



# A novel approach for the synthesis of nanocrystalline zinc oxide powders by room temperature co-precipitation method

V.R. Kumar<sup>a</sup>, P.R.S. Warier<sup>a,\*</sup>, V.S. Prasad<sup>b</sup>, J. Koshy<sup>a</sup>

<sup>a</sup> Department of Physics, University College, Trivandrum 695034, Kerala, India

<sup>b</sup> National Institute for Interdisciplinary Science and Technology, CSIR, Trivandrum 695019, Kerala, India

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## ABSTRACT

A single step co-precipitation route has been employed for the first time in the preparation of ZnO nanoparticles using ammonium hydroxide and zinc nitrate tetrahydrate. The X-ray diffraction analysis revealed that the synthesized powder has the hexagonal (wurtzite) structure. The as-prepared ZnO powder was well crystalline, without any calcination. This is a promising result compared to those mentioned in the literature, in which crystallization of ZnO nanoparticles was detected at  $> 300$  °C. The average crystallite size of the as-prepared ZnO nanopowder is 20–40 nm. The nanocrystalline ZnO could be sintered to ~95% of the theoretical density at 1300 °C in 4 h.

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## 1. Introduction

Transition metal oxides with nanostructure have attracted considerable interest in many areas of chemistry, physics and materials science [1]. Zinc oxide nanoparticles are used in a variety of applications such as UV absorption, antibacterial treatment [2], catalyst [3], photocatalyst [4] and additive in many industrial products. It is a technologically important material due to its wide range of optical and electrical properties as well as semiconductor crystal with a large binding energy (60 meV) and wide band gap (3.37 eV). It is also used in the fabrication of solar cells [5], gas sensors [6,7], luminescent materials [8], transparent conductor, heat mirrors and coatings.

Different physical methods such as pulse laser deposition [9,10], vapor phase transparent process [11], chemical vapor deposition [12] and vapor transparent deposition have been developed for the preparation of nanosized ZnO. The solid state route, a well known method for synthesizing the oxide powders, has difficulties on fine particle distribution because of abnormal grain growth at high temperature. As another way of synthesis of powder, wet chemical preparation, such as sol-gel [13,14] and precipitation method [15,16], could have merits of the uniform particle distribution as well as lower temperature process, but induce impurities in the particles from starting materials and metal ions having a different melting temperature, respectively.

Synthesis of zinc oxide nanopowder by gel combustion method was reported in the literature [17]. But the as-prepared powder was amorphous in nature and a calcination temperature of 500 °C was desired to change amorphous particles to a crystalline phase. In hydrothermal synthesis of ZnO nanocrystals [18], a calcination process was carried out over a temperature of 400–450 °C. Nanosized ZnO particles were successfully synthesized at low temperature by a polymerized complex method via an organochemical route [19] where crystallization of the ZnO particles was detected at 300 °C. In the reports for the synthesis of ZnO powders by polymeric precursor method [20], the precursor was calcined at 600 °C for 1 h to obtain nanocrystalline ZnO powders.

The objective of our work is to investigate the synthesis of phase pure ZnO, without the need for any type of thermal treatment, using a simple room temperature co-precipitation method. In this paper, we report for the first time the synthesis of phase pure nanoparticles of ZnO by a single step co-precipitation route. This involves the precipitation of zinc nitrate tetrahydrate with ammonium hydroxide. The zinc hydroxide precipitate thus formed is transformed into zinc oxide monohydrate ( $\text{ZnO} \cdot \text{H}_2\text{O}$ ) at room temperature. The as-synthesized powders are characterized by XRD, FT-IR, SEM, EDX and TEM. The sintering of the nanopowder obtained by co-precipitation route is also presented.

## 2. Material and methods

Solution of 0.1 M of tetrahydrated zinc nitrate (99.9%) dissolved in distilled water was prepared. To this, under magnetic stirring, ammonium hydroxide was added a drop at a time to complete the precipitation under controlled pH, leading to the formation of a white

\* Corresponding author. Tel.: +91 471 2313540; fax: +91 471 2475830.

E-mail address: [prswarrier@yahoo.com](mailto:prswarrier@yahoo.com) (P.R.S. Warier).

gel. This gel was then collected and washed with distilled water to completely remove all the ammonium nitrate formed. The gel was dried at room temperature for 48 h.

