



# Efficient visible light photocatalytic oxidation of NO with hierarchical nanostructured 3D *flower-like* BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions



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## ABSTRACT

Bismuth oxyhalides (BiOX, X = Cl, Br, I) as effective photocatalysts have attracted a wide attention for its outstanding performance on air purification with solar energy. In this work, a series of band-gap engineered BiOCl<sub>x</sub>Br<sub>1-x</sub> homogeneous solid solution materials were explored as efficient visible-light induced photocatalysts. The BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solution photocatalysts with 3D hierarchical nanostructures have been successfully synthesized through a facile template free hydrothermal method. The prepared BiOCl<sub>x</sub>Br<sub>1-x</sub> possess a single tetragonal crystal structure without any secondary phases in spite of x varying from 0 to 1 indicating a homogeneous solid-solution characteristic. However, the band gaps of BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions are modulated from 3.30 to 2.75 eV by decreasing x from 1 to 0, which extends the light absorption from 375 nm to 450 nm. The obtained BiOCl<sub>0.5</sub>Br<sub>0.5</sub> sample displays enhanced photocatalytic activity for the oxidation of NO, with a good stability under visible light. The existence of hydroxyl radicals and super oxygen radicals confirm its photocatalytic activities. The highly enhanced visible light photocatalytic activity of BiOCl<sub>0.5</sub>Br<sub>0.5</sub> can be ascribed to the large specific surface area, hierarchical structures and the modified band structures. Furthermore, the modified band-gap adapts the balance between adequate redox potentials and effective visible light absorption. The present work provides novel insights into the design and synthesis of 3D hierarchical nanostructures with band-gap engineering to explore novel photocatalysts.

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## 1. Introduction

Since environmental pollution has exceeded the capacity of material self-purification, semiconductor photocatalysis has attracted a wide attention, particularly in the field of air and water purification [1–3]. TiO<sub>2</sub> is by far the leading commercial photocatalyst characterized by high activity, notable stability, simple processing and low cost [4]. Unfortunately, the efficiency of utilization of visible light is low due to the wide band gap. In recent years, hierarchical porous nanomaterials assembled from low dimensional nanoscale building blocks exhibited superior photocatalytic activity [5]. A high performance photocatalyst requires efficient separation and low recombination of photogenerated holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) to ensure that the oxidation and

reduction reactions can occur favourably in the valence band (VB) and conduction band (CB) of a semiconductor photocatalyst [6,7]. Many reports shows that 2D nanosheets favour the transfer of e<sup>-</sup> and h<sup>+</sup> to the crystal surface and avoid the e<sup>-</sup> and h<sup>+</sup> recombination [8–11]. Fabrication of hierarchical semiconductor materials assembled from 2D nanostructures showed higher photocatalytic activity than single 2D nanostructures because they can accelerate the separation process of photogenerated carriers and provide more active sites [10,11].

Bismuth oxyhalides (BiOX, X = Cl, Br, I) have lately gained considerable attention as effective photocatalysts. BiOX features unique crystal structures consisting of [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> slabs and interleaved halogen ion layers [12–14]. These layered crystal structures are favourable to the formation of a self-built internal static electric field, which is very beneficial to the separation and migration of photogenerated carriers [15,16]. In order to further enhance the visible light photocatalytic activities, BiOX-based heterojunction composite materials have been developed such as BiOI/Ag<sub>3</sub>PO<sub>4</sub> [17],

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BiOCl/WO<sub>3</sub> [18], BiOI/Bi<sub>2</sub>MoO<sub>6</sub> [19], BiOCl/BiOI [20], BiOBr/C<sub>3</sub>N<sub>4</sub> [21], BiOCl/C<sub>3</sub>N<sub>4</sub> [22], BiOBr/Bi<sub>2</sub>O<sub>3</sub> [23]. Another strategy to enhance the photocatalytic efficiency of BiOX system is to fabricate solid-solution photocatalysts, with aiming at engineering the band-gap. This strategy has succeeded in many examples for the elimination of pollution, such as BiOCl<sub>x</sub>Br<sub>1-x</sub> [24], BiOCl<sub>x</sub>I<sub>1-x</sub> [25]. These nanomaterials exhibited efficient visible light photocatalytic activities comparing to pure BiOX in degradation of various pollutants. Though the photocatalytic mechanism and active species in degradation of various pollutants have been intensively studied, as far as we knew, these in the oxidation of NO is still ambiguous.

In this study, we use a facile template free hydrothermal method to prepare 3D flowerlike BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions composed with 2D nanosheets and explore the photocatalytic activities of oxidizing NO. The prepared microstructure-modulated solid solution of 3D BiOCl<sub>x</sub>Br<sub>1-x</sub> hierarchical catalysts exhibit enhanced photocatalytic oxidation activity and durability under visible light illumination for the removal of 600 ppb level of nitric oxide (NO) in air. The structural features of the BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions were characterized in detail. And theoretical calculations of electronic band structures have been implemented to study the photocatalytic activities.

