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Soluble starch-modulated solvothermal synthesis of grain-like $Bi_{24}O_{31}Br_{10}$ hierarchical architectures with enhanced photocatalytic activity

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ABSTRACT

Hierarchically structured $Bi_{24}O_{31}Br_{10}$ photocatalysts were synthesized by a facile solvothermal method with the help of soluble starch. As-prepared samples were characterized by XRD, SEM, EDS, TEM, FTIR and N_2 adsorption. It was found that starch played a key role in shaping morphology of $Bi_{24}O_{31}Br_{10}$, and especially a novel grain-like $Bi_{24}O_{31}Br_{10}$ hierarchical architecture could be obtained by adding the right amount of starch. The forming mechanisms of different microstructures were proposed. The photocatalytic performances of the obtained samples were also investigated by degradation of Rhodamine B (RhB) under visible light illumination. Starch-modulated $Bi_{24}O_{31}Br_{10}$ photocatalysts exhibited obviously enhanced photocatalytic activity, whose mechanism was discussed. The present work demonstrated a novel strategy to modulate the structures, morphologies and properties of materials, which can be extended to other photocatalysts.

1. Introduction

Recently, oxygen-rich bismuth oxybromides such as $Bi_{24}O_{31}Br_{10}$, $Bi_4O_5Br_2$ and Bi_3O_4Br, have attracted much attention as a kind of promising photocatalysts [1–4]. On the one hand, these compounds possess similar layered structure to bismuth oxybromide (BiOBr), which induces an effective separation of photo-generated electron-hole pair. On the other hand, they display narrower band gaps than BiOBr due to smaller value of Br:O ratio, which present stronger absorption in the visible light range. Among these oxygen-rich bismuth oxybromides, $Bi_{24}O_{31}Br_{10}$ is of great research interest owing to its high thermal stability and relatively superior catalytic activity under visible light irradiation [5]. For instance, Xiao et al. [6] reported an enhanced photocatalytic activity of $Bi_{24}O_{31}Br_{10}$ toward the degradation of TC compared with BiOBr microspheres. Nonetheless, the practical application of $Bi_{24}O_{31}Br_{10}$ is still limited by its insufficient photocatalytic efficiency, and more efforts need be made to further enhance its activity.

As is well known, the photocatalytic properties of inorganic materials are closely related to their morphologies and structures [7–9]. Self-assembling hierarchical nanostructures not only increase specific surface area but also shorten the diffusion length of photo-generated charge carriers, which result in strong adsorptivity and effective separation of electron-hole pairs and thus favor the enhancement of photocatalytic activity. Therefore, the fabrication of photocatalysts with high-quality hierarchical nanostructures has become a research hotspot [10,11]. A hydrothermal/solvothermal strategy with the help of various organic surfactants is a universal and effective approach to synthesize morphology and size-controlled photocatalysts, by which photocatalysts with various morphologies such as hierarchical nanospheres [12], nanoflower [13] and other complex nanostructures [14,15], have been well prepared. In spite of these accomplishments, the organic surfactants used such as polyvinyl pyrrolidone(PVP) [16], 2-bromoethylamine hydrobromide (C2H6BrN·HBr,BTH) [17] and citric acid(CA) [18], are often environmentally harmful and high cost. It is necessary to find green and cheap alternative materials, which can exhibit the same functions as surfactants. Recently, starch has been widely used in preparing photocatalysts. For example, Gül Avcı et al. [19] and Kochkar et al. [20] have prepared flower shaped ZnO crystals and

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mesoporous TiO_2 nanocrystalline by using starch. Inspired by the aforementioned concepts, we infer that $Bi_{24}O_{31}Br_{10}$ photocatalysts with high-quality hierarchical nanostructures can be synthesized with the assistance of starch. If successful, it may provide us with a new way of thinking to design other photocatalyst materials.

Given the foregoing, herein, we focused on the preparation of $Bi_{24}O_{31}Br_{10}$ photocatalysts with high-quality hierarchical nanostructures by using soluble starch as a structural agent. The obtained products not only show high specific surface area but also high quantum efficiency, which synergistically promoted visible-light photocatalytic activity.

2. Experimental

2.1. Sample preparation

All the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (China), and used as received without further purification. $Bi_{24}O_{31}Br_{10}$ photocatalysts were synthesized by a facile solvothermal process with the help of starch. Briefly, 4 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ and a desired amount of starch were orderly added in 35 ml of glycerol (Gr) under magnetic stirring. Then another 35 ml Gr solution containing 4 mmol of hexadecyltrimethylammonium bromide (CTAB) was added into the above solution and stirred for 30 min. After added 6 ml of 2 M NaOH solution, the precursor solution was transferred into a 100 ml Teflon-lined autoclave, which was sealed and heated at 160 °C for 16 h. The autoclave was allowed to cool down to room temperature. The products were collected and washed repeatedly, and then dried at 80 °C overnight. Starch removal from the samples was carried out by ethanol/water refluxing method. The mass of starch used was 0 g, 0.2 g, 0.4 g, 0.8 g and 1.2 g. Accordingly, the final samples were denoted as BOB-S0, BOB-S0.2, BOB-S0.4, BOB-S0.8 and BOB-S1.2.

