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Solid phase fabrication of Bismuth-rich $Bi_3O_4Cl_xBr_{1-x}$ solid solution for enhanced photocatalytic NO removal under visible light

Yang Bai[a], Ping Yang[a,c], Pingquan Wang[a,*], Zhou Fan[a], Haiquan Xie[b], Po Keung Wong[d], Liqun Ye[a,b,**]

[a] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
[b] Engineering Technology Research Center of Henan Province for Solar Catalysis, Collaborative Innovation Center of Water Security for Water Source Region of Mid-line of South-to-North Diversion Project of Henan Province, Nanyang Normal University, Nanyang 473061, China
[c] College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China
[d] School of Life Sciences, The Chinese University of Hong Kong, Shatin, N.T, Hong Kong Special

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ABSTRACT

A new bismuth-rich $Bi_3O_4Cl_xBr_{1-x}$ solid solution photocatalyst was firstly synthesized through a solid phase conversion method. The X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), high-resolution transmission electron microscopy (HRTEM), UV–vis diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), and photoluminescence spectroscopy (PL) were used to characterize the physico-chemial properties of samples. Results demonstrated that $Bi_3O_4Cl_{0.5}Br_{0.5}$ had a higher activity than that of Bi_3O_4X (X = Cl, Br) for photocatalytic NO removal. The valence band XPS and photoelectrochemical analyses, theoretical calculation and scavenger trapping experiment indicated that $Bi_3O_4Cl_{0.5}Br_{0.5}$ had higher photocatalytic oxidation ability and effective prohibition the recombination of photo-induced charged carriers. This study suggested that solid solution should be effective approach to improve the photocatalytic activity of bismuth-rich photocatalysts for air purification.

1. Introduction

Environmental and energy crises are the crucial focus for human existence and development. The semiconductor photocatalysis is an efficient route to solve these issues. In the last few decades, TiO_2 and ZnO as the traditional photocatalysts that exhibited the narrow visible light response scope owing to their broad band gap, which limits the application of sunlight [1,2]. In order to improve the photocatalytic practical application, a multitude of workers devote themselves to researching new photocatalytic materials. For instances, sulfide-based, silver-based, and bismuth-based semiconductors photocatalysts were reported [3].

BiOX (X = Cl, Br and I) semiconductors were the most important bismuth-based photocatalysts. It displayed outstanding photocatalytic activity due to their unique layered structure with the $[Bi_2O_2]$ slabs intersected by double slabs of halogen atoms [4,5]. For instance, a series of BiOX photocatalysts ware reported by Zhang's group, which displayed notably photocatalytic property through visible light irradiation [6–9]. Our group also fabricated numerous BiOX photocatalysts with superior activities for photocatalytic H_2 evolution and dye degradation [10–12]. Meanwhile, many strategies, such as facet engineering [14–19], doping [20,21], and coupling [22–25], have been used to improve the BiOX practical application. Recently, the strategies of solid solution, and bismuth-rich were used to improve the photocatalytic activity and stability of BiOX. Solid solution is alloy phase in which the solute atoms dissolve into the solvent lattice and remain the solvent type. And our previous work proved that solid solution can enhance exciton photocatalytic process for effective pollutant degradation [26]. For Bi-O-X photocatatytic materials, $BiOCl_xI_{1-x}$, $BiOBr_xI_{1-x}$, $BiOCl_xBr_{1-x}$ were prepared by solvothermal method. And they displayed more excellent photocatalytic activity for dye degradation than the corresponding monomers [27–29]. For bismuth-rich strategy, Bi_5O_7Br and Bi_5O_7I can availably activated molecular oxygen and nitrogen, respectively [30,31]. $Bi_{12}O_{17}X_2$ (X = Br and Cl) showed effective photocatalytic activities for generation H_2 and degradation Rhodamine B (RhB) under visible light [32–34]. Photocatalytic reduction of Cr(VI) and degradation of dye were

* Corresponding author.
** Corresponding author at: Engineering Technology Research Center of Henan Province for Solar Catalysis, Collaborative Innovation Center of Water Security for Water Source Region of Mid-line of South-to-North Diversion Project of Henan Province, Nanyang Normal University, Nanyang 473061, China.
E-mail addresses: baiyanghyq@foxmail.com (P. Wang), yeliquny@163.com (L. Ye).

