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# Simple non-basic solution route for the preparation of zinc oxide hollow spheres

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## ABSTRACT

Despite considerable efforts undertaken in a rapidly developing area of materials research, controlled synthesis of nanostructured ZnO is still a matter of intensive research. Herein, we report a facile base free approach for the fabrication of nanostructured ZnO hollow spheres. In the synthesis, ethylene glycol has been introduced as solvent and crystal-growth modifier and zinc acetate has been used as zinc precursor and also a source of soft template. ZnO nanoparticles of diameter  $\sim 25$  nm are assembled into highly regular hollow spheres. The powder X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDS), photoluminescence (PL) and UV–visible spectroscopy have been used to characterize the crystal structure, morphology, composition and optical properties. Powder XRD pattern of ZnO confirms the formation of the wurtzite structure. Presence of oxygen deficiency in the prepared ZnO product is revealed by Raman and EDS studies. Strong emission at 422 nm with three weak emissions at 400, 484 and 529 nm were observed by PL spectrum. The growth mechanism for the formation of ZnO hollow spheres has been discussed on the basis of the growth model for the polar ZnO crystals.

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## 1. Introduction

Nowadays, hollow spheres of nanometer to micrometer dimensions have attracted great interest because of their low density, high surface-to-volume ratio, large surface area and also their ability to interact with ions not only at the surface but also throughout the bulk of the materials [1]. Because of these excellent properties, hollow structured microspheres are widely used as artificial cells, catalysts, fillers, and for controlled release of drugs, dyes, cosmetics and inks [2–7]. A significant number of inorganic hollow structured materials such as CuO/Cu<sub>2</sub>O, TiO<sub>2</sub>, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>,  $\beta$ -Ni(OH)<sub>2</sub>,  $\alpha$ -MnO<sub>2</sub>, CuS, Sb<sub>2</sub>S<sub>3</sub>, CdMoO<sub>4</sub>, ZnWO<sub>4</sub> [8–19] and ZnO [20–22] have been reported. ZnO hollow structured microspheres were usually synthesized through thermal evaporation process [23–27] and hydrothermal method [20,28–30]. Thermal evaporation process usually involves the disadvantages related to requiring special equipment, high temperature ( $> 500$  °C) and vacuum condition. In hydrothermal method, templates were generally employed for creating hollow structures. Most commonly used templates are spherobacterium, sulfonated polystyrene, pickering emulsion, surfactant vesicles and liquid droplets [20,28–32]. This template dependent hydrothermal method always requires extremely complicated synthetic procedures

such as fabrication of templates, introduction of surface functional groups, deposition of the target material and post removal of the templates. The use of templates therefore, results in high cost, low product yield and time consuming synthesis procedure. Recently, template free hydrothermal method is also reported for the preparation of hollow structured ZnO microspheres [33]. However, inorganic or organic bases are commonly used in this approach. Therefore, a direct fabrication of hollow structured ZnO microspheres at low cost remains a challenge for the materials scientists. In recent years, base free approaches have been reported for the fabrication of ZnO nanoparticles [34], flower [35] and nanorods [36] but not for the fabrication of ZnO hollow structured microspheres.

In this paper, we demonstrate a novel low temperature and template/base free approach to synthesize large scale hollow structured ZnO microspheres. The key point of the successful realization is that we use an ethylene glycol to control the growth rate of ZnO crystals and water bubbles as source of soft template for the formation of microspheres with hollow interior.

## 2. Experimental

### 2.1. Materials preparation

Analytical pure grade chemicals were used without further purification. In a typical solvothermal synthesis, 0.5 g of zinc

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acetate was dissolved in 13 ml of ethylene glycol taken in a Teflon lined stain less autoclave and stirred for 20 min. The obtained clear solution was kept at 160 °C for 1 d. After the solvothermal process, the autoclaves were cooled to an ambient temperature and the resultant white solid was extracted by centrifugation. Then the obtained solid product was washed with distilled water followed by ethanol and finally dried at 70 °C for 2 h.

