Catalysis Communications 80 (2016) 15–19

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Mannitol ligand-assisted assembly of BiOBr photocatalyst in the cationic micelles of cetylpyridinium bromide

Yanfen Fang [a,b], Tingting Hua [b], Weiyong Feng [b], David M. Johnson [a,b], Yingping Huang [a,b,*]

[a] Innovation Center for Geo-Hazards and Eco-Environment in Three Gorges Area, Yichang 443002, Hubei Province, China
[b] Engineering Research Center of Eco-environment in Three Gorges Reservoir Region, Ministry of Education, China Three Gorges University, Yichang, Hubei 443002, China

ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form 2 March 2016
Accepted 4 March 2016
Available online 5 March 2016

Keywords:
BiOBr
Ligand-assisted assembly
Photocatalysis
CPB micelles
Photodegradation

ABSTRACT

This is the first report on ligand-assisted assembly of BiOBr. BiOBr, using cetylpyridinium bromide (CPB) as Br source and surface template, was prepared with water with the presence of three polyhydroxyl alcohols. Based on SEM, HR-TEM and XRD, mannitol results in different particle morphologies. Rather than smooth microspheres, projections form that double surface area. BiOBr prepared in mannitol displayed the highest photocatalytic activity and tripled the oxygen consumption rate compared to the other preparations. The Bi^{3+}–mannitol complex competes with hydroxide for Bi^{3+} in the CPB micelles and limits the availability of BiO^{+}, altering the assembly process. A four-step mechanism for ligand-assisted assembly of BiOBr in mannitol is proposed.

1. Introduction

Nanoparticulate photocatalysts have excellent potential for removing refractory organic pollutants from wastewater. One of the most promising photocatalysts is BiOBr, which readily degrades dyes [1–3], amino acids [4], microcystins [5] and cylindrospermopsin [6]. Compared with the corresponding bulk nanostructures, BiOBr hierarchical nanomaterials possess improved removal efficiency of pollutants owing to their large surface area and unique surface property [7–15]. Consequently, much research work focused on the fabrication and application of 3D hierarchical nanostructures of BiOBr. Recent studies have demonstrated that the self-assembly process can be manipulated to obtain 3D BiOBr architectures using microwave-assisted solvothermy [7–11], solvent mediated solvothermy [12–14], aerogel hydrothermy [15] and ionothermy [16] methods, and the resulting photocatalysts displayed higher efficiencies for pollutant removal under visible light irradiation.

Recent studies indicated that the presence of mannitol can assist assembly of BiOBr with interesting 3D heirarchical architectures. For example, Chen. et al. reported that mannitol can mediate the microwave synthesis of BiOX (X = Cl, Br, I) with hierarchical assembly structures [11]. They also proposed that formation of the nanostructure in the presence of mannitol is attributed to the selective adsorption on the nuclei [17,18] and the high viscosity of mannitol [11]. Previously, we found that cationic surfactant cetylpyridinium bromide (CPB) can be used as the bromine source and template to guide the evolution of nanostructures by formation of micelles during the hydrothermic synthesis of BiOBr photocatalyst. In that study, only the common layered BiOBr nanomaterial, rather than the desirable hierarchical assembly structures, was obtained in the absence of any alcohol [19]. An ultrathin BiOBr nanosheet was also prepared in the presence of mannitol in the polymer Polyvinyl Pyrrolidone (PVP) micelle [20]. However, the assembling chemistry of the mannitol-guided formation of nanostructure occurring in the micelles has not been adequately described.

It is known that Bi^{3+} exists only at pH ≤ 1 in aqueous solution. Above this pH, deposition of $Bi(OH)_3(s)$ would be formed. However, Bi^{3+} is soluble in alkaline solutions of mannitol, clearly indicating that mannitol successfully competes with OH^- for Bi^{3+} by forming a metal–ligand complex [21]. The underlying reason for the formation of metal–ligand complex may come from the polyhydroxyl characteristics of the mannitol, which makes mannitol a good multi-dentate ligand with the capability of strongly interacting with the Bi^{3+} ions. During synthesis of BiOBr nanostructures, the rate of the nuclei formation and growth would largely determine the morphology and the catalytic properties of the obtained materials. The formation of complex between the precursor Bi^{3+} and alcohol would have important influence on the reaction rate and consequently the properties of the BiOBr photocatalyst. When the reaction is carried out in micelle, the reaction rate can also be controlled by the availability of the precursors within micelle. In previous studies on the synthesis of BiOBr nanostructures in micelles, the Bi^{3+} species are usually incorporated before micelle formation, which would have a facile access to the Bi^{3+} species and lead to a rapid nuclei formation and particle

