



# Bismuth-rich strategy induced photocatalytic molecular oxygen activation properties of bismuth oxyhalogen: The case of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$



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## ABSTRACT

Molecular oxygen activation is very important for photocatalytic degradation of organic pollutants. In this paper,  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$  nanosheets with {100} facets exposure were successfully synthesized by hydromel method and characterized. The size of a single nanosheet is about 5  $\mu\text{m}$  in width and 10–30 nm in thickness, which results in a large ratio of surface to thickness and higher exposure ratio of {100} facets. The Mott–Schottky test revealed that the conduction band minimum (CBM) of  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$  is more negative than  $\text{BiOCl}$  due to the bismuth-rich strategy. And the photocatalytic results showed that as-synthesized  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$  showed higher photocatalytic properties than  $\text{BiOCl}$  for activate molecular oxygen to generate superoxide radical ( $\text{O}_2^{\bullet-}$ ) under visible light ( $\lambda > 420\text{ nm}$ ) irradiation, and generate hydroxyl radical ( $\bullet\text{OH}$ ) under UV–vis light irradiation. This strategy in this work may potentially be extended to other bismuth-based photocatalysts for molecular oxygen activation.

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## 1. Introduction

Photocatalysis technology has been studied widely since the photocatalytic splitting of water by  $\text{TiO}_2$  electrodes was discovered in 1970s [1]. Due to its potential applications in environmental pollution purification and energy conversion, semiconductor photocatalysis technology has been considered as a green technology to completely eliminate the organic pollutants in an environmentally friendly manner [2–11]. There is no doubt that the photocatalyst is the most important part of the photocatalytic technology. Therefore, the development of high-performance photocatalysts has attracted great attentions and many new photocatalysts such as oxides, sulfides, element, and polymers semiconductor photocatalysts were studied.

Recently,  $\text{BiOX}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) photocatalysts have been widely studied for their outstanding optical, electrical and catalytic properties.  $\text{BiOX}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) are a new inorganic graphene type photocatalysts which exhibit excellent photocatalytic activities and has attracted much attention all over the world due to their unique layer structures and appropriate band gaps [12–23]. Among all the

$\text{BiOX}$  samples,  $\text{BiOCl}$  displays the best photocatalytic activity under UV light irradiation. For instance, Zhang and co-workers reported  $\text{BiOCl}$  exhibited better performance than  $\text{TiO}_2$  (P25, Degussa) on photocatalytic degradation of methyl orange (MO) [24]. However,  $\text{BiOCl}$  can not show high photocatalytic reduction activity caused by the lower position conduction band minimum (CBM) as well as can not be excited under visible light irradiation. DFT calculations indicated that the position of CBM is mainly determined by the  $\text{Bi } 6p$  of  $\text{BiOCl}$ . This suggested that an effective way to regulate the CBM position of  $\text{BiOX}$  is adjustment content of bismuth. For example, Huang found that the increments of the content of bismuth in bismuth titanate  $\text{Bi}_x\text{Ti}_y\text{O}_z$  can improve the position of CBM [25]. It indicates that the bismuth-rich strategy is feasible to improve the position of CBM and thus enhancing the photocatalytic reduction activity for  $\text{Bi}_x\text{O}_y\text{X}_z$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) photocatalysts. For instances, by bismuth-rich strategy,  $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$  displayed high photocatalytic activity the  $\text{Cr(VI)}$  reduction and  $\text{H}_2$  production from water [26].  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$  was synthesized by electrolytic corrosion of metal Bi, or calcination precursor, and it also showed high photocatalytic activity [27,28]. However, to the best of our knowledge, there are no reports about hydrothermal synthesis and photocatalytic molecular oxygen activation of  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ .

Molecular oxygen ( $\text{O}_2$ ) is the most inexpensive and green oxidant for oxidation reaction. Unfortunately, because of spin forbidden reactions,  $\text{O}_2$  cannot oxidize degrade most organic

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pollutants under ambient conditions [29]. Therefore, we all know that the reactive oxygen species (ROS, such as  $O_2^{\bullet-}$ ,  $H_2O_2$ , and  $\bullet OH$ ) are suggested as the main reactive species for photocatalytic degradation of pollutants. In photocatalytic process, molecular oxygen activation is occurred when photogenerated electrons on the surface of semiconductors reacting with  $O_2$  to produce  $O_2^{\bullet-}$  via one-electron reduction process, and then the  $O_2^{\bullet-}$  can be reduced to  $\bullet OH$  via two-electron reduction process [30,31]. So, it is very important to enhance the photocatalytic activity for molecular oxygen activation. In this work, via bismuth-rich strategy,  $Bi_{24}O_{31}Cl_{10}$  nanosheets with  $\{100\}$  facets exposure were synthesized, and its photocatalytic activity for molecular oxygen activation also were studied. The results showed that  $Bi_{24}O_{31}Cl_{10}$  activated molecular oxygen to generate  $O_2^{\bullet-}$  under visible light ( $\lambda > 420$  nm) irradiation, and generate hydroxyl radical ( $\bullet OH$ ) under UV–vis light irradiation.

## 2. Experimental

### 2.1. Materials and preparation

$Bi(NO_3)_3 \cdot 5H_2O$ , NaCl, Nitroblue tetrazolium (NBT), and ammonia solution ( $NH_3$ , 25–28%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ethanol were brought from Tianjin Kermel Chemical Reagent Co., Ltd. All the reagents we used were analytically pure without further purification.

