Microwave Assisted Synthesis of Polycrystalline Flower-like Zinc Oxide Nanostructure Using Dicationic Ionic Liquid

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(Received: 05 Sep. 2010 and Accepted: 12 Nov. 2010)

Abstract:
In this paper, synthesis of the flower-like zinc oxide was performed using microwave assisted dicationic ionic liquid [mmp(im)$_2$]Br$_2$. The polycrystalline flower-like zinc oxide nanostructure was obtained when a suitable mole ratio (ionic liquid /zinc acetate) and short duration microwave was used. X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra were employed to characterize of the as-synthesized zinc oxide. The SEM image illustrates that the surface of flower-like zinc oxide is polycrystalline with nanoparticles of about 48 nm. The samples fabricated in presence and absence of ionic liquid exhibited (UV, green-yellow) and (UV, blue, green) emission, respectively, while Commercial ZnO exhibited UV and green emission.
Keywords: *Zinc oxide; Flower-like; Polycrystalline; Ionic liquid; Luminescence*

1. INTRODUCTION

Room temperature ionic liquids (RTIL) have been widely studied in organic chemistry as new types of environmentally friendly reaction media, owing to their unique properties such as extremely low volatility, wide temperature range in liquid state, ionic conductivity and non-flammability [1]. A variety of inorganic nanostructures have been fabricated via various RTIL involved processes, including, TiO_2 nanoparticles and nanotubular [2, 3], Bi_2Se_3 nanosheets [4], CdS hallow nanospheres [5], gold nanoparticles [6], CdF_2 nanoflakes [7], ZnO nanorods [8-10] flower-like ZnO [11, 12] ZnO particles [13] and iron oxide nanorod and nanocubs [14]. However, in contrast to their application in organic chemistry the use of ionic liquid (IL) in inorganic synthesis is still in its primary stage. In recent years, the microwave method has been rapidly developed for synthesis of nanomaterial. Ionic liquids are excellent microwave absorbing agents due to their high ionic conductivity and polarizibility, thus leading to a high heating rate and a significantly shortened reaction time [15, 16]. Luminescence spectroscopy is known to be an effective method for evolution of surface defects and optical properties. Generally, the UV emission is due to the recombination of photo-generated electrons and holes, while the visible emission is associated with oxygen vacancies [17]. Presence of oxygen vacancy and existence of defect in the structure of zinc oxide makes the ZnO nanostructures ideal gas sensors and photocatalyst [18-21]. Furthermore, room temperature ferromagnetism property of zinc oxide was strongly related to the presence of oxygen vacancy defect [22]. Hence, new strategy synthesis of zinc oxide is important for tailoring of gas sensor and room temperature ferromagnetism devices.

In this paper, a simple and rapid one-step method by microwave assisted ionic liquid [mmp(im)$_2$]Br$_2$ was

proposed for the synthesis of polycrystalline flower-like zinc oxide nanostructure. X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra have been employed for characterization of the as-synthesized ZnO samples.

2. EXPERIMENTAL

The IL used in this study was synthesized according to the procedures reported in the literature [23]. Figure 1 shows the structure of the IL used in this study.

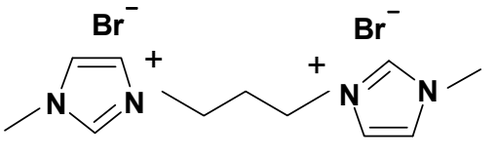

Figure 1: *The structure of the dicationic IL used in this study.*

Zinc acetate-2-hydrate and Commercial ZnO were purchased from Aldrich and Merk, respectively. Sodium hydroxide was used without further purification. Zinc acetate dihydrate was dissolved in double distilled water under vigorous stirring and, NaOH solution (mole ratio of OH^-/Zn^{2+} = 15:1) was added drop wise until the solution become transparent, and a solution of the IL in double distilled H_2O was added and stirred for about 5 min (mole ratio of IL/Zn^{2+} = 0.75:10, 1:10 and 2:10). 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 75% of the microwave output power was used to irradiate the mixture for 1 min (on for 30 s, off for 7 s). The product was separated by decantation, washed with double distilled water several times and dried. Furthermore, the experiment was carried out in absence of IL under the same condition.

The structure and morphology of the products were characterized by 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.