## 2.2. Materials characterization

Powder X-ray diffraction data were recorded on a X'pert PRO PANalytical X-ray diffractometer with graphite monochromatized Cu K $\alpha$  radiation. The morphology of the product was examined by a JEOL-JSM-6490 LV scanning electron microscope and a CM12 Philips transmission electron microscope equipped with EDS (Kevex Sigma TM Quasar, USA). Raman spectrum was recorded at room temperature with a confocal laser micro-Raman spectrometer (LABRM-HR). The absorption spectrum was recorded using a Shimadzu visible spectrometer (UV-3101) at room temperature. Photoluminescence studies were carried out on a Perkin-Elmer LS-55 luminescence spectrometer using Xe lamp with an excitation wavelength of 325 nm at room temperature.

## 3. Results and discussion

### 3.1. Powder X-ray diffraction

The powder XRD patterns of the solvothermally derived ZnO products obtained at 120 °C, 140 °C and 160 °C for 1 d are shown in Fig. 1. The diffraction pattern obtained at 120 °C (Fig. 1(a)) agrees well with that of layered hydroxide of zinc acetate (LHZA) having features of lamellar compounds related to brucite-type layers [37]. The LZHA exhibited layered structures as evidenced from their X-ray diffraction (XRD) patterns, which showed intense (001) diffraction peaks in the low angle range and asymmetric reflections in the range of high angles. Such features can be explained on the basis of stacking order of brucite-like sheets parallel and equidistant but twisted and/or translated

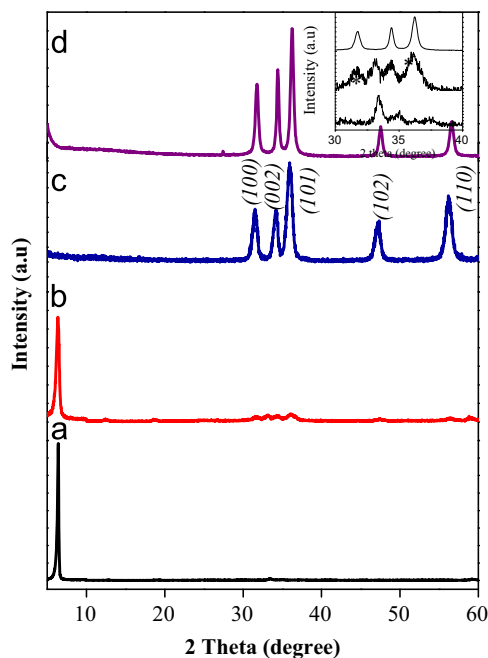


Fig. 1. Powder XRD pattern of the ZnO product prepared at (a) 120 °C, (b) 140 °C, (c) 160 °C and (d) 180 °C for 1 d.

against each other [38–40]. The product obtained at 140 °C (Fig. 1(b)) represents a mixture of both LHZA and ZnO (marked by \*). Whereas, phase pure ZnO can be obtained when the temperature increases to 160 °C and 180 °C (Fig. 1(c) and (d)). All the diffraction peaks of the XRD pattern can be assigned to the hexagonal phase of wurtzite ZnO structure with lattice constants  $a=0.3249$  nm and  $c=0.5206$  nm, which is in good agreement with the reported literature values of ZnO (JCPDS 36-1451).

### 3.2. Scanning electron microscopy

The SEM images of the products prepared at 120 °C, 140 °C, 160 °C and 180 °C for 1 d are shown in Fig. 2. The product obtained at 120 °C shows wire-like morphology (Fig. 2(a)). The product prepared at 140 °C (Fig. 2(b)) exhibits a micrometer sized spheres with uniform diameter. The diameter of the spheres is found to be in range of 1–1.5  $\mu$ m. It is clear that lots of microspheres with hollow interior were observed at 160 °C (Fig. 2(c)). Close examination reveals that the surface of the spheres is not smooth, indicating that the spheres are made by the self-assembly of small ZnO nanoparticles. The ZnO product prepared at 180 °C (Fig. 2(d)) also shows the existence of hollow spheres besides the nanoparticles.

