

Influence of the pH Value on the Compositions and Properties of Bismuth Oxyiodides Photocatalysts by Hydrothermal Synthesis and Their Activity

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Abstract

A series of bismuth oxyiodides were prepared using autoclave hydrothermal methods. In the preparation procedure, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in HNO_3 , NaOH aqueous solution was added to adjust the pH value, and KI aqueous solution was then added to the suspension. The composition and morphologies of the bismuth oxyiodides were controlled by adjusting certain growth parameters, including reaction pH and temperature. The prepared samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, UV-vis diffuse reflectance spectra, and Brunauer-Emmett-Teller surface areas. Results show that a series of changes in the compounds occurred at different pH values and hydrothermal reactions, described as $\text{BiOI} \rightarrow \text{Bi}_4\text{O}_5\text{I}_2 \rightarrow \text{Bi}_7\text{O}_9\text{I}_3 \rightarrow \text{Bi}_5\text{O}_7\text{I} \rightarrow \alpha\text{-Bi}_2\text{O}_3$. We demonstrate that bismuth oxyiodides can be selectively prepared through adjusted pH value under the hydrothermal method. UV-Vis spectra show bismuth oxybromide materials to be indirect semiconductors with an optical bandgap of 1.65-3.2 eV. The photocatalytic activity of the samples was evaluated by photodegradation of Crystal Violet (CV) under visible light irradiation. Finally, intermediates of the process were separated, identified, and characterized by HPLC-ESI-MS techniques. The reaction mechanisms proposed in this study are useful for future application of this technology for dye degradation.

Keywords: Bismuth oxyiodide, Visible-light-responsive photocatalyst, Autoclave hydrothermal

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1 Introduction

Two of the most urgent issues currently facing modern society are depletion of energy resources and deterioration of the natural environment. Semiconductor-based photocatalysis is attracting extensive interest as a type of “green” technology to alleviate both of these problems by splitting water for green energy hydrogen production and degrading toxic pollutants [1]. However, the widely used photocatalyst TiO_2 is only active in the UV range [2], so developing more efficient visible-light-driven photocatalysts is indispensable. Although dye sensitization or doping of other elements makes the utilization of visible light possible [3], stable and efficient dyes are rare while dopants act as recombination centers for photogenerated electrons and holes. Therefore, many researchers have focused on the design and development of new single-phase effective photocatalysts under visible light irradiation.

The bismuth-based layered structure compounds, including the Aurivillius family, Sillen family, and Aurivillius – Sillen intergrows [4], have been extensively investigated as visible-light-driven photocatalysts because of their unique layered structure and high activity. The formed internal electric fields between the slabs are beneficial to inducing the efficient separation of photogenerated electron-hole pairs and then improving the photocatalytic activity of catalysts [5]. Bismuth oxyhalides, BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), belong to the family of main group multi-component metal oxyhalides V–VI–VII, an important class of ternary compounds, which have induced significant recent interest because of their unique and excellent optical, electrical, magnetic, and photoluminescence properties and their

potential photocatalytic abilities [6-7].

Bismuth oxyiodides, V-VI-VII ternary compounds with layered structures, have attracted recent attention because of their promising application as efficient photocatalysts [8-9]. Four different bismuth oxide iodides, including BiOI [6], Bi₄O₅I₂ [8], Bi₇O₉I₃ [7], and Bi₅O₇I [5], are known. Among them, BiOI and Bi₅O₇I have been reported to exhibit catalytic activity on degrading organic model pollutants by visible-light [6-7, 9], which may benefit from their special electronic structures. The conduction band bottom of these bismuth oxyiodides is mainly composed of Bi 6p orbits, and the valence band top primarily consists of Bi 6s, O 2p, and I 5p [10]. The Bi 6s and O 2p levels in bismuth oxides form dispersed hybridized valence bands [11], and incorporating I 5p orbits makes the valence band of bismuth oxyiodides more dispersed [5], which favors the migration of photogenerated holes and oxidation reaction. The internal electric fields between positive Bi_xO_yⁿ⁺ slabs and anionic iodide slabs induce efficient separation of photogenerated electron-hole pairs and improve the photocatalytic activity of the catalyst. Therefore, bismuth oxyiodides, with layered structures, are expected to demonstrate visible-light photocatalytic activity. This paper first reports the synthesis of bismuth oxyiodide powders with different compositions through autoclave hydrothermal treatment. The influences of precipitation pH on the compositions and photocatalytic properties of the bismuth oxyiodides were investigated from aqueous solutions. To our knowledge, this is the first report of photocatalytic activity comparing four bismuth oxyiodides with their composites.