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evaluated by the $Bi_{24}O_{31}X_{10}$ (X = Br and Cl) [35–38]. $Bi_4O_5X_2$ (X = Br and I) displayed remarkable photocatalytic performance for H_2 production, CO_2 conversion, and degradation of 4–tert–butylphenol [39–41]. In this work, the strategies of bismuth-rich and solid solution were combined to enhance the photocatalytic activity of BiOX.

One of the most common gaseous pollutants is nitrogen monoxide (NO) [42]. At present, the physical adsorption and thermal catalysis methods are the traditional techniques, which cannot eliminate NO at low concentration (ppb) levels in indoor air [43]. Taking into consideration environmental cleaning, photocatalysis has received significant attention, which especially for the decontamination of air pollutants at low concentrations. Recently, BiOX was used for NO removal, and showed higher efficiency than TiO_2 system [44]. For example, *Dong* fabricated the single-crystal nanoplates of BiOX (X = Cl, Br, I) utilizing removal of NO [45]. The BiOI hollow microspheres were performed by Zhang's group, which applied for the photocatalytic removal of NO [46]. The BiOBr microspheres also showed exceedingly photocatalysis activity of NO removal [42]. However, there is no report on Bi_3O_4X (X = Cl and Br) photocatalytic activity for NO removal. In this work, bismuth-rich $Bi_3O_4Cl_xBr_{1-x}$($x = 0$, 0.15, 0.35, 0.5, 0.65, 0.85, 1) solid solution was firstly synthesized through the solid phase conversion method. The photocatalytic data showed than $Bi_3O_4Cl_{0.5}Br_{0.5}$ can remove 60% NO within 10 min under visible light irradiation, which has the higher degradation rate than that of pure Bi_3O_4X (X = Br and Cl).

2. Experimental section

2.1. Materials

Bismuth nitrate ($Bi(NO_3)_3$•$5H_2O$), potassium bromide (KBr), potassium chloride (KCl),bismuth oxide(Bi_2O_3), and ethyl alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All materials were of analytic reagent and without further treatment.

2.2. Synthesis

BiOX: BiOX (X = Cl, Br) was fabricated via the hydrothermal method. Four mmol $Bi(NO_3)_3$•$5H_2O$ was dispersed in 35 mL deionized water under stirring, KX (X = Br or/and Cl; 4 mmol) was respectively dissolved in another 35 ml deionized water stirring for 30 min. Then KX solution was slowly pour into the $Bi(NO_3)_3$·$5H_2O$ solution with serially stirring for 30 min. Transferred the suspension solution into a 100 ml Teflon-lined autoclave, kept at 160 °C for 16 h, and cooled to room temperature. BiOX was obtained by centrifuging, washing with deionized water and ethyl alcohol several times, and drying at 60 °C for 12 h.

$Bi_3O_4Cl_xBr_{1-x}$: $Bi_3O_4Br_xCl_{1-x}$, Bi_3O_4Cl, and Bi_3O_4Br were synthesized through the solid-state reaction with Bi_2O_3 and BiOX. Stoichiometric proportion of 2 mmol Bi_2O_3 and 2 mmol BiOX (X = Br, or/and Cl) were mixed with grinding and annealed at 600 °C for 6 h with the 5 °C/min heating rate, and then chilled to room temperature.