The effect of solvothermal time on the formation of self assembled hollow spheres is investigated. It is also found that the formation of ZnO hollow spheres has been influenced significantly by the solvothermal time. The products prepared at 160 °C for 3 and 6 h exhibit irregular morphologies as shown in Fig. 3(a) and (b). Whereas, the product prepared at 160 °C for 12 h shows hollow spheres (Fig. 3(c)).

### 3.3. Transmission electron microscopy

Fig. 4 shows the TEM image and corresponding SAED pattern taken on the surface of the ZnO hollow spheres prepared at 160 °C for 1 d. The ZnO hollow spheres were composed of nanoparticles with a diameter of  $\sim$ 25 nm. All of these nanoparticles are single crystalline in nature and can be indexed as the hexagonal ZnO phase as evidenced from the SAED pattern (inset of Fig. 4). This result is consistent with the XRD results.

### 3.4. Energy-dispersive X-ray spectroscopy

The chemical purity of ZnO as well as its stoichiometry was investigated using EDS analysis. The EDS spectrum (Fig. 5) clearly indicates that the hollow spheres are composed of Zn and O. The Cu peak arises from the copper grid. Quantitative elemental analysis reveals that the atomic ratio of Zn:O is 56.2:43.8, indicating the presence of oxygen deficiency, which might have been caused during the rapid formation of ZnO under solvothermal condition. This is confirmed by both Raman and photoluminescence studies.

### 3.5. Raman spectroscopy

ZnO crystal exhibits the hexagonal wurtzite structure, which belongs to the space group  $C_{6v}$  [41]. According to the selection rules of phonon resonance modes, Raman-active modes for wurtzite ZnO are  $A_1+2E_2+E_1$  [42]. The  $A_1$  and  $E_1$  modes are polar and can be split into the transverse optical (TO) and longitudinal optical (LO) phonon modes. The  $E_2$  mode is nonpolar optical phonon mode that is composed of two modes with a low and a high frequency. Fig. 6 demonstrates the room temperature Raman spectrum of the ZnO hollow spheres in the wave number range 50–700  $cm^{-1}$ . Vibration peaks can be clearly observed at 100  $cm^{-1}$ , 332  $cm^{-1}$  and 440  $cm^{-1}$ . The two strong peaks at

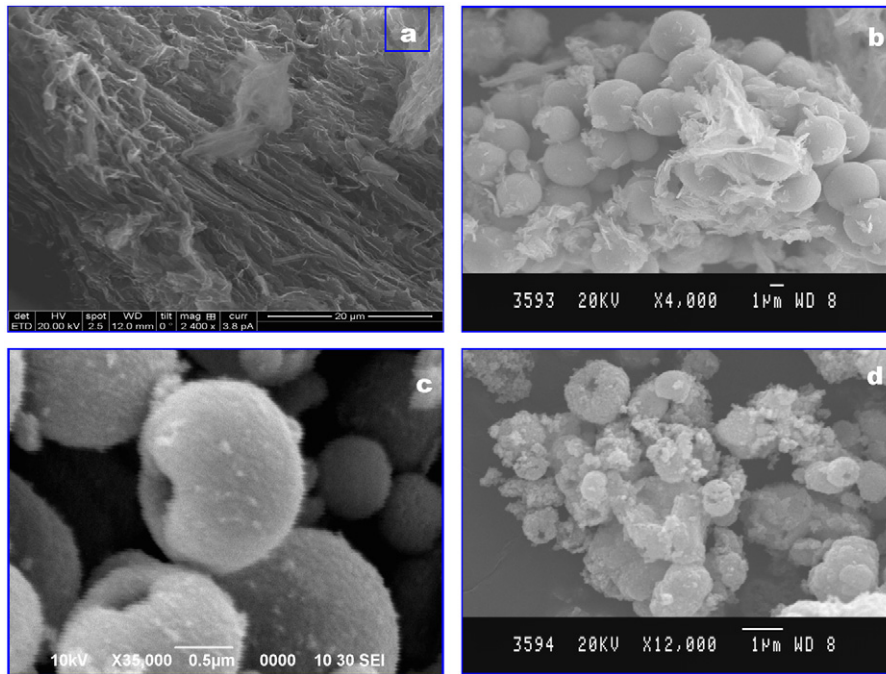


Fig. 2. SEM images of the ZnO products prepared at (a) 120 °C, (b) 140 °C, (c) 160 °C and (d) 180 °C for 1 d.

