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Adsorption/photocatalytic performances of hierarchical flowerlike $BiOBr_xCl_{1-x}$ nanostructures for methyl orange, Rhodamine B and methylene blue



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ABSTRACT

We synthesized hierarchical flower-like BiOBr_xCl_{1-x} ($0 \le x \le 1$) microspheres in ethylene glycol solvent and examined their fundamental properties by scanning electron microscopy (SEM), X-day diffraction (XRD), UV-visible absorption, Raman, photoluminescence spectroscopy, and BET surface area measurement. Additionally, their adsorption and photocatalytic performance were tested using methyl orange (MO), Rhodamine B (RhB), and methylene blue (MB). The adsorption performance was found to be in the order of BiOCl < BiOBr_xCl_{1-x} < BiOBr for MO under dark conditions. For the selected BiOBr_{0.7}Cl_{0.3} catalyst, the adsorption ability was found to be in the order of MO < RhB < MB owing to electrostatic interactions between the catalyst and the dye. The photocatalytic dye degradation performance occurred in the order of MB < MO < RhB as a result of light absorption by the dye followed by good electron transfer from the conduction band of the dye to that of the catalyst. An indirect chemical probe method was used to examine the roles of active species in the dye-sensitized photodegradation mechanism, which were found to be in the order of $\cdot OH \approx \cdot O_2^- < h^+$ under visible light irradiation.

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1. Introduction

In recent years, pollutant removal from water has been extensively investigated using bismuth oxyhalide, BiOX (X=Br, Cl, I), catalysts [1–32]. One of the merits of BiOX is that their photocatalytic activities during dye degradation are superior to commercial TiO₂ under visible light irradiation [1,15,22,31]. In addition, the band gaps of BiOX can be tuned within 3.4–1.7 eV by varying the halides (X=Br, Cl and I) and the relative composition of two different halides (BiOX_xX'_{1-x}) [13]. Facial hydrothermal

http://dx.doi.org/10.1016/j.mssp.2014.06.043 1369-8001/© 2014 Elsevier Ltd. All rights reserved. and solvothermal methods have commonly been employed using different chemicals, compositions, and reaction temperatures to synthesize catalysts with various morphologies [1,4,5–7]. Selection of a solvent and controlling the ratio of a mixed solvent are major factors determining the morphology of synthesized catalysts [3]. Zhang et al. synthesized various BiOBr nanosheets with different thicknesses and ratios of exposed {1 0 0} facets by controlling the reaction temperature and solvent [3]. Generally, catalysts with different facets show different adsorption ability and charge separation ability; accordingly, the catalytic performance can be enhanced by controlling the facets [1–3]. Hybridization of two different materials has been employed to enhance their catalytic performance [1–3,29]. In hybrid systems, one material absorbs light to excite the electrons

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in the valence band into the conduction band, after which the electron can be transferred into the conduction band of the other material [9–11,17,29]. As a result, the photodegradation performance is greatly enhanced. Two major morphologies of 2D sheets and 3D hierarchical flower-like structures have commonly been reported for BiOX catalysts. By adding surfactants such as cetyltrimethylammonium bromide (CTAB), different flow-like structures were obtained [16]. The photocatalytic performance of BiOX has been tested for MO, RhB, and MB. Additionally, the removal of phenols [15,24] and Cr(IV) ions [16] has been demonstrated, and the antibacterial photocatalytic activity was also tested [14].

In the present study, we synthesized hierarchical flower-like $BiOBr_xCl_{1-x}$ ($0 \le x \le 1$) microspheres by varying the relative composition of Br and Cl and tested the adsorption and photocatalytic activity for MO, RhB, and MB. These dyes have different molecular structures, and show different UV-visible absorption bands beyond the band edges of the $BiOBr_xCl_{1-x}$ microspheres; therefore, they comprise a good model system for investigation of adsorption and photocatalytic degradation mechanisms of a catalyst. Although extensive dye degradation studies using BiOX catalysts have been performed, the results presented herein provide deeper insight into the origins of adsorption ability and photocatalytic activity, as well greater scientific insight.

