Comparative Study of Structural and Optical Properties of ZnO Nanoparticles Capped with Hexamine and Tetraoctylammonium Bromide as Surfactants

FOZIA Z. HAQUE* and MOHAMMAD RAMZAN PARRA

Department of Physics, Maulana Azad National Institute of Technology, Bhopal (India).

ABSTRACT

We have developed a simple hydrothermal route for the production of ZnO nanostructures at reaction temperature of 90$^{R°}$C. This is a fast, simple, and reproducible method which does not require any template, catalyst, but can control the morphology of ZnO crystals. The influence of time-period of heat-treatment was investigated for the formation of ZnO nanostructures. The presence of surfactants [Hexamethylenetetramine (Hexamine) and tetraoctylammonium bromide (TOAB)] on the surface of zinc oxide (ZnO) nanoparticles resulted variation in their optical properties and structural growth. For structural study and analysis, the fabricated micro/nanostructures were characterized using scanning electron microscopy (SEM). The results of investigation show a preferential growth by the selective capping hexamethylenetetramine. We demonstrate the optical properties of our chemically synthesized structures using photoluminescence spectroscopy.

INTRODUCTION

In the past, the formation of semiconductor nanostructures with controlled dimension and different morphologies is the point of research. Nanoscale structures are expected to be manipulated into well-defined configuration in order to build integrated systems. Different nanostructures synthesized from semiconductor materials are of particular interest primarily because of their unique physical properties. Among the promising optoelectronic semiconductors, ZnO with a direct wide band gap (3.37 eV) and high exciton binding energy (60 meV), is one of the most important functional materials. So far, the growth of controlled microstructures, especially the novel well-organized hierarchical structures, has been performed by several methods, such as, conventional thermal evaporation and condensation method [1] solution-phase growth [2], and electrochemical deposition [3]. Gas phase synthesis techniques have been used to grow branched nanocrystals for several material systems [4–6], but the equipments are complex, expensive, and consume high levels of energy. Many types of branched nanocrystals have also been produced with solution-phase synthesis process, which offers the potential for low-cost, industry-scale manufacturing [7, 8]. The interest in micro and nanostructured ZnO materials has taken more relevance due to its wide range of applications, which makes it thermally and chemically stable [9]. These properties make ZnO feasible for applications in many fields, such as energy conversion [10-12], optoelectronics [13-15] and sensing devices [16-19], in particular when it is synthesized in one-dimensional (1D) geometry [20-22]. Hexagonal structure among all the geometries, the most feasible for such type of applications are nanowires [9, 23-25], nanobelts [26, 27], nanotubes and nanorods, and arrays of them [28, 29]. Most of the properties of ZnO strongly depend on its structures, including the morphology, size and aspect ratio [30]. These structural characteristics have an important role in many optoelectronic applications. Therefore, as an attractive functional

material, the synthesis of ZnO with different morphology is attractive for exploring various functions of ZnO. Zinc oxide nanostructures can be synthesized either through gas-phase or through solution-phase synthesis. Some commonly used gas-phase methods are vapor-phase transport, which includes vapor–solid (VS) and vapor–liquid–solid (VLS) growth, physical vapor deposition (PVD), chemical vapor deposition (CVD). In the solution-phase synthesis, the growth process is carried out in a liquid. Normally aqueous solutions are used and the process is then referred to as hydrothermal growth process. One of the most energy-efficient strategies for synthesizing ZnO micro/nanorods is the hydrothermal process that does not require high temperature and complex vacuum environment. The hydrothermal process induces an epitaxial, anisotropic crystal growth in a solution (normally aqueous solution). Hydrothermal deposition techniques in aqueous solution are based on heterogeneous nucleation and subsequent crystal growth on a specific substrate, have attracted much attention to prepare ZnO nanorod films [31, 32]. The aqueous solution usually contain zinc source [Zn $(NO_3)_2$, Zn $(CH_3COO)_2$] and some additives, such as complex or chelating agents (urea, hexamethylenetetramine, ethane-1, 2-diamine). By means of controlling process-parameters, well-aligned single-crystalline hexagonal rods of ZnO were grown along the c-axis direction in a perpendicular fashion onto the substrates. It was reported by Sugunan *et al.* [33] that hexamine, a non-ionic tertiary amine derivative and a non-polar chelating agent, would preferentially attach to the non-polar facets of the ZnO crystal as it builds up, there by exposing only the (0 0 1) plane for epitaxial growth [33].

In our synthesis process, we have used hexamine (HMT) and tetraoctylammonium bromide (TOAB) as capping agents, hexamine having the advantage that it preferentially attaches to the non-polar facets of the grown ZnO micro-rods. The influence of time-period of heat-treatment was observed for the formation of ZnO nanostructures. We investigate the influence of these surfactants on ZnO nanoparticles using fluorescence emission techniques. For this study, nanoparticles have been prepared by the hydrothermal method in aqueous medium in the presence of different surfactants.

EXPERIMENTAL

Chemicals used

All chemicals used in this study were of analytical grade and were used without further purification. Zinc nitrate hexahydrate (Zn $(NO_3)_2 \cdot 6H_2O$) procured from Merck with 99% purity, was used as the zinc cation precursor chemical, hexamethylenetetramine (HMT, $C_6H_{12}N_4$) and tetraoctylammonium bromide (TOAB, $[CH_3(CH_2)_7]_4N$ Br) procured from RANKEM with 99% purity as the hydroxide anion precursor chemical .

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized using simple hydrothermal