3. RESULTS AND DISCUSSION

The conditions of typical samples are listed in Table 1.

Figure 2 shows the SEM image and XRD pattern of sample 1. In this experiment zinc oxide was synthesized in absence of IL. The SEM image illustrates agglomerated flower-like zinc oxide. The position of the diffraction peaks (XRD) is in good agreement with the JCPDS file of ZnO (JCPDS card No. 36-1451).

Sample 2 was prepared in presence of the IL (mole ratio of IL/Zn^{2+}=0.75:10). The XRD pattern of sample 2 indicated that the product consists of two types of peaks, which can be well indexed to the ZnO and $Zn(OH)_2$ reported in JCPDS file (No.36-1451 and No.38-0385) (Figure 3A). The SEM image of this product is shown in Figure 4a.

When the product was transferred to the furnace and heated at 180ºC for 1 hour, pure ZnO was obtained (see Figures 3B, XRD pattern and 4b, SEM image).

Table 1: *Experimental conditions for the prepared zinc oxide*

Sample No.	Precursors	% Microwave Out put power	Time of reaction (min)	Mole ratio of IL/Zn^{2+}	Product	Morphology
1	Zinc acetate/NaOH	75	1.5	-	ZnO	Fig. 2
2	Zinc acetate/NaOH	75	1	0.75:10	ZnO + $Zn(OH)_2$	Fig. 4a
3	Zinc acetate/NaOH	75	1	1:10	ZnO	Fig. 4c
4	Zinc acetate/NaOH	75	1	2:10	ZnO	Fig. 4d

