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Microwave-assisted synthesis of hierarchical $Bi_7O_9I_3$ microsheets for efficient photocatalytic degradation of bisphenol-A under visible light irradiation

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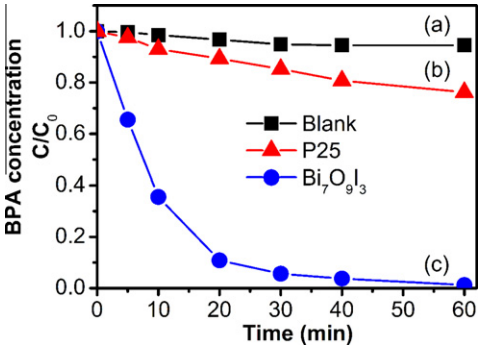
HIGHLIGHTS

- Hierarchical $Bi_7O_9I_3$ microsheets are synthesized using microwave route.
- Photocatalyst is $Bi_7O_9I_3$ microsheets.
- $Bi_7O_9I_3$ microsheets have visible-light photocatalytic ability to bisphenol-A.
- The photocatalysis of bisphenol-A over $Bi_7O_9I_3$ microsheets is investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and energy-saving microwave heating route for rapid synthesis of $Bi_7O_9I_3$ sheet-like hierarchical architectures has been demonstrated. The visible-light-induced photocatalytic performances of the prepared materials for the degradation of bisphenol-A (BPA, a known endocrine disrupting chemical) are studied systematically. Using $Bi_7O_9I_3$ photocatalyst synthesized by 400 W microwaves heating 180 s and with a catalyst dosage of 1 g L^{-1} in 20 mg L^{-1} aqueous solution of BPA, a degradation percentage of 99% is obtained under visible-light irradiation for 60 min. The photocatalytic reaction follows pseudo first-order kinetics according to the Langmuir–Hinshelwood model, and the reaction rate constant of the optimal sample is over 16 times greater than that of the commercial Degussa P25 catalyst based on TiO_2. In addition, two main intermediates are identified using liquid chromatography combined with mass spectrometry (LC–MS) technique, and subsequently, a simple and direct photodegradation mechanism is proposed. Furthermore, the as-synthesized photocatalysts exhibit a high mineralization capacity of BPA and good stability during the photodegradation reaction, suggesting a promising prospect in the practical application of the photodegradation of organic pollutants.

1. Introduction

Bisphenol-A [2,2-bis(4-hydroxyphenyl)propane; BPA], an important raw organic chemical material, has been widely used in household and commercial products, including the lining of food cans, dental sealants, polycarbonate plastics, and epoxy resins. However, it is also notably recognized as an endocrine disrupting chemical (EDC) and is highly toxic to aquatic organisms [1,2]. Thus, the removal of BPA in aquatic environment is a necessary topic for environmental protection [3,4].

So far, several methods have been developed to remove BPA from aqueous solutions, including physical absorption [5], filtration [6], microbial degradation [7], UV photolysis [8], ultrasonic degradation [9], electrochemical techniques [10], Fenton reactions [11], ozone oxidation [12], and photocatalytic degradation [13–16].

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Among these methods, photocatalytic degradation is a promising one due to its advantages for the removal of BPA such as high degradation and mineralization efficiency, low toxicity, and operating under ambient conditions [17–19]. Though the photocatalytic reaction of BPA by TiO_2 has been extensively studied, the practical application of TiO_2 is still limited due to its wide band gap energy (only effective under ultraviolet irradiation at $\lambda < 380$ nm). What's more, it is well known that the photocatalysts with nanosize are difficult to be separated completely from a slurry system after photocatalytic reaction owing to their small size, which seriously limits their practical application [20]. Therefore, the exploitation of novel, effective, visible-light-driven and easily reused photocatalysts is necessary to overcome these drawbacks.

Recently, as a new family of promising photocatalysts, bismuth oxyhalides (BiOX, X = F [21], Cl [22], Br [23], and I [24]), have demonstrated remarkable photocatalytic activities due to their uniquely layered structures with an internal static electric field perpendicular to each layer, which can induce effective separation of photogenerated electron–hole pairs, and thus achieve a high photocatalytic performance. Other complex bismuth oxyhalides, such as Bi_3O_4Cl [25], Bi_4NbO_8Cl [26], $PbBiO_2Cl$ [27], $Bi_4O_5I_2$ [28], and Bi_5O_7I [29], have been investigated and show good photocatalytic ability under visible light irradiation for the degradation of various organic contaminants. In our previous work [30], a novel hierarchical $Bi_7O_9I_3$ micro/nano-architecture was synthesized using a facile oil-bath procedure, which showed high photocatalytic activity in the decomposition of phenol under visible light irradiation and could easily be recycled, suggesting it could be a promising photocatalyst in the treatment of wastewaters containing organic pollutants. However, until now, there have been very few studies on the synthesis of $Bi_7O_9I_3$ materials and their photocatalytic properties for the degradation of organic pollutants.