2 Experimental

2.1 Materials

The purchased Bi (NO₃)₃•5H₂O, CV dye (TCI), and KI (Katayama) were obtained and used without any further purification. Reagent-grade nitric acid, sodium hydroxide, ammonium acetate, and HPLC-grade methanol were obtained from Merck. The de-ionized water used in this study was purified with a Milli-Q water ion-exchange system (Millipore Co.) for a resistivity of 1.8×10⁷ Ω-cm.

2.2 Synthesis of bismuth oxybromide

5 mmol of Bi (NO₃)₃ were first mixed in a 100 mL flask, followed by adding 5 mL of 4M HNO₃ with continuous stirring.

Table 1: Bismuth oxyiodides obtained under different reaction conditions.

Samples	pH	T(°C)	t(h)
BI-1-130-12	1	130	12
BI-1-180-12	1	180	12
BI-1-230-12	1	230	12
BI-1-280-12	1	280	12
BI-2-130-12	2	130	12
BI-2-180-12	2	180	12
BI-2-230-12	2	230	12
BI-2-280-12	2	280	12
BI-3-130-12	3	130	12
BI-3-180-12	3	180	12
BI-3-230-12	3	230	12
BI-3-280-12	3	280	12
BI-4-130-12	4	130	12
BI-4-180-12	4	180	12
BI-4-230-12	4	230	12
BI-4-280-12	4	280	12
BI-5-130-12	5	130	12
BI-5-180-12	5	180	12
BI-5-230-12	5	230	12
BI-5-280-12	5	280	12
BI-6-130-12	6	130	12
BI-6-180-12	6	180	12
BI-6-230-12	6	230	12
BI-6-280-12	6	280	12
BI-7-130-12	7	130	12
BI-7-180-12	7	180	12
BI-7-230-12	7	230	12
BI-7-280-12	7	280	12
BI-8-130-12	8	130	12
BI-8-180-12	8	180	12
BI-8-230-12	8	230	12
BI-8-280-12	8	280	12
BI-9-130-12	9	130	12
BI-9-180-12	9	180	12
BI-9-230-12	9	230	12
BI-9-280-12	9	280	12
BI-10-130-12	10	130	12
BI-10-180-12	10	180	12
BI-10-230-12	10	230	12
BI-10-280-12	10	280	12
BI-12-130-12	12	130	12
BI-12-180-12	12	180	12
BI-12-230-12	12	230	12
BI-12-280-12	12	280	12
BI-13-130-12	13	130	12
BI-13-180-12	13	180	12
BI-13-230-12	13	230	12
BI-13-280-12	13	280	12

2 M of NaOH was added dropwise to adjust the pH value to

1-14 and when a white precipitate was formed, 2 mL of KI was also added dropwise. The solution was then stirred vigorously for 30 min and transferred into a 30 mL Teflon-lined autoclave, which was heated to 130-280 °C for 12, 24, and 36 h and then naturally cooled to room temperature. After the reaction was completed, the resulting solid product was collected by filtration, washed with deionized water and methanol to remove any possible ionic species in the product, and then dried at 60 °C overnight. The samples are listed in **Table 1**.

