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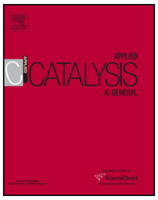

Synthesis of BiOBr/carbon quantum dots microspheres with enhanced photoactivity and photostability under visible light irradiation

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ABSTRACT

In this paper, BiOBr/carbon quantum dots (CQDs) microspheres were successfully synthesized via a facile solvothermal method followed by a hydrothermal process. Then, the structures, morphologies, optical properties, and photocatalytic performances were investigated in detail. Research showed that the BiOBr/CQDs microspheres exhibited significantly enhanced photocatalytic performance as compared with pure BiOBr. When the CQDs introduction was appropriate, the highest photodegradation rate (0.0296 min^{-1}) would be obtained in the photocatalysis process of rhodamine B (RhB) which was about 5.3 times higher than that of pure BiOBr under visible light irradiation. As for *p*-Nitrotoluene (PNP), it could not be photodegraded by pure BiOBr while the BiOBr/CQDs microspheres displayed obvious photocatalytic activity. In this photocatalytic system, the enhanced photoactivity was mainly attributed to the fast interfacial charge transfer ability and enhanced light harvesting for the appropriate CQDs introduction.

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1. Introduction

In recent years, photocatalysis technology, offers a "green" technology for completely eliminating various kinds of contaminants (especially some azodyes) and obtaining ideal hydrogen energy from sunlight and water [1–4], is considered as a very important method for relieving or resolving current environmental issue and energy crisis. Particularly, bismuth oxyhalides (BiOX, X = Cl, Br, and I) have been widely studied due to their excellent photoelectric property and catalytic performance [5–11]. Among numerous BiOX semiconductors, BiOBr was greatly investigated for its appropriate band gap and excellent visible light photocatalytic activity [12–14]. However, the photocatalytic acticity of the pure BiOBr semiconductor was limited by its low separation efficiency of the photoexcited electron-hole pairs. In order to improve photocatalytic activity of BiOBr semiconductor, BiOBr has been modified by SiO_2 [15], Fe_3O_4/$mSiO_2$ [16], MoS_2 [17], BiOI [18–21], $Bi_{24}O_{31}Br_{10}$ [22], $NiFe_2O_4$/BiOBr [23], WO_3/Bi_2WO_6 [24], Bi_2O_3 [25], nitrogen-doped graphene [26], $BiPO_4$ [27], TiO_2 [28,29], Bi_2WO_6 [30,31], Ag_3PO_4 [32], $CoFe_2O_4$ [33], CdS [34] and Ag_2CO_3 [35] etc. However, these large-size materials can hardly build perfect interacted interfaces with BiOBr, the surface defects could act as recombination centers of photoexcited electron-hole pairs which may limit the photocatalytic activity [36,37].

Carbon quantum dots (CQDs), a new class of carbon nanomaterials with size less than 10 nm, were first obtained during purification of single-walled carbon nanotubes through preparative electrophoresis in 2004 [38]. As a group of newly emerged fluorescent nanomaterials, CQDs have shown tremendous potential as versatile nanomaterials for a wide range of applications, including chemical sensing, biosensing, bioimaging, drug delivery, photodynamic therapy, photocatalysis and electrocatalysis [39]. Compared to conventional semiconductor quantum dots, the unique attributes of CQDs, for example their benign chemical composition, tunable fluorescence emissions, facile functionalization and excellent physicochemical and photochemical stability (non-photobleaching or non-photoblinking), render them very attractive for technical applications [39]. Together with other advantages such as low cost and ease of synthesis [40], CQDs are in a favorable position for achieving unprecedented performance.

CQDs are typically quasi-spherical nanoparticles comprising amorphous to nanocrystalline cores with predominantly graphitic or turbostratic carbon (sp^2 carbon) or graphene and graphene oxide sheets fused by diamond-like sp^3 hybridised carbon insertions [39], which provide the CQDs with superior electron transfer and reservoir ability [37]. In addition, the up-converted photoluminescence

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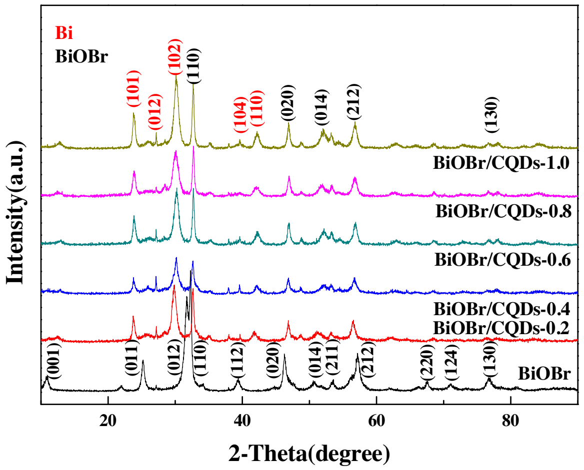

Fig. 1. XRD patterns of BiOBr/CQDs materials with different CQDs amounts.

(PL) behavior of CQDs can expand the light utilization range of nanomaterials from UV to visible range and enhance photo-induced electron transfer [39]. Therefore, a series of CQDs-based photocatalysts have been synthesized to improve the photocatalytic activity of semiconductors, such as CQDs/Cu_2O [41], CQDs/Fe_2O_3 [42], CQDs/Bi_2MoO_6 [43], CQDs/TiO_2 [44], CQDs/Ag_3PO_4 [45], CQDs/Fe_3O_4 [46] and CQDs/Bi_2WO_6 [36]. However, the binding form between CQDs and semiconductors as well as functional mechanism of CQDs for photocatalytic activity improvement is far from clear. Therefore, it was highly desirable to solve the problems aforementioned in order to further improve the performance of CQDs by appropriate means so as to acquire satisfactory high-efficient photocatalytic activity of CQDs-based materials.

