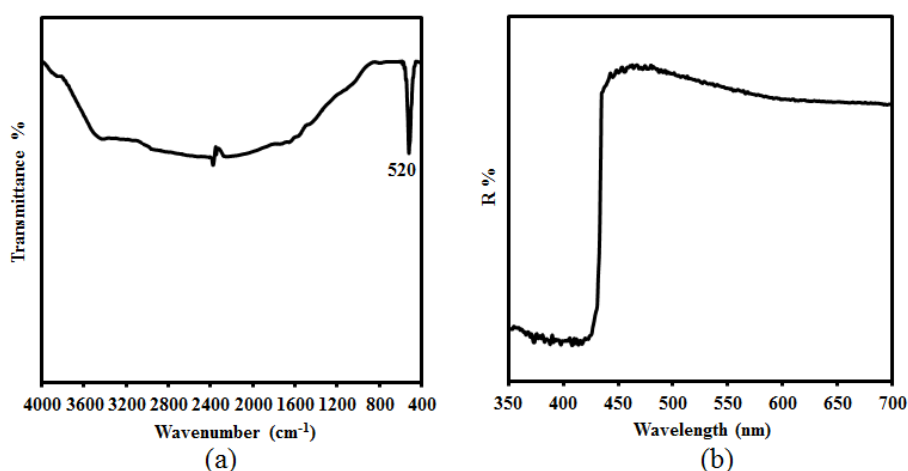


Figure 2. (a) FTIR spectrum and (b) UV-vis DRS spectrum of as-prepared flower-like BiOBr hierarchical structures.

The photocatalytic activities of the as-prepared BiOBr samples were evaluated by the SSY degradation under visible light irradiation (Figure 3). SSY is an important synthetic chemical which extensively used in food, pharmaceutical and cosmetic industries. Several recent cases of SSY contamination to food products have been reported in several countries [15]. Indeed, the complex molecular structure of SSY was difficult to be degraded by microorganisms, thus threatening the water ecology. Various *in vivo* tests also showed that SSY can cause chromosomal aberration in the liver and germinative cells, DNA fragmentation and increase of morphological abnormalities in spermatozooids of mice [15],[16]. Blank experiment of SSY photolysis indicated that the self-degradation of SSY in the absence of catalysts can be neglected. However, when the catalysts were used, the degradation of SSY obviously accelerated with increasing of the irradiation time. It was apparent that the flower-like BiOBr showed higher photocatalytic activity than those of 2D BiOBr nanosheets and commercially available TiO₂ photocatalysts. Within the reaction time, the degradation efficiency of SSY achieved 53.5%, however, for BiOBr nanosheets and TiO₂ the degradation efficiencies were only 46.2% and 41.4%, respectively.

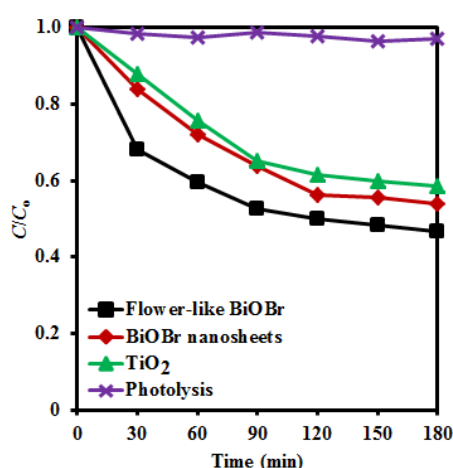


Figure 3. C/C_0 versus time curves of photodegradation of SSY.

The enhanced photocatalytic performance over flower-like BiOBr can be ascribed to the unique hierarchical porous surface structure with good crystallinity and optical properties, which could lead to efficient separation of electron-hole pairs and generation of large number of reactive oxygen species.

