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Preparation, photoluminescence and photocatalytic activity of micro and nanosized flower-like ZnO

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Abstract: In this paper, micro and nanosized flower-like ZnO were successfully prepared by a microwave route without assistance of surfactant and template, employing zinc acetate and sodium hydroxide or ammonia as the starting materials. Nanosized flower-like was obtained when ammonium hydroxide solution was used. X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra were employed to characterization of the as synthesized ZnO. The photocatalytic activity of micro and nanosized flower-like ZnO was compared by photocatalytic decolorization of Congo red azo dye. Results show that the photocatalytic efficiency of micro sized flower-like ZnO to be remarkably greater than that nanosized flower-like ZnO.

Keywords: *Luminescence; Photocatalyst; Microwave; ZnO*

Introduction

Zinc oxide with a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV), is currently attracting worldwide intense interests because of its importance in fundamental studies and its numerous applications especially as optoelectronic materials [1]. The size and morphology of ZnO particles have great influences on their performances. Because of the materials properties depend on their size and shape, new synthetic strategies in which the size and the shape of nanostructures can be easily tailored are important. Recently, efforts have been made for the synthesis of ZnO particles with controlled morphologies. Zinc Oxide is used for a wide variety of industrial applications, such as semiconductors and photocatalysts [2, 3]. ZnO has been widely used as a photocatalyst, owing to its high activity, low cost and environmentally friendly feature [4]. There are numerous methods for the preparation of flower-like ZnO [5, 6]. Microwave radiation is a special heat-treatment method, and under this condition, reaction time can be greatly reduced, and it has been used to synthesize various materials [7-9]. In this paper, micro and nanosized flower-like ZnO were synthesized by microwave method. X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra were employed to characterization of the as synthesized ZnO.

Furthermore, photocatalytic activities of the micro and nanosized ZnO were investigated.

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Experimental procedure

All reagents were analytic grade and used without further purification. Zinc acetate dihydrate (0.80 g) was dissolved in double distilled water (40 mL) under vigorous stirring and, 4M NaOH or ammonium hydroxide 25% was added drop wise until the solution become transparent, and stirred for about 5 min. Finally, 10 ml of the mixture was loaded into a 50 ml capacity pyrex bottle. The reaction vessel was placed in a microwave oven (Daewo, KOR-63A5, 800W) and 25-100% of the microwave output power was used to irradiate the mixture for 1-2 min (on for 30 s, off for 7 s). The product was separated by decantation, washed with double distilled water several times and dried. The structure and morphology of the product were characterized by using XRD (Holland Philips Xpert X-ray diffractometer with Cu-Kα radiation) and SEM (Holland Philips XL30 microscope with an accelerating voltage of 25 kV). The PL spectra were recorded on a Varian Cary-Eclipse spectrometer.

Furthermore, the efficiency of micro and nanosized flower-like ZnO was compared by photocatalytic decolorization of Congo red azo dye. The amount of Photo catalyst and concentration of congo red azo dye solution were chosen 0.5 g/l and 5 mg/l respectively. Photocatalytic experiments were performed in opened Pyrex vessel. The radiation source, a UV lamp, (30W, UV-C, $\lambda = 253.7$ nm) was irradiated perpendicularly to the surface of solution, and distance between the UV source and vessel containing reaction mixture was fixed at 15 cm. Air was blown into the reaction by an air pump to maintain the solution saturated with oxygen during the course of the reaction. The progress of photocatalytic decolorization was measured by UV-Vis spectrophotometer (Shimadzu UV 2100).

Result and discussions

The conditions of some typical samples synthesized by microwave heating are listed in Table 1.

The morphology of the ZnO product was visualized by SEM. Figure 1 shows the SEM images of samples.

Here, the effect of mole ratio OH^-/Zn^{2+} and microwave output power on the morphology and sized were studied. Results show that, micro flower-like ZnO can be obtained with mole ratio $OH^-/Zn^{2+} = 15$ and under microwave irradiation with 25-100% output power.