2.3 Characterization

The precipitates were further characterized. Powder X-ray diffraction (XRD) was performed on a MAC Science, MXP18 X-ray diffractometer with Cu K α radiation, and operated at 40 kV and 80 mA. FE-SEM-EDS measurements were conducted with a field-emission microscope (JEOL JSM-7401F) at an acceleration voltage of 15 kV and an HRXPS measurement was conducted with ULVAC-PHI XPS. The Al K α radiation was generated with a voltage of 15 kV.

2.4 Photocatalytic reaction

Photocatalytic activities of bismuth oxyiodides were studied by degrading CV under visible light irradiation of a 20 watt lamp. An average irradiation intensity of 5.2 W/m² was maintained throughout the experiments and was measured by an internal radiometer. Aqueous dispersions of CV (100 mL, 10 ppm) and the given amount of catalyst powder were placed in a Pyrex flask. The pH value of the dispersions was adjusted by adding either NaOH or HNO₃ solutions. Before irradiation, the dispersions were magnetically stirred in the dark for 30 min to reach an adsorption/desorption equilibrium between the dye and the catalyst surface under ambient air-equilibrated conditions. At the given irradiation time intervals, 5 mL of aliquot was collected and centrifuged to remove the catalyst. The supernatant was analyzed by HPLC-ESI-MS

3 Results and Discussion

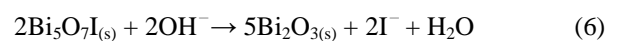
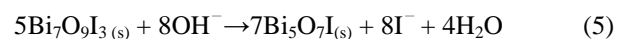
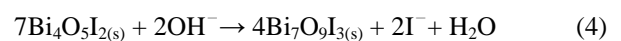
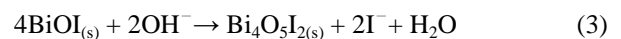
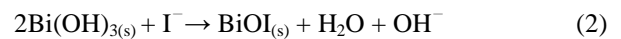
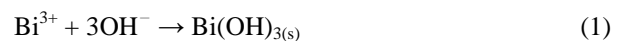
3.1 Characterizations of as-prepared powders

3.1.1 XRD analysis

The X-ray diffraction data of bismuth oxyiodide samples

prepared with different hydrothermal parameters are shown in **Figure 1**. All the bismuth oxyiodide samples synthesized using the hydrothermal method described at different temperatures and pH are BiOI (JCPDS 73-2062), Bi₄O₅I₂ [12], Bi₇O₉I₃ [12], and Bi₅O₇I (JCPDS 40-0548) phases.

Figure 1 shows the XRD patterns of as-prepared powders as a function of precipitation pH values, which displays that all the powders are well crystallized. For the samples synthesized at pH 3.0, the diffraction data obtained match well with the tetragonal phase BiOI [7], and no peaks of any other phases or impurities were detected. As the pH value was increased to 2, a new diffraction peak around 2 θ of 29.58 appeared along with those for the tetragonal BiOI, which could be identified as the characteristic peaks of Bi₄O₅I₂. This indicates that the samples obtained at pH 2 are composed of BiOI and Bi₄O₅I₂. Similarly, as the pH value was increased to 3, a new diffraction peak appeared, which could be identified as the characteristic peaks of Bi₇O₉I₃. This indicates that the samples obtained at pH 3-6 are composed of BiOI, Bi₄O₅I₂, and Bi₇O₉I₃. When the pH value was increased to 8-10, the characteristic peaks of Bi₄O₅I₂ disappeared and Bi₅O₇I₃ appeared. When the pH value was further increased to 8-10, the samples obtained are composed of Bi₇O₉I₃ and Bi₅O₇I. When the pH value was increased to 12, the characteristic peaks of Bi₇O₉I₃ disappeared, and the diffraction peaks matched well with the Bi₅O₇I pattern. The diffraction peaks of the sample prepared at pH 13 are those of the monoclinic phase Bi₅O₇I and Bi₂O₃, in which no impurity peaks were detected. By controlling the pH of the reaction, different compositions of bismuth oxyiodide were obtained. The possible processes for the formation of bismuth oxybromides can be described as follows [Eqs. (1)–(6)]:



These equations show that BiOI formed at the onset of the

reaction, then OH^- gradually substituted I^- in the basic conditions, which resulted in the reduced content of I^- in the products. Increasing the pH, $\text{Bi}_4\text{O}_5\text{I}_2$, $\text{Bi}_7\text{O}_9\text{I}_3$, $\text{Bi}_5\text{O}_7\text{I}$,

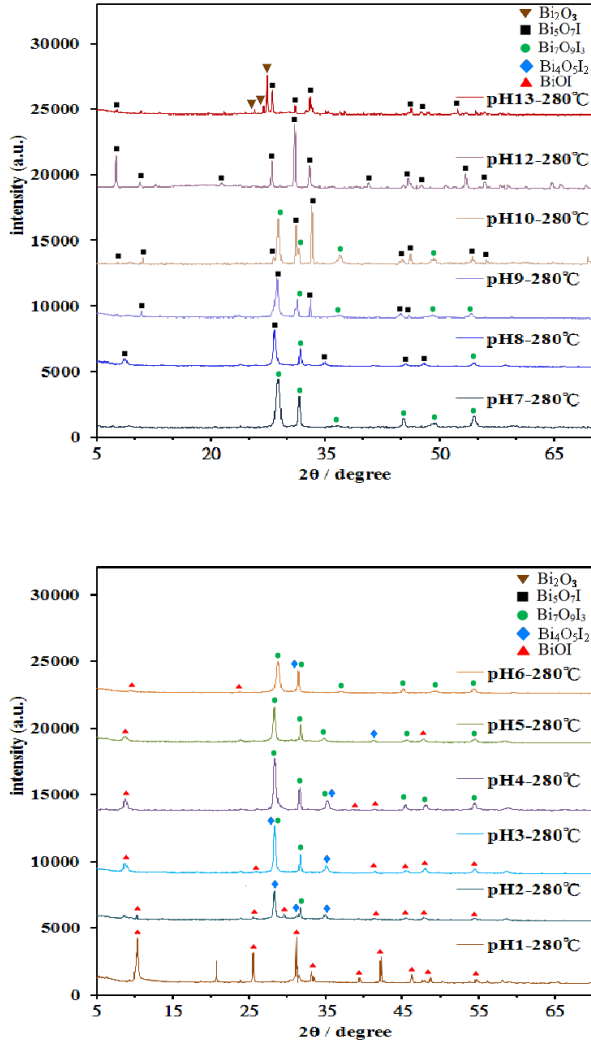


Figure 1: XRD patterns of as-prepared under different pH value, at 280 °C for 12 h

and Bi_2O_3 could be gradually obtained [9]. The higher the pH value, the lower the I^- content in the products, until the content of I^- in the products was fully replaced by OH^- , finally resulting in the formation of Bi_2O_3 under strong basic conditions. However, BiOI is the exclusive product at pH 1, $\text{Bi}_7\text{O}_9\text{I}_3$ is the exclusive product at pH 7 under higher temperature, $\text{Bi}_5\text{O}_7\text{I}$ is the exclusive product at pH 12. Generally, there is a competitive relationship between the OH^- and Br^- ions in basic solution.

3.1.2 SEM-EDS analysis

Bismuth oxyiodides were prepared with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

and KI by the hydrothermal method under different pH value and temperature. The surface morphology of the photocatalysts was examined by FE-SEM-EDS (**Figure 2**). These samples displayed the powders, irregular nanosheets and nanoplatelets resulted in rectangular-slat shapes with a lateral size of several micrometers and a thickness between 5 and 10 nm. EDS further confirmed the elementary chemical composition of the synthesized products in **Table 2**. The EDS and HR-XPS results show that the product's main elements are bismuth, oxygen, and iodine.