2. Experimental

2.1. Catalysts preparation

BiOBr_xCl_{1-x} (x=1, 0.7, 0.5, 0.3 and 0.0) catalysts were synthesized as follows. Stoichiometric amounts of Bi(NO₃)₃ · 5H₂O (98.0%, Junsei, Japan), KCl (99.0%, Daejung, Korea) and KBr (99.0%, Daejung, Korea) were completely dissolved in 25.0 mL ethylene glycol (99.0%, Samchun, Korea) solvent, after which the solutions were transferred to a 120 mL Teflon bottle. The bottle was then capped and placed in an oven (120 °C) for 12 h, after which the white products were centrifuged and washed with Millipore water and ethanol several times.

2.2. Catalysts characterization

The surface morphology of the dried products was subsequently evaluated by scanning electron microscopy (SEM, Hitachi SE-4800), while the powder X-ray diffraction patterns were observed using a PANalytical X'Pert Pro MPD diffractometer with Cu $K\alpha$ radiation applied at 40 kV and 30 mA. Additionally, the UV-vis absorption spectra of the powder samples were obtained using a Varian Cary 5000 UV-visible-NEAR IR spectrophotometer, while the Raman spectra were taken using a Bruker Senterra Raman spectrometer with a laser wavelength of 532 nm. A Thermo Scientific Nicolet iS10 spectrometer was employed to obtain the FT-IR spectra, photoluminescence spectra were recorded using a SCINCO FluoroMate FS-2 and the Brunauer-Emmett-Teller (BET) surface area was determined using a ChemBET TPR/TPD analyzer (Quantachrome Ins.) equipped with a thermal conductivity detector.

2.3. Adsorption and photocatalytic activity tests

For the adsorption and photocatalytic reactions, 50 mg of catalyst was dispersed in 100 mL of dye solution (MO, RhB and MB) with a concentration of 10 or 50 mg/L. The adsorption and photodegradation performance was then examined using a UV-vis absorption spectrometer (Jasco V-530) with adsorption and photodegradation time under dark and light (daylight and incandescent) irradiation conditions, respectively. The daylight was sunlight passing through the window of our laboratory. Although the light intensity could not be measured, this did not impair the results and discussion. For the incandescent light, we used a 60 W incandescent lamp with a distance of 50 cm above the dye solution. The dry powder catalyst was found to be stable under visible light conditions; therefore, we excluded catalyst degradation from the discussion. In addition, since the UV light contained in the daylight and incandescent light was minor, we excluded the effect of UV light from evaluation of the visible light photocatalytic degradation. To examine the photodegradation mechanism, isopropyl alcohol (IPA), benzoquinone (BQ) and EDTA were added as active species scavengers for 'OH, O_2^- and h⁺, respectively, in the dye solution [33–35]. Upon irradiation with visible light, we measured a change in UV-vis absorption intensity of the dye solution. Photoluminescence spectroscopy was employed to detect active 'OH radicals using terephthalic acid solution with the catalyst [34]. After visible light irradiation, the photoluminescence from the solution was measured using a SCINCO FluoroMate FS-2 spectrometer.

3. Results and discussion

3.1. Morphology and growth mechanism

Fig. 1 shows the SEM images of $BiOBr_xCl_{1-x}$ (x=0, 0.3, 0.7 and 1) catalysts prepared in EG (HO-CH₂-CH₂-OH). The morphologies of all samples were similar and consisted of hierarchical flower-like structures with white color. Under water conditions, the morphology was found to be 2D-nanosheets, which was less active than the flower-like structures for photocatalytic dye degradation (data not shown). The flower-like spheres were typically 2-3 µm in diameter, and appeared to be aggregates of 2Dnanosheets formed by a 3D-assembly process. The microspheres could be formed by the following 3D-assembly growth mechanism. BiOX seeds are initially formed by a reaction of $Bi^{3+} + X^- + H_2O \rightarrow BiOX + 2H^+$. The seeds then initially grow into sheets, after which the smaller sheets dissolve and re-grow on larger particles via the Ostwald ripening process. Consequently, the 3D-self-assembly process minimizes the surface energy to form hierarchical spheres, as illustrated in Fig. 2 [5,25].

3.2. Crystal structure

Fig. 3 shows the powder XRD patterns of $BiOBr_xCl_{1-x}$ (x=1, 0.7, 0.3, and 0.0) catalysts prepared in EG. The XRD patterns of the BiOCl matched those of tetragonal (*P4*/*nmm*) BiOCl (JCPDS 1-085-0861) well. The three major



Fig. 1. SEM images of BiOBr_xCl_{1-x} ($0 \le x < 1$) catalysts. Insets show the optical microscopy images of the corresponding powder samples.



