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Hydrothermal fabrication and enhanced photocatalytic activity of hexagram shaped InOOH nanostructures with exposed {0 2 0} facets

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ABSTRACT

Hexagram shaped InOOH nanostructures with exposed {0 2 0} facets were synthesized in large quantities via the hydrothermal reaction of $InCl_3$ with NaAc, ethylene glycol and H_2O system at 180–220 °C for 12 h. The six constituent nanocones of the hexagram shaped nanostructure grew along the directions perpendicular to $(2\,0\,0)/(\bar{2}\,0\,0)$, $(1\,0\,1)/(\bar{1}\,0\,\bar{1})$ and $(\bar{1}\,0\,1)/(1\,0\,\bar{1})$ facets of the orthorhombic InOOH through the oriented attachment process, and the top and bottom surfaces of the hexagrams were dominantly enclosed by the {0 2 0} facets. The {0 2 0} facets were stabilized by ethylene glycol, which was employed to control the growth of InOOH crystals. When the hydrothermal reaction temperature increased, the size of hexagram shaped InOOH nanostructures decreased, their specific surface area and the texture coefficient (TC) of (0 2 0) plane increased, and thus their photocatalytic activity was enhanced. The hexagram shaped InOOH nanostructures obtained at 220 °C showed higher intrinsic photocatalytic activity than Degussa P25 TiO_2 for degradation of rhodamine B. The superior intrinsic photocatalytic activity was attributed to the high percentage of exposed {0 2 0} facets of the hexagram shaped nanostructures.

1. Introduction

Since discovery of water photolysis on a TiO_2 electrode in presence of UV by Fujishima and Honda in 1972 [1], semiconductor photocatalysis has received much attention as a potential solution to the worldwide energy shortage and for counteracting environmental degradation [2]. During the past decades, the photocatalytic activities of TiO_2 [3–5], WO_3 [6,7] ZnO [8,9], In_2O_3 [10,11], α-Fe_2O_3 [12], CdS [13], ZnS [13], ZnSe [14], $NiO_x/In_{1-x}Ni_xTaO_4$ [15], etc. in the degradation of toxic organic pollutants and splitting of water have been widely studied [16]. Recently, Li et al. reported the photocatalytic activity of InOOH nanoparticles with irregular morphologies for the degradation of benzene and rhodamine B (RhB) [17,18]. However, the photocatalytic activities of InOOH with well-defined geometric shapes have never been investigated until now.

As we know, semiconducting nanocrystals with well-defined sizes and geometric shapes display chemical and physical properties that differ from those of the bulk materials and have enormous potentials as fundamental building blocks for nanoscale electronic and photonic devices [19,20]. As for InOOH, an n-type semiconductor with a wide band gap of 3.5 eV, nanofibers [21], nanowires [22], nanorods [23,24], nanotubes [24,25], multipods [26], hollow microspheres [27], urchin-like structures [11], and 3-D architectures [28] have been synthesized via various wet chemical methods, but these InOOH nanostructures are simply employed as precursors for synthesis of In_2O_3 nanocrystals with well-defined geometric shapes, and their crystal structure, physical and chemical properties have hardly been studied. To the best of our knowledge, the photocatalytic activity of single crystalline hexagram shaped InOOH nanostructures have never been reported until now.

Herein, we demonstrate the facile fabrication of hexagram shaped InOOH nanostructures with dominant {0 2 0} surfaces in the $InCl_3$-ethylene glycol (EG)-NaAc-H_2O hydrothermal system. Average size, specific surface area and the texture coefficient (TC) of (0 2 0) plane of the hexagram shaped InOOH nanostructures can be adjusted by changing the hydrothermal reaction temperature. The growth mechanism and photocatalytic activities of the InOOH hexagram in the degradation of RhB were investigated in detail. The as-prepared hexagram shaped InOOH nanostructure with exposed {0 2 0} facets shows higher intrinsic photocatalytic than Degussa P25 TiO_2 for degradation of rhodamine B.

2. Experimental

2.1. Preparation

All reagents used were of analytical grade and were directly used as received without any further purification. 0.510 M aqueous

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solution of $InCl_3$ was obtained by dissolving 15.000 g of $InCl_3 \cdot 4H_2O$ in 100.0 mL of 0.12 M hydrochloric acid.

The hexagram shaped InOOH nanostructures. In a typical procedure, 0.88 ml of 0.510 M $InCl_3$ aqueous solution, 5.0 mL of water and 0.367 g of $NaAc \cdot 3H_2O$ were put into a beaker of 50 mL capacity, stirred to form a clear solution (pH of about 6). Then 24.0 mL of EG was added into the clear solution under stirring. After 10 min, the mixed solution was transferred into a Teflon-lined autoclave of 50 mL capacity. The autoclave was sealed and heated at 180–220 °C for 12 h. After hydrothermal treatment, the autoclave was cooled down to room temperature naturally. The resulting white products were isolated by centrifugation, washed with water and absolute ethanol, and finally dried in air at room temperature.

2.2. Characterization

The as-prepared products were characterized and analyzed using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and infrared (IR) spectroscopy. The XRD analysis was performed using a Rigaku D/MAX2500VB+ X-ray diffractometer with Cu Kα (λ = 1.541 Å) radiation at 40 kV and 100 mA. Each specimen was scanned at a step size of 0.02° and a scanning speed of 4°/min with diffraction angles varying between 20° and 70°. SEM images were obtained on a FEI Quanta 200 scanning electron microscope at an accelerating voltage of 20 kV. TEM and electron diffraction images were obtained using a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. Samples for TEM were prepared by dispersing InOOH powder on a carbon-coated copper grid. IR spectrum was recorded using a Nicolet Avatar 360E.S.P Fourier transform IR spectrophotometer at room temperature. The specific surface area was measured by nitrogen adsorption/desorption using Brunauer–Emmett–Teller (BET) method on an ASAP 2020 Surface and Porosimetry Analyzer (Micromeritics, USA).

2.3. Evaluation of photocatalytic activity

RhB was selected as model organic compounds to examine the photocatalytic activity of the InOOH hexagram shaped nanostructures. 30.0 mg of the as-prepared photocatalysts was added to 30.0 mL of 2.5×10^{-5} M RhB aqueous solution to get a suspension. The suspension was magnetically stirred for 30 min in the dark to establish an adsorption/desorption equilibrium between the dye and the photocatalyst. Then the mixed solution was irradiated with a 300 W medium-pressure mercury-vapor lamp at a distance of about 8 cm (XPA-7 photochemical reactor, Xujiang Electromechanical Plant, Nanjing, China). At a given irradiation time interval, 5 mL of sample was withdrawn from the test tube for analysis. Sample solutions were obtained by centrifugation, and their absorption spectra were measured by on a Hitachi U-3900 spectrophotometer using deionized water as reference. For comparison, the photocatalytic activities of commercial TiO_2 (Degussa P25) were also tested under the same reaction conditions and with the equal catalyst weight as that employed for InOOH.

3. Results and discussion

3.1. Morphology and crystal structure

The morphology and crystal structure of the as-synthesized samples were investigated by SEM and XRD. Fig. 1a and b shows the typical SEM images of the sample prepared at 180 °C for 12 h. It can be observed that the sample consists almost entirely of hexagram-shaped nanostructures with six symmetric arms extending radically from the center. The average size was

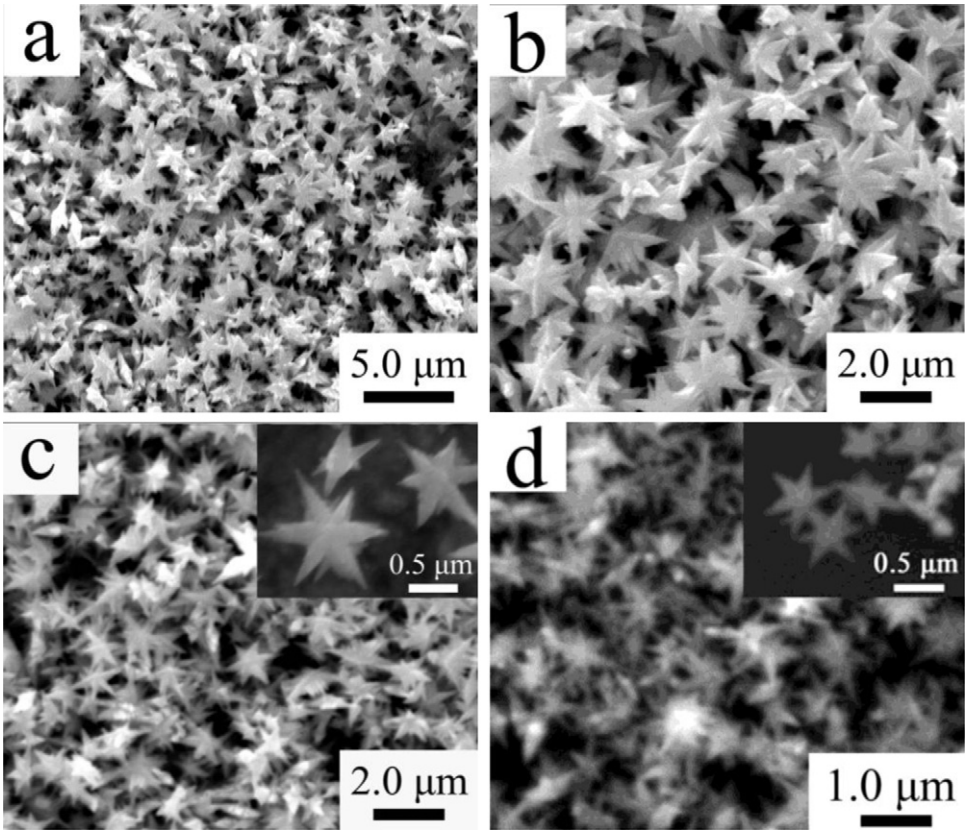

Fig. 1. SEM images of hexagram shaped InOOH nanostructures prepared at 180 °C (a) and (b), 200 °C (c) and 220 °C (d) for 12 h.