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Small angle neutron scattering and photoluminescence property of wet chemistry process synthesised ZnO nanoparticles

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We report the synthesis of zinc oxide (ZnO) nanoparticles from aqueous solution at 25°C and subsequent heating of the solution at 115°C by the suitable selection of the solution chemistry and the control of the alkaline conditions. The structure of the synthesised ZnO particles was studied by X-ray diffraction (XRD), confirming the formation of Wurtzite structure. The optical property of synthesised ZnO nanoparticles is investigated through room temperature photoluminescence (PL) measurement. The PL of ZnO nanoparticles shows a strong UV emission band at approximately 385 nm, a blue–green band at approximately 473 nm and a very weak green band at approximately 554 nm, although polydispersity of the sample shows no presence on the PL spectrum. Small angle neutron scattering is used to determine the size and the size distribution of ZnO nanoparticles. The SANS data analysis and model fitting predict the size as about 18–20 nm, which is closely matched with XRD and transmission electron microscopy results with Gaussian distribution.

Keywords: ZnO; photoluminescence; X-ray diffraction; neutron scattering

1. Introduction

Zinc oxide (ZnO) is an environmentally friendly transparent semiconductor with a large band gap of 3.37 eV. ZnO nanoparticles have received considerable attention because of their potential applications in various electronic circuits and electric power systems as well as in the chemical sensors technology, optics, catalysis, transparent electrodes for solar cell, preparation of UV protection films, antibacterial agent [1], photonic material [2] and for gas sensing [3]. In most cases, the generation of nanosize ZnO is highly desirable. Most recently, interest on ZnO nanoparticles for potential applications in solar cell has also been renewed. The production of ZnO nanoparticles in aqueous solutions at temperatures different from ambient conditions has been investigated from both the scientific and technological points of view. In this respect, various approaches like spray pyrolysis, thermal decomposition, chemical vapour deposition, laser ablation, etc., have been used for the synthesis of nanomaterials and structures [4–8]. Chemical synthesis is one

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of the important techniques, which can be performed using different precursors and synthesis conditions like temperature, time, concentration, pH of reactants, etc., [9]. Optimisation of those parameters leads to nanoparticles of different size, shape and showing different optical properties. In a more general case, ZnO formation from aqueous solution involves the formation of $Zn(OH)_2$ as an intermediate phase, which is dehydrated only after a subsequent heating at a temperature near 100°C or even higher.

In this study, ZnO nanoparticles are synthesised by a simple wet chemical method at room temperature under ambient atmosphere. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy were used to characterise the ZnO nanoparticles. A more quantitative structural analysis, size, and size distribution of ZnO nanoparticles, was carried out by small angle neutron scattering (SANS) for the first time.

2. Experimental

2.1. *Chemical and synthesis*

To synthesise ZnO nanoparticles, 2 gm of zinc acetate dehydrated powder ($Zn(C_2H_3O_2)_2 \cdot 2H_2O$, 99.999%, Aldrich) was put into 210 mL of distilled water under vigorous stirring. After 20 min of stirring, 20 mL of 2 M NaOH aqueous solution was added into the above aqueous solution. The white aqueous solution maintaining the pH 12 was heated at the temperature of 115°C for 5 h. The resulting white solid products were filtered, washed with distilled water and finally with methanol to remove any ions remaining in the final products. The solid powder was dried in air at 70°C for 24 h. A final dried sample was annealed at 300°C for 5 h.

2.2. *Characterisation*

A structure analysis was conducted using TEM (Hitachi 7600) and XRD (Panalytical). The PL spectra were recorded at room temperature using an excitation source at 325 nm. SANS measurements of ZnO nanoparticles suspended in di-methyl sulfoxide (DMS) were carried out at the NG7 30 m small neutron scattering instrument at the NIST Center for Neutron Research of the National Institute of Standards and Technology. Incident neutron wavelength of 6 Å, with a varying sample-to-detector distance of 1, 15 and 4.5 m detector 25 mm offset, yields a scattering angle range of $0.0009\,\text{Å}^{-1} < q < 0.4\,\text{Å}^{-1}$, where $q = 4\pi/\lambda \sin(\theta/2)$ is the magnitude of momentum transfer vector and θ is the scattering angle. After correction for background and detector efficiency and conversion to an absolute scale using direct beam intensity, the 2D intensity was circularly averaged to yield the total structure factor, $S(q)$ [10].