For the syntheses of  $Bi_{24}O_{31}Cl_{10}$  nanosheets, 0.004 mol of  $Bi(NO_3)_3 \cdot 5H_2O$  and 0.004 mol of NaCl were dissolved in 24 mL of distilled water at room temperature with continuous stirring, and then ammonia solution was added dropwise to adjust the pH value of the solution to 10.3. The resulting solution were transferred into a 50 mL Teflon-lined stainless steel autoclave filled up to 80% of the total volume followed by a hydrothermal treatment at 160 °C for 18.5 h. After the reaction, the precipitate was collected, washed with deionized water and ethanol several times and dried at 60 °C in air. For comparison, BiOCl was obtained by using the same procedure without adding  $NH_3 \cdot H_2O$ .

### 2.2. Characterization

The crystalline phase of the samples was characterized by X-ray diffraction (XRD) by a Bruker D8 advance X-ray diffractometer at room temperature with Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm) and the  $2\theta$  ranging from 5 to 80°. Their size and morphology were inspected with scanning electron microscope (SEM, FEI, QUANTA 200). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) image was obtained by a JEOL JEM-2100 (RH) with operating at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with an Ar K $\alpha$  X-ray source. UV–vis diffuse reflectance spectra (DRS) were obtained using a Shimadzu UV-3600 spectrometer by using  $BaSO_4$  as a reference. Photoluminescence (PL) spectra of the samples were recorded on a Fluorescence Spectrophotometer (Varian, CARY Eclipse).

### 2.3. Photocatalytic properties for molecular oxygen activation

The photocatalytic activities were evaluated under visible light ( $\lambda > 420$  nm) or UV–vis light irradiation. The light was emitted by a 500 W high pressure xenon lamp (Changzhou Yuyu Electro-optical Device Co., Ltd. China). The visible light was obtained with a 420 nm cut-off filter using. Typical photocatalytic process is arranged in this way: 100 mL aqueous suspension of substrate (NBT ( $1.25 \times 10^{-5}$  mol/L) solution; TA ( $5 \times 10^{-4}$  mol/L) and NaOH ( $2 \times 10^{-3}$  mol/L) solution) were placed in a beaker, and then 20 mg

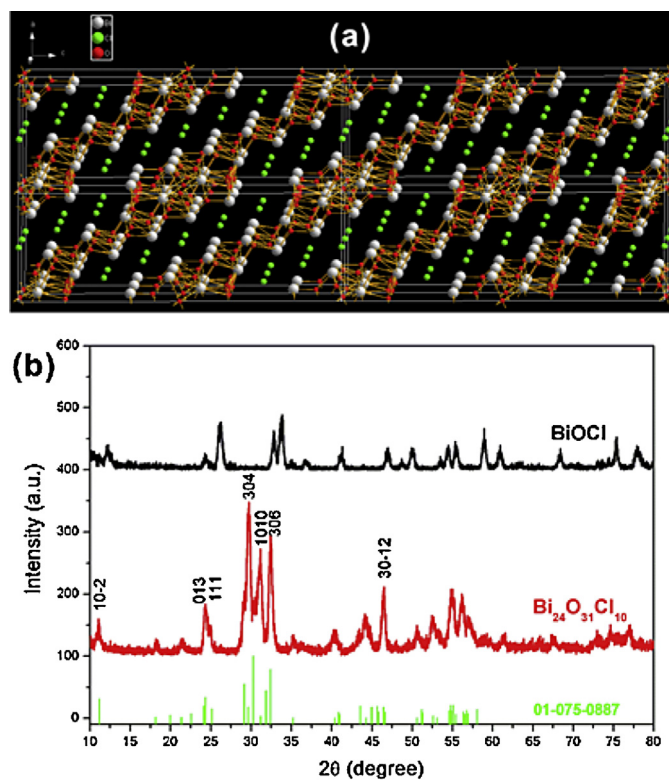


Fig. 1. (a) Schematic diagram of crystal structure of  $Bi_{24}O_{31}Cl_{10}$ , and (b) XRD patterns of as-prepared  $Bi_{24}O_{31}Cl_{10}$  and BiOCl.

photocatalysts were added. Prior to irradiation, the suspensions were sonicated for 20 min and then were continuously stirred in dark for 30 min to reach adsorption-desorption equilibrium. The suspensions were kept under constant air-equilibrated conditions during irradiation. A magnetic stirrer was employed for continuous mixing. At the given time intervals, 6 mL suspensions was sampled, centrifuged, filtered and measured every 20 min. The upper clear liquid of TA–NaOH solution was analyzed by recording by PL spectra (Varian, CARY Eclipse) with  $\lambda_{exc} = 315$  nm. The NBT solution was detected with UV–vis spectra (Perkin Elmer, Lambda 650s).

### 2.4. Electrochemical measurements

The Mott–Schottky curves were collected with an electrochemical analyzer (CHI660D, CHI Shanghai, Inc.) in a standard three electrode system. The  $Bi_{24}O_{31}Cl_{10}$  photoanode ( $1 \times 1$  cm $^2$ ), platinum plate, saturated calomel electrode (SCE), and saturated KCl solution were used as working, counter, reference electrodes, and electrolyte, respectively. The working electrode was prepared via the dip-coating method. The Mott–Schottky measurements were monitored with independence-potential model to evaluate the band positions of  $Bi_{24}O_{31}Cl_{10}$ . And they were monitored at a fixed frequency of 100 Hz with 10 mV amplitude at various potentials.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1a shows the schematic diagram of crystal structure of  $Bi_{24}O_{31}Cl_{10}$ . And Fig. 1b displays the XRD patterns of as-prepared  $Bi_{24}O_{31}Cl_{10}$  and BiOCl nanosheets prepared by hydrothermal process, respectively. XRD analysis of the samples showed that they were both well crystallized. They can well be indexed to the hexagonal structures of BiOCl (JCPDS File No. 73-20600), and monoclinic

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