Fig. 2. Proposed growth mechanism of the hierarchical flower-like nanostructures.

peaks were positioned at 2θ =25.9°, 32.6° and 33.5°, which were assigned to the (1 0 1), (1 1 0) and (1 0 2) planes, respectively. Our results are consistent with those of previous studies [30]. As the composition of Br increased, the XRD patterns (e.g., (1 1 0) and (1 0 2) planes) showed a gradual change to the crystal structure of BiOBr. These findings indicate that BiOBr_xCl_{1-x} is likely a good hybrid state, which was also confirmed by the UV–vis absorption spectra (shown below). For the BiOBr, the XRD patterns matched those of tetragonal (*P*4/*nmm*) BiOBr (JCPDS 1-073-2061) well [15]. For this sample, the XRD peak corresponding to the (011) planes was reduced significantly when compared to other samples.

3.3. Optical properties and band gaps

The UV–vis reflectance absorption spectra for the $BiOBr_xCl_{1-x}$ catalyst are displayed in Fig. 4. The absorbance (*Y*-axis) was converted from diffuse reflectance by the Kubelka–Munk method. The band gap of each sample was measured by taking the absorption edge of the two extrapolated straight lines, which are shown in the inset



Fig. 3. Power X-ray diffraction patterns of $BiOBr_xCl_{1-x}$ ($0 \le x \le 1$) catalyts.

of Fig. 4. In this study, the band gap of BiOCl was measured to be \sim 3.2 eV. As the composition of Cl increased, the band gap decreased. The band gaps of 3.01, 2.90, 2.81 and 2.73 eV were measured for the BiOBr_{0.3}Cl_{0.7}, BiOBr_{0.5}Cl_{0.5}, BiOBr_{0.7}Cl_{0.3} and BiOBr catalysts, respectively. The band gaps were reported to differ slightly depending on the structures and compositions. A smaller band gap of 2.9 eV was reported for square-like BiOCl nanoplates [22]. Zhu et al. was able to tune the band gap of 3D BiOCl hierarchical structures from 3.05 eV to 3.32 eV by changing the ratio of urea/Bi³⁺ during synthesis [25]. Band gaps of 2.52 eV and 2.64 eV were reported for BiOBr sheets [2] and microspheres [15], respectively. Zhang et al. also obtained 3D flower-like microspheres in a glycol solvent by the solvothermal method, and measured band gaps of 3.1 eV, 2.61 eV and 2.6 eV for BiOCl, BiOClBr and BiOBr, respectively [7].

3.4. Photoluminescence spectra

Fig. 5 displays the photoluminescence (PL) of the BiOBr_x Cl_{1-x} catalysts taken under the same conditions (photon flux, slit widths, and an excitation wavelength of 280 nm). The luminescence occurs via recombination of an electron in the conduction band and a hole in the valence band. When the recombination rate is increased, the electron and hole become less involved in the photocatalytic reaction [14]. As a result, the catalyst showing a higher PL intensity will exhibit a lower photocatalytic activity. For the PL of BiOCl, two broad PL regions were found at around 360 nm and 440 nm, and the peak at 360 nm was 2 × stronger than that at 440 nm. As the composition of Br increased, the former peak decreased significantly, while the latter peaks showed a slight decrease. For the PL of BiOBr, only a broad PL region was observed at 440 nm. The integrated PL



Fig. 4. UV–vis diffuse reflectance absorption spectra of BiOBr_xCl_{1-x} $(0 \le x \le 1)$ catalyts. Inset shows the plot of $[ah\nu]^{1/2}$ versus $h\nu$ for the selected BiOBr and BiOCl samples.



Fig. 5. Photoluminescence spectra of $BiOBr_xCl_{1-x}$ ($0 \le x \le 1$) catalysts.

intensity was found to be in the order of BiOBr < BiOBr_{0.7} Cl_{0.3} < BiOBr_{0.5}Cl_{1-0.5} < BiOBr_{0.3}Cl_{0.7} < BiOCl. Based on these results, BiOBr is a more efficient photocatalyst than BiOCl. Qin et al. performed visible light photocatalytic experiments using BiOCl and BiOBr microspheres for the removal of MO and found that BiOBr was more efficient than BiOCl [2], which is consistent with our PL results.