3. Results and discussion

A typical TEM image is presented in Figure 1, showing that ZnO nanoparticles are nearly spherical in shape. The size of the particles is about 15–20 nm. The size and the size distribution were estimated more quantitatively using a small neutron scattering study.

Figure 2 shows the XRD pattern of ZnO nanomaterials, synthesised by wet chemical method. Powder ZnO particle in 1 mm capillary was used to perform XRD measurement at an angle between 20° and 75°. The XRD peaks indicate that ZnO nanoparticles have wurtzite structure, well matched with standard ZnO according to the Joint Committee on

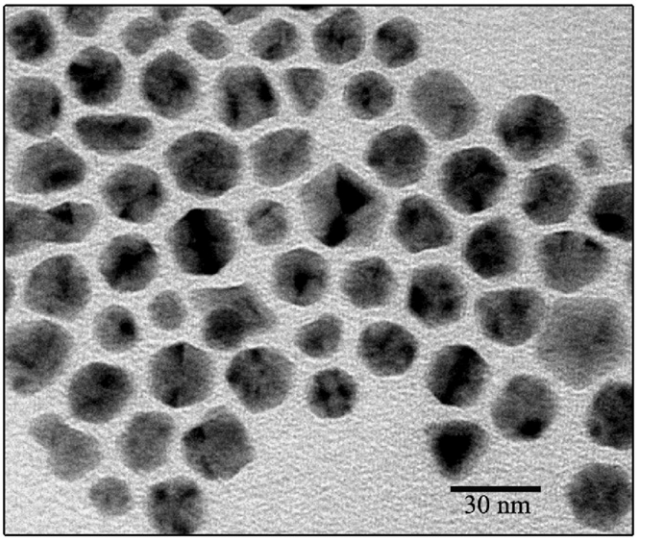

Figure 1. TEM micrograph of ZnO nanoparticles. ZnO is shown spherical in shape in the micrograph.

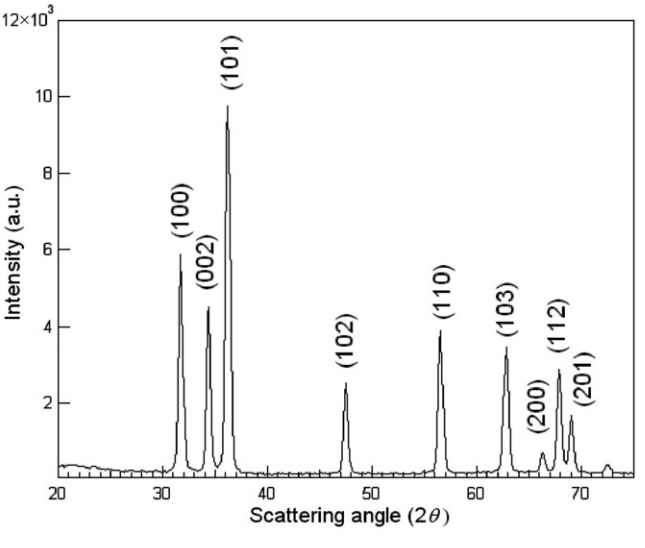

Figure 2. XRD pattern of ZnO nanoparticles.

Powder Diffraction Standard (JCPDS) card number 36–1451. Traditionally, the broadening of the peaks in the XRD pattern of solid powder indicates that the size of ZnO particles is in the nanorange. The crystalline domain diameter of the ZnO particles was estimated from the full width at half maximum (FWHM) of the XRD peaks according to the Debye–Scherrer formula [11,12],

$$d = \frac{K\lambda}{B\cos\theta}, \tag{1}$$

where d is the particle size, λ the wavelength of X-ray radiation, B the FWHM of the peak, θ the angle of diffraction and K the correction factor contributed from the geometry of the crystallites. Borchet et al. [13] modified the Scherrer Equation (1) for more precise calculations by adopting the geometrical factor $K = 0.9$ of the nanoparticles [14]. The broadening of Bragg reflections is basically determined by the number of unit cells along the columns perpendicular to the diffraction planes. For spherical particles of diameter, the length of such columns of unit cells varies within the given particles. The calculation of the particle size with Scherrer equation will lead to an effective diameter (d), which is smaller than the geometric diameter or the average grain diameter (d_g) ($d = 3/4d_g$). Detailed description can be found in an article by Natter et al. [15]. Therefore, Equation (1) becomes

$$d = \frac{(3)0.9\lambda}{4B\cos\theta}. \tag{2}$$

The average particle size of the ZnO nanoparticles calculated from the diffraction peaks observed through the Scherrer formula is 20 nm, which is similar to the TEM result.

