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# A series of bismuth-oxychloride/bismuth-oxiodide/graphene-oxide nanocomposites: Synthesis, characterization, and photocatalytic activity and mechanism

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## ABSTRACT

This is the first report that a series of bismuth oxychloride/bismuth oxyiodide/graphene oxide ( $\text{BiO}_m\text{Cl}_n/\text{BiO}_x\text{I}_y/\text{GO}$ ) nanocomposites with different GO contents are synthesized through a simple hydrothermal method and characterized using X-ray diffraction, transmission electron microscopy, scanning electron microscopy energy-dispersive spectroscopy, Fourier transform infrared, X-ray photoelectron spectroscopy, and diffuse reflectance spectroscopy. The  $\text{BiO}_m\text{Cl}_n/\text{BiO}_x\text{I}_y/\text{GO}$  composites exhibit excellent photocatalytic activities in the degradation of crystal violet (CV) and phenol under visible light irradiation. The order of rate constants appears  $\text{BiOCl}/\text{Bi}_3\text{O}_4\text{Cl}/\text{BiOI}/\text{Bi}_7\text{O}_9\text{I}_3/\text{GO} > \text{BiOCl}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{BiOI}/\text{GO} > \text{BiOCl}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{BiOI}/\text{GO} > \text{BiOCl}/\text{Bi}_3\text{O}_4\text{Cl}/\text{BiOI}/\text{Bi}_7\text{O}_9\text{I}_3/\text{GO} > \text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{Bi}_5\text{O}_7\text{I}/\text{GO} > \text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{Bi}_5\text{O}_7\text{I}/\text{GO} > \text{Bi}_4\text{O}_5\text{I}_2 > \text{Bi}_7\text{O}_9\text{I}_3 > \text{BiOI} > \text{Bi}_5\text{O}_7\text{I} > \text{BiOCl} > \text{GO}$  for photocatalytic degradation of CV. The photocatalytic activity of  $\text{BiOCl}/\text{Bi}_3\text{O}_4\text{Cl}/\text{BiOI}/\text{Bi}_7\text{O}_9\text{I}_3/\text{GO}$  composites reaches a maximum rate constant of  $0.422 \text{ h}^{-1}$ , which is 2.3 times higher than that of  $\text{BiOCl}/\text{Bi}_3\text{O}_4\text{Cl}/\text{BiOI}/\text{Bi}_7\text{O}_9\text{I}_3$ , 9 and 2 times higher than that of BiOI and  $\text{Bi}_4\text{O}_5\text{I}_2$ , and 18 and 12 times higher than that of BiOCl and  $\text{Bi}_3\text{O}_4\text{Cl}$ . When being irradiated, it can produce two major active species, superoxide radical ( $\text{O}_2^{\cdot-}$ ) and hydroxyl radical ( $\cdot\text{OH}$ ), and a minor active species, singlet oxygen ( $^1\text{O}_2$ ), for the CV degradation.

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## 1. Introduction

Semiconductor photo-catalysis driven by visible light has sparked great research interest because it provides a valuable method for solving environmental pollution and energy supply problems. An environmentally potent and cheap photo-catalyst is an important component for practical applications of photo-catalysis [1]. The study of visible-light-driven photo-catalysts has attracted considerable attention as an alternative to the elimination of toxic materials from wastewater. The photo-catalytic degradation of CV dyes was researched using several systems to produce active species including  $\text{TiO}_2$  [2], ZnO [3],  $\text{BaTiO}_3$  [4], BiOI [5],  $\text{Bi}_2\text{WO}_6$  [6],  $\text{BiO}_x\text{Cl}_y/\text{BiO}_m\text{I}_n$  [7],  $\text{BiOBr}/\text{BiOI}$  [8],  $\text{PbBiO}_2\text{Br}/\text{BiOBr}$  [9],  $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$  [10],  $\text{Bi}_2\text{SiO}_5/\text{g-C}_3\text{N}_4$  [11], and  $\text{BiOI}/\text{GO}$  [12].

A simple and effective strategy for improving the photocatalytic activity of a photo-catalyst is the incorporation of a hetero-structure because hetero-composites (or heterojunction) have great potential for tuning the desired electronic properties of photo-catalysts and efficiently separating photo-induced

electron-hole pairs [13,14]. A new group of advantageous photocatalysts,  $\text{BiOX}$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) [15,16], have demonstrated unusual photo-catalytic efficiency because their unique layered structure features an internal static electric field vertical in each layer that may occasion more effective separation of photo-induced charge carriers.  $\text{BiOX}$  has received increasing interests because of its suitable energy gaps, stability, and relatively superior photo-catalytic activities [17,18]. It was reported that the band gaps of BiOI [19], BiOBr [8], BiOCl [20],  $\text{BiO}_x\text{Cl}_y/\text{BiO}_m\text{I}_n$  [7], and  $\text{Bi}_2\text{O}_3$  [21] were 1.75, 2.61, 3.37, 1.78–2.95, and 2.30 eV, respectively. It seemed that the gaps of all these semiconductors were in the visible-light range to catalyze the photocatalytic reaction.