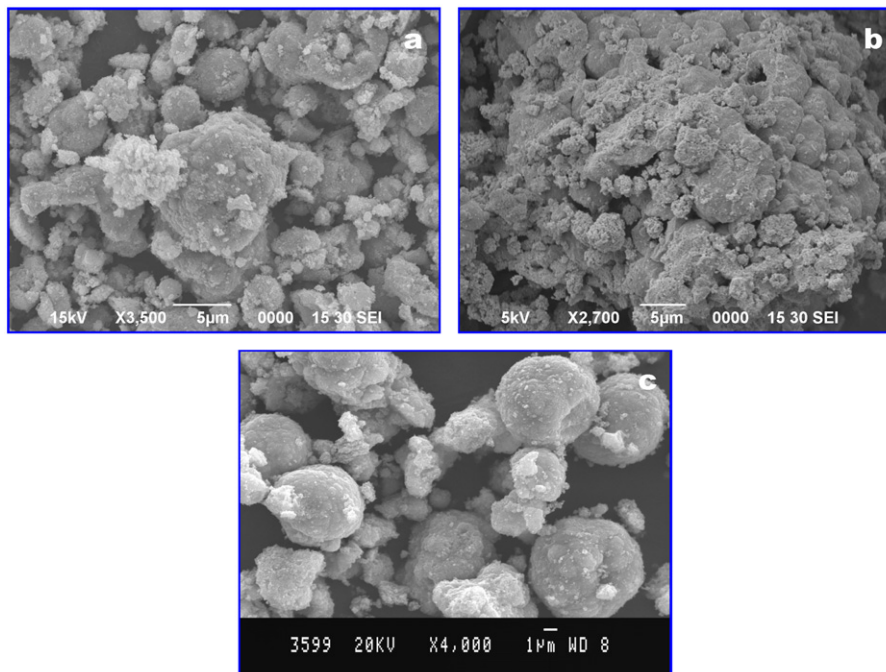


Fig. 3. SEM images of the ZnO products prepared at 160 °C for (a) 3, (b) 6 and (c) 12 h.

$100\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  can be assigned to the two non polar optical phonon ( $E_2$ ) modes of the ZnO hollow spheres at low and high frequency respectively, which are associated with oxygen deficiency. The peak at  $332\text{ cm}^{-1}$  is attributed to the  $2E_2$  mode. A strong intensity of the  $E_2$  modes implies that the ZnO hollow spheres are severely oxygen deficient [43].

### 3.6. Optical properties

PL study is an effective technique to evaluate both ZnO defects and its optical property available as a photonic material. Fig. 7

represents the photoluminescence spectrum of the ZnO hollow spheres obtained with an excitation wavelength of 325 nm. ZnO hollow spheres exhibit a strong emission at 422 nm with three weak emissions at 400, 484 and 529 nm. The UV emission at 400 nm is attributed to the near-band-edge emission of ZnO, originating from the excitonic transitions between the electrons in the conduction bands and the holes in the valence bands (VB) [35]. It is known that visible luminescence mainly originates from defect states such as Zn interstitials ( $Zn_i$ ) and oxygen vacancies. The strong emission peak centered at 422 nm can be assigned to the recombination of an electron at  $Zn_i$  and a hole in the

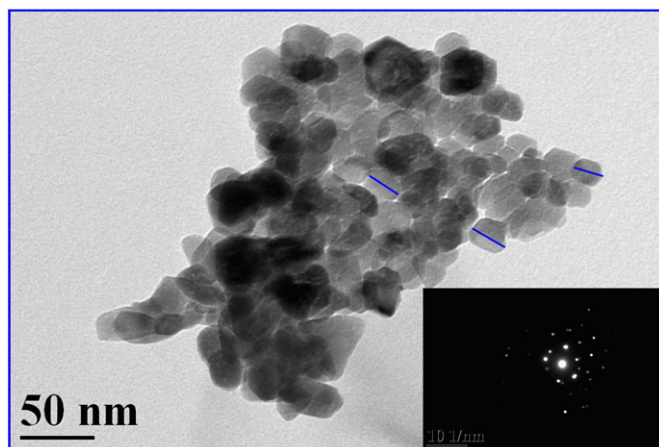


Fig. 4. TEM image and SAED pattern (inset) of the ZnO products prepared at 160 °C.

