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Optical Properties of ZnO Nanoparticles Prepared by Chemical Method Using Poly(vinyl pyrrolidone) as Capping Agent†

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Zinc oxide nanoparticles are synthesized by chemical method using poly(vinyl pyrrolidone) as capping agent. ZnO nanoparticles are characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, photoluminescence and UV-visible diffuse reflectance/absorption spectroscopy. The XRD pattern of ZnO nanoparticles suggests that the synthesized ZnO nanocrystallites have hexagonal wurtzite structure. SEM and TEM images reveal the shape and size of the ZnO nanoparticles. The presence of functional groups is analyzed by FTIR spectroscopy. The UV-visible absorption spectrum of the ZnO nanoparticles shows blue-shift in wavelength corresponding to bulk. The photoluminescence spectrum exhibits a UV emission at 397 nm, a green emission at around 540 nm and a blue emission at 469 nm.

Key Words: ZnO nanoparticles, Chemical synthesis, Structural studies, Optical properties.

INTRODUCTION

In recent years, research on semiconductor nanomaterials stimulated great interest because of their unique optical and electrical properties. ZnO is a *n*-type semiconductor that displays a hexagonal crystalline wurtzite-type structure, with space group $P6_3mc$ and lattice parameters of a = b = 0.3250 nm and c = 0.5207 nm[1]. The importance of ZnO is due to its extraordinery physical properties, such as high conductance, good chemical and thermal stability[2], wide and direct band gap of 3.37 eV[3] and a high exciton binding energy of 60 MeV[4]. In addition, it has good radiation resistance[5] and is harmless to the environment[6]. This material has technological applications, such as opto-electronic devices, chemical sensors[7], catalysts, pigments, cosmetics, varistors and gas sensors[8]. Different techniques are employed to produce ZnO nanostructures, such as molecular beam epitaxy, thermal decomposition, hydrothermal method, synthesis by vapour phase, precipitation, sol-gel and solochemical method. Among the techniques employed, those belonging to the chemical routes are suitable for the preparation of ZnO nanostructures in industrial scale since they are relatively cheap and provide a high uniformity of the final product[9].

For preparing high-quality ZnO nano powders, the chemical precipitation method has advantage to obtain highly crystallized powders and with high purity without the necessity of any posterior treatments. The particle properties, such as morphology and size can be altered *via* this method by adjusting the parameters, like reaction temperature, concentration and reaction time. Due to the simplicity, versatility and low cost of this route, the chemical precipitation method is a process extremely viable for industrial production of zinc oxide[10].

In this study, ZnO nanoparticles are synthesized in short reaction time and in relatively low temperature by the chemical precipitation method using zinc nitrate hexahydrate, KOH and poly(vinyl pyrrolidone) (PVP) without any posterior treatments. The synthesized ZnO nanoparticles were subjected to various characterization methods to analyze their structural and phase formation, morphology and size, functional group assignments and optical properties.

EXPERIMENTAL

The source materials, such as zinc nitrate hexahydrate [$(Zn(NO_3)_2{\cdot}6H_2O$], potassium hydroxide and poly(vinyl pyrrolidone) [C_6H_9NO] were of analytical grade and used as purchased. Solutions were prepared by dissolving appropriate amount of the compounds in double distilled water.

Synthesis of cauliflower-like ZnO nanoparticles: In this method, 0.5 M aqueous solution of zinc nitrate hexahydrate and 1 M aqueous solution of potassium hydroxide were prepared

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in distilled water to form 100 mL solution. Poly(vinyl pyrrolidone) was added as capping agent. The reaction solution was heated at 50 ºC under continuous stirring for 1 h. The precipitate formed was collected and washed with ethanol and dried at room temperature. The dried precipitate was calcined at 600 ºC in air for 1 h.

Characterization of ZnO nanoparticles: The structural and phase formation of the samples were identified by Reich Seifert XRD 3000 diffractometer using CuK$_\alpha$ (λ = 1.5406 Å). The morphology and size of the ZnO nanoparticles were evaluated by scanning electron microscopy (SEM, FEI-Quanta 250) and transmission electronic microscopy (TEM, FEI-Technai Sprit). The presence of functional groups is analyzed by FTIR spectroscopy (JSO DEBYEFLEX 2002). UV-VIS measurements were made by Lamda 650 UV-VIS diffuse reflectance spectrometer (PerkinElmer) and room temperature photoluminescence spectrum was measured by a luminescence spectrometer (LS/55, Perkin-Elmer).

RESULTS AND DISCUSSION

Structural and phase formation: The XRD pattern of the synthesized poly(vinyl pyrrolidone) capped ZnO sample is shown in Fig. 1. The XRD pattern of the sample reveals that all peaks correspond to the characteristic peaks of the hexagonal wurtzite structure of ZnO (space group P6$_3$mc and lattice parameters of a = b = 0.3250 nm and c = 0.5207 nm) according to the JCPDS number of 36-1451[11]. No peaks of any other phase are detected, indicating that the ZnO sample obtained by the current synthetic route is highly pure. The sharp peaks indicate that the products are well crystallized.

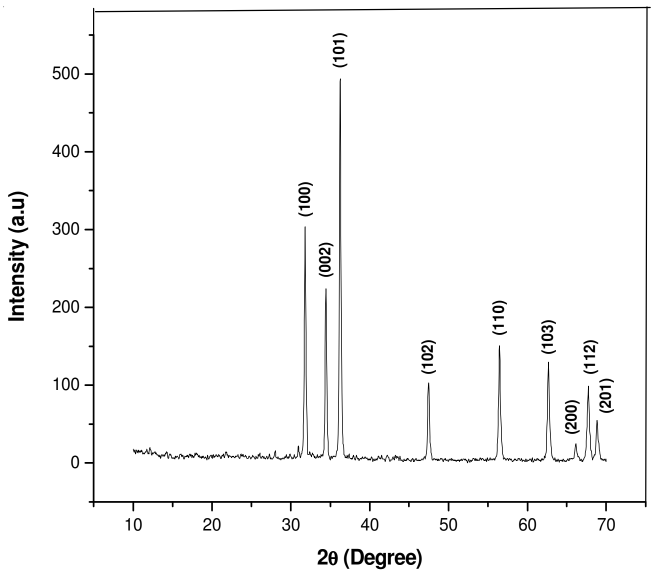
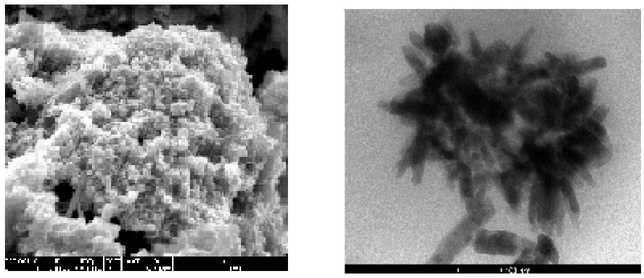


Fig. 1. XRD pattern of ZnO nanoparticles

Morphology and size: The SEM image of ZnO sample is shown in Fig. 2(a). The SEM image demonstrates the existence of bulk quantity of flower-like bunches. Each bunch is gathered by closely packed nanometer scale rods and forms a cauliflower-like structure.

The TEM image of ZnO sample is shown in Fig. 2(b). ZnO nanorods holding the cauliflower shaped structure is



(a) (b)

Fig. 2. (a) SEM image, (b) TEM image

observable from the image. The diameter of the stalk is in the range of 50 nm and that of the individual rods giving the cauliflower shape are 25 nm.

Functional groups: The FTIR spectrum of the ZnO nanoparticles which was acquired in the range of 4000-400 cm^{-1} is shown Fig. 3.

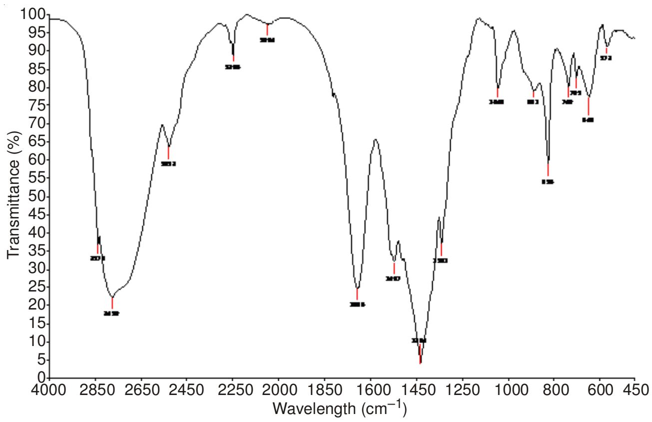


Fig. 3. FTIR spectrum of ZnO sample

The band located at 550-650 cm^{-1} is correlated to the stretching mode of Zn-O[12]. The band at 3450 cm^{-1} corresponds to O-H mode of vibration. The stretching mode vibration of C=O is observed at 1656 cm^{-1}. The band at 2953 cm^{-1} is assigned to the asymmetrical stretching vibration of CH_2. The absorption band at 1384 cm^{-1} corresponds to the bending vibration of CH_2. The stretching vibration of C-N is observed at 1291 cm^{-1}.

Optical properties: The UV-VIS absorption spectrum of the ZnO sample is shown in Fig. 4. The absorption peak of the ZnO sample occurs at 365 nm which is lower than that of bulk ZnO (373 nm). Compared to bulk ZnO the ZnO sample synthesized in the present work exhibits a blue-shift in cut off wavelength which may be ascribed to size effect and their unique morphology[13]. The diffuse reflectance spectrum of the sample is shown in Fig. 5. The low reflectance values of the sample indicate high absorption in the corresponding wavelength region. The observed band gap for the ZnO sample using UV-VIS absorption spectrum is 3.42 eV which is in good agreement with that of the bulk ZnO (3.37 eV).

Room temperature photoluminescence spectrum of the ZnO sample excited by 350 nm UV light from a He-Cd laser is shown in Fig. 6. The photoluminescence from ZnO consists of three emission bands at room temperature, a near-band-edge (UV) emission and two broad, deep-level (visible) emissions.

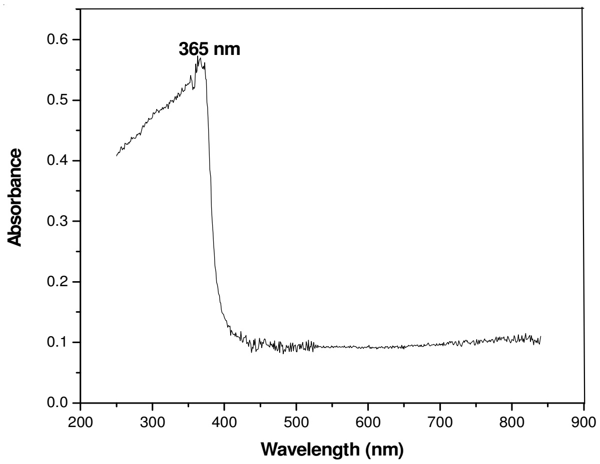


Fig. 4. UV-VIS absorption spectrum

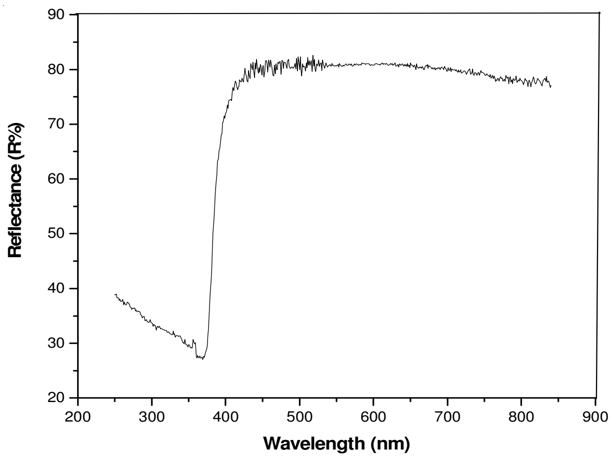
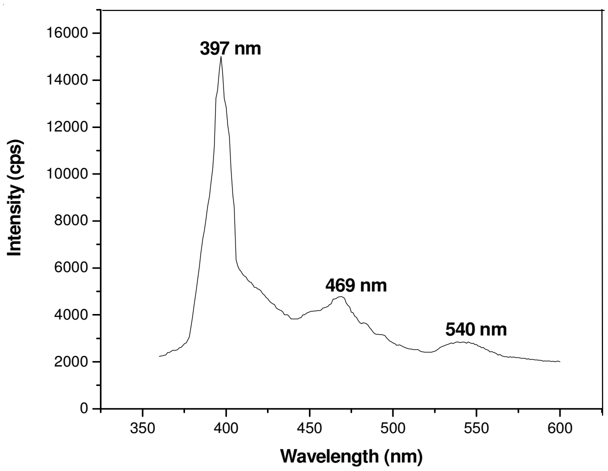


Fig. 5. UV-VIS diffuse reflectance spectrum



Fig, 6. Photoluminescence spectrum of ZnO sample

The visible emission is usually considered to be related to various intrinsic defects produced during the preparation ZnO nanoparticles. Normally these defects are located on the surface of the ZnO nanostructure. For the prepared ZnO nanoparticles, a sharp UV emission peak at 397 nm and a broad green emission peak at 540 nm were observed in the photoluminescence spectrum. The UV emission at 397 nm corresponds to the near band-edge emission resulting from the recombination of free excitons; the green emission at 540 nm is commonly referred to the singly ionized oxygen vacancy; and the emission results from the radiative recombination a photo generated hole with an electron occupying the oxygen vacancy[14]. The visible emission at 469 nm is likely attributed to electron transition, mediated by defect levels in the band gap.

Conclusion

ZnO nanoparticles were prepared by a cost effective and simple chemical technique using zinc nitrate hexahydrate, potassium hydroxide and poly(vinyl pyrrolidone) as capping agent. The XRD analysis confirmed that the nanoparticles have the hexagonal wurtzite-type structure of ZnO. SEM image of the sample showed cauliflower-like morphology. The TEM image of the sample showed that the nanoparticles have predominantly, a nanometric rod-like morphology with a diameter of 25 nm. The FTIR spectrum revealed the functional group assignments of the synthesized ZnO nanoparticles. The UV-VIS absorption spectrum of the the ZnO sample exhibits a blue-shift in wavelength with respect to the bulk. The observed band gap using UV-VIS absorption spectrum of the sample is in good agreement with that of the bulk. Room temperature photoluminescence spectrum of the poly(vinyl pyrrolidone) capped ZnO nanoparticles showed a strong UV emission, which represents a good nanomaterial as for the applications in various fields of nanoscience and technology.

REFERENCES

1. R. Liu, A.A. Vertegel, E.W. Bohannan, T.A. Sorenson and J.A. Switzer, *Chem. Mater.*, **13**, 508 (2001).
2. R. Kaur, A.V. Singh, K. Sehrawat, N.C. Mehra and R.M. Mehra, *J. Non-Cryst. Solids*, **352**, 2565 (2006).
3. J. Kubota, K. Haga, Y. Kashiwaba, H. Watanabe, B.P. Zhang and Y. Segawa, *Appl. Surf. Sci.*, **216**, 431 (2003).
4. S. Singh, P. Thiyagarajan, K.M. Kant, D. Anita, S. Thirupathiah, N. Rama, B. Tiwari, M. Kottaisamy and M.S.R. Rao, *J. Phys. D: Appl. Phys.*, **40**, 6312 (2007).
5. D.C. Reynolds, D.C. Look and B. Jogai, *J. Appl. Phys.*, **89**, 6189 (2001).
6. C. Wu, X. Qiao, J. Chen, H. Wang, F. Tan and S. Li, *Mater. Lett.*, **60**, 1828 (2006).
7. R. Hong, T. Pan, J. Qian and H. Li, *Chem. Eng. J.*, **119**, 71 (2006).
8. J.-H. Park, S.-G. Oh and B.-W. Jo, *Mater. Chem. Phys.*, **87**, 301 (2004).
9. Y. Hu and H.J. Chen, *J. Nanopart. Res.*, **10**, 401 (2008).
10. M.R. Vaezi and S.K. Sadrnezhaad, *Mater. Des.*, **28**, 515 (2007).
11. R. Zhang and L.L. Kerr, *J. Solid State Chem.*, **180**, 988 (2007).
12. H.M. Ismail, *J. Anal. Appl. Pyrol.*, **21**, 315 (1991).
13. X.M. Hou, F. Zhou and W.M. Liu, *Mater. Lett.*, **60**, 3786 (2006).
14. Y. Dai, Y. Zhang, Y. Bai and Z.L. Wang, *J. Chem. Phys. Lett.*, **375**, 96 (2003).