The synthesized material was characterized by powder X-ray diffraction (XRD) using a X-ray diffractometer (Model Bruker D-8) with nickel filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The infrared (IR) spectra of the samples were recorded in the range  $400\text{--}4000 \text{ cm}^{-1}$  on a Thermo-Nicolet Avatar 370 Fourier transform infrared (FT-IR) spectrometer using KBr pellet method. The particle size and morphology of the co-precipitated powders were observed by scanning electron microscope (JEOL, Model-JSM-6390LA, Analytical SEM) and transmission electron microscope (TEM, JEOL 2010Fas). The chemical composition of the powder was analyzed by the scanning electron microscope in conjunction with energy dispersive X-ray (EDX) analysis.

Green pellets of 14 mm diameter and  $\sim 2 \text{ mm}$  thickness were obtained by pressing the nanopowders uniaxially at 350 MPa using 5% polyvinyl alcohol as binder. The sintering of the pellets was carried at  $1300 \text{ }^\circ\text{C}$  for 4 h in air with a heating/cooling rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . The bulk density of the sintered pellets was determined using Archimedes method. The microstructure of the sintered sample after thermal etching was investigated by scanning electron microscope.

### 3. Results and discussion

Fig. 1a shows the XRD pattern of as-prepared powder obtained by the co-precipitation route. All of the indexed peaks in the obtained spectrum are well matched with that of bulk ZnO (JCPDS Card No. 36-1451) which confirms that the synthesized powder possesses a wurtzite hexagonal structure with lattice parameters  $a$  and  $c$  of  $0.3251 \text{ nm}$  and  $0.5207 \text{ nm}$ , respectively. No other peaks related to impurities were detected in the spectrum within the detection limit of the X-ray diffraction, which further confirms that the synthesized powders are phase pure ZnO. The crystallite size estimated from X-ray line broadening using Scherrer equation was  $\sim 36 \text{ nm}$ . In order to distinguish the effect of crystallite-size-induced broadening and strain-induced broadening at FWHM of the XRD profile, the Williamson–Hall plot [21] is performed and is shown as the inset in Fig. 1. The grain size and strain of the as-prepared sample are found to be  $42 \text{ nm}$  and  $8.8 \times 10^{-4}$ , respectively. Fig. 1b–c shows the XRD patterns of the nanopowders calcined at  $200 \text{ }^\circ\text{C}$  and  $600 \text{ }^\circ\text{C}$  for 1 h. No structural changes were

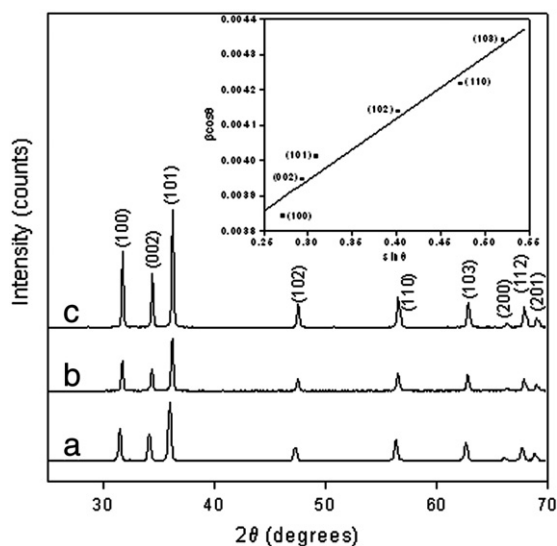


Fig. 1. XRD patterns of the (a) as-prepared ZnO and that heated at (b)  $200 \text{ }^\circ\text{C}$  and (c)  $600 \text{ }^\circ\text{C}$  (Inset shows the Williamson–Hall plot of nanocrystalline ZnO).

observed in the heated samples compared to the as-prepared powder, which indicates that phase formation was completed during the precipitation process at room temperature without the need for any calcination step.

The composition and quality of the product were analyzed by the FT-IR spectroscopy. Fig. 2 shows the FT-IR spectrum of the co-precipitated ZnO powder. The band at  $490 \text{ cm}^{-1}$  is correlated to zinc oxide. The band around  $3445 \text{ cm}^{-1}$  is characterized as water molecules (O–H stretching modes in crystallization water). The weak band at  $1640 \text{ cm}^{-1}$  corresponds to H–O–H bending vibration.

The particle size of powders can be determined from the TEM picture. The TEM method is better than X-ray line broadening in that it is direct and less likely to be affected by experimental errors and/or other properties of the particles such as internal strain or distribution in the size of the lattice parameter. Fig. 3a is the TEM micrograph of ZnO powders synthesized through room temperature co-precipitation. The average grain size observed from the micrograph is about  $20\text{--}40 \text{ nm}$ , and which is in agreement with the calculation using Scherrer's equation. The scanning electron micrograph and EDX spectrum of ZnO nanopowders synthesized through co-precipitation route are shown in Fig. 3b–c, respectively. The SEM picture clearly indicates that the powders were homogeneous and agglomerated. EDX spectrum furnishes various elements in the as-prepared sample.