Herein, BiOBr first absorbed the light and transferred the electron from valence band to the conduction band, leading to the generation of the separated electron-hole pairs. Then, the reactive oxygen species such as $\bullet\text{OH}$, superoxide oxide anion radical ($\text{O}_2^{\bullet-}$) and hydroperoxyl radical (HO_2^{\bullet}) can be generated, which significantly degraded the organic pollutants adsorbed on the catalyst surface. To reveal the $\bullet\text{OH}$ involved in the photocatalytic degradation of SSY, PL spectroscopy technique with terephthalic acid as a probing molecule was employed (Figure 4). It was apparent that the $\bullet\text{OH}$ formation rate in the presence of flower-like BiOBr was higher than the BiOBr nanosheets and TiO_2 , revealing an improved photocatalytic activity of the as-prepared flower-like BiOBr.

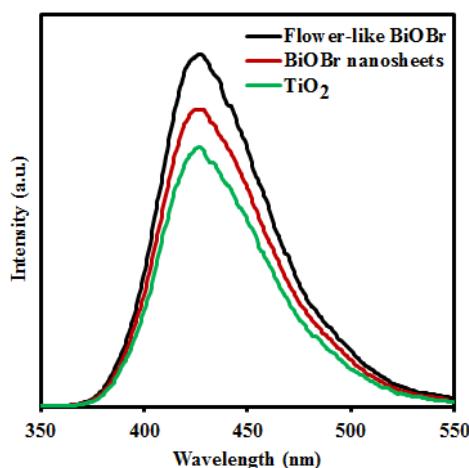


Figure 4. PL spectra of different photocatalysts in an aqueous basic solution of terephthalic acid after 180 min irradiation.

Furthermore, the degradation of colourless BPA and MP were performed to further ascertain the visible light photocatalytic activity of as-prepared BiOBr samples (Figure 5). Like SSY, BPA and MP are toxic and resistant to biodegradation [17]. Although the activities were poor, the flower-like BiOBr hierarchical structures still showed their visible light photocatalytic activity without the photosensitization effect. These results also suggested that the as-prepared BiOBr samples showed different activities in photocatalytic degradation of different organic pollutants, nevertheless, they could enhance the degradation of pollutants mentioned above owing to the catalytic ability.

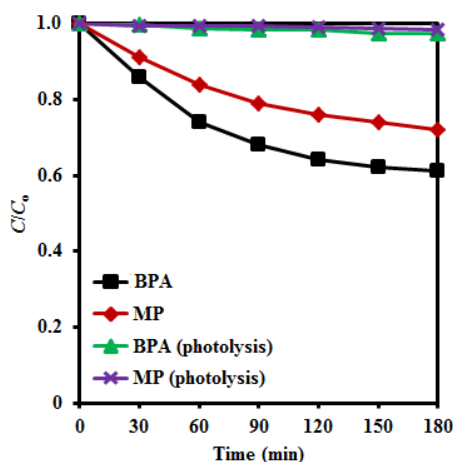


Figure 5. Photocatalytic degradation of several other organic pollutants by flower-like BiOBr.

4. Conclusions

In conclusion, 3D flower-like BiOBr hierarchical structures were successfully prepared in this study. The prepared BiOBr samples were characterized by FESEM, EDX, XRD, FTIR and UV-vis DRS measurements. Under visible light irradiation, the flower-like BiOBr demonstrated enhanced photocatalytic activity in comparison with BiOBr nanosheets and commercial TiO₂. The characterization results and theoretical analysis suggested the flower-like BiOBr as efficient photocatalysts can be rationally ascribed to the unique hierarchical porous surface structure with good crystallinity and optical properties which could enhance the electron-hole pairs separation and generated large number of reactive oxygen species. In addition to the facile preparation method and enhancement photocatalytic performance, preliminary results also demonstrated the prepared flower-like BiOBr were promising catalysts for environmental remediation. Further studies on these catalysts will be helpful to understand the exact growth mechanism of the flower-like BiOBr and to optimize their catalytic performance, which can be an interesting topic to address in future studies.

5. References

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