



Facile synthesis and photocatalytic activity of La-doped BiOCl hierarchical, flower-like nano-/micro-structures



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ABSTRACT

A series of La-doped BiOCl hierarchical, flower-like nano-/micro-structures (NMFs) with ginkgo-leaf-like “petals” were prepared by etching La-doped Bi₂O₃ films in HCl solution at room temperature. For the La-doped Bi₂O₃ films, they were fabricated through hot-dipping Bi₂O₃ thin films in La₂O₃ powder at 650 °C. Microstructure examination revealed that the ginkgo-leaf-like La-doped BiOCl petals have a multilayered structure consisting of several ultra-thin nanosheets with different radii due to the external-to-internal etching process. The investigation on their formation mechanism revealed that the La-doped BiOCl hierarchical NMFs grew anisotropically through Ostwald ripening mechanism. Besides, the photodegradation of rhodamine B under simulated sunlight irradiation revealed that the La-doped BiOCl hierarchical NMFs possessed higher performance than pure BiOCl sample. And the active species trapping tests indicated that the photogenerated holes were the main active radicals for the degradation of rhodamine B.

1. Introduction

As a member of V-VI-VIIA groups compound semiconductors, bismuth oxychloride (BiOCl) protrudes outstandingly among its congeners in optical, catalytic, luminescent, electrical and gas sensitive properties. Consequently, it has various promising applications in industries, like paints in cosmetic industry [1], photocatalysts for degrading many organic dyes such as rhodamine B (RhB), ciprofloxacin and eosin Y under visible-light irradiation [2,3], high-performance electrocatalysts for air electrode of Al-air batteries [4], and gas sensors to CO, CO₂ and O₂ [5,6].

To date, many approaches have been proposed to synthesize various forms of BiOCl materials, including electrospinning, solvothermal synthesis, hydrolysis, hydrothermal synthesis, sonochemical route, refluxing method, solution oxidation process, and electrochemical route [7–14]. And a variety of BiOCl materials with different nano-/micro-structures, like one dimensional nano-rods/wires, two dimensional nano-plates/sheets and three dimensional hierarchical architectures, have been fabricated. However, most of their aggregates are powders or particles, which have some inevitable problems [15,16]. (i) They are not easily applied to continuous flow system. (ii) The suspended catalyst powders or particles tend to aggregate, especially when they are of high concentration, weakening their photocatalytic activity. And (iii)

the separation of the photocatalysts with organic pollutants is very difficult and expensive; so they cannot be recycled and reused, preventing some special applications such as battery electrode or photocatalysis reaction. Therefore, many scientists have still striven to synthesize various BiOCl materials with specific nano-/micro-structures.

On the other hand, although BiOCl has attracted considerable attention for potential photocatalytic application, its large band-gap (about 3.46 eV [17]) makes it useful only under ultraviolet irradiation, hindering its applications under visible light, the main part (about 96%) of the natural solar light. In order to improve the absorption and utilization efficiency of BiOCl for visible light, the modification of BiOCl has been a hot topic in this field. And it has been reported that the visible light driven photocatalytic activity of BiOCl can be improved to some extent by changing the crystal structure, band gap or surface microstructure. For example, Xie *et al.* [18] synthesized Sn-doped BiOCl photocatalysts at room temperature via an oxidation-reduction method, indicating that Sn(10%)-doped BiOCl sample exhibited higher photocatalytic degradation on benzoic acid and RhB than the other Sn-doped BiOCl and pure BiOCl ones due to its narrowed band gap (2.91 eV). Ding *et al.* [19] synthesized Er³⁺ doped BiOCl hierarchical microspheres by a solvothermal method. The presence of Er³⁺ did not affect the microstructure and morphology of BiOCl, but the Er³⁺ doped BiOCl microspheres exhibited an enhanced photocatalytic activity for the

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degradation of RhB under visible light ($\lambda > 420$ nm) irradiation. The enhanced activity was attributed to the up-conversion resulted in by the dopant that could transform visible into ultraviolet light. Besides, La doping is also an effective way to improve the catalytic activity of some oxide semiconductors photocatalysts. Not only can La present as stable La^{3+} ion because there existed no variable valence state for it, but also improve the quantum yield of the doped oxides by prolonging the life of the photo-generated carries because of the shallow potential trap formed by its full electronic configuration [20]. For instance, Yang *et al.* [21] prepared La doped Bi_2O_3 by an impregnation method, indicating that an appropriate amount of La doping can effectively prevent the transformation of Bi_2O_3 from tetragonal to monoclinic phase. Their UV–vis absorption spectra revealed an extension of light absorption into the visible region (higher than 550 nm). The doped La would partially substitute bismuth in the lattice of Bi_2O_3 , existing in a form of Bi-O-La chemical bond, and a new complex metal oxide compound ($\text{La}_{0.176}\text{Bi}_{0.824}\text{O}_{1.5}$) appeared in the catalysts, which could inhibit the recombination between photoelectrons and holes, leading to enhanced photocatalytic quantum efficiency. Sun *et al.* [20] synthesized La-doped TiO_2 film by a sol-gel method. La^{3+} dispersed into TiO_2 in the form of mainly La_2O_3 and partly Ti-O-La bond. And La doping can inhibit the phase transformation of TiO_2 by enhancing its phase transformation temperature, and is also beneficial for the formation of TiO_2 in smaller particle size and thus with large surface area. However, the application of La doping into BiOCl to improve its photocatalytic properties has not been reported.