## 2. Experimental

### 2.1. Chemicals and synthesis of BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solution photocatalysts

All chemical reagents used in this study were analytical grade without further purification. BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions were synthesized by a simple template free method at 150 °C. In a typical synthesis, 2 mmol stoichiometric amounts of NaCl and NaBr were dissolved in 40 mL of deionized water. 2 mmol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was added into the above solution slowly with stirring for 2 h. After stirring continuously for 2 h, 1.0 g of NaOH was added under vigorous stirring for 5 h. Then, the solution was transferred to a 50 mL sealed teflon-lined steel autoclave. The Teflon-lined steel autoclave was heated at 150 °C for 12 h. After the Teflon-lined steel autoclave was cooled to ambient temperature, the sediments obtained was washed several times with distilled water and dried at 50 °C for 24 h. Depending on the molar ratio of NaCl and NaBr (1:0, 0.875:0.125, 0.75:0.25, 0.5:0.5, 0.375:0.625, 0.25:0.75, 0.125:0.875, 0:1), Different BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions were synthesized by adjusting x from 0 to 1 and labelled as sample S1 (BiOBr), S2 (BiOCl<sub>0.125</sub>Br<sub>0.875</sub>), S3 (BiOCl<sub>0.25</sub>Br<sub>0.75</sub>), S4 (BiOCl<sub>0.375</sub>Br<sub>0.625</sub>), S5 (BiOCl<sub>0.5</sub>Br<sub>0.5</sub>), S6 (BiOCl<sub>0.625</sub>Br<sub>0.375</sub>), S7 (BiOCl<sub>0.75</sub>Br<sub>0.25</sub>), S8 (BiOCl<sub>0.875</sub>Br<sub>0.125</sub>) and S9 (BiOCl), respectively. It was well known that the hydrolysis of Bi(NO<sub>3</sub>)<sub>3</sub> in water produced the BiONO<sub>3</sub> [26]. The formation of BiOCl<sub>x</sub>Br<sub>1-x</sub> solid solutions from the starting compounds follow the Eqs. (1)–(3).



### 2.2. Characterization

X-ray diffraction (XRD) analysis was conducted by using a PANalytical X'pert diffractometer operating at 40 kV and 40 mA using Cu K $\alpha$  radiation. Raman spectra were measured by using a LabRAM HR800 Raman spectrometer by exciting the samples with 532 nm laser. Field emission scanning electron microscopy (FE-

SEM, TESCAN MARI3) and transmission electron microscopy (TEM, FEI TECNAI G2 F20) were applied for the morphologies, sizes and structures of the samples. The UV–vis diffuse reflection spectra (DRS) were measured using a UV–vis spectrophotometer (Shimadzu UV3600) equipped with an integrating sphere assembly, using BaSO<sub>4</sub> as reflectance sample. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi with an Al K $\alpha$  X-ray source on the samples. The energy calibrations were referenced the C 1s peak at 284.6 eV to eliminate the charging of the sample during analysis. The photoluminescence (PL) spectra of the generated  $\cdot\text{OH}$  adduct TAOH was measured on a fluorescence spectrophotometer at 425 nm (Shimadzu RF-5301pc). Fluorescence was induced by excitation at 315 nm.

### 2.3. Photocatalytic experiments

The photocatalytic activity of BiOCl<sub>x</sub>Br<sub>1-x</sub> samples in the experiments was investigated by oxidizing NO at ppb levels in a continuous flow reactor at room temperature (The schematic flow diagram of reactor system are shown in Fig. S1 of Supplementary Material). Detailed reactor setup have been reported in previous studies [10]. A 100 W commercial tungsten halogen lamp was vertically placed outside the reactor with a distance of 30 cm. For the photocatalytic activity test, a 400 nm UV cutoff filter was used to eliminate the ultraviolet light. 0.2 g photocatalyst was dispersed in 20 mL water and ultrasonic treatment for 20 min then, the suspension was dispersion into a dish with a diameter of 10 cm and dried at 50 °C. The solid photocatalyst was finally coated on the dish uniformly. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N<sub>2</sub> balance). The initial concentration of NO was diluted to about 600 ppb by the air steam. The desired relative humidity (RH) level of the NO flow was set at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 2.4 L min<sup>-1</sup> by a mass flow controller. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The concentration of NO<sub>x</sub> was continuously measured by a chemiluminescence NO<sub>x</sub> (NO + NO<sub>2</sub>) analyser. The removal efficiency ( $\eta$ ) of NO is calculated as  $\eta$  (%) = (1 - C/C<sub>0</sub>) × 100%, where C<sub>0</sub> is the initial concentration of NO, and C is the concentration of NO<sub>x</sub> (NO + NO<sub>2</sub>) after photocatalytic reaction for time t.

### 2.4. Quantified detection of active species ( $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ )

The amount of  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  generated was quantitatively detected by terephthalic acid (TA) and nitroblue tetrazolium (NBT) transformation, respectively [27–29]. TA can react with  $\cdot\text{OH}$  to form highly fluorescent 2-hydroxyterephthalic acid (TAOH), which can be detected by a fluorescence spectrophotometer. The PL intensity of TAOH is proportional to the amount of  $\cdot\text{OH}$  produced during the photocatalytic process. NBT, which can react with  $\cdot\text{O}_2^-$  and displays a maximum absorbance at 259 nm, was selected to determine the amounts of  $\cdot\text{O}_2^-$  generated over the photocatalysts. The production of  $\cdot\text{O}_2^-$  was quantified by recording the concentration of NBT on a UV-3600 spectrophotometer.

### 2.5. Photoelectrochemical measurements

Photoelectrochemical properties were determined using a CHI-660B electrochemical system (China) at 0.0 V with a light intensity of 100 mW cm<sup>-2</sup>. The as-synthesized BiOCl<sub>x</sub>Br<sub>1-x</sub> samples were coated on indium-tin oxide (ITO) glass as the working electrode. A platinum plate and saturated Ag/AgCl electrode were utilized as the counter electrode and reference electrode, respectively. The

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