The sintering behavior of ZnO nanoparticles synthesized through the single step co-precipitation route was studied. The relative green density of the specimen used for the sintering study was  $55 \pm 2\%$  for a pressure of 350 MPa. A sintered density of  $\sim 95\%$  of the theoretical value was obtained on sintering the compacted specimen at  $1300 \text{ }^\circ\text{C}$  with 4 h plateau. Fig. 3d shows the SEM image of the sintered specimen. No cracks were observed on the surface due to densification.

### 4. Conclusions

Nanometric ZnO particles were successfully synthesized through a novel room temperature co-precipitation method. XRD results showed that obtained ZnO nanoparticles were composed of hexagonal wurtzite phase with very good crystallinity. The particle size obtained from Scherrer formula and Williamson–Hall plot was in good agreement with TEM results ( $20\text{--}40 \text{ nm}$ ). The method has an advantage in that phase pure ZnO nanoparticles can be obtained by a single step process without the need for any calcination step. The ZnO nanoparticles could be sintered to  $\sim 95\%$  of the theoretical density at  $1300 \text{ }^\circ\text{C}$  in 4 h.

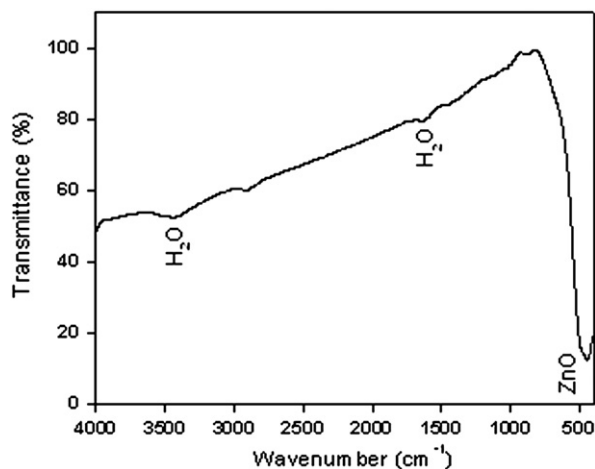


Fig. 2. FT-IR spectrum of as-synthesized ZnO nanopowder.

