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Original research article

Template-free hydrothermal synthesis of Flower-like hierarchical zinc oxide nanostructures

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ABSTRACT

Flower-like hierarchical zinc oxide nanostructures have been successfully synthesized by a facile and template-free hydrothermal method from zinc acetate ($Zn(AC)_2$) and potassium hydroxide (KOH) only. Furthermore, the effects of alkaline mineralizer type on product synthesis by hydrothermal processing have been studied. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscope, UV–vis spectrophotometry and Raman-scattering spectroscopy. When the type of mineralizer was KOH, the shape of ZnO sample has presented flower-like hierarchical nanostructures with diameters of 2–4 μm. Photocatalytic activity of the hierarchical ZnO nanostructures was evaluated by the degradation of methylene blue (MB) under UV light illumination. The as-prepared ZnO nanostructures exhibited a significantly enhanced photocatalytic activity than commercial ZnO. This was mainly attributed to the unique morphology and higher surface area.

1. Introduction

With rapid development of global economy and continuous improvement of people living standard, the ecological balance is damaged significantly, environmental pollution problems are becoming more and more serious. Especially, the pollutions come from industrial waste soluble organic dyes and organic chemicals, when these pollutants release into the environment, they effectively disturb the ecosystem and pose a direct threat to the water resources. Hence, it is needed to search for a new pollution treatment technology for the efficient degradation of this harmful and widely used dye [1–3]. Among several advanced processes, photocatalytic oxidation process attracts considerable attention as a technology for removing organic pollutants from water. It provides an interesting route for the destruction of the toxic and hazardous pollutants up to completely mineralize into H_2O and inorganic ions. The mechanism about photocatalytic oxidation processes has been discussed extensively in literature [4–8].

As one of the most important semiconductor photocatalysts, ZnO has presents itself as one of the promising photocatalyst for the photocatalytic degradation of organic dyes and chemicals due to its versatile properties such as direct and wide band gap (~3.37 eV), large exciton binding energy (60 meV), semiconducting, piezoelectric and pyroelectric properties and so on [9–13]. Moreover, compared with TiO_2, ZnO has receiving much attention due to its lower cost, very simple synthesis process and has the similar band gap energy around 3.2 eV. In this paper, that is flower-like hierarchical zinc oxide nanostructures which are assembled by nanosheets are synthesized by hydrothermal method successfully. Our method does not require either complicated apparatus nor other additives [14]· This is a facile and economical route to prepare flower-like hierarchical zinc oxide nanostructures. Additionally, the as-prepared flower-like hierarchical ZnO nanostructures show a high specific surface area and exhibit a significantly enhanced photocatalytic activity in the photodegradation of MB.

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2. Experimental

Flower-like hierarchical ZnO nanostructures were synthesized by a simple hydrothermal method. All chemicals used in this work were analytical-grade reagents without any further purification. In a typical experiment, 10 ml 0.1 M zinc acetate aqueous solution and 10 ml 1 M potassium hydroxide aqueous solution were added to 20 ml double distilled water. After vigorous magnetic stirring for 30 min, the resulting mixed solution was transferred into a 50 ml Teflon-lined stainless steel autoclave and heated at 120 °C for 8 h. The precipitates were centrifuged, washed with water and alcohol several times, and finally dried in an oven at 60 ℃ for 24 h.

The X-ray powder diffraction (XRD) data were collected on an X'Pert MPD Philips diffractometer. Scanning electron microscopy (SEM) images were performed by using a FE-SEM JEOL-6700F microscope operating at 20 kV. The UV–vis spectra were recorded in the range of 200–600 nm by a Thermo Scientific Evolution system (300 UV–vis spectrophotometer, USA). The Raman spectra (Invia, Renishaw, Gloucestershire, UK) were excited by a 532 nm Nd: YAG laser at room temperature.

The photocatalytic performance of the as-prepared samples was monitored using UV–vis spectrophotomer by photocatalytic degradation of MB. The samples (1.5 g/l)

were dispersed in the 100 ml MB aqueous solution (10 mg/l). The mixed suspensions

were magnetically stirred for 30 min in the dark to attain an adsorption–desorption equilibrium and irradiated by 365 nm UV light. At certain time intervals (15 min), 2 ml of the mixed suspensions were extracted and centrifugated to remove the photocatalyst. The degradation of MB was observed by recording the decrease in optical absorption peak at 663 nm with increasing time of light irradiation. The photocatalytic cycling stability of the as-prepared samples was tested by degradation of MB solution at the same condition, the cycle was repeated with three times, and the solid powder obtained was used the next photocatalytic degradation test after filtering and drying when the photocatalytic reaction was end every time.

3. Results and discussions

The XRD patterns of the synthesized flower-like hierarchical ZnO nanostructures are shown in Fig. 1. All the peaks in Fig. 1 are well-matched with the hexagonal wurtzite structure of ZnO (JCPDS 36–1451). No other diffraction peaks were detected, indicating that no impurity existed in the pattern which confirms the well-crystallinity and purity of as-synthesized ZnO nanostructures.

The morphologies of the synthesized flower-like hierarchical ZnO nanostructures were investigated by field emission scanning electron microscopy (FESEM), as are shown in Fig.2. The low resolution FESEM image shows that the synthesized nanostructures are grown in large density and possessing multilayered structure. The average diameter of the grown nanostructures was determined in the range of 2–4 μm. The high resolution FESEM image shows that most of the synthesized nanostructures exhibit almost uniform morphologies, are constructed by ZnO nanosheet and the surface of the nanosheet is relatively smooth, about 60 nm in thickness. Further composition of the synthesized nanostructures is confirmed by FESEM-EDS. Except for C (because the sample were decomposed on the conductive adhesive) and Au (because its surface was sprayed with gold), the peaks corresponding to zinc and oxygen were detected as shown in Fig.2(c), without any other peak related to impurity which confirmed that the synthesized nanostructures were composed of zinc and oxygen.

Initial nucleation that occurs during hydrothermal reactions are expressed in the following chemical equations:

$$Zn^{2+} + 2\ OH- \rightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

$$Zn(OH)_2 + 2\ OH- \leftrightarrow [Zn(OH)_4]^{2-} \quad (3)$$

$$Zn^{2+} + 2\ OH- \leftrightarrow ZnO + H_2O \quad (4)$$

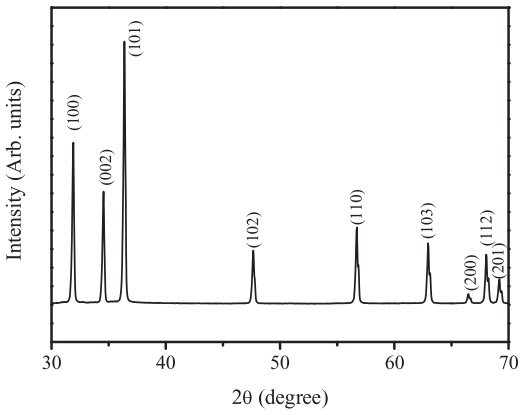

Fig. 1. XRD patterns of the synthesized flower-like hierarchical ZnO nanostructures.