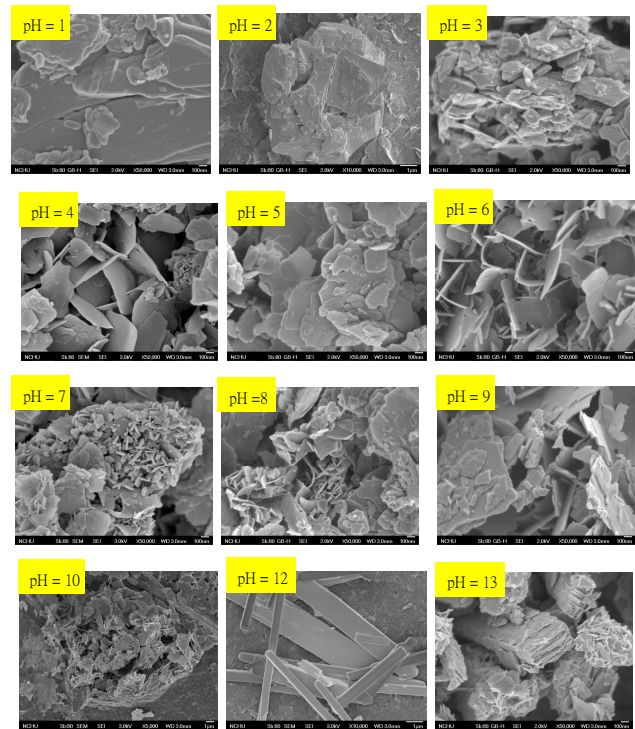


Figure 2: SEM images of bismuth oxyiodides prepared by the hydrothermal autoclave method at 280 °C, 12 h; for pH= 1-13.

3.1.3 XPS analysis

XPS was employed to examine the purity of the prepared bismuth oxyiodides products, and the spectra are shown in **Figure 3**. **Figure 3(a)** shows the total survey spectra of the Bi 4f, I 3d, and O 1s XPS of the four bismuth oxyiodide samples. The characteristic binding energy value of 157.9 eV for Bi 4f_{7/2} (**Figure 3 (b)**) reveals a trivalent oxidation state for bismuth. An additional spin-orbit doublet with binding energy of 155.5 eV for Bi 4f_{7/2} was also observed in all samples, suggesting that certain parts of bismuth existed in the (+3-x) valence state. This indicated that the trivalent bismuth was partially reduced to the lower

valence state by the hydrothermal autoclave method. A similar chemical shift of approximately 2.4-2.6 eV for Bi 4f_{7/2} was also observed [13]. They concluded that Bi (+3-x) formal oxidation state was most likely attributed to the substoichiometric forms of Bi within the Bi₂O₃ layer, and formation of the low oxidation state resulted in oxygen vacancy in the crystal lattice. However, we assumed that Bi (+3-x) formal oxidation state was most likely attributed to the substoichiometric forms of Bi at the outer site of the particles, and formation of the low oxidation state resulted in oxygen vacancy in the crystal surface. The binding energy of 629.7 eV and 618.0 eV were referred to the I 3d_{5/2} and 3d_{3/2} respectively, which can be assigned to the I at the monovalent oxidation state.

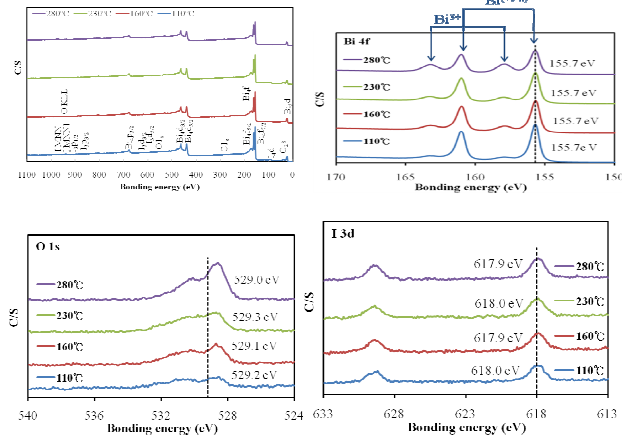


Figure 3. High resolution XPS spectra of the bismuth oxyiodide prepared by the hydrothermal autoclave method at 280 °C, 12 h, pH= 12.

