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Ionic liquid-induced double regulation of carbon quantum dots modified bismuth oxychloride/bismuth oxybromide nanosheets with enhanced visible-light photocatalytic activity

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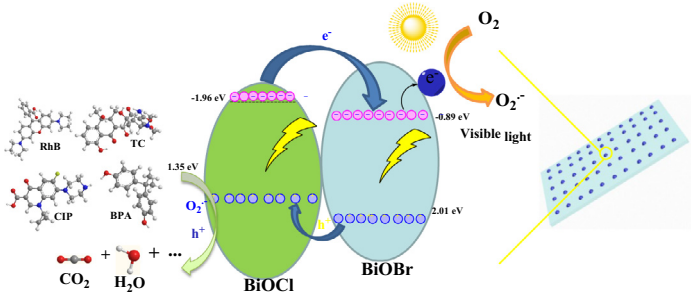
GRAPHICAL ABSTRACT



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ABSTRACT

The efficient separation of photoexcited electron-hole pairs acts as a significant factor and challenge for the enhanced photocatalytic activity of the photocatalyst. To pursue higher photocatalytic activity, carbon quantum dots (CQDs) modified bismuth oxychloride (BiOCl)/bismuth oxybromide (BiOBr) nanosheet photocatalyst has first been synthesized via an in situ ionic liquid-induced strategy. The bridge function of the ionic liquid ensures the uniform dispersal of CQDs on the surface of the BiOCl/BiOBr material. After the introduction of CQDs, the CQDs/BiOCl/BiOBr composite photocatalyst displayed enhanced photocatalytic activity for the photodegradation of several different types of organic contaminants such as rhodamine B, tetracycline hydrochloride, ciprofloxacin, and bisphenol A under the irradiation of visible light, and the BiOCl/BiOBr material loading with 5 wt% CQDs showed the best photocatalytic performance. The characterization results revealed that the introduction of CQDs could simultaneously improve the visible light absorption properties and separation efficiency of photoexcited electron-hole pairs. The electron spin resonance and radical quenching experiments demonstrated that during the photocatalytic reactions, holes and superoxide radicals were the main active species involved in the degradation of the contaminants, and the possible photocatalytic mechanism is presented. Therefore, this work provides an efficient pathway for the improved activity of the photocatalyst.

1. Introduction

Photocatalysis, a very promising technique, can be applied in environmental remediation and the transformation of solar energy

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into chemical power [1,2]. A variety of photocatalysts such as (oxy) nitrides [3], oxides [4], plasmonic photocatalysts [5], and elemental photocatalysts [6] have been tested to attain the high-efficiency photocatalytic activity. Nevertheless, in practical applications, the performance of photocatalysts is greatly limited by two factors: (a) the narrow absorption range of visible light and (b) the inefficient separation and transport of photoexcited electron-hole pairs.

As one of the new layered materials, bismuth oxyhalides (BiOX, X = Cl, Br, I) have attracted growing research attention because of their excellent electrical, optical, and catalytic properties [7]. In all the BiOX photocatalysts, bismuth oxychloride (BiOCl) displays the highest photocatalytic activity under UV illumination [7,8]. Bismuth oxyiodide (BiOI) shows the best visible light absorption capacity because of its small energy gap. Bismuth oxybromide (BiOBr) reveals the highest photocatalytic oxidation and reduction activity under full light irradiation based on the appropriate band gap [7]. Nevertheless, the photocatalytic performance of individual bismuth oxyhalide is still limited to its low absorption of visible light, low transfer efficiency of photogenerated charges and high recombination rate of photoexcited electron-hole pairs. To improve the photocatalytic performance of BiOX, construction of BiOX-based composites with metallic salts (such as AgX [9], $ZnFe_2O_4$ [10], and $NaBiO_3$ [11]), metal oxides (such as Fe_3O_4 [12], Bi_2O_3 [13], TiO_2 [14], and WO_3 [15]) and precious metals (such as Pt [16]) have been reported. In addition, BiOX/BiOY (X, Y = Cl, Br, I) have drawn increasing research attention for their light absorption ability, unique layered structure and effective separation of photogenerated carriers [17]. Li et al. [17] first developed a novel process for the solvent-thermal synthesis of BiOCl/BiOBr microspheres by employing ionic liquid as reaction solvents. An improved photocatalytic performance of BiOCl/BiOBr material has been obtained compared to BiOBr or BiOCl. Zhang [18] introduced microwave-assisted coprecipitation for the synthesis of heterostructured BiOCl/BiOBr photocatalyst. Comparing to BiOCl/BiOBr synthesized by the hydrothermal method, BiOCl/BiOBr synthesized by a microwave-assisted method showed a higher degradation rate of RhB. The high photocatalytic activity of BiOCl/BiOBr resulted mainly from the effective separation of photoexcited electron-hole pairs. However, it was difficult to regulate the size and crystal structure of BiOCl/BiOBr material using the microwave-assisted method. In addition, the narrow absorption of visible light and inefficient separation of photogenerated charge carriers for BiOCl/BiOBr material still remain, in spite of the improved photocatalytic activity of BiOBr or BiOCl.