3.5. Raman spectra

Fig. 6 displays the Raman spectra of the $BiOBr_xCl_{1-x}$ $(0 \le x \le 1)$ microspheres. Three major bands were commonly observed in the spectra. For BiOX (X=Br, Cl and I) with a tetragonal P4/mmm space group, the vibrational modes are described as 4, $\Gamma = 2A_{1g} + B_{1g} + 3E_g + 2E_u + 2A_{2u}$, where A_{1g} , B_{1g} , and $3E_g$ are Raman active, and others are IR active [11,20]. For the BiOBr catalyst, the strongest band was observed at 110 cm⁻¹, which was assigned to the A_{1g} mode of internal Bi-Br stretching. The band at 159 cm⁻ was attributed to the $E_{\rm g}$ mode of internal Bi-Br stretching [1]. The weakest band at around 380 cm^{-1} was attributed to the E_g/B_{1g} modes of oxygen atoms [9,18]. As the Cl composition increased, the bands gradually shifted to a longer wavenumber. For the BiOCl catalyst, the three bands (A_{1g} , E_g and E_g/B_{1g} modes) became stronger and positioned at 144 cm^{-1} , 200 cm^{-1} and 395 cm^{-1} , respectively (Fig. 6).

3.6. Adsorption and photocatalytic activity of MO

We first tested the adsorption of MO for various $BiOBr_xCl_{1-x}$ ($0 \le x \le 1$) catalysts under dark conditions (Fig. 7). We monitored the maximum band at 464 nm, which was associated with the azo (-N=N-) bond of MO. The adsorption performance was found to be in the order $BiOCl < BiOBr_{0.3}Cl_{0.7} < BiOBr_{0.5}Cl_{0.5} < BiOBr_{0.7}Cl_{0.3} < BiOBr.$ Next, the BET surface area was measured to evaluate the adsorption performance. The BET surface areas were found to be 16.9–20.8 m²/g for $BiOBr_xCl_{1-x}$ ($0 \le x < 1$) catalysts



Fig. 6. Raman spectra of $BiOBr_xCl_{1-x}$ ($0 \le x \le 1$) catalysts.

prepared in ethylene glycol (Table 1), which was not consistent with the adsorption performance. These findings indicate that other factors such as surface charges of the catalysts also play a role in adsorption [3]. Zhang et al. employed Zeta potential measurement to directly measure the surface charge of a BiOX catalyst, and explained the adsorption performance by introducing electrostatic interactions between the dye and the catalyst [3].

For a selected BiOBr_{0.7}Cl_{0.3} catalyst, we tested the photodegradation of MO, RhB, and MB, which show UV–vis absorption bands at around 450 nm, 550 nm and 650 nm, respectively. The adsorption and photodegradation tests for MO are displayed in Fig. 8. Upon subjecting the samples to adsorption for 4 h, the absorption peak was decreased by about 40%. However, under irradiation by daylight, the peak decreased by more than 60%. After 10 h, the UV–vis absorption intensity and color of the MO solution were drastically diminished when compared with those measured under dark conditions.

3.7. Adsorption and photocatalytic activity of RhB

The adsorption and photocatalytic activity of RhB solution (10 mg/L) are displayed in Fig. 9. Under dark conditions, the UV–vis absorption peak at 550 nm decreased sharply within 10 min. Upon adsorption for 3 h, the absorption peak was decreased by about 60%. The red color of the catalyst powder reflects dye adsorption; however, under irradiation by daylight (or incandescent

Table 1 Summarized BET surface areas of $BiOBr_xCl_{1-x}$ catalysts.