Table 1 Experimental conditions for some typical flower-like ZnO samples

sample No.	Precursors	% Microwave Out put power	Time of reaction	$[OH]/[Zn^{2+}]$	product	Morphology
1	Zinc acetate/NaOH	25	2 min	15:1	ZnO	Micro Flower
2	Zinc acetate/NaOH	50	1.5 min	15:1	ZnO	Micro Flower
3	Zinc acetate/NaOH	75	1.5 min	15:1	ZnO	Micro Flower
4	Zinc acetate/NaOH	100	1 min	15:1	ZnO	Micro Flower
5	Zinc acetate/NH_4OH	25	2 min	-	ZnO	Micro Flower
6	Zinc acetate/NH_4OH	50	1.5 min	-	ZnO	Micro Flower
7	Zinc acetate/NH_4OH	75	1.5 min	-	ZnO	Micro Flower
8	Zinc acetate/NH_4OH	100	1 min	-	ZnO	Nano Flower
9	Zinc acetate/NaOH	25	2 min	30:1	No Product	-
10	Zinc acetate/NaOH	50	1.5 min	30:1	No Product	-
11	Zinc acetate/NaOH	75	1.5 min	30:1	No Product	-
12	Zinc acetate/NaOH	100	1 min	30:1	No Product	-
13	Zinc acetate/NaOH	100	6 min	30:1	No Product	-

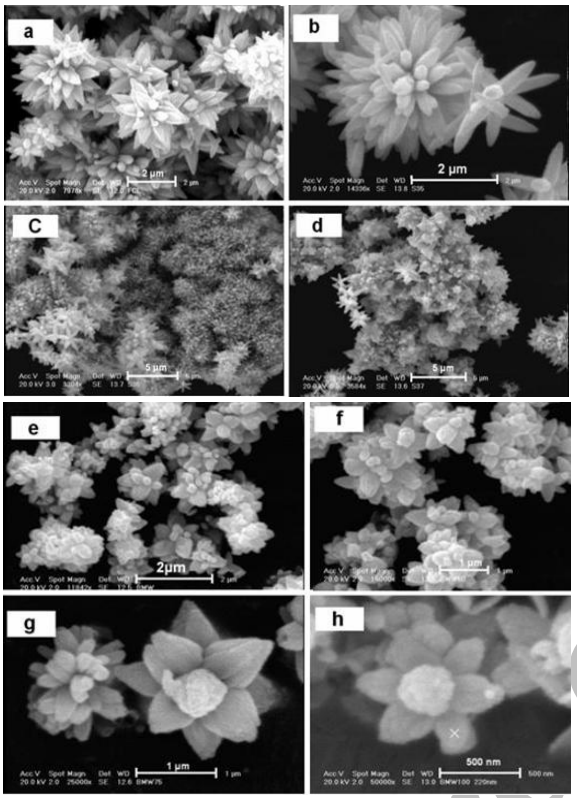

Figure1 SEM images of samples (1-8) according to Table 1, (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, (f) sample 6, (g) sample 7 and (h) sample 8.

At the mole ratio OH^-/Zn^{2+} = 30 the product was not formed. According to SEM image (Figure 1h) the nanosized flower-like zinc oxide was obtained when ammonium hydroxide solution and 100% microwave out put power was used. In the present work, the duration of microwave heating process was very short (1-2 min). The microwave irradiation played a critical role in the rapid formation of flower-like ZnO. During the microwave irradiation, the heating phenomenon was occurred by the interaction of the dipole molecules such as H_2O with the high frequency electromagnetic radiation [10]. Figure 2 shows XRD patterns of the samples 2 and 8. All the diffraction peaks are in agreement with the JCPDS file of ZnO (JCPDS No. 36-1451), which can be indexed as a hexagonal phase of ZnO.