The optical property of the ZnO nanoparticles was investigated through the measurement of PL spectra at room temperature using 300 nm wavelength of light source. Figure 3 shows the PL spectra recorded at the room temperature of ZnO nanoparticles. Room

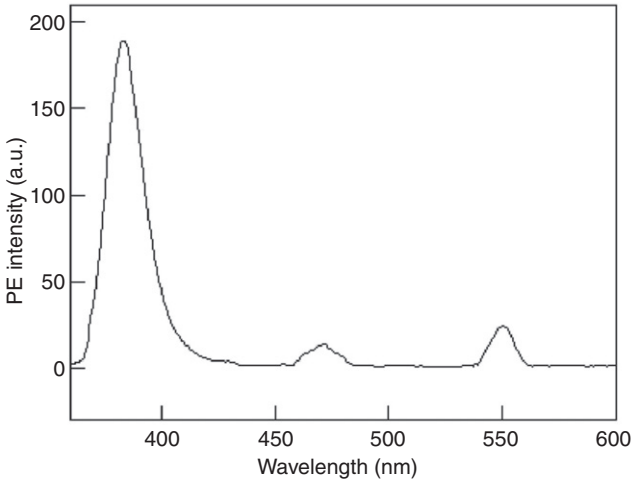

Figure 3. Room temperature of photoluminescence (PL) spectra of ZnO nanoparticles.

temperature PL of ZnO particles shows three emission bands: a strong UV emission band at approximately 385 nm, a weak blue band at approximately 473 nm and a very weak green band at 554 nm. The strong UV emission indicates the exciton recombination-related near-band edge emission of ZnO [16,17]. The blue–green emissions may be due to a surface defect in the ZnO particles [18,19]. The weak green band emission corresponds to the single ionised oxygen vacancy in ZnO or zinc interstitials and this emission is from the recombination of photo-generated hole with the singly ionised charge state of the specific defect [20–23]. The low intensity of the green emission is possibly due to the low density of oxygen vacancies during the preparation of ZnO particles, whereas the strong UV emission intensity at room temperature should be attributed to high-purity ZnO nanoparticles with perfect crystallinity. The size distribution of ZnO nanoparticles, as observed by SANS, does not effect the PL spectra, which further confirms the presence of a surface defect on the nanoparticles.

Scattering technique is a unique tool to investigate the size and the size distribution of nanoparticles [13,23,24]. SANS scattering is one of the best techniques to study particle size and distribution of nanoparticles as well as other structure-related parameters. As is well known, particle size distribution is an important feature of nanopowders. Assuming that there is no interparticle interference to the scattering spectra and for a dilute system of spherical, or spheroidal, and randomly oriented particles, the scattered intensity, $I(q)$, is given by

$$I(q) = AF(q) + \text{Bkg}, \tag{3}$$

where A is an adjustable constant that accounts for instrumental and other experimental factors, $F(q)$ the form factor for individual sphere, $S(q)$ the structure factor that results from interparticle interference and Bkg the background scattering. The form factor for spherical particles with polydisperse radius can be expressed as

$$F(q) = \frac{\text{scale}}{V_p} \int_0^\infty P(q) f(r) \mathrm{d}r, \tag{4}$$

where $f(r)$, the normalised Gaussian distribution of the radius, is expressed as

$$f(r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2} \left(r - r_{\text{avg}}\right)^2 \right], \tag{5}$$

where the polydispersity is equal to σ/r_{avg}, r and r_{avg} are the radius of the particles and average radius assumed in the model fitting, respectively. The form factor of the sphere, $P(q)$, can be expressed as [25]

$$P(q) = \left[\frac{3V(\Delta\rho)\sin(qr) - qr\cos(qr)}{(qr)^2} \right]^2, \tag{6}$$

where $\Delta\rho$ is the difference in scattering length density (SLD) between ZnO nanoparticles and solvent used for the suspension of particles.