2.2. Materials characterization

The crystalline structures of samples were characterized by X-ray powder diffraction (XRD, Bruker D8 Advance X-ray diffractometer). The morphologies were examined by a field-emission scanning electron microscope (SEM, FEI Quanta-250) equipped with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscopy (TEM, Tecnai G2 F20). N_2 sorption was used to determine the specific surface area and pore size distribution. FT-IR spectra were recorded by using Vertex70 FTIR spectrometer.The optical property was analyzed by UV–vis diffuse reflectance spectra (DRS, Varian Cary 300).

2.3. Photocatalytic and electrochemical performances

The photocatalytic activity of as-obtained samples was determined by degradation of Rhodamine-B (RhB) under visible light irradiation. A 150W tungsten–halogen lamp (Beijing Institute of Opto-Electronic Technology) was selected as the visible light source. In each experiment, 0.1 g of photocatalyst was added into 100 ml of 10 mg/l RhB solution. Before irradiation, the suspension was stirred for 10 min in the dark. At given irradiation time intervals, 3 ml of suspension was taken and centrifuged. The concentration of remnant pollutant was determined by UV–vis spectrophotometer at the characteristic wavelength of 553 nm for RhB.

2.4. Photocurrent measurement

Transient photocurrent measurements and electrochemical impedance spectroscopy (EIS) were performed on a CHI660B electrochemical workstation with a standard three-electrode configuration. A platinum plate was used as counter electrode, and Ag/AgCl electrode (saturated KCl) as the reference electrode. The working electrodes were prepared as follows: 2 mg catalysts were added into the mixture solution of 0.2 ml ethanol and 0.2 ml EG to produce slurry. 20 μl of the suspension was dropped on $1.5 \times 1.5\ cm^2$ fluorine-tinoxide (FTO) glass, and then dried under ambient conditions. The electrolyte was 0.5 M Na_2SO_4 aqueous solution. A 300 W Xenon lamp was utilized as the irradiation source for photocurrent measurements, and the amplitude of the sinusoidal wave for EIS measurements was set up as 10 mV. Both photocurrent and EIS measurements were carried out at room temperature.

3. Results and discussion

3.1. Characterization

The effect of soluble starch on crystal structure of $Bi_{24}O_{31}Br_{10}$ was investigated by X-ray powder diffraction (XRD). The results are presented in Fig. 1. All peaks can be readily indexed to pure monoclinic phase $Bi_{24}O_{31}Br_{10}$ (JCPDS card no.75-0887), and no impurity such as Bi_2O_3, BiOBr and other oxygen-rich bismuth oxybromides is found, indicating the negligible effect of starch on the formation of $Bi_{24}O_{31}Br_{10}$. There is no evidence for amorphous starch, which may be related to the low content of starch. In addition, it is found that, for all samples, the diffraction peak at around 31.8°, which corresponds to (117) plane, is sharper than those at 24.0°, 29.8°, 46.0° and 54.6°, indicating an anisotropic growth of Bi24O31Br10 crystals. When different amount of starch is used, all the diffraction peaks are broadened in different degrees. It suggests that adding starch may reduce the crystal size of Bi24O31Br10, which is confirmed by the following SEM and TEM.

The morphology and microstructure of the $Bi_{24}O_{31}Br_{10}$ samples synthesized without or with different amount of starch were characterized by SEM. As shown in Fig. 2, the amount of starch used has a crucial influence on size and shape of $Bi_{24}O_{31}Br_{10}$. In the absence of starch, BOB-S0 sample presents irregular hierarchical structures assembled by curly nanosheets, which have a thickness of ~20 nm and a size of 100–200 nm in the other two dimensions (Fig. 2a). With adding a small quantity of starch (0.2 g), as-obtained

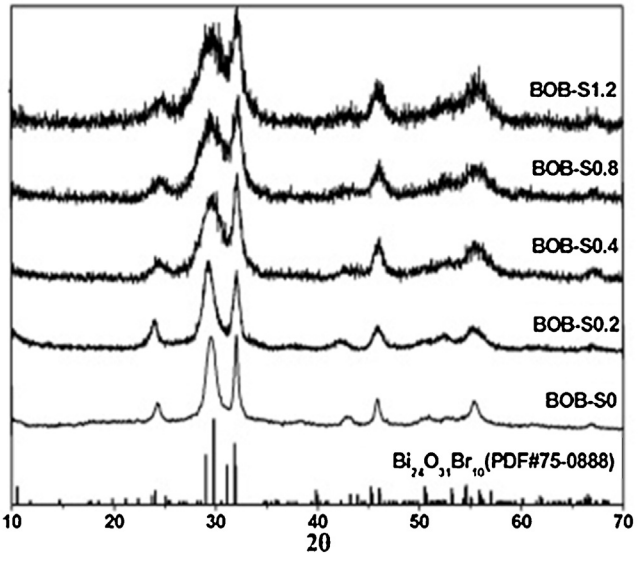

Fig. 1. XRD patterns of as-prepared samples synthesized with different amount of starch.