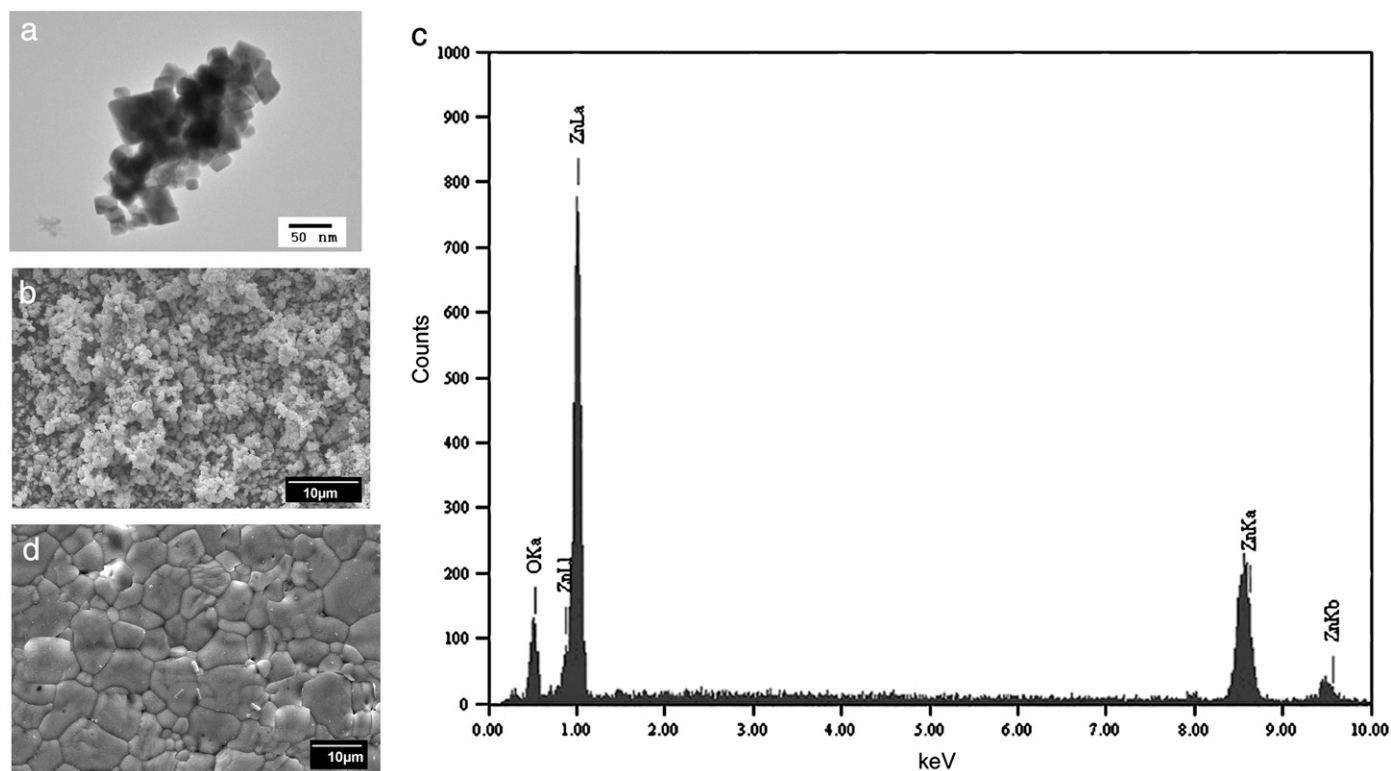


Fig. 3. (a) TEM bright field image (b) SEM secondary electron image and (c) EDX spectrum of as-synthesized ZnO nanopowder; (d) SEM micrograph of sintered pellet of ZnO.

## References

- [1] Hu JT, Odom TW, Leiber CM. *Acc Chem Res* 1999;32:435–45.
- [2] Sanchez L, Peral J, Domenech X. *Electrochim Acta* 1996;41:1981–5.
- [3] Huang WJ, Fang GC, Wang CC. *Colloids and Surfaces A Physicochem Eng Aspects* 2005;260:45–51.
- [4] Li Yansheng, Jiao Zhenhua, Yang Nan, Gao Hong. *J Environ Sci* 2009;21:569–72.
- [5] Matsubara K, Fons P, Iwata K, Yamada A, Sakurai K, Tampo H, et al. *Thin Solid Films* 2003;369:431–2.
- [6] Zhang Q, Xie C, Zhang S, Wang A, Zhu B, Wang L, et al. *Sens Actuators B* 2005;110:370–6.
- [7] Lin HM, Tzeng SJ, Hsiau PJ, Tsai WL. *Nanostruct Mater* 1998;10:465–77.
- [8] Zhang J, Yu W, Zhang L. *Phys Lett A* 2002;299:276–81.
- [9] Nakata Y, Okada T, Maeda M. *Appl Surf Sci* 2002;197:368–70.
- [10] Yoo YZ, Jin ZW, Chikyow T, Fukumura T, Kawasaki M, Koinuma H. *Appl Phys Lett* 2002;81:3798–800.
- [11] Chen BJ, Sun XW, Xu CX, Tay BK. *Phys E* 2004;21:103–7.
- [12] Zhang Ning, Yi Ran, Shi Rongrong, Gao Guanhua, Gen Chen, Liu Xiaohe. *Mater Lett* 2009;63:496–9.
- [13] Sumetha Suwanboon. *ScienceAsia* 2008;34:31–4.
- [14] Bahsi ZB, Aslan MH, Ozer M, Oral AY. *Cryst Res Technol* 2009;44:961–6.
- [15] Lingna W, Mamoun M. *J Mater Chem* 1999;9:2871–8.
- [16] Hong RY, Li JH, Chen LL, Liu DQ, Li HZ, Zheng Y, et al. *Powder Technol* 2009;189:426–32.
- [17] Riahi-Noori N, Sarraf-Mamoory R, Alizadeh P, Mehdikhani A. *J Ceram Process Res* 2008;9:246–9.
- [18] Sridevi D, Rajendran KV. *Bull Mater Sci* 2009;32:165–8.
- [19] Kwon Yong Jae, Kim Kyoung Hun, Lim Chang Sung, Shim Kwang Bo. *J Ceram Process Res* 2002;3:146–9.
- [20] Santi Maensiri, Paveena Laokul, Vinich Promarak. *J Cryst Growth* 2006;289:102–6.
- [21] Williamson GK, Hall WH. *Acta Metall* 1953;1:22–31.