Figure 4 shows the SANS pattern along with the fitted curve of ZnO-suspended nanoparticles. The experimental results are well fitted with spherical form factor with Gaussian distribution function. The model fitting using Equations (3)–(6) revealed that the average size of ZnO nanoparticles is 18–20 nm, which is closely matched with the

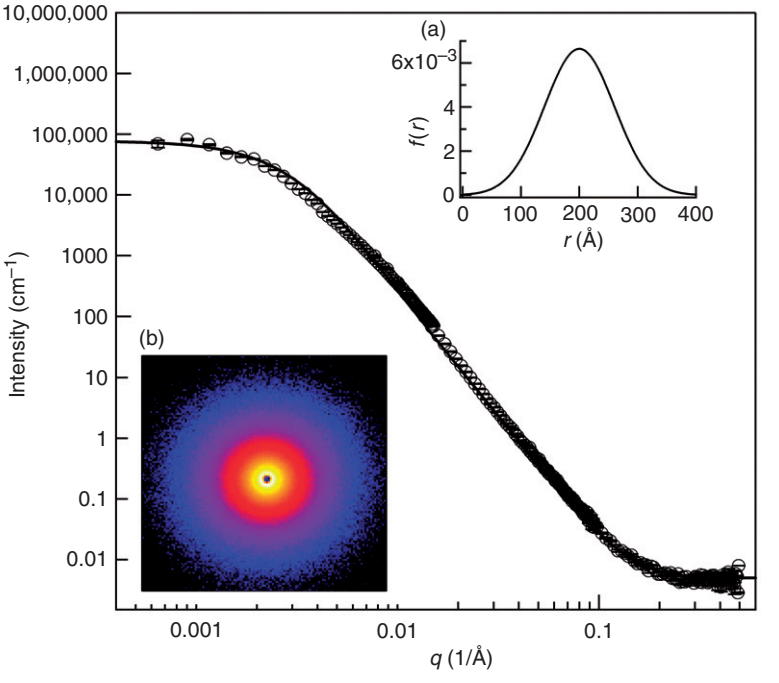

Figure 4. SANS spectra of ZnO nanoparticles. The symbols represent experimental data and the solid line through the symbols is best fit with sphere model with Gaussian distribution function. Inset A shows the size distribution of ZnO nanoparticles. Inset B shows SANS pattern of ZnO nanoparticles suspended in di-methyl sulfoxide (DMS).

XRD and TEM results and polydispersity is 0.75, indicating the more uniform size of the nanoparticles synthesised. The inset A of Figure 4 demonstrated the Gaussian distribution of ZnO nanoparticles.

4. Conclusion

In summary, ZnO nanoparticles have been successfully synthesised using zinc acetate and NaOH in wet chemistry method. The structure and size of ZnO particles are determined using XRD. The SANS technique is used to calculate the size and size distribution of the ZnO nanoparticles. The SANS data model fitting revealed that the size of ZnO nanoparticles is in the order of 18–20 nm and polydispersity is 0.75, indicating a very uniform and narrow size distribution. The size of ZnO nanoparticles obtained from SANS data analysis is closely matched with XRD and TEM results.

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References

[1] L. Zhang, Y. Ding, M. Povey, and D. York, *ZnO nanofluids – A potential antibacterial agent*, Prog. Nat. Sci. 18 (2008), pp. 939–944.

[2] J. Xie, H. Deng, Z.Q. Xu, Y. Li, and J. Huang, *Growth of ZnO photonic crystals by self-assembly*, J. Cryst. Growth 292 (2006), pp. 227–229.

[3] C. Liewhiran and S. Phanichphant, *Improvement of flame-made ZnO nanoparticulate thick film morphology for ethanol sensing*, Sensors 7 (2007), pp. 650–675.

[4] T. Liu, O. Sakurai, N. Mizutani, and M. Kato, *Preparation of spherical fine ZnO particles by the spray pyrolysis method using ultrasonic atomization techniques*, J. Mater. Sci. 21 (1986), pp. 3698–3702.

[5] R.S. Yadav, R. Mishra, and A.C. Pandey, *Particle size distribution study by small-angle X-ray scattering technique and photoluminescence property of ZnO nanoparticles*, J. Exp. Nanosci. 4 (2009), pp. 139–146.

[6] B. Chiou, Y.J. Tsai, and J. Duh, *Thermal evolution in synthesized ZnO varistors by the urea process*, J. Mater. Sci. Lett. 7 (1988), pp. 785–786.

[7] M.S. El-Shall, D. Graiver, and U. Pernisz, *Synthesis and characterization of nanoscale zinc oxide particles.1. Laser vaporization condensation technique*, Nano Struct. Mater. 6 (1995), pp. 297–300.

[8] H. Usui, Y. Shimizu, T. Sasaki, and N. Koshizaki, *Photoluminescence of ZnO nanoparticles prepared by laser ablation in different surfactant solutions*, J. Phys. Chem. B 109(1) (2005), pp. 120–124.

[9] M. Muhammed, *Chemical methods for the synthesis of nanophase materials*, Analysis 24 (1996), pp. M12–M13.

[10] S.R. Kline, *Reduction and analysis of SANS and USANS data using IGOR Pro*, J. Appl. Cryst. 39(6) (2006), pp. 895–900.

[11] M. Maleki, M.S. Ghamsari, Sh. Mirdamadi, and R. Ghasemzadeh, *A facile route for preparation of CdS nanoparticles*, Semicond. Phys. Quantum Electron. Optoelectron. 10 (2007), pp. 30–32.

[12] B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Lebanon, Indiana, USA,1978.

[13] H. Borchert, E.V. Shevchenko, A. Robert, I. Mekis, A. Kornowski, G. Grubel, and H. Weller, *Determination of nanocrystal sizes: A comparison of TEM, SAXS, and XRD studies of highly monodisperse $COPt_3$ particles*, Langmuir 21 (2005), pp. 1931–1936.

[14] H.P. Klug and L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed., John Wiley & Sons, New York, 1974.

[15] H. Natter, M. Schmelzer, M.S. Löffler, C.E. Krill, A. Fitch, and R. Hempelmann, *Grain-growth kinetics of nanocrystalline iron studied in situ by synchrotron real-time X-ray diffraction*, J. Phys. Chem. B 104 (2000), pp. 2467–2476.

[16] K. Vanheusden, W.L. Warren, C.H. Sesger, D.R. Tallant, J.A. Voigt, and B.E. Gnage, *Mechanisms behind green photoluminescence in ZnO phosphor powders*, J. Appl. Phys. 79 (1996), pp. 7983–7990.

[17] S.C. Lyu, Y. Zhang, H. Ruh, H. Lee, H. Shim, E. Suh, and C.J. Lee, *Low temperature growth and photoluminescence of well-aligned zinc oxide nanowires*, Chem. Phys. Lett. 363 (2002), pp. 134–138.

[18] J. Wang and L. Gao, *Hydrothermal synthesis and photoluminescence properties of ZnO nanowires*, Solid State Commun. 132 (2004), pp. 269–271.

[19] S. Maensiri, C. Masingboon, V. Promarak, and S. Seraphin, *Synthesis and optical properties of nanocrystalline V-doped ZnO powders*, Opt. Mater. 29 (2007), pp. 1700–1705.

[20] S. Monticone, R. Tufeu, and A.V. Kanaev, *Complex nature of the UV and visible fluorescence of colloidal ZnO nanoparticles*, J. Phys. Chem. B 102 (1998), pp. 2854–2862.

[21] B.D. Yao, Y.F. Chan, and N. Wang, *Formation of ZnO nanostructures by a simple way of thermal evaporation*, Appl. Phys. Lett. 81 (2002), pp. 757–759.

[22] A.B. Djurišić, Y.H. Leung, K.H. Tam, Y.F. Hsu, L. Ding, W.K. Ge, Y.C. Zhong, K.S. Wong, W.K. Wong, W.K. Chan, H.L. Tam, K.W. Cheah, W.M. Kwok, and D.L. Phillips, *Defect emissions in ZnO nanostructures*, Nanotechnology 18 (2007), p. 095702.
[23] R.S. Yadav and A.C. Pandey, *Small angle X-ray scattering and photoluminescence study of ZnO nanoparticles synthesized by hydrothermal process*, J. Exp. Nanosci. 2 (2007), pp. 177–182.
[24] A.K. Keshari and A.C. Pandey, *Size and distribution: A comparison of XRD, SAXS and SANS study of II–VI semiconductor nanocrystals*, J. Nanosci. Nanotech, 8 (2008), pp. 1221–1227.
[25] R.J. Roe, *Method of X-Ray and Neutron Scattering in Polymer Science*, Oxford University Press, New York, 2000.