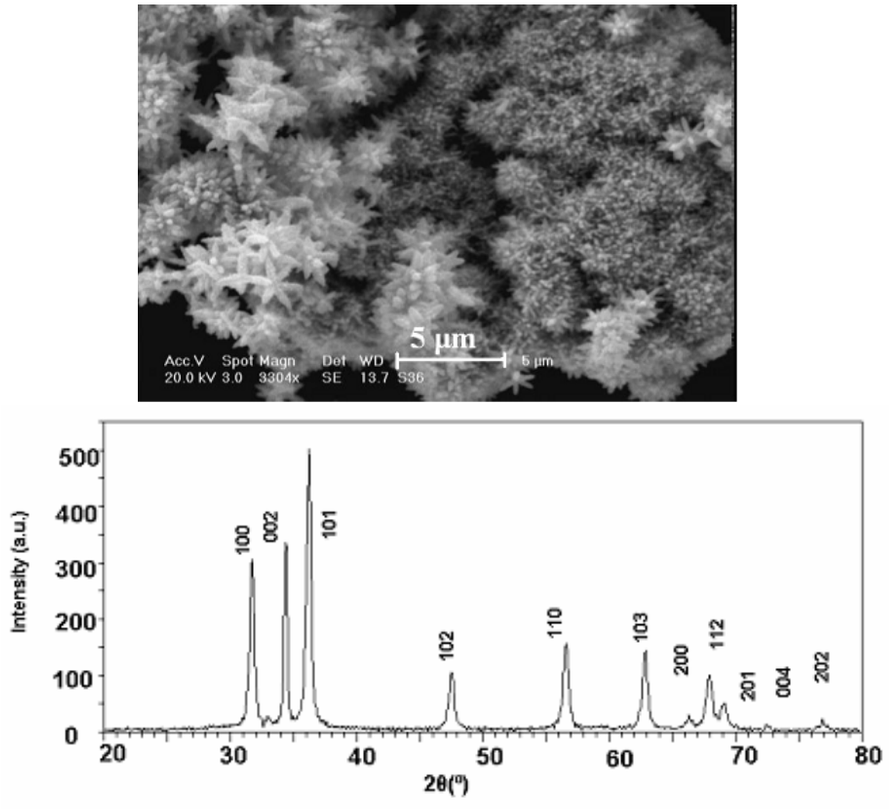

Figure 2: *SEM image and XRD pattern of the sample 1.*

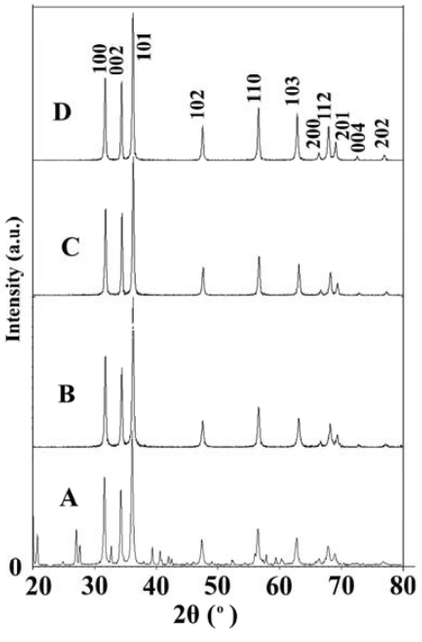

Figure 3: *XRD pattern of the: (A) as-prepared product, mole ratio of IL/Zn^{2+} = 0.75:10, sample 2 (B) annealed sample 2 at 180 °C for 1 hour (C) as-prepared product, mole ratio of IL/Zn^{2+} = 1:10, sample 3 (D) as-prepared product, mole ratio of IL/Zn^{2+} = 2:10, sample 4.*

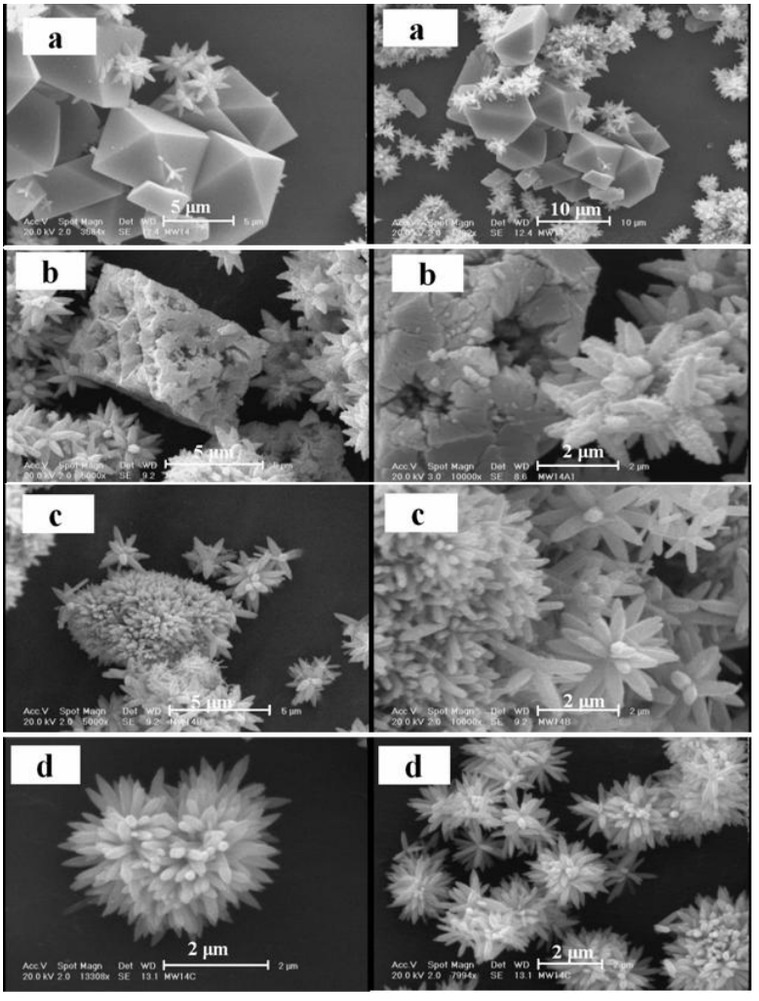

Figure 4: *SEM images of the: (a) as-prepared product, mole ratio of IL/Zn^{2+} = 0.75:10, sample 2 (b) annealed sample 2 at 180 °C for 1 hour, (c) as-prepared product, mole ratio of IL/Zn^{2+} = 1:10, sample 3 (d) as-prepared product, mole ratio of IL/Zn^{2+} = 2:10, sample 4.*