Therefore, in this work, we present a simple approach to prepare La-doped BiOCl films, which are composed of hierarchical, flower-like nano-/micro-structures (NMFs) with ginkgo-leaf-like “petals”, by etching La-doped Bi_2O_3 films in HCl acid at room temperature. For the applied La-doped Bi_2O_3 films, they were fabricated through hot-dipping Bi_2O_3 thin films in La_2O_3 powder at 650 °C. Special emphasis was paid on the effects of the hot-dipping time in La_2O_3 and etching time in HCl acid on the composition, structure and photocatalytic properties of the as-prepared La-doped BiOCl films. The formation mechanism was proposed. And the mechanism for their improved photocatalytic performances was also suggested.

2. Experimental section

2.1. Samples preparation

P-type conducting silicon wafers purchased from GRINM Advanced Materials Co. Ltd (China) were used as the substrates. Before use, the substrates were ultrasonically cleaned in absolute alcohol and de-ionized water for 20 min, respectively, and then completely dried in an open oven. All the applied chemicals were of analytical grade and used as received without further purification. Among them, HCl acid was bought from Beijing Chemical Works (China), and the others were from Xilong Chemical Co. Ltd (China). In a typical process, Bi_2O_3 films were first prepared onto silicon substrates by covering the substrates with Bi_2O_3 powder and then heating at 800 °C for 1 h in a muffle furnace (KSL-1100, Hefei Kejing Materials Technology Co. Ltd, China). After heating, extra Bi_2O_3 powder became a chunk, which could be peeled off from the substrate, and thus thin Bi_2O_3 film was left on it. Then, the Bi_2O_3 film was covered with La_2O_3 powder and heated at 650 °C for 5, 10, 20, 30 and 40 min, respectively. After that, the samples were further etched in HCl aqueous solution (HCl:H₂O = 1:100) for 120 s. Finally, the etched samples were rinsed by de-ionized water and dried by N₂ flow. For comparison, a non-doped, pure BiOCl film was also prepared by the same process.

2.2. Materials characterization

The phase composition of the samples were identified by grazing incidence X-ray diffraction (GI-XRD, D/max-RB, Cu K α radiation,

$\lambda = 1.5418$ Å) in a 2θ range of 10° to 90° under a continuous scanning mode with a scanning rate of 6°/min at an incidence angle of 1° of the X-ray. The morphology of the samples was observed by field emission scanning electron microscope (SEM, S4800). The samples were also examined by transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN, America) and high-resolution transmission electron microscopy (HRTEM). X-ray photoelectron spectroscopy (XPS, non-monochromated Mg K α radiation, photon energy 1253.6 eV) was performed to characterize the chemical state and composition of the samples, during which the spectrometer was calibrated by the binding energy of C1s line (285 eV). The UV–vis absorption spectra were recorded on a Cary 5000 UV–vis spectrometer (Varian) equipped with a DRA-CA-30I integrating sphere for solid-phase characterization.

2.3. Photocatalytic activity

The photodegradation of model dye RhB under simulated sunlight irradiation (SSI) was carried out to evaluate the photocatalytic activity of the obtained La-doped BiOCl hierarchical NMFs. The samples were set on the bottom of a glass tube with the substrate surface covered with the La-doped BiOCl hierarchical NMFs toward the light (provide by an 8 W halogen lamp, which emits light with a wavelength approximately in the range of 400–790 nm). Then the glass tube was filled with 5 mmol·L⁻¹ RhB solution, keeping the ratio of the mass of the La-doped BiOCl catalyst (mg) to the volume of the RhB solution (mL) equal to 1:1. After the light irradiation for each 10 min, 3 mL of the reactive solution was withdrawn from the reaction system for the measurement of the remnant RhB content in it by an UV–vis spectroscope (SP-752). After the measurement, the reactive solution was immediately poured back into the glass tube to keep the reaction in almost the same state. For comparison, the photocatalytic activity of the pure BiOCl sample was also examined under the same conditions.

2.4. Active species trapping experiments

In order to examine the active species generated in the photocatalytic process, 1 mM benzoquinone (BQ, a quencher of superoxide radicals $\cdot\text{O}_2^-$ [22]), 1 mM triethanolamine (TEOA, a scavenger of holes h^+ [22]), and 1 mM isopropanol (IPA, a capturer of hydroxyl radicals $\cdot\text{OH}$ [23]) were added into the reaction system, respectively, together with the prepared catalyst before light irradiation. And all the other experimental parameters during the tests were kept as those of the above RhB photodegradation experiments.

3. Results and discussion

3.1. Composition and microstructure

Typical XRD patterns of the La-doped BiOCl films produced from Bi_2O_3 films via hot-dipping in La_2O_3 powder at 650 °C for different times followed by etching in HCl acid for 120 s are shown in Fig. 1a. For comparison, that of the sample without La_2O_3 hot-dipping is also presented. As is seen from this figure, all the diffraction peaks of the samples, whether they were hot-dipped in La_2O_3 powder or not, can be assigned to those of the tetragonal phase of BiOCl with a space group of P4/nmm (JCPDS card no. 85-0861). Because there are no other diffraction peaks detected, it can be concluded that the applied Bi_2O_3 films were converted into BiOCl during the present etching processes. But due to the detection limit of XRD, no new phase in correlation with the doped La^{3+} ions could be identified. And the strong and sharp diffraction peaks indicated that the samples prepared by this approach are well crystallized. However, when Bi_2O_3 was hot-dipped in La_2O_3 powder for increasing time up to 20 min, a peak shift to large angle of 2θ could be easily observed. From the XRD patterns as shown in Fig. 1a, the lattice constants of *a* and *c* of the BiOCl phase were calculated, and the results are displayed in Fig. 1b as a function of the La_2O_3 hot-

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