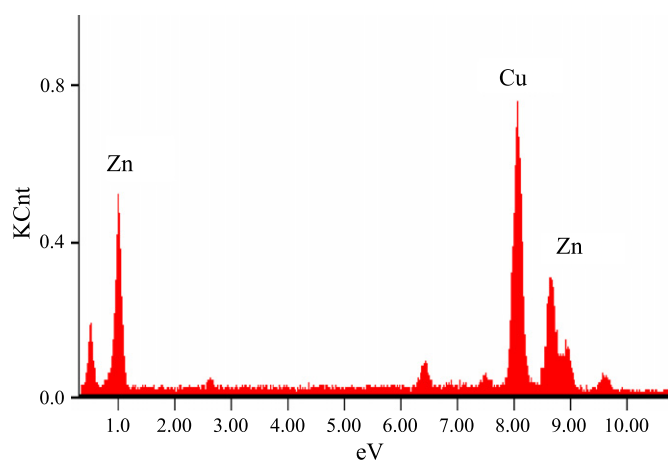


Fig. 5. EDS spectrum of ZnO product prepared at 160 °C for 1 d.

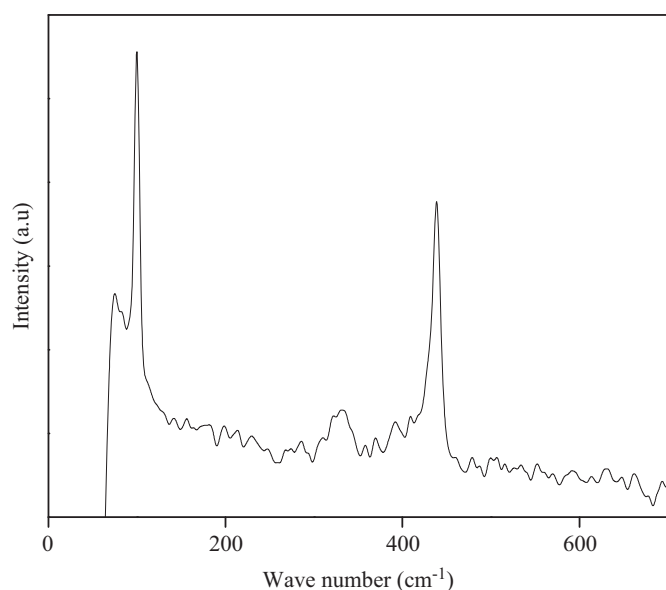


Fig. 6. Raman spectrum of ZnO hollow spheres prepared at 160 °C for 1 d.

**valence band.** The weak emission peak around 530 nm may be related to the singly ionized oxygen vacancy [43] and the mechanism of the emission at 485 nm is not yet clear. The