3.1.4 UV-vis diffuse reflectance spectroscopy

The UV-vis adsorption spectra of synthesized catalysts are shown in **Figure 4**. Their corresponding band gap energies were calculated, which are close to 2.22-2.76 eV. Compared to P25, bismuth oxyiodides exhibit pronounced light absorbance abilities at $\lambda > 400$ nm, suggesting their potential photocatalytic activity under visible light. The steep shape and strong absorption in the visible region indicate that the visible light absorption was because of the intrinsic band gap transition between the valence band and the conduction band, rather than transition from the impurity levels [14]. The difference of band gap energy in the prepared bismuth oxyiodides can be ascribed to their individual composition with various characteristics.

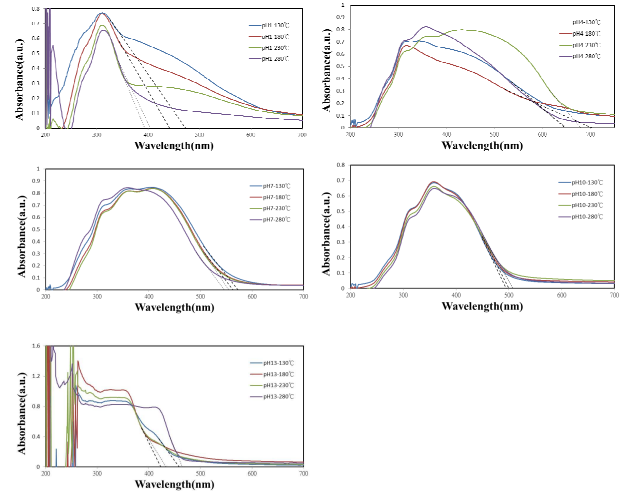


Figure 4: UV-vis absorption spectra of the prepared bismuth oxyiodide catalysts under temperature. (a) pH = 1; (b) pH = 4; (c) pH = 7; (d) pH = 10; (e) pH = 13.

3.2 Evaluation of Photocatalytic Activity

Photocatalytic performance of the bismuth oxyiodide catalysts were evaluated by degrading CV under visible light or UV irradiation with 0.5 g/L of catalyst added. The degradation efficiencies as a function of reaction time are illustrated in **Figure 5**. In the absence of catalysts, CV could not be degraded under visible or UV light irradiation. The removal efficiency was enhanced significantly in the presence of bismuth oxyiodides catalysts. After 24 h irradiation, bismuth oxyiodides showed superior photocatalytic performance, with CV removal efficiency up to 99.9%. The superior photocatalytic ability of bismuth oxyiodides may be ascribed to their efficient utilization of visible light and the high separation efficiency of the electron-hole pairs to their hierarchical structure.

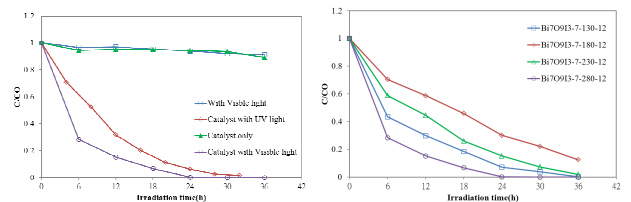


Figure 5: Photocatalytic degradation of CV by the resulting bismuth oxyiodide catalysts under visible light irradiation. (a) Control experiments; (b) Temp=130-280 °C, at pH 7 for 12 h.

4 Conclusion

The prepared bismuth oxyiodide catalysts of different phases, removed nearly 100% of CV from solution after 24 h under visible light irradiation, and the high photoactivity can be attributed to their relatively efficient utilization of visible light. Both removal efficiencies and kinetic analysis demonstrated the superior photocatalytic ability of bismuth oxyiodides.

Acknowledgments

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