Materials Research Bulletin 48 (2013) 3723–3728

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Pencil-like zinc oxide micro/nano-scale structures: Hydrothermal synthesis, optical and photocatalytic properties

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ARTICLE INFO

Article history:
Received 1 March 2013
Received in revised form 2 May 2013
Accepted 27 May 2013
Available online 10 June 2013

Keywords:
A. Inorganic compounds
B. Chemical synthesis
C. X-ray photoelectron spectroscopy
D. Optical properties

ABSTRACT

Zinc oxide micro/nanopencils have been successfully synthesized by hydrothermal process using zinc acetate and diamines as structure-directing agents. The morphology, the structure, the crystallinity and the composition of the materials were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The optical properties of synthesized ZnO were investigated by UV–vis spectroscopy. The photocatalytic activity of the material has been evaluated by the degradation of methylene blue under UV irradiation. As a result, after the lapse of 150 min, around 82% bleaching was observed, with ZnO nanopencils yielding more photodegradation compared to that of commercial ZnO (61%).

1. Introduction

In recent years, controlling the morphology and size of inorganic materials has attracted intensive attention due to the fact they play very important roles in determining optical, electrical, and other physicochemical properties [1–4]. Due to decrease in particle size, novel properties resulting from quantum effects have been observed [5]. Nanocrystalline metal oxides play a very important role in materials science. The synthesis of inorganic nanocrystals with tunable morphology is currently an active field of research in modern materials chemistry due to their wide application in catalysis, energy conversion, optoelectronics, microelectronics, optics, and biology [6–8]. Efforts have been devoted to controllable synthesis of inorganic materials with various morphologies for exploring its potential applications in various fields. One-dimensional (1D) nanostructures, such as nanowires, nanotubes, nanobelts, and nanorods, have been prepared and exhibit lots of special properties in optical, electronic, and mechanical properties [9–17]. Among the fine, structured semiconducting materials, ZnO is a wide direct band gap (3.37 eV) semiconductor material with a large exciton binding energy (60 meV). Besides, its nontoxicity, inexpensive and chemical stability has made ZnO a promising material in various fields including photocatalysis [18], solar cells [19], sensors [20], nanogenerators [21], room-temperature UV laser [22], optical waveguides [23], and so on. More recently, improved optimized routes, simple solution and hydrothermal treatment, for fabrication of nanostructured products have been also reported [24]. It is noticed that morphology of the synthesized nanostructures strongly depends on the synthesis route and the structure directing agents [25–27].

This paper deals with the synthesis of zinc oxide (ZnO) micro/nanopencils by hydrothermal reaction of zinc acetate $Zn(CH_3COO)_2{\cdot}2H_2O$ and diamines $H_2N(CH_2)_nNH_2$ ($n = 3$, 4 or 6) which could allow control the size and the morphology. A study of the photocatalytic activity is reported. Although many methods have been developed to elaborate nanostructured zinc oxide, to the best of our knowledge, it is the first report of ZnO micro/nanopencils synthesis using $Zn(CH_3COO)_2{\cdot}2H_2O$ and diamines $H_2N(CH_2)_nNH_2$ (with $n = 3$, 4 or 6) as structure-directing agents, and no report on the photocatalytic activity of ZnO nanopencils has been conducted so far.

2. Experimental

2.1. Hydrothermal synthesis

All of the chemical reagents were analytical grade. They were purchased from Acros Organics and used without further purification. Zinc oxide micro/nanopencils were prepared from

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http://dx.doi.org/10.1016/j.materresbull.2013.05.116

$Zn(CH_3COO)_2{\cdot}2H_2O$, diamines [$H_2N$–$(CH_2)_n$–$NH_2$ with n = 3 (DAP), 4 (DAB) and 6 (DAH)], NaOH and distilled water (5 mL) in the molar ratio 1:1:10. Once introduced in the above-mentioned order, reactants were stirred for few minutes. The resulting mixture was transferred into a Teflon-lined stainless autoclave (47 mL capacity). The autoclave was sealed and maintained at 180 °C for 4 h. The system was then naturally cooled to room temperature. In the series of syntheses, the diamine was changed at the designed molar ratio. The resulting white powder was washed with water and acetone to remove the residues of diamines. It was then left to dry for four hours at 80 °C. The pH of the solution remains close to pH ≈ 13 during the whole synthesis.