Considering the superiorities of BiOBr and CQDs above mentioned, the BiOBr/CQDs microspheres were successfully prepared via a facile hydrothermal route followed by a hydrothermal process. The structures, morphologies, optical properties were investigated in detail, and the photocatalytic activities of BiOBr/CQDs materials were also evaluated sufficiently by the photocatalytic degradation of two different kinds of model pollutants (RhB and PNP). The relationships between the structure of the photocatalyst and the photocatalytic activities were also discussed in detail. Ultimately, the mechanism of pollutant photodegradation in this system was studied and proposed.

2. Experimental section

2.1. Photocatalyst synthesis

All chemicals were purchased from J&K Chemical and were used as received.

The BiOBr microspheres were synthesized by a facile solvothermal method. In a typical procedure, 14 mmol Bi $(NO_3)_3 \cdot 5H_2O$ and 10 mmol KBr was dissolved in 80 mL of ethylene glycol by ultrasonic. Then, the solution was transferred into a 100 mL teflon-lined stainless-steel autoclave and kept at 180 °C for 8 h. After the reaction finished, the resulting samples were collected and separated by centrifugation and washed with deionized water and absolute ethanol followed by drying via the vacuum freeze-drying technology [47,48].

The synthesis of BiOBr/CQDs materials was carried out according to a previous report with little modification [49]. Firstly, 1.0 g as-prepared BiOBr microspheres were dispersed in 100 mL deionized water by ultrasonic for about 5 min. Then the stoichiometric (0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g) citric acid and 2.68 mL ethylenediamine was added into the above system under continuous mechanical stirring. The above mixture was transferred into 100 mL teflon-lined stainless-steel autoclave and heated at 180 °C for 8 h and cooled down to room temperature. The acquired product was subjected to centrifugation and washed several times with deionized water and absolute ethanol followed by drying via the vacuum freeze-drying technology centrifugation. The resulting sample was coded as BiOBr/CQDs-α, and α denotes the mass of citric acid.

2.2. Photocatalyst characterization

The crystalline phases of BiOBr/CQDs materials were determined by X-ray power diffraction (XRD) analysis using a Bruker AXS D8-advance X-ray diffractometer with Cu-Kα radiation. The elements and chemical states on the surface of BiOBr/CQDs materials were determined by X-ray photoelectron spectroscopy (XPS) using an Axis Ultra instrument (Kratos Analytical, Manchester, U.K.) under ultrahigh vacuum condition ($<10^{-6}$ Pa) with a monochromatic Al Kα X-ray source (1486.6 eV). Fourier transform-infrared (FT-IR) spectra were measured on a PerkinElmer 580BIR spectrophotometer using KBr pellet technique. Thermogravimetric analysis (TG) was performed on a Q5000IR (TA Instruments, US) apparatus. Scanning electron microscopy (SEM) micrographs were observed on a JEOL-JSM-6700F. Transmission electron microscopy (TEM) micrographs were observed on a JEOL JEM-2100F. N_2 adsorption/desorption isotherms were obtained on a TriStar II 20 apparatus. UV–vis diffuse reflectance spectra (DRS) were performed on a Shimadzu UV-3600 spectrometer ($BaSO_4$ power as substrate). The Photoluminescence (PL) spectra of BiOBr/CQDs materials were detected on a Varian Cary Eclipse spectrometer.

2.3. Photocatalytic activity test

The photocatalytic activity of the as-prepared BiOBr/CQDs materials with different CQDs contents was investigated by the photodegradation of 20 mg/L RhB and 20 mg/L PNP under visible light (a 300 W Xe arc lamp with a UV cutoff filter (400 nm)). In a typical process, 100 mg BiOBr/CQDs samples were added into 100 mL RhB or 100 mL PNP. Prior to irradiation, the suspension was stirred in the dark for 30 min to ensure adsorption-desorption equilibrium. During the photodegradation process, 3 mL suspension was sampled at certain time intervals and centrifuged at 13000 rpm for 3 min to remove the BiOBr/CQDs microspheres for analysis. The concentration of RhB and PNP samples were analyzed on an UV–vis spectrophotometer (UV-2450, Shimadzu) at wavelength of 553 nm and 317 nm, respectively.

2.4. Free radical trapping experiments

For detecting the active species during photocatalytic reactivity, hydroxyl radicals ($^{\bullet}OH$), superoxide radicals ($O_2^{\bullet-}$), holes (h^+) and electrons (e^-) were investigated by adding 1.0 mM IPA (a quencher of $^{\bullet}OH$) [50,51], 1 mM *p*-benzoquinone (BQ, a quencher of $O_2^{\bullet-}$)[36,50], 1 mM KI (a quencher of h^+)[15] and 1 mM tertiary butanol (TBA) for e^-, respectively. The method was similar to the former photocatalytic activity test.

3. Results and discussion

3.1. Compositional and structural information

The phases of the BiOBr/CQDs microspheres with different CQDs contents were investigated by X-ray diffraction (XRD), and the diffraction spectra were shown in Fig. 1. The peaks located at 10.9°, 25.3°, 31.8°, 32.3°, 33.3°, 39.4°, 40.6°, 47.0° and 56.4° can be indexed to the (001), (011), (012), (110), (003), (112), (013), (113) and (114)

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