Samples	BiOBr	BiOBr _{0.7} Cl _{0.3}	BiOBr _{0.5} Cl _{0.5}	BiOBr _{0.3} Cl _{0.7}	BiOCl
Surface area (m²/g)	18.7	18.0	20.8	20.2	16.9



Fig. 7. Adsorption performance of 50 mg BiOBr_xCl_{1-x} ($0 \le x \le 1$) catalysts for MO (50 mg/L=ppm, 100 mL) with time under dark conditions. UV-vis absorption spectra are shown for the selected BiOBr catalyst sample.

light) the peak showed a sharper decrease. The RhB photodegraded much faster than the MO. Interestingly, under daylight irradiation for 5 min, the peak at 550 nm decreased by about 70%, and was completely suppressed within 2 h. Moreover, the original color of the dye solution disappeared completely. Finally, the catalyst powder turned yellowish-white (the original color of the catalyst), reflecting the complete photodegradation of the dye on the catalyst surface. We also observed a change in UV-vis absorption peak with increasing light irradiation time. It appears that the dye was first broken by active species such as $^{\circ}O_{2}^{-}$ radical to produce secondary products, which show UV-vis absorption in the shorter wavelength region. When $^{\circ}O_2^{-}$ radical scavenger was added during the photodegradation we observed no change in peak position (discussed later below). This indicates that oxygen plays a crucial role in the formation of the secondary products.



Fig. 8. Adsorption test (closed circle) of 50 mg BiOBr_{0.7}Cl_{0.3} catalyst for MO (10 mg/L, 100 mL) in the dark, and photodegradation test (open circle) under daylight conditions with time. Insets show the corresponding UV–vis absorption spectra with time, and the photos of the final solutions.

3.8. Adsorption and photocatalytic activity of MB

We further tested the catalyst with MB, which showed a major UV–vis absorption band at 650 nm (Fig. 10). The adsorption of the dye on the catalyst surface was initially very rapid, then continued gradually. During adsorption under dark conditions for 24 h, the peak decreased by about 70%. Interestingly, although the adsorption of MB was better than that of MO and Rh B, the MB photodegraded much more slowly. The high adsorption performance of MB and Rh B was attributed to the electrostatic interactions between the positively charged ions of the dye and the negatively charged surface of the BiOBr_{0.7}Cl_{0.3} catalyst [2]. For photodegradation, the performance was found to be in the order of RhB \ge MO > MB for the BiOBr_{0.7}Cl_{0.3} catalyst. These findings are consistent with



Fig. 10. Adsorption test (closed circle) of 50 mg $BiOBr_{0.7}Cl_{0.3}$ catalyst for MB (10 mg/L, 100 mL) in the dark, and photodegradation test (open circle) under bright conditions with time. Insets show the corresponding UV–vis absorption spectra with time.



Fig. 9. Adsorption test (closed square) of 50 mg BiOBr_{0.7}Cl_{0.3} catalyst for RhB (10 mg/L, 100 mL) in the dark, and photodegradation tests under daylight (closed circle) and incandescent light (closed triangle) conditions. Inset photos show red and white colors of the catalysts after adsorption and photodegradation experiments, respectively. The corresponding UV–vis absorption spectra (right) are displayed for the daylight condition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. Photocatalytic degradation of RhB with BiOBr_{0.7}Cl_{0.3} catalyst in the absence and presence of scavengers (BQ, EDTA and IPA) under visible light irradiation for 3 h. The corresponding UV-vis absorption spectra are shown on the right.

those reported in previous studies [1,13]. Chang et al. conducted a similar experiment evaluating BiOCl and BiOBr catalysts using RhB, MO and MB dye solutions [13] and found that RhB was most efficiently photodegraded on the catalysts, which was attributed to its having the most positive LUMO. Zhang et al. used BiOBr catalysts to decompose three different dyes and found that decomposition occurred in the order RhB \ge MO > MB [2].

3.9. Photodegradation mechanism of the dyes over $BiOBr_xCl_{1-x}$ catalysts

During the photodegradation of a dye, major active species of hydroxyl radicals ('OH), superoxide radicals $(^{\circ}O_2^{-})$, electrons (e^{-}) and holes (h^+) are commonly formed. Several techniques have been employed to examine the roles of these active species and detect reaction intermediates, including DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) EPR (electron paramagnetic resonance) spin trapping techniques [36,37], LC-MS (liquid chromatography-mass spectrometry) [38] and LC-SIR (selected ion recording)–MS [39,40] and HPLC (high performance liquid chromatography)-MS [41,42]. Since we could not use these powerful techniques, we employed an indirect chemical probe method in which active species scavengers were added during the photoreaction, after which the dye degradation was examined by UV-vis absorption spectroscopy [33-35,37,43].