2.3. Characterization

X-ray diffraction (XRD) analyzed the phase and crystal structure of the samples was conducted by a Bruker D8 diffractometer using Cu Ka radiation, and the scanning region was from 5° to 70° with the 2θ sweep speed of 6 min^{-1}. Morphology of the photocatalysts was observed by a Quanta 450 scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were obtained by a JEOL JEM-2100F (UHR) field emission transmission electron microscopy. UV–vis diffuse reflectance spectroscopy (DRS) of samples were obtained by a UV–vis spectrometer (Perkin Elmer, Lambda 650 s, $BaSO_4$ as a reference) with a scanning range of 200–800 nm. X-ray photoelectron spectroscopic (XPS) results of samples was determined by a Thermos Scientific ESCALAB 250XI X-ray photoelectron spectrometer (Al Ka, 150 W, and C1s 284.6 eV). PL spectra of the samples were determined by a FLS920 Multifunction Steady State and Transient State Fluorescence Spectrometer (Edinburgh Instruments) at room temperature.

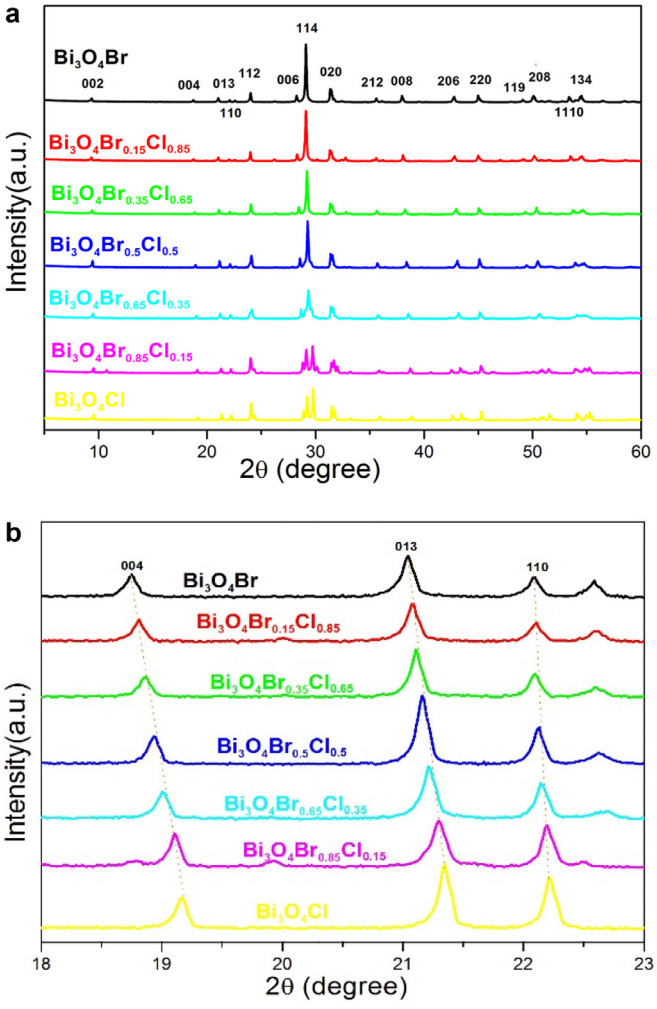

Fig 1. XRD patterns of $Bi_3O_4Cl_xBr_{1-x}$($x = 0$, 0.15, 0.35, 0.5, 0.65, 0.85, 1): (a) 5°–70°, and (b) 18°–23°.

2.4. Photocatalytic NO removal experiments

Photocatalytic NO removal experiments were conducted at room temperature in a consecutive flow quartz reactor ($H = 10$ cm; $L = 30$ cm; $W = 15$ cm). In the middle of the reactor, putted a sample dish (diameter, 12 cm) including the 0.12 g of sample was unrolled on it. A 30 Watt LED lamp ($\lambda = 448$ nm) was used as the simulated visible light source. NO gas was from a compressed gas cylinder at a concentration of 48 ppm NO (N_2 balance, BOC gas) with traceable National Institute of Stands and Technology (NIST) standard. Diluted the initial concentration of NO to about 600 ppb by the air supplied by a zero air generator (Thermo Environmental Inc. model 111). The humidity grade of the NO flow was kept at 70% by passing the zero air streams through a humidification chamber. The gas streams were pre-mixed totally through

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