BiOCl, a novel layered ternary semiconductor, has been drawn much attention for its remarkable photo-catalytic performance, which is comparable to or even better than that of  $\text{TiO}_2$  because of its open crystalline structure. However, the activity of BiOCl nanosheets is still far from satisfaction owing to the rapid recombination of photogenerated excitons and the indigent harvest of sunlight. However, because the valence band for bismuth oxyiodides ( $\text{BiO}_m\text{I}_n$ ) contains mostly  $\text{I}_{5p}$  and  $\text{O}_{2p}$  orbitals, whereas the conduction band is based on the  $\text{Bi}_{6p}$  orbital [22], iodine-poor  $\text{BiO}_m\text{I}_n$  could be demonstrated to have band-gap energy lower than it of  $\text{Bi}_2\text{O}_3$  but higher than it of BiOI [23]; hence, these materials

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might be used as visible-light responsive photocatalysts. In particular, the structure and composition of  $\text{BiO}_m\text{I}_n$  strongly influence their optical, electronic, oxidizing abilities, and other physicochemical properties, offering an opportunity to obtain novel photocatalysts for effective degradation of environmental and toxic pollutants. Following Keller and Kramer [24] who have first reported the practically unlimited solubility of the  $\text{BiOX}/\text{BiOY}$  ( $X, Y = \text{Cl, Br, I}$ ) systems, several articles were published disclosing the successful synthesis and the unique photocatalytic properties of similar oxyhalide materials. However, the synthesis methods, characterization, and evaluated properties of a series of  $\text{BiOX}/\text{BiOY}$  have remained rare until recently.

Graphene (GR) and its derivatives are excellent electron mediators due to their unique two-dimensional structures and superior conductivity, and have attracted numerous attentions recently [25]. Furthermore, it can be easily produced from graphite, which is cheap and naturally sufficient. According to a report, the theoretically specific surface area of GR reaches  $2630 \text{ m}^2/\text{g}$ . Therefore, it can be used as an ideal support material with improved interfacial contact and enhanced adsorption activity. GR has a powerful but flexible structure with high carrier mobility. Thus, a GR-based hybrid photocatalyst will show excellent photocatalytic efficiency, such as,  $\text{BiOI}/\text{GR}$  [26] and  $\text{BiOBr}/\text{GR}$  [27].

Two specific branches of GR research dealt with graphene oxide (GO) and reduced graphene oxide (rGO). This could be considered as a precursor of semiconductor/GO (or rGO) synthesis by either chemical or thermal processes. A previous study showed that the incorporation of GO with a metal oxide could enhance the photocatalytic activity [28]. Apparently, photocatalysis enhancement through GO is because a conjugate structure provides a pathway for the transport of charge carriers. Song et al. [29] synthesized an  $\text{Ag}/\text{Ag}_2\text{CO}_3/\text{rGO}$  composite that exhibited enhanced photocatalytic performance for the photocatalytic oxidation of organic pollutants. Metal oxide semiconductors finds unparalleled opportunity in wastewater purification under UV-vis light, largely encouraged by their divergent admirable features like stability, non-toxicity, ease of preparation, suitable band edge positions and facile generation of active oxygen species in the aqueous medium. Currently, many studies reported that the integration of GO and semiconductor or metal oxide photocatalyst, such as  $\text{Bi}_4\text{O}_5\text{I}_2$  [12],  $\text{BiOI}$  [26],  $\text{MoS}_2$  [30],  $\text{ZnO}$  [31],  $\text{Co}_2\text{O}_3/\text{TiO}_2$  [32],  $\text{TiO}_2$  [33],  $\text{BiVO}_4$  [34],  $\text{SrTiO}_3$  [35], and  $\text{BiFeO}_3$  [36], could form hybrid materials with superior photocatalytic activity. It is found that the  $\text{BiO}_x\text{I}_y/\text{GO}$  (or rGO, GR) composite shows higher photocatalytic activities than  $\text{BiO}_x\text{I}_y$  and GO (or rGO, GR) do for the photocatalytic degradation of dyes [37,38].

Previous studies showed that the incorporation of GO with a metal oxide could enhance photocatalytic activity. According to our literature search, a series of  $\text{BiO}_m\text{Cl}_n/\text{BiO}_x\text{I}_y/\text{GO}$ -assisted photocatalytic degradation of CV dyes under visible light irradiation has never been reported. This study synthesizes a series of  $\text{BiO}_m\text{Cl}_n/\text{BiO}_x\text{I}_y/\text{GO}$  nanocomposites with different GO contents, synthesizes through a simple hydrothermal method, and compares their photocatalytic activities in degrading CV in aqueous solutions under visible light irradiation. Possible photo-degradation mechanisms are proposed and discussed in this research. The study is useful in synthesizing  $\text{BiO}_m\text{Cl}_n/\text{BiO}_x\text{I}_y/\text{GO}$  and degrading dye for the future applications of environmental pollution and control.

