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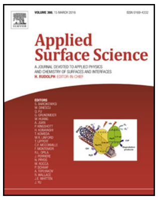

The highly enhanced visible light photocatalytic degradation of gaseous *o*-dichlorobenzene through fabricating like-flowers $BiPO_4$/BiOBr p-n heterojunction composites

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ABSTRACT

In this paper, in order to enhance photo-induced electron-hole pairs separation of BiOBr, flowers-like $BiPO_4$/BiOBr p-n heterojunction composites was fabricated by a mixing in solvent method. The as-prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), UV–vis absorption spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), and N_2 adsorption-desorption. Meanwhile, their photocatalytic properties were investigated by the degradation of gaseous *o*-dichlorobenzene under visible light irradiation. Due to its strong adsorption capacity and the formation of p-n heterojunction, compared with $BiPO_4$ and BiOBr, the $BiPO_4$/BiOBr composites showed higher photocatalytic activity in the degradation of gaseous *o*-DCB under visible light. Among them, 2% $BiPO_4$/BiOBr showed the maximum value of the activity, whose degradation rate was about 2.6 times as great as the pure BiOBr. Furthermore, the $OH^\bullet$ was confirmed the main active species during the photocatalytic process by the trapping experiments. The outstanding performance indicated that the photocatalysts could be applied to air purification for chlorinated volatile organic compound.

1. Introduction

During the incineration of municipal solid and medical wastes, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), which are as volatile organic compounds (VOCs), are produced [1,2]. These pollutions have attracted much attention for their carcinogenicity, high toxicity and persistent in the environment. Generally, 1, 2-dichlorobenzene (*o*-DCB), as typical chlorinated benzene, is usually chosen as the model compound owing to the dangers and complexities of PCDDs/PCDFs [3–6]. Up to now, the main removal methods for chlorinated benzenes are catalytic oxidation or combustion, and are studied by some research groups in the world. However, there exist some disadvantages for these methods, such as the consumption of large amounts of energy and producing many secondary pollutants. Photocatalytic oxidation technology, which is as advanced oxidation processes, has been attracted for environmental contaminations degradation because it can completely decompose pollutions into carbon dioxide and water at ambient conditions [7–15]. At present, although TiO_2 has been extensively investigated and widely employed, it is limited to utilization due to its low seperation efficiency of photo-induced electron-hole pairs and wide bandgap [16–18]. Hence, visible-light-driven photocatalysts is necessary, and the research has received particular interest in recent years.

Recently, bismuth oxyhalide BiOX (X = F, Cl, Br, I), a new family of promising photocatalysts, has been attracted in potential application [19–27]. Among them, BiOBr is of great research interset attracted in potential application as a visible light photocatalyst due to its stability, suitable band gap and excellent photocatalytic activity [23,28,29]. BiOBr is characterized by $[Bi_2O_2]$ slabs interleaved by double slabs of bromine atoms, which is p-type semiconductor. The intrinsic layered structure, which can lead to a strong internal electric field between the Br negative layer and $[Bi_2O_2]$ positive layer, can effectively enhance the separation probability of the photo-induced electron-hole pairs and favor the enhancement of the photocatalytic activity. Nonetheless, the pho-

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tocatalytic activity of BiOBr is usually unsatisfactory due to the rapid recombination of photo-induced electron-hole pairs and it needs some further improvements [27,30–32]. On the one hand, in order to effectively remove pollutions, various micro- and nanomaterials have already adopted, such as microspheres, nanotubes and nanospheres and so on [33]. Among them, BiOBr microspheres have attracted much attention owing to its large surface area, which can enhance the physical adsorption [29]. On the other hand, p-n heterojunction, which can be as an efficient and promising method for enhancing the photocatalytic activity of BiOBr, can extend the probability of photo-induced electron-hole separation via an additional internal electric field [27,34–36]. Up to now, some p-n heterojunction photocatalysts have been developed, for example BiOBr nanosheets@TiO_2 nanobelts [37], BiOBr/$CoFe_2O_4$ [9] and Bi_2WO_6/BiOBr [38]. The results indicate that these p-n junction photocatalysts display much higher photocatalytic activity than the individual compound. Recently, $BiPO_4$, which is used as a new n-type semiconductor photocatalyst, has been reported to possess excellent photocatalytic activity in the UV region [39,40]. PO_4^{3-}, which possesses a large negative charge, is postulated to help the electron-hole pairs separation, which plays an important role in its excellent photocatalytic activity. Duo et al. fabricated $BiPO_4$/BiOBr via a facile one-step hydrothermal method and $BiPO_4$/BiOBr composite displayed higher photocatalytic activity than pure $BiPO_4$ and BiOBr for the degradation of Rhodamine B under visible light irradiation [41]. Dong et al. reported that BiOBr/rod-like $BiPO_4$ were synthesized by a two-step method and it performed optimal photocatalytic activity of degrading Rhodamine B under visible light [42]. Furthermore, $BiPO_4$ nanoparticles/BiOBr hierarchical microspheres were fabricated by Liu et al. and it exhibited obviously increased photocatalytic activity in degradation of Rhodamine B [43]. However, in these reports, the fabricated $BiPO_4$/BiOBr composite is mainly used in degradation of liquid phase pollutions.