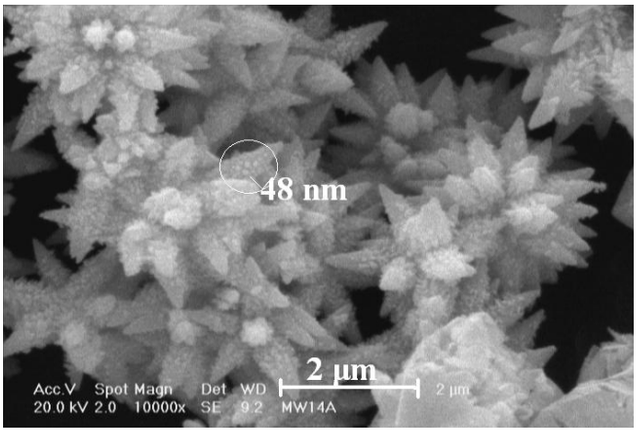

Figure 5: *SEM image of the polycrystalline flower-like zinc oxide.*

Increasing the mole ratio of IL/Zn^{2+} (1:10 or 2:10) led to pure zinc oxide (sample 3 and 4). The phase characteristics of the products were determined by using XRD pattern of the samples. All the reflections were indexed as pure hexagonal ZnO phase which were in good agreement with the data reported for Zincite [JCPDS 36-1451] (Figure 3C and 3D). XRD patterns indicated that the products were pure powders with no observable peaks relevant to such impurities as $Zn(OH)_2$. Figures 4c and 4d show the morphologies of zinc oxide prepared in presence of the IL with mole ratio of IL/Zn^{2+} = 1:10 and 2:10, respectively. It is obvious from the results that suitable mole ratio of the IL/ Zn^{2+} played an important role in the morphology and purity of zinc oxide. The SEM image illustrates that the polycrystalline flower-like zinc oxide has nanoparticles on the surface with average size of about 48 nm (Figure 5**)**.

In the present work, the duration of microwave heating process was very short (1 min). The microwave irradiation played a critical role in the rapid formation of flower-like zinc oxide. During the microwave irradiation, the heating phenomenon was occurred by the interaction of the dipole molecules with the high frequency electromagnetic radiation [24]. Polar molecules such as H_2O and ionic liquid have high dipole moments that make them appropriate solvents for microwave-assisted reactions. For the growth process of the flower-like ZnO crystals a possible formation process of ZnO was suggested as follows. Zinc hydroxide $[Zn(OH)_4]^{2-}$ species could be easily formed, and served as growth units for the formation of ZnO nuclei and epitaxial growth of ZnO nuclei into flower-like structures. The overall reaction may be simplified as follows:

$$[Zn(OH)_4]^{-2} \xrightarrow{\text{Microwave irradiation}} ZnO + H_2O + 2\,OH^-$$

In this investigation, the formation of ZnO flower-like is due to the initial formation of nuclei by the microwave radiations, and then the IL molecules may serve as a growth controller [25]. As it is known, ZnO is a polar crystal, O^{2-} is in hexagonal closest packing, and each Zn^{2+} lies within a tetrahedral group of four oxygen ions [26]. The IL is

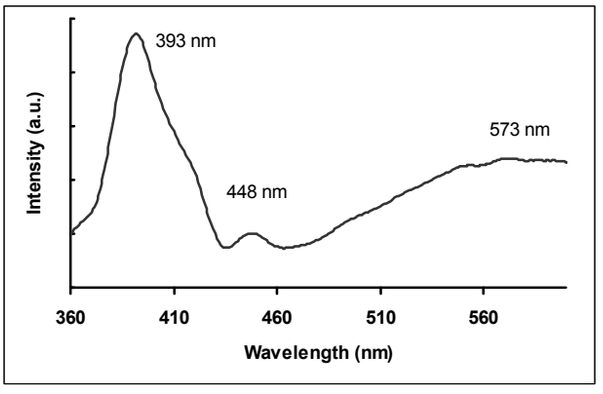

Figure 6: *Room temperature PL spectrum of the zinc oxide produced in absence of IL, sample 1.*