Fig. 11 displays the photocatalytic degradation of RhB with BiOBr_{0.7}Cl_{0.3} catalyst in the absence and presence of scavengers (IPA, BQ and EDTA) under visible light irradiation for 3 h. For a dye solution without a scavenger, the UV–vis absorption intensity was decreased by 50% upon visible light irradiation for 3 h. Upon addition of scavengers for 'OH, 'O₂⁻ and h⁺ species, the dye degradations were all dramatically suppressed. The order was found to

be 'OH \approx 'O₂⁻ < h⁺ under visible light irradiation, indicating that the active species are formed and play important roles in the dye degradation. The formation mechanism of the active species is discussed in greater detail below. It is well known that BiOX (X=Cl, Br and I) catalysts are stable under a photocatalytic reaction [14]. We also confirmed by XRD (not shown here) that our synthesized catalysts were stable after the photocatalytic dye degradation reaction.

We further confirmed the formation of 'OH radical by photoluminescence spectroscopy using terephthalic acid and displayed in Fig. 12 [34,37,40,44]. When 'OH radicals are formed they react with terephthalic acid to form 2hydroxyterephthalic acid, which shows a luminescence peak at 425 nm under an excitation wavelength of 315 nm. We observed no emission signal after 3 h; however, the luminescence peak at 425 nm clearly appeared after visible light irradiation for 30 h. This result confirms that 'OH radical was produced, and that it was involved in the photocatalytic dye degradation reaction.

Based on the photodegradation performance of the three different dyes and the indirect chemical probe method, we propose the following photocatalytic dye sensitized mechanism [6,45], which is displayed in Fig. 13.

$$Dye + Visible light \rightarrow Dye(e^{-}_{CB} + h^{+}_{VB})$$
(1)

BiOBr_xCl_{1-x}(e⁻_{CB})+O₂(or surface O)→
$$^{\circ}O_2^{-}$$
(or $^{\circ}O^{-}$)
+BiOBr_xCl_{1-x} (3)

$$H_2 O \rightarrow H^+ + O H^- \tag{4}$$

$$H_2O + BiOBr_xCl_{1-x}(h^+_{VB}) \rightarrow OH + H^+$$
(5)

$$^{\circ}O_{2}^{-}(\text{or }^{\circ}O) + \text{H}^{+} \rightarrow ^{\circ}O_{2}\text{H}(\text{or }^{\circ}O\text{H})$$
(6)

$$O_2^-, h^+ \text{ or }OH + Dye/Dye^+ \rightarrow degradation products (7)$$

Under visible light irradiation, a dye absorbs visible light, after which an electron in the valence band (VB) of the dye is



Fig. 12. Photoluminescence spectra of terephthalic acid solution with $BiOBr_{0.7}Cl_{0.3}$ catalyst after visible light irradiation for 3 (broken black line) and 30 (thick blue line) hours. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 13. Photocatalytic degradation mechanism of a dye over the ${\rm BiOBr}_x{\rm Cl}_{1-x}$ catalysts.

Table 2

Summary of studies using $BiOBr_xCl_{1-x}$ catalysts.

photoexcited into the conduction band (CB) as in reaction (1). Direct photoexcitation from the VB of the catalyst to the CB is less likely because the band gap edge is located below 450 nm, which prevents the catalyst from absorbing visible light (Fig. 3). For the three dyes, negligible photodegradation was observed when there was no catalyst, indicating that an interfacial charge transfer process should be included in the reaction mechanism [6,45,53,54]. Electron transfer to the CB of the $BiOBr_xCl_{1-x}$ catalyst then occurs in reaction (2), where it reacts with adsorbed molecular oxygen (or atomic oxygen) to form ${}^{\circ}O_2^{-}$ (or ${}^{\circ}O^{-}$) radicals, as shown in reaction (3). The dye with a positive state (dye⁺) readily reacts with O_2^- to finally dissociate [46-48]. As shown in Fig. 11, the dye degradation was suppressed when the O_2^- radicals were scavenged. In (4), (5) and (6), active 'OH radicals may be formed and play a role in dye degradation. The formation of 'OH radicals was confirmed by photoluminescence spectroscopy (Fig. 12) or the scavenger test (Fig. 11).