* Corresponding author at: Innovation Center for Geo-Hazards and Eco-Environment in Three Gorges Area, Yichang 443002, Hubei Province, China.
E-mail addresses: huangyp@ctgu.edu.cn, chem_ctgu@126.com (Y. Huang).

http://dx.doi.org/10.1016/j.catcom.2016.03.002
1566-7367/

growth. One less-reported way to control the availability of the Bi^{3+} species is to introduce them after the formation of the micelle, in which the Bi^{3+} species have to penetrate the micelles into the reaction sites and hence leading to a more controllable reaction.

This project is aimed to understand the assembling chemistry of the mannitol-guided formation of nanostructure occurring in the micelles. For this purpose, the effects of a series of alcohols with different hydroxyl (ethylene glycol (E_2), glycerol (G_3) and mannitol (M_6)) on the self-assembly of BiOBr was systematically studied to show the role of the interaction strength between the precursor Bi^{3+} and polyhydroxyl alcohol in the assembly. In addition, the solution of pre-formed Bi^{3+}–alcohol complex was introduced micelle suspension of surfactant cetylpyridinium bromide (CPB) to control the rate of nuclei formation and growth process. Particle morphologies were characterized in detail. The photocatalytic activity of each BiOBr was compared by using Sulforhodamine B (SRB) and Salicylic acid (SA) as model substrates. The results showed that the effects of mannitol on the formation of BiOBr nanostructure stems mainly come from its strong coordination with the Bi^{3+}. A four step process describing the self-assembly of BiOBr in mannitol was proposed to explain the unique morphology of BiOBr-M_6. The BiOBr photocatalyst prepared in the mannitol exhibited the highest photocatalytic activity.

2. Experimental

2.1. Catalyst preparation

Four BiOBr samples were synthesized using our previously patented method [19] and the only change is the solvent. $Bi(NO_3)_3 \cdot 5H_2O$ (0.002 mol) was dissolved in four different solvents (15 mL) of ethylene glycol (E_2), glycerol (G_3), mannitol (M_6) and dilute acidic water (W_0). CPB (0.003 mol) was dissolved in 60 mL of water to reach a concentration of 0.04 mol/L with the solutions placed in a 40 °C water bath. A yellow precipitate was formed after adding $Bi(NO_3)_3 \cdot 5H_2O$ solution dropwise, and the mixture was stirred vigorously at room temperature for 1 h. The suspension was transferred to a 100 mL Teflon-lined autoclave for 17 h at 170 °C. The precipitate was collected after samples cooled to room temperature, washed with de-ionized water, and air-dried at 50 °C. BiOBr nanomaterials were named BiOBr-G_2, BiOBr-G_3, BiOBr-M_6 and BiOBr-W_0 according to the solvent, respectively. The weight percentage (wt.%) and viscosity of four solvents in synthesis process were calculated [22–23] and shown in Table S1.

2.2. Catalyst characterization

The crystal structure of each BiOBr preparation was characterized by X-ray diffractometry (XRD) (Ultima IV, Rigaku, Japan) with Cu Kα radiation (λ = 1.54178 Å). The specific surface area and pore size of BiOBr were determined using a BET surface area and pore size analyzer (ASAP 2020, Micrometrics, USA). Scanning electron microscopic (SEM) images were obtained on JEOL (JSM 6380-LA, Japan). High-resolution transmission electron microscope (TEM and HRTEM) was used to observe the morphology on JEOL (JEM-2100f, Japan). FT-IR spectrum was recorded on Nicolet iS5 (Thermo, USA). The UV–visible diffuse reflectance spectra (UV–Vis DRS) of the catalysts were recorded (U-3010, Hitachi, Japan) using spectral grade BaSO4 as the reference material.