Therefore, in this paper, in order to improve the separation efficiency of photo-induced electron-hole pairs of BiOBr under visible light, on the one hand, the morphology of BiOBr was controlled by fabrication method. On the other hand, heterojunction was formed between BiOBr and $BiPO_4$, which was prepared by a mixing in solvent method. Furthermore, the mechanism of enhancing photocatalytic performance of gaseous *o*-DCB over $BiPO_4$/BiOBr composite has been discussed in detail with spectral characterization.

2. Experimental

All chemicals were used as received without any further modification. $Bi(NO_3)_3 \cdot 5H_2O$, ethylene glycol, hexadecyltrimethylammonium bromide (CTAB), Na_2CO_3, $Na_3PO_4 \cdot 12H_2O$, H_3PO_4 and anhydrous ethanol were purchased from Tianjin Kermel Chemical Reagents Development Centre.

2.1. Synthesis of flowers-like BiOBr microspheres

BiOBr was synthesized by a solvothermal method. 0.5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was added into 5 mL ethylene glycol. Then 0.5 mmol CTAB was added into the mixture under stirring. Subsequently, Na_2CO_3 was added in drops until the value of pH was 3. After being stirred for 30 min, the resulting solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 130 °C for 6 h. The products were washed three times with distilled water and anhydrous ethanol respectively before it dried at 120 °C.

2.2. Synthesis of $BiPO_4$ nanoparticles

$BiPO_4$ was synthesized by solvothermal process. Typically, 3 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was soluted into 100 mL ethylene glycol under magnetic stirring. Then 3 mmol $Na_3PO_4 \cdot 12H_2O$ was added into the mixture and stirred for 1 h. Subsequently, 30 mL of H_3PO_4 (12 M) was added into the solution. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 6 h. The products were washed three times with distilled water and anhydrous ethanol respectively before it dried at 60 °C for 12 h.

2.3. Synthesis of $BiPO_4$/BiOBr p-n heterojunction composites

The $BiPO_4$/BiOBr p–n junction composites with different amount of $BiPO_4$ were prepared using a mixing in solvent method. Typically, BiOBr powder was immersed into a certain amount of $BiPO_4$ with anhydrous ethanol as solvent under stirring. The as-prepared $BiPO_4$/BiOBr powder was aged at room temperature overnight and then dried at 70 °C for 12 h. The prepared samples were denoted as x% $BiPO_4$, where x refers to the weight ratio of $BiPO_4$ (x = 1%, 2%, 3%, 4% and 5%).

2.4. Characterization of $BiPO_4$/BiOBr p-n heterojunction composites

The morphology of materials was observed using a scanning electron microscope (SEM, JSM-5600LV, Oxford, UK). Crystallographic, crystallinity, and purity information were recorded by X-ray diffraction (XRD) using a powder X-ray diffractometer (Bruker D8, Germany, $\lambda = 1.5406$ Å) with a scan rate of $0.02^\circ\ s^{-1}$ over a 2θ range from 10 to 70°. The pore structure of the obtained sample was characterized by N_2 adsorption using an adsorption apparatus (Quantachrome autosorb-iQ-2MP gas sorption analyzer). Specific surface area of the samples was determined from the Brunauer-Emmett-Teller (BET) equation, and pore volume was determined from the total amount adsorbed at relative pressures near unity. UV–vis diffuse reflectance spectra (DRS) of the products were collected on an UV–vis spectrophotometer (UV-2600, Shimadzu, Japan). The transmission IR spectra were recorded through FTIR spectroscopy (Bruker VERTEX 70 equipped with a DTGS detector, Germany) with a resolution of $1\ cm^{-1}$ ranging from 4000 to $500\ cm^{-1}$. The photoluminescence (PL) spectra were measured using a Cary-300 spectrofluorometer (Agilent) with excitation wavelength 380 nm. The electron spin resonance (ESR) signals of the radicals trapped by 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) were detected at ambient temperature with a Bruker (E500) spectrometer. The irradiation source was a Quanta-Ray Nd: YAG pulsed laser system ($\lambda = 532$ nm, 10 Hz). The settings for the ESR spectrometer were as follows: center field = 3510 G; sweep width = 200 G; microwave frequency = 9.85 GHz; modulation frequency = 100 kHz and power = 20 mW. To minimize measurement error s, the same quartz capillary tube was used throughout the ESR measurements.

2.5. Photocatalytic activity test

The removal efficiency of gaseous *o*-DCB was evaluated in a home-built in situ quartz reaction cell. For visible light, a 500 W Xenon lamp equipped with a UV-cut off filter ($\lambda > 400$ nm) was chosen. The photocatalysts (0.02 g) pressed into the wafer profile were fixed to the holder of the cell and then the system was sealed up. At that time, the reaction conditions were under a dry air atmosphere and the temperature was about 30 °C. The pollutant was brought into the reaction cell by injecting liquid *o*-DCB (5 μL) into a rubber hose with a micro syringe. After an hour of volatilization and adsorption in the dark, the gaseous *o*-DCB would reach equilibrium on the surface of these catalysts, and at that moment the concentration of *o*-DCB was designated as the initial value. During the photocatalytic reaction, the pollutant concentration was detected at regular intervals through injecting the gas mixture (1 mL) from

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