



Hierarchical bismuth oxychlorides constructed by porous nanosheets: Preparation, growth mechanism, and application in photocatalysis

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ABSTRACT

Hierarchical structures bismuth oxychlorides (BiOCl) were synthesized *via* a solvothermal process assisted with citric acid using methanol as a solvent. The as-synthesized hierarchical structures were constructed by porous nanosheets. The crystal growth and morphology structures of BiOCl were significantly influenced by the amount of citric acid, the solvothermal time and the solvent used in reaction. Based on the electron microscope observations, the growth of such architectures has been proposed as an Ostwald ripening process followed by self-assembly. Pore-size distribution analysis revealed that both mesopores and macropores existed in the product. UV–vis spectroscopy was employed to estimate the band gap energies and light utilization efficiency of the BiOCl hierarchical structures. Moreover, the adsorption capability and photocatalytic activities of BiOCl hierarchical structures were evaluated on the degradation of rhodamine B and methyl orange under either UV light or simulated sunlight illumination, respectively. The results assumed that BiOCl hierarchical structures sample showed much higher photocatalytic activity than the conventionally prepared sample and commercial TiO₂ (Degussa, P25).

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1. Introduction

Environmental problems associated with organic and toxic water pollutants are more and more urgent in the area of environmental remediation [1,2]. Heterogeneous photocatalysis is an emerging technique valuable for water and air purification and remediation using semiconductors as environmental photocatalysts. Photocatalysis by polycrystalline semiconductor oxides is an unconventional technology that has traditionally been applied (sometimes

coupled to other technologies) to degrade organic and inorganic pollutants both in vapor and liquid phase. Its main advantages consist not only under general mild conditions, but also in the possibility to abate refractory, very toxic and non biodegradable molecules. At present, photocatalytic degradation of organic pollutants is attracting extensive interest for its potential applications in remedying environmental pollution [3]. In general, the photocatalytic properties of photocatalyst relate primarily to the amount of catalysts surface active sites, which depend on the BET surface area of catalysts, light utilization, and other structural properties (e.g. phase composition, crystallinity, size distribution) [4]. Therefore, great research efforts have been made on the synthesis of

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nanometer- and micrometer-size anisotropic materials with controlled shape of the architectures. Among various morphological structures, in particular, microscale architectures composed of nanosheets have the advantages of both a microstructure and a nanostructure, e.g. high surface-to-volume, anti-aggregation ability, and abundant electronic transport paths, which could be expected to enhance physical and chemical performance of catalysts [5,6].

Bismuth oxychloride (BiOCl), one of the important main group multi-components V–VI–VII semiconductors, has drawn considerable attention for its potential applications as a novel photocatalyst due to its unique layered structures and high chemical stability [7]. BiOCl is known to be a tetragonal layered structure consisting of [Cl–Bi–O–Bi–Cl] sheets stacked together by nonbonding interactions through the Cl atoms along the *c*-axis. The strong internal static electric fields perpendicular to the Cl layer and the bismuth oxide-based fluorite-like layer enable the effective separation of the photogenerated electron–hole pairs, and these results in a high photocatalytic performance [8–10]. To date, various morphologies such as nanoplates [11], nanobelts [12], nanosheets [13], microspheres [14], and flower-like hierarchical structures [15], have been synthesized *via* different synthetic routes, e.g. sonochemistry, ionothermal synthesis, hydrolytic, hydro-/solvothermal, etc. For flower-like BiOCl hierarchical structures, they have been reported by several research groups over the past few years [16–21]. Generally, the solvent in the solvothermal method has a crucial effect on the formation of BiOCl hierarchical structures. Qin et al. synthesized hierarchical BiOX (X=Cl, Br and I) microspheres by a generalized ionic liquid-assisted solvothermal method [22]. Zhu et al. prepared hierarchitectured BiOCl with different morphologies and microstructures by a template-free solvothermal method [23]. Xia et al. synthesized BiOCl with uniform flower-like microspheres and porous nanospheres structures through a one-pot ethylene glycol (EG)-assisted solvothermal process in the presence of reactable ionic liquid 1-hexadecyl-3-methylimidazolium chloride ([C₁₆mim]Cl) and [C₁₆mim]Cl–PVP composite system [14]. Wang et al. synthesized BiOCl micro-flowers in water and glycerol solvent *via* a facile hydrothermal route [24]. In these studies, polyols e.g. ethylene glycol or glycerol were used as solvent. However, to the best of our knowledge, it is still rare in literature about the preparation of BiOCl hierarchical structures through a solvothermal route using methanol as a solvent. Citric acid (CA) can strongly complex metal ions and significantly alters the surface properties. It has been widely used as chelating agent in sol–gel, hydrothermal and solvothermal routes to prepare nanoparticles [25,26].

In our previous work, it has been shown that the flower-like BiOCl hierarchical structures could be prepared through a solvothermal synthesis assisted with CA using methanol as a solvent [27]. However, the formation mechanisms of BiOCl hierarchical structures are still unclear. Herein, in the present work, we investigated the formation mechanisms of BiOCl hierarchical structures by controlling the amount of CA, the solvothermal time and the solvent used in reaction. Furthermore, the relationship between

the structures of the photocatalyst and the photocatalytic activities was also discussed in detail.

2. Experimental

2.1. Starting materials

All major chemicals were of AR grade and used without further purification. Bismuth nitrate (Bi(NO₃)₃·5H₂O) was purchased from Guangdong Guanghua Chemical Factory Co., Ltd. China. Potassium chloride (KCl) was supplied by Xilong Chemical Co., Ltd., China. Methanol and citric acid were obtained from Beijing Chemical Works, China. And distilled water was used in all experiments.

2.2. Preparation of BiOCl photocatalysts

Flower-like BiOCl hierarchical structures were synthesized *via* a facile solvothermal method. In a typical procedure, 0.005 mol of Bi(NO₃)₃·5H₂O was dissolved in 30 mL of methanol, being followed by dissolution of 0.005 mol KCl and 0.005 mol CA (molar ratio of CA/Bi³⁺=1) into the above solution. After further stirring for 0.5 h, the mixture was transferred into 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 150 °C for 12 h, and then cooled to room temperature. The precipitate was washed with distilled water and ethanol, and then dried under vacuum at 60 °C for 12 h. To understand the role of CA and the formation process of the flower-like BiOCl hierarchical structures, controlled experiments were carried out by varying the amount of CA added (CA/Bi³⁺=0, 0.375, 0.625 and 2) and the reaction times (0.5, 1, 3, 6 and 24 h), while keeping other experimental conditions unchanged. To investigate the effect of solvent on the final product, distilled water was used as solvent to synthesize BiOCl. Other conditions were the same.

2.3. Catalyst characterization

The crystallographic phases were characterized by X-ray diffraction (XRD) analysis using graphite monochromatized Cu K α radiation (Rigaku, D/MAX 2200 PC). The measurements were carried out at 40 kV tube voltages and 200 mA current. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific Escalab 250 spectrometer with monochromatized Al K α excitation, and C 1s (284.6 eV) was used to calibrate the peak positions of the elements. The morphology of samples was evaluated by field emission scanning electron microscopy (FESEM, JEOL-6340F) with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were taken over a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. The UV–vis diffuse reflectance spectra were obtained using a Scan UV–vis spectrophotometer (Shimadzu, UV-3600) with BaSO₄ as reference. The specific surface areas (BET) of the powder samples were determined by the amount of nitrogen adsorption at 77 K (BET, NOVA-2200e).

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