2.2. Characterization techniques

X-ray powder diffraction data (XRD) were obtained on a X'Pert Pro Panalytical diffractometer with CuKα radiation (λ = 1.5418 Å) and graphite monochromator. The XRD measurements were carried out by applying a step scanning method (2 range from 3 to 70), the scanning rate is 0.017 s^{-1} and the step time is 1 s. Scanning electron microscopy (SEM) images were recorded on a Cambridge Instruments Stereoscan 120. Fourier-transform infrared spectra (FTIR) were recorded from 4000 to 400 cm^{-1} on a Nicolet 380 spectrometer in pellets of samples dispersed in KBr. Raman spectroscopy was performed using a Jobin Yvon T 64000 spectrometer (blue laser excitation with 488 nm wavelength and < 55 mW power at the sample). X-ray photoelectron spectroscopy (XPS) experiments were performed using a Shimadzu ESCALAB, at room temperature. UV–vis spectra were recorded on Shimadzu UV3101PC Visible spectrophotometer in the Wavelength range of 200–800 nm. The photocatalytic activity of ZnO nanopencils and commercial ZnO was tested by methylene blue (MB) degradation under UV light at room temperature. Experiments were performed in a Vossloh schwabe (1 L) reactor containing 10 mL of MB solution with an initial concentration of 10 mg L^{-1} and the loading of the catalyst is 1 g L^{-1}. The irradiation source was under the irradiation of UV lamp (6 W) with a maximum emission at 365 nm immersed within the reactor in a double wall jacket for water circulation to avoid the heating of mixture. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure adsorption/desorption equilibrium. At regular time intervals, suspension samples were collected and centrifuged to separate solid particles. The filtrates were analyzed by recording the variation of the absorption band maximum at 365 nm in the UV–vis spectrum of MB using a Hach RD/4000 UV–vis spectrophotometer. The MB concentration was calculated by Beer–Lambert equation.

3. Results and discussion

3.1. X-ray diffraction

Powder X-ray diffraction patterns of the resulting samples are shown in Fig. 1. As indicated, all of diffraction peaks can be ascribed to the pure hexagonal phase of ZnO (wurtzite structure, space group P_3^6mc). The cell parameters are calculated to be $a = b$ = 3.25 Å and c = 5.25 Å according to JCPDS card No. 36-1451. All peaks appear at 2θ = 31.827, 34.478, 36.310, 47.589, 56.649, 62.911, 66.430, 67.001 and 69.132, corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2) and (2 0 1), respectively. The results indicate that the products consist of pure phase and no characteristic peaks can be found from other phases or impurities. Additionally, the sharp and the small values of the full widths at half maxima (FWHM) of the XRD peaks reveal that the as-synthesized materials are of high purity and good crystallinity. It is well known that the growth rate of the different planes family follows the sequence (0 0 1) > (1 0 1) > (1 0 0) [28,29]. But in this study the (1 0 1) peak is the most intense peak, that shows (1 0 1) plane is preferred growth plane. Maybe this rearrangement of the order of growth rate among (0 0 1), (1 0 0), and (1 0 1) surfaces are due to synthesis condition [29]. The average crystallite size of the as-synthesized materials was calculated by using Scherrer's formula:

$$L = \frac{0.89\lambda}{\beta \cos\theta}$$

where L is the average crystallite size, λ = 0.154056 nm, β is the half maximum peak width and θ is the diffraction angle in degrees [30]. The average crystallite size values, calculated from XRD patterns of the samples synthesized with DAP, DAB and DAH, have been found to be about 87 nm, 89 nm and 90 nm, respectively. It is clear that the hydrocarbon chain length of the diamines has no significant influence on the crystallite size.

3.2. Scanning electron microscopy

Further structural characterization of the ZnO was performed by SEM. It was found that the different structure-directing agents lead to the different morphologies of samples as shown in SEM micrographs (Fig. 2). In fact, ZnO grew in all diamines, but the

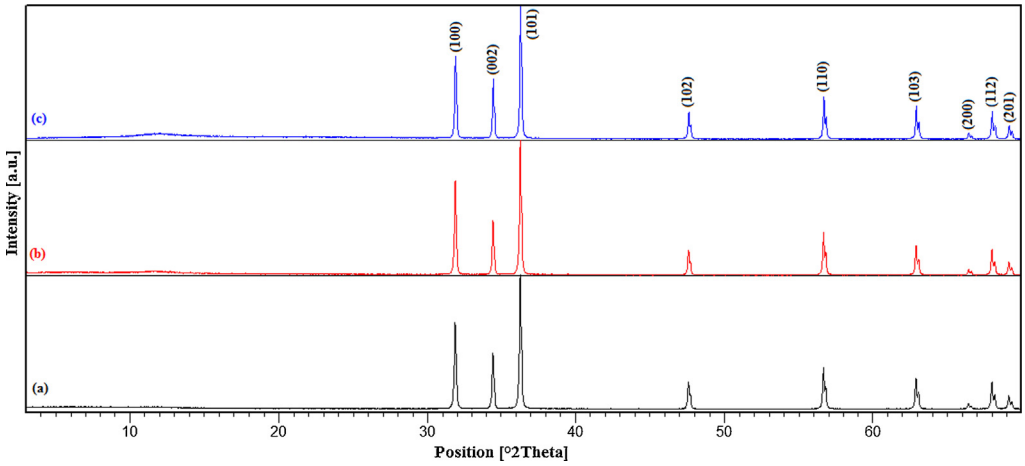

Fig. 1. XRD patterns of the as-synthesized ZnO using DAP (a), DAB (b) and DAH (c) as structure-directing agents.