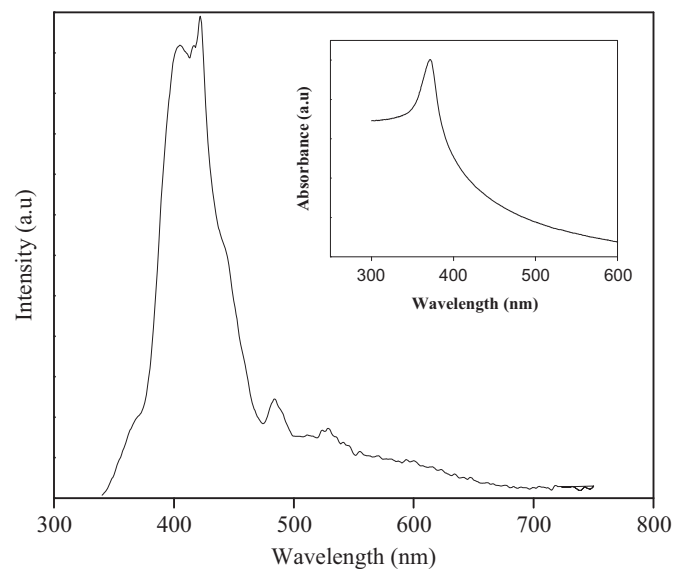


Fig. 7. Room temperature PL spectrum of ZnO products. The inset is the UV-vis absorption spectrum of ZnO products prepared at 160 °C for 1 d.

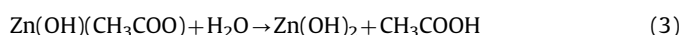
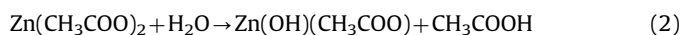
absorption peak centered for 378 nm can be clearly observed (inset of Fig. 7). The corresponding value of direct optical band gap is found to be 3.40 eV. This value is quite comparable to the earlier reported value of 3.32 eV for ZnO nanoparticles [44].

### 3.7. Growth mechanism

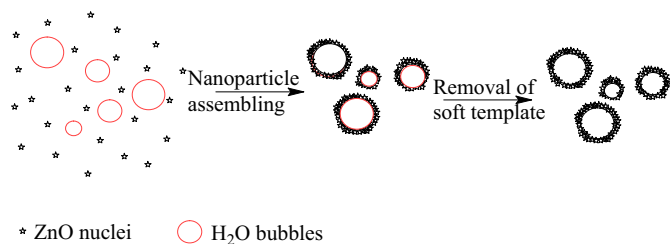
Once the zinc acetate is dissolved in ethylene glycol and subjected to solvothermal treatment, the following series of reactions take place: (i) First, zinc acetate dihydrate undergoes dehydration with the formation of anhydrous zinc acetate and water with the removal of coordinate water molecules:



(ii) The formed anhydrous zinc acetate undergoes hydrolysis with dissociated water molecules (in the previous step) to form basic zinc acetate according to the Eq. (2). (iii) Basic zinc acetate solution is boiled continuously for several hours, acetic acid will evaporate off and only pure basic zinc hydroxide is left behind in the process as shown in Eq. (3). (iv) Finally, ZnO is obtained by dehydration of zinc hydroxide according to the Eq. (4) [45]:



The formation mechanism of ZnO hollow spheres in zinc acetate–ethylene glycol system was investigated. We speculate that ethylene glycol may not only be the solvent but also act as a crystal growth modifier. It is difficult to obtain the spherical ZnO structure without the help of spherical template owing to its different growth rates of ZnO crystal in different directions [46]. Ethylene glycol serves as growth inhibitor due to presence of two functional hydroxyl (–OH) groups [36]. The two hydroxyl groups present at both ends could effectively attach to the (0001) surface of ZnO crystals due to slightly positive charged Zn surface [36]. In addition to this, the hydroxyl groups of ethylene glycol could also form hydrogen bonds with the negatively charged (10 $\bar{1}$ 0) and (01 $\bar{1}$ 0) planes of ZnO [47]. These surface interactions can inhibit the growth of the ZnO crystals in all directions and help the formation of ZnO nanoparticles. The formed ZnO



**Fig. 8.** Schematic illustration of the possible formation mechanism of ZnO hollow spheres.

nanoparticles have tendency to aggregate around the gas liquid interface (water bubbles) due to their high surface energy. Finally, they emerge as hollow spheres. The overall schematic representation of growth process for the hollow spheres is shown Fig. 8.

#### 4. Conclusion

In summary, we have demonstrated a simple solvothermal approach to synthesize hollow structured ZnO microspheres. Ethylene glycol plays a vital role for the formation of hollow spheres by controlling the growth of ZnO crystals during solvothermal condition. This simple and novel method can be adopted for the preparation of other metal oxides hollow structure.

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