2.3. Activity test

All degradation experiments were carried out in a Pyrex vessel (70 mL) with SRB (1.0×10^{-5} mol/L) or SA (2.0×10^{-4} mol/L) and BiOBr. The solution pH was adjusted to 7.0 and reaction volume was 50 mL prior to irradiation, the suspension was stirred in the dark for 30 min to ensure establishment of the adsorption/desorption equilibrium on the surface of BiOBr. At pre-set time intervals, 3 mL samples were collected, centrifuged, filtered (Millipore, 0.45 μm) and the extent of degradation was monitored. SRB was determined by UV–Vis spectrophotometry at 565 nm (Perkin Elmer, USA). SA was determined using a Waters 2998 photodiode array (PDA) detector and a C_{18} reverse-phase column (5 μm, 4.6 mm i.d. × 250 mm, Kromasil). The mobile phase was methanol and phosphate (KH_2PO_4, pH 3.5) ($V:V = 45:55$) and the stationary phase was a C_{18} column using a column temperature of 30 °C, a flow rate of 0.70 mL/min and wavelength detection at 278 nm. The fluorescence method [24] was used for indirect detection of •OH and the variation of H_2O_2 concentration during degradation was determined by the DPD method [25]. During the degradation, O_2 consumption was obtained by the dissolved oxygen meters (Thermo Orion 3-Star, USA) in a sealed Pyrex vessel (20 mL) with 10 mL of SRB (1.0×10^{-5} mol/L) and 4 mg catalyst.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD

XRD results are displayed in Fig. 1. The diffraction peaks of BiOBr are 10.9°, 25.2°, 31.7°, 46.2°, 50.6°, 56.2°, 57.2°, indicating tetragonal geometry (JCPDS 85–0862) but lattice parameters (a = b = 3.920 nm, c = 8.110 nm). The seven strong diffraction peaks (001/101/110/220/104/114/212) indicate that BiOBr crystals grow anisotropically along the crystal face. The diffraction peaks of BiOBr synthesized using mannitol were not as strong as those of the others due to the amorphicity of the residual of mannitol in the sample as shown in IR spectra (Fig. S3).

3.1.2. Morphology

SEM, TEM and HR-TEM images for each of the BiOBr preparations are shown in Fig. S1. The SEM (a) images show that all four preparations have a lamellar structure composed of stacked discs ~600 nm across. BiOBr-M_6 is composed of spherical nanostructures of diameter 1–3 μm. The TEM (b) images give a more detailed view of particle morphology and structure, showing spheres composed of closely packed, multifaceted sheets (~200 nm). The HR-TEM (c) images show a typical lattice distance ranging from 0.2721–0.2779 nm, indicating exposed (110) facets [26]. Lattice parameters were calculated by reduced fast Fourier transformation (Reduced-FFT) (c, inset). The spacings calculated, 0.277 nm and 0.196 nm, correspond to facets (110) and (200), oriented at 45°. The electron diffraction spots were distinct, indicating that BiOBr is well crystallized. It is clear from the particle morphologies that mannitol strongly affects the self-assembly of BiOBr. Chen et al. prepared BiOBr with multilayered, fan-like quasi-microspheres in which the nanoplates interconnected to form a central shaft and proposed that mannitol restricts intrinsic anisotropic growth [17]. The nanoplates of different BiOBr preparations stack in ways that give different 3D structures, but mannitol does not affect the intrinsic BiOBr structure.

3.1.3. BET surface areas

Table 1 lists the specific surface areas and adsorption capacities of each BiOBr preparation and Fig. S2 shows the Brunauere Emmette Teller (BET) Plots of samples. The BET surface areas of BiOBr-W_0, BiOBr-E_2 and BiOBr-G_3 were 5.32, 6.13 and 7.06 m^2/g, respectively, whereas the BET specific surface area of BiOBr prepared in mannitol (M_6) was 11.92 m^2/g. Both measures of Langmuir specific surface area and monolayer adsorption capacity for BiOBr-M_6 are remarkably higher than those of the other BiOBr preparations.

3.1.4. Absorption

The UV–Vis DRS of each catalyst is displayed in Fig. 2. The band gap potential (E_g) of BiOBr can be calculated using Kubelka–Munk function ($(\alpha h\nu)^2 = A(h\nu - E_g)^2$). The calculated E_2 of four catalysts were: BiOBr-M_6, 2.78; BiOBr-G_3, 2.82; BiOBr-E_2, 2.89 and BiOBr-W_0, 2.91. Although