## 2. Experimental Details

### 2.1. Materials

Graphite (Showa), isopropanol,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  (Merck),  $\text{KMnO}_4$  (Shimakyu),  $\text{NaNO}_3$ ,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , and  $\text{KI}$  (Katayama), CV dye

(TCI), *p*-benzoquinone (Alfa Aesar), sodium azide (Sigma), and ammonium oxalate (Osaka) were purchased and used without further purification. Reagent-grade sodium hydroxide, nitric acid, ammonium acetate, and high pressure liquid chromatography (HPLC)-grade methanol were obtained from Merck.

### 2.2. Instruments and analytical methods

Crystallinity and phase analysis was performed by powder X-ray diffraction (XRD) using a MAC Science MXP18 equipped with Cu-K $\alpha$  radiation and operated at 40 kV and 80 mA. Nanostructures were visualized by high-resolution transmission electron microscopy (HR-TEM). Images, selected area electron diffraction patterns, high resolution transmission electron microscopic (HRTEM) images, and energy-dispersive X-ray spectra (EDS) were obtained using a JEOL-2010 with an accelerating voltage of 200 kV. Al-K $\alpha$  radiation was generated at 15 kV. Surface morphology and composition were also visualized by a field emission scanning electron microscope electron-dispersive X-ray spectroscopy (FE-SEM-EDS). FE-SEM-EDS measurement was conducted using a JEOL JSM-7401F at an acceleration voltage of 15 kV. High resolution X-ray photoelectron spectroscopic measurement was conducted using an ULVAC-PHI. Binding energies were corrected to the C 1s peak at 284.6 eV and surface atomic compositions calculated via correction for the appropriate instrument response factors. Photoluminescence (PL) measurement was conducted on Hitachi F-7000. Ultraviolet photoelectron spectroscopic measurement was performed using an ULVAC-PHI XPS, PHI Quantera SXM. Brunauer-Emmett-Teller (BET) specific surface areas of samples ( $S_{\text{BET}}$ ) were measured with an automated system (Micrometrics Gemini) by using nitrogen gas as the adsorbate at liquid nitrogen temperature. Textural properties were characterized by nitrogen porosimetry on a surface area analyzer, to calculate pore size distributions and BET surface areas. The HPLC-PDAESI-MS system consisted of a Waters 1525 binary pump, 2998 photodiode array detector, and 717 plus autosampler, a ZQ2000 micromass detector. LC-MS analysis was undertaken to identify products of CV photodegradation. The amount of residual dye at each reaction cycle was determined by HPLC-PDA. Transmission FT-IR and ATR/FT-IR spectra were acquired with a Nicolet 5700 Fourier Transform Infrared spectrometer (Thermo) equipped with a Greasby-Specac advanced overhead (specaflo) ATR system P/N 1401 series.

### 2.3. Synthesis of $\text{BiO}_m\text{Cl}_n/\text{BiO}_x\text{I}_y/\text{GO}$

GO was synthesized by stirring 1 g powdered flake graphite and 0.5 g  $\text{NaNO}_3$  into 23 mL  $\text{H}_2\text{SO}_4$  at 0 °C ice bath. While maintaining vigorous agitation, 3 g  $\text{KMnO}_4$  was added to the suspension. The ice bath was then removed, and the temperature of the suspension was brought to 35 °C and maintained at that temperature overnight. Then, 3 g  $\text{KMnO}_4$  was added to the suspension, which was allowed to stand for 3 h. After 3 h, 46 mL  $\text{H}_2\text{O}$  was slowly stirred into the paste, causing violent effervescence and the temperature increasing to 95 °C. The diluted suspension, now brown in color, was maintained at this temperature for 15 min. The suspension was then further diluted to approximately 140 mL with warm water and treated with 30% (w)  $\text{H}_2\text{O}_2$  to reduce the residual  $\text{MnO}_4^-$  and  $\text{MnO}_2$  to bleach soluble  $\text{Mn}(\text{SO}_4)_2$ . Upon the treatment with peroxide, the suspension turned bright yellow. The suspension was filtered, and a yellow-brown filter cake was obtained. After washing the cake three times with a total of 140 mL warm water, the GO residue was dispersed in 100 mL of 10%  $\text{HCl}$ . Dry GO was obtained through centrifugation followed by drying in the oven at 60 °C overnight [12,39].

Five mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was first mixed in a 50-mL flask and then added 5 mL 4 M ethylene glycerol and GO powder. With con-

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