To further enhance the photocatalytic activity of BiOX, carbon quantum dots (CQDs) have been introduced to extend the absorption of visible light and raise the separation efficiency of photoexcited electron-hole pairs [19]. Carbon quantum dots are a novel type of carbon-based material with one dimension less than 10 nm in size. They are composed of sp^2/sp^3 hybridized carbon atoms, have various surface functional groups and exhibit composition-dependent fluorescence [19]. CQDs have been widely used in a train of significant fields, for example, bio-imaging [20], catalysis [21], sensors [22], and photovoltaic devices [23], owing to the properties of easy functionalization, low toxicity, wonderful biocompatibility and fine resistance to photobleaching [24,25]. Meanwhile, due to the excellent properties of the electron transfer/reservoir, CQDs have been successfully doped into photocatalysts to improve the photocatalytic activity, for example, Fe_2O_3 [26], ZnO [27], Ag_3PO_4 [28], TiO_2 [29], BiOX [30], Bi_2WO_6 [31], $BiVO_4$ [32].

In this work, we report a one-step ionic liquid in situ induced solvent-thermal method for the preparation of two-dimensional CQDs/BiOCl/BiOBr composites with regulable loading amounts of CQDs for improving the degradation rate of rhodamine B (RhB), tetracycline hydrochloride (TC), ciprofloxacin (CIP) and bisphenol A (BPA) under visible light. The relationship between the photocatalyst structure and the photocatalytic activity is studied in detail. The photocatalytic reaction mechanism in this system is investigated by radical quenching experiments and electron spin resonance (ESR) analysis. This study could provide new sights into the design of more composite photocatalyst materials for the potential application to environmental remediation.

2. Experimental section

2.1. Material preparation

All the reagents were of analytical grade and used without further purification. The ionic liquid $[C_{16}mim]Cl$ (1-hexadecyl-3-methylimidazolium chloride) (99%) and $[C_{16}mim]Br$ (1-hexadecyl-3-methylimidazolium bromide) (99%) were purchased from Shanghai Chengjie Chemical Co., Ltd.

2.2. Synthesis of the photocatalysts

CQDs were prepared by a simple one-step process and then handled by freeze-drying [33]. Citric acid (1.05 g) was dissolved in 10 mL deionized water, and 335 μL of ethylenediamine was then added. The mixture was then poured into a 25 mL Teflon-lined autoclave and reacted at 200 °C for 5 h, then cooled. The reddish-brown liquid was subjected to dialysis for 20 h to obtain the CQDs solution. Finally, the CQDs solid was obtained after freeze drying. The CQDs modified BiOCl/BiOBr composites were prepared via a facile solvent-thermal process. A given mass of CQDs and 0.48 g $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in 9 mL, 0.1 M mannitol solution under magnetic stirring and defined as solution A. Ionic liquid $[C_{16}mim]Cl$ (0.17 g) and ionic liquid $[C_{16}mim]Br$ (0.19 g) were poured into 9 mL, 0.1 M mannitol solution to define solution B. B was added into A dropwise under continuous stirring and stirred for 0.5 h. The mixture was then poured into a 25 mL Teflon-lined autoclave and reacted at 140 °C for 24 h. The composites that were obtained were centrifuged at high speed and washed with hot deionized water and ethanol five times, respectively. Finally, the composites were dried at 50 °C for 24 h. The added amount of CQDs in the CQDs/BiOCl/BiOBr composites was regulated to 1 wt %, 3 wt%, 5 wt% and 7 wt%, by regulating the mass ratio of CQDs to BiOCl/BiOBr. The BiOCl/BiOBr, BiOCl and BiOBr were also synthesized by a similar method without adding CQDs.

2.3. Characterization

The phase composition of the photocatalysts was characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, Japan) employing Cu Kα as the source of radiation, λ = 1.54056 Å at scan speed of 7°·min^{-1} over a range of 10–80°, operating at 40 mA and 40 kV. The morphology and nanosheet size of the materials were investigated by scanning electron microscope (SEM, JSM-7001F, JEOL, Japan), as well as by transmission electron microscope (TEM, JEM-2010, JEOL, Japan). The chemical states of the photocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS) with a monochromatic Mg-Kα source operating at 20 kV. The UV–vis spectra of the prepared materials were obtained via a UV–vis spectrometer (UV-2450, Shimadzu, Japan) by the diffuse reflectance method with $BaSO_4$ powder as the substrate. A certain amount of photocatalyst was mixed with the $BaSO_4$ powder and then tabletted for measuring. The Tauc equation was then used to calculate the band gap of BiOCl, BiOBr and BiOCl/BiOBr. The specific surface area and gas adsorption isotherms of the materials at 77 K were measured by adsorption-desorption of N_2 on a TristarⅡ 3020 surface area and