Finally, to show the originality and new physical insights of the present study, we summarized previous studies conducted using the same catalysts in Table 2. BiOBr_xCl_{1-x} catalysts were commonly synthesized by hydrothermal and precipitation methods [49-52]. However, we employed a solvothermal method under ethylene glycol conditions and obtained 3D flower-like nanostructures. Gnayem and Sasson reported 3D flower-like structures, but they used a precipitation method in water and tested the photocatalytic activities of RhB and acetophenone [49]. Although the photocatalytic activity of $BiOBr_xCl_{1-x}$ with plate morphology was fully tested for RhB [50–52], no study of MO and MB with $BiOBr_xCl_{1-x}$ catalysts has been reported to date. However, in the present study, we further examined the photocatalytic degradation of MO and MB under visible light with 3D flower-like nanostructures and presented new experimental results. The recent researches of BiOXrelated catalysts have been reviewed by Ye et al.[55] and Zhao et al. [56] in greater detail.

4. Conclusions

Hierarchical flower-like $BiOBr_xCl_{1-x}$ ($0 \le x \le 1$) microspheres were successfully synthesized in ethylene glycol

Experimental condition and method	Morphology and test systems	Experimental data shown
$Bi(NO_3)_3\cdot 5H_2O,$ KCl, KBr, acetic acid, and surfactant in water. Precipitation at room temp. $[49]$	3D flower-like, RhB and acetophenone. Highest activity for BiOCl _{0.875} Br _{0.125}	SEM, XRD, BET. UV–vis absorption
Bi(NO ₃) ₃ ·5H ₂ O and NH ₄ OH in water by the hydrothermal method, followed by treatment with HCl and HBr [50]	Stacked 2D plates, RhB. Highest activity for BiOCl _{0.5} Br _{0.5}	SEM, XRD, BET. UV-vis absorption
Bi(NO ₃) ₃ · 5H ₂ O, KCl and KBr in water at 160 °C (12 h). Hydrothermal method [51]	2D-lamellar plates. RhB, 2-propanol	SEM, XRD, BET. UV-vis absorption. Raman, photocurrent measurements, electronic structure calculations
$Bi(NO_3)_3 \cdot 5H_2O$, KCl and KBr in ethanol. Precipitation at room temp. [52]	2D-lamellar Plates. RhB. Highest activity for BiOCl _{0.5} Br _{0.5}	XRD, HRTEM, UV–vis absorption, BET
Bi(NO ₃) ₃ ·5H ₂ O, KCl and KBr in EG at 120 °C (12 h). Solvothermal method (this study)	3D flower-like. MO, RhB and MB. Highest activity for BiOCl _{0.3} Br _{0.7}	SEM, XRD, BET. UV–vis absorption, Raman, PL, OH radical formation test

solvent by a solvothermal method. The adsorption and photocatalytic performance were tested for MO, RhB and MB.

This study presented several important findings:

- (1) The BiOBr_xCl_{1-x} catalyst showed band gaps in the range of 3.2 eV and 2.73 eV, which were dependent on the relative composition of Br and Cl.
- (2) Composition was an important factor for adsorption. The adsorption performance occurred in the order of $BiOCl < BiOBr_xCl_{1-x} < BiOBr$ for MO under dark conditions.
- (3) Methylene blue was found to be the most easily removed by adsorption. The adsorption performance was in the order of MO < RhB < MB for the selected BiOBr_{0.7}Cl_{0.3} catalyst, which was a result of electrostatic interactions between the catalyst and the dye.
- (4) RhB was the most easily photodegraded among the three different dyes. Under visible light irradiation, the dye degradation was found to be in the order of $MB < MO \ll RhB$ owing to light absorption by the dye followed by a charge transfer from the conduction band of the dye to that of the catalyst. The charge transfer process plays a major role in the photocatalytic activity.
- (5) For the photocatalytic dye degradation, the roles of active species were found to be in the order of $^{\circ}OH \approx ^{\circ}O_2^- < h^+$ under visible light irradiation based on the indirect chemical probe method. Photoluminescence spectra of terephthalic acid solution confirmed the formation of $^{\circ}OH$ radical over the catalyst during photoirradiation.

The present study provides information that will enable understanding of the adsorption and photodegradation mechanism, which will allow efficient development of an appropriate catalyst for such reactions.

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