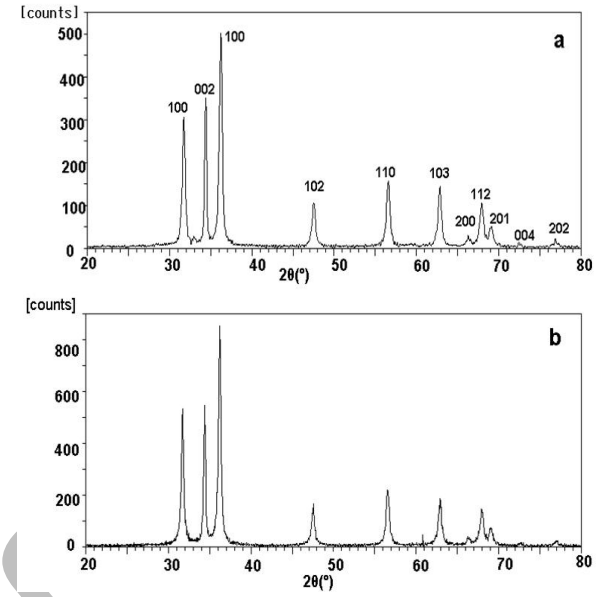

Figure 2 X-ray diffraction patterns for the products (a) micrsized flower-like ZnO,sample 2, according to Table 1 (b) nanosized flower-like ZnO, sample 8, according to Table 1

The decolorization of Congo red dye using photocatalytic reaction for the nano and micro sized ZnO was studied. Results show that the photocatalytic efficiency of micro sized flower-like ZnO to be remarkably greater than that nanosized flower-like ZnO (Figure 3).

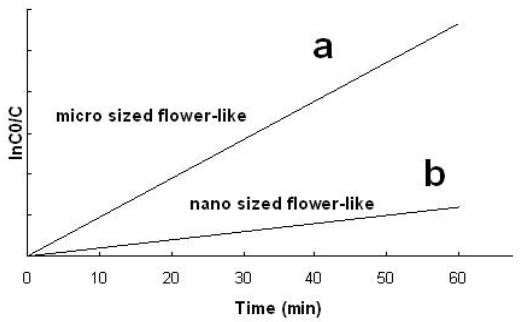

Figure 3 photocatalytic activity of the micro (a) and nanosized flower-like ZnO (b), sample 2 and 8 according to Table 1, respectively

The photoluminescence (PL) technique has been widely used to investigate the structural and proper-

ties of the active sites on the surface of metal oxides [11]. Also,the PL technique has been useful in the field of photocatalysis over semiconductors for understanding the surface processes. PL spectrum is an effective way to study the electronic structure, optical and photochemical properties of semiconductor materials [12]. Therefore, it is of great significance for environmental photocatalysis. We used the PL spectroscopy as an effective method for evaluating ZnO defects. The PL spectrum of the nano and micro sized flower-like ZnO were measured by an excitation wavelength of 325 nm at room temperature. Figure 4 shows the PL spectra of the micro and nanosized flower-like ZnO. The photoluminescence spectrum for micro sized flower-like ZnO (Figure 4a) shows a UV emission at 390 nm, the UV peak is due to the recombination of photo-generated electrons and holes [13].

Furthermore, PL spectrum reveals blue emissions with a strong band at 446 nm and weak band at 418 nm. They are attributed to the transition between the vacancy of oxygen and interstitial oxygen [14]. An emission was observed at 593 nm, which was due to the single ionized oxygen vacancy in the zinc oxide crystal [14]. In contrast, PL spectrum for nanosized flower-like ZnO reveals a UV emission at 388 nm and visible emission at 593 nm (Figure 4b). The PL

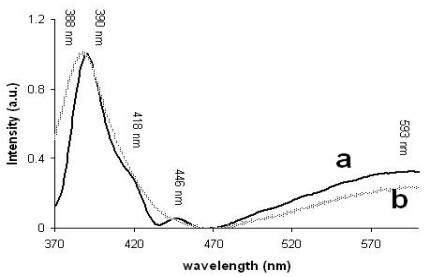

Figure 4 PL spectra of the micro (a) and nanosized flower-like ZnO (b), sample 2 and 8 according to Table 1, respectively

emission can be ascribed to the presence of defects in the crystalline structures discussed and, therefore, the formation of states within the band gaps.

Conclusions

In summary, a simple and rapid one-step method was proposed to fabricate micro and nanosized flower-like ZnO. The nanosized flower-like zinc oxide was obtained when ammonium hydroxide solution and 100% microwave out put power was used. Furthermore, Results show that the photocatalytic efficiency of micro sized flower-like ZnO for decolorization of Congo red dye to be remarkably greater than the nanosized flower-like ZnO. The PL spectrum for nanosized flower-like ZnO reveals a UV emission at 388 nm and visible emission at 593 nm. In contrast, PL spectrum for micro sized flower-like ZnO reveals a UV emission at 390 nm and visible emission at 593, 446 and 418 nm.

Acknowledgements

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