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Synthesis of bilayer ZnO nanowire arrays: Morphology evolution, optical properties and photocatalytic performance

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Abstract

A novel hierarchical zinc oxide three-dimensional architecture of densely packed and well-aligned bilayer ZnO nanowire arrays was synthesized via a hydrothermal process. For ZnO nanowire growth, a layer of dense zinc microplatelet arrays was first obtained on copper foil by an electroplating method. Uniform ZnO nanowires were grown vertically on both surfaces of zinc microplatelet in hydrothermal solution only containing ammonia water. The obtained ZnO nanowire arrays possessed high packing density and uniform size, demonstrating a rapid nucleation and growth process in the initial stage of growth. But then Ostwald ripening dominated the morphology evolution of hierarchical ZnO architecture due to a low degree of supersaturation of ZnO. XRD and HRTEM characterizations confirmed ZnO possessing a highly crystalline nature with preferential (002) orientations along the *c*-axis direction. With the decrease of ZnO nanowire size, the absorption spectra of hierarchical ZnO film exhibited an increase of visible light absorption and slight red-shift of band gap, whereas its emission spectra exhibited a decrease of photoluminescence intensity, which can be ascribed to the increase of defects in ZnO structure with size decrease. The photocatalytic experiment indicated that the hierarchical nanostructure film had superior photocatalytic performance in the degradation of methyl orange solution under ultraviolet irradiation. The work also presented a simple approach for further practical application of ZnO nanowire arrays to nanoscale optoelectronic device.

Keywords: D. ZnO; Hierarchical architecture; Hydrothermal method; Photocatalysis

1. Introduction

ZnO is an important metal oxide semiconductor material with wide band gap (3.37 eV) and large exciton binding energy(60 eV) [1]. One-dimensional (1D) ZnO nanostructures are of special interest due to their unique catalytic, electrical and optical properties, which are related with their high aspect ratio, the quantum size confinement effect, and more direct conduction path for electron transport [2–4]. Self-assembly of 1D ZnO nanostructure into highly ordered hierarchical architectures with morphology uniformity and narrow size distribution has attracted much attention owing to its promising applications to nanodevices, such as field emission transistors [5] and solar cells [6]. There have been many reports about the physical and chemical methods to fabricate ordered hierarchical heterostructure based on 1D ZnO nanostructure, including metal organic chemical vapor deposition (MOCVD), thermal vapor deposition, pulsed laser deposition, molecular beam epitaxy, electron beam evaporation, spray pyrolysis, electrochemical deposition, and hydrothermal synthesis [7–15]. Among them, hydrothermal process is a low cost and large scale method. However, almost all the templated hydrothermal synthesis methods rely on pre-made ZnO seed layer on the substrate prior to the actual hydrothermal synthesis to promote high density nucleation and oriented growth [8]. Thus, a simple, facile, and seed-free method to fabricate ordered hierarchical ZnO architectures would be of great interest. Koh and Loh [16]reported the synthesis of hexagonally packed zinc oxide nanorod bundles on hydrotalcite (HTLc) sheets

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by reacting zinc acetate with aluminum-coated silicon in alkali hydrothermal condition. Liu et al. [17] described the synthesis of ZnO/Zn–Al layered double hydroxide hierarchical heterostructures using an Al substrate suspended in a $Zn(CH–CO_2)_2$ aqueous solution. Lupan et al. [18] reported a template-free solution growth self-assembly technique to synthesize densely packed and aligned bilayer ZnO nanorod arrays through the formation of a thin layer of hydrotalcite-like zincowoodwardite in a hydrothermal reaction process. In the examples above, the Zn–Al layered double hydroxide seemed to be essential for the growth of self-assembled ZnO nanorod arrays.

Naturally, the photocatalytic performance of the hierarchical ZnO nanostructure is fascinating. Recent researches revealed that the hierarchical ZnO nanostructure has much improved photocatalytic activity due to higher specific surface area, hierarchical porous surface structure, and more surface defects [19–22]. It is also confirmed that constructing hierarchical structure based on 1D or 2D structures on desired substrate is an efficient way not only to achieve integration of catalysis-recycle but also to keep the outstanding photocatalytic performance unchanged [23].