Microwave heating has been widely applied in chemical reactions and materials synthesis with several advantages compared with conventional heating, such as rapid heating, faster kinetics, homogeneity, higher yield, better reproducibility, and energy savings [31]. Previously, several bismuth-containing photocatalytic materials, such as Bi_2O_3 [32], Bi_2S_3 [33], Bi_2WO_6 [34], Bi_2MoO_6 [31], $BiVO_4$ [35], $BiFeO_3$ [36], and BiOBr [37] have been successfully synthesized by the microwave-assisted method. We synthesized hierarchical $Bi_7O_9I_3$ microsheets through a novel and fast microwave heating route and subsequently studied their photocatalytic performance in removing BPA in aqueous solutions under visible light irradiation. In the present study, the morphology, structure and photoabsorption property of the as-synthesized hierarchical $Bi_7O_9I_3$ microsheets were characterized, the optimal conditions of synthesis and photocatalytic degradation were explored, and a possible photocatalytic degradation mechanism was proposed.

2. Experimental

2.1. Materials and methods

The BPA was purchased from Sinopharm Group Chemical Reagent Co. Ltd. Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) and potassium iodide (KI) were bought from Tianjin Kermel Chemical Reagent Co. Ltd. Ethylene glycol (EG) was obtained from Chinasun Specialty Products Co. Ltd. All chemicals were used as received without further purification. Distilled water was used to prepare the solutions in the experiments.

In a typical synthesis, 0.485 g $Bi(NO_3)_3{\cdot}5H_2O$ and 0.166 g KI were dissolved completely in 50 mL EG by stirring at room temperature using a 150 mL round flask as the container. Then, the reaction was performed in a microwave chemical reactor (MCR-3, at a fixed frequency of 2.45 GHz and a maximum output of 800 W, Beijing Rui Cheng Wei Industry Equipment Co. Ltd., China) equipped with in situ magnetic stirring and a condensing apparatus. After completion of the reaction, the mixture was continuously stirred for 30 min until it reached room temperature; then, the precipitates were collected by centrifugation, washed several times with distilled water and ethanol, and finally dried in an oven overnight at 60 °C. The five typical samples synthesized under different microwave irradiation powers and reaction times are denoted as S1 (400 W, 180 s), S2 (240 W, 180 s), S3 (560 W, 180 s), S4 (400 W, 120 s), and S5 (400 W, 240 s), respectively.

2.2. Characterization and photocatalytic measurement

The morphologies and microstructures of as-prepared samples were analyzed by a scanning electron microscope (SEM, JSM-6510, JEOL, Japan). Crystalline phases of the obtained samples were identified by powder X-ray diffractometer (XRD, Y2000, Dandong, China) with Cu Kα as the radiation source for a 2θ range of 10–80°. The average crystallite size of catalysts was estimated using the Debye–Scherrer equation:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where D is the average crystallite size (nm), K is a constant which is taken as 0.89 here, λ is the wavelength of the X-ray radiation (nm), β is the full width at half maximum (FWHM) after subtraction of equipment broadening, and θ is the Bragg angle of the peak.

The UV–vis diffuse reflection spectra (DRS) were obtained using a UV–vis spectrophotometer (UV-3010, Hitachi, Japan). The band gap energy (E_g) of these samples was evaluated using the following equation [38]:

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (2)$$

where α, ν, E_g and A are the absorption coefficient, light frequency, band gap energy, and a constant, respectively. Among them, n depends on the characteristics of the transition in a semiconductor. For BiOX, the value of n is 4 for their indirect transition [39,40]. Then band gap energies (E_g values) of BiOX can be thus estimated from a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($\alpha h\nu$).

The specific surface area was measured by nitrogen adsorption–desorption isotherms at 77 K according to the Brunauer–Emmett–Teller analysis (BET, ASAP 2020, Micromeritics, USA). A desorption isotherm was used to determine the pore size distribution using the Barrett–Joyner–Halenda (BJH) method.

The photocatalytic degradation experiments were performed in a photochemical reactor (XPA-VII, Nanjing Xujiang Machine-electronic Plant, China), equipped with a 1000 W Xe lamp combined with a 420-nm cut-off filter as the light source. In each experiment, a certain amount of the as-synthesized $Bi_7O_9I_3$ catalyst (varying from 0.2 to 2.0 g L^{-1}) was added to a 50 mL reaction solution containing BPA with various initial concentrations (ranging from 10 to 50 mg L^{-1}). Prior to irradiation, the solution with the catalyst was stirred for 1 h in the dark to allow the system to reach adsorption equilibrium. During the photocatalytic process, approximately 2.5 mL of the suspension was taken out at a specified time, and subsequently, the solids were removed from the solution using a 0.45 μm nitrocellulose filter and the filtrate were then identified using UV–vis spectroscopy (UV-1800, Shimadzu, Japan, $\lambda = 276$ nm) to obtain the BPA concentrations in the solution. The total organic carbon concentration was measured by an automatic total organic carbon analyzer (TOC-V, Shimadzu, Japan).

2.3. Intermediates analysis

The BPA and its intermediates in the solution were separated using high-performance liquid chromatography (HPLC, LC-10AT,