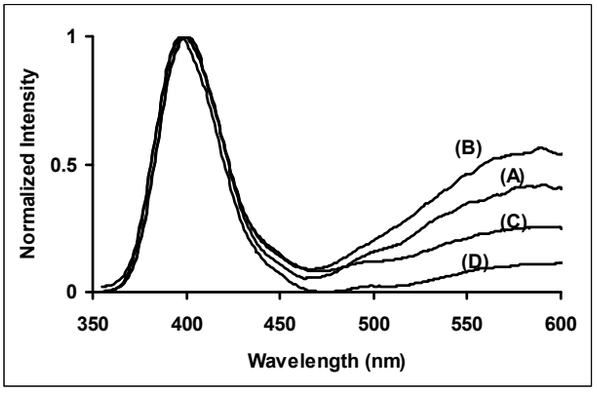

Figure 7: *Room temperature PL spectra of the ZnO produced in presence of IL: (A) as-prepared product, mole ratio of IL/Zn^{2+} = 0.75:10, sample 2 (B) annealed sample 2 at 180 °C for 1 hour, (C) as-prepared product, mole ratio of IL/Zn^{2+} = 1:10, sample 3 (D) as-prepared product, mole ratio of IL/Zn^{2+} = 2:10, sample 4.*

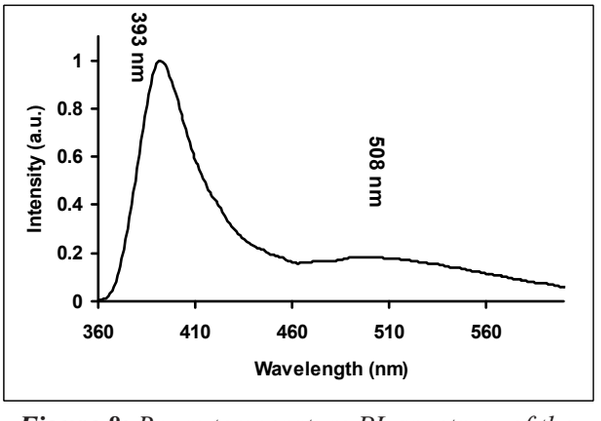

Figure 8: *Room temperature PL spectrum of the Commercial zinc oxide.*

ionic compound, which completely ionize in water. The cations of ionic liquid can be easily absorbed on the surface of the O^{2-}- terminated by electrostatic force, and the hydrogen bond, formed between the hydrogen atom at position 2 of the imidazole ring and the oxygen atoms of O–Zn, may act as an effective bridge to connect the O^{2-}-terminated plane of the produced nuclei of metal oxide and cations of ionic liquids [12, 27, 28].

In other experiments, PL spectra of the ZnO products were measured by an excitation wavelength of 325 nm at room temperature to examine the quality of the product. The PL spectrum of the sample 1 indicates a strong UV emission bond at 393 nm, blue emission at 448 nm and green emission at 540-573 nm (Figure 6).

The PL spectra of zinc oxide fabricated in presence of IL (samples 2, 3 and 4) are shown in Figure 7. The emission bonds show a strong UV emission at about (396-401 nm) and a green-yellow emission peak (540-584 nm). PL spectrum of the sample 2 annealed at 180°C for 1 hour shows a strong green-yellow emission band (Figure 7 B). This indicates the presence of large quantities of defect centers. Generally, the green emission (500-570nm) corresponds to the singly ionized oxygen vacancy in zinc oxide [29-31].

PL spectrum of the commercial zinc oxide is shown in Figure 8. The fluorescence spectrum of commercial zinc oxide shows a strong UV emission at 393 nm and a weak green emission at about 508 nm. A comparison between PL spectra of the commercial zinc oxide with prepared samples show a rising trend in the green emission range of 500-570 nm for the prepared samples. The result could be attributed to the increasing of oxygen vacancy; however there is no upward trend for the commercial Zinc oxide.

4. CONCLUSIONS

In summary, results show that short duration of microwave (1 min) and suitable mole ratio of IL/Zn^{2+} = 1:10 led to rapid formation of polycrystalline flower-like zinc oxide. This product consists of nanoparticles on the surface with grain size of about 48 nm. The photoluminescence spectrum of this sample exhibited strong UV emission at 401 nm and a green-yellow emission at 540-584 nm. Generally, the UV peak is due to the recombination of photo-generated electrons and holes, while the visible emission is associated with oxygen vacancies. On the basis of our experimental results, presence of the IL plays an important role in photoluminescence properties.

ACKNOWLEDGMENTS

This work was supported by Tarbiat Modares University. The authors are grateful for the financial support

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