In the present work, a novel hierarchical ZnO 3D architecture was synthesized by self-assembly of densely packed and well-aligned bilayer ZnO arrays. In this process, a layer of dense zinc microplatelet (MP) arrays on copper foil was first formed by a common electrodepositing method. Then, uniform bilayer ZnO nanowire arrays grew symmetrically and vertically on both surfaces of zinc MP in ammonium-based hydrothermal condition. The morphology evolution of hierarchical assembly induced by temperature and time was observed. The photocatalytic activity and reusability of the as-synthesized ZnO hierarchical nanostructures were evaluated by the photodegradation of methyl orange (MO) under ultraviolet (UV) irradiation. The relationship among the morphology, size, optical properties, and photocatalytic performance was also discussed.

2. Experimental section

2.1. Materials and reagents

The reagents used in the experiments were of analytical grade and utilized without further purification. Zn foil (99.9%), copper foil (99.9%, $20 \times 40 \times 0.1$ mm^3), zinc chloride ($ZnCl_2$), potassium chloride (KCl), boric acid (H_3BO_3), gelatin, ammonia ($NH_3 \cdot H_2O$, 25%) were obtained from Sinopharm Chemical Reagents Co. Ltd.

2.2. The preparation of zinc-electroplated Cu foil

Zinc MP arrays were prepared by the electrodepositing method as reported before [24]. The detail is as follows: A copper foil was rubbed with fine sandpaper and cleaned with dilute hydrochloric acid, acetone, and distilled water in turn in an ultrasonic bath. A zinc foil was also rubbed with fine sandpaper and then cleaned with absolute ethanol and distilled water in an ultrasonic bath, respectively. A mixture consisting of 0.40 M $ZnCl_2$, 2.50 M KCl, 0.40 M HBO_3, and 2 g L^{-1} gelatin was prepared and used as the electrolytic solution. The electrodeposition experiment was carried out at the room temperature in a single cell unit at a constant voltage of 0.4 V, using the cleaned Cu foil as cathode and the zinc foil as anode. After 30 min electrodeposition, the Zn-electrodeposited copper foil was obtained.

2.3. The preparation of ZnO nanostructure

In a typical reaction process, 40 mL of distilled water with a stationary concentration of ammonia hydroxide (0.1 M) was added into a Telfon beaker and the Zn-electrodeposited copper foil was placed vertically against the wall of Teflon beaker. Then, the Teflon beaker was sealed into a stainless steel autoclave and maintained at a certain temperature for the desired test time. After the reaction was complete, the autoclave was naturally cooled to the room temperature. The foil was taken out and washed with distilled water and absolute ethanol, and directly used in photodegradation experiment or dried under vacuum at 60 °C for 4 h for the following characterization.

2.4. Characterization

The morphologies of the products were studied by SEM (Hitachi, S-3400N). The structure characterization of the products was carried out by using X-ray diffraction (XRD, D/max-γB) equipped with Cu Kα radiation over a range from 20° to 80°. The high resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL) with selected-area electron diffraction (SAED) was used to obtained the HRTEM image and SAED pattern of single nanowire. Compositions of the nanowires were determined by energy-dispersive X-ray spectroscopy (EDS, OXFORD, attached on the TEM). Ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS) of the products was tested using an Ocean Optics optical fiber spectrometer (Maya 2000 pro). The spectra were recorded timely in the range of 250–650 nm using $BaSO_4$ as the reference standard. Photoluminescence (PL) spectroscopy of products was taken at room temperature on a Perkin-Elmer Lambda S55 spectrofluorometer using a Xe lamp with an excitation wavelength of 325 nm.

2.5. Photocatalytic test of ZnO nanostructures

The photocatalytic activity of the as-synthesized ZnO products was evaluated by the degradation of methyl orange (MO) solution under UV irradiation. In a typical experiment, the ZnO film was suspended in a quartz reactor filled by 80 mL of 10 mg/L MO aqueous solution. The solution was stirred for 30 min in the dark in order to achieve the absorption equilibrium, which was then irradiated under the high pressure mercury lamp (300 W, dominant wavelength 365 nm). During the irradiation, 3 mL aliquots were taken from the reactor at a 30-min interval and the absorbance of MO solutions at 465 nm were measured on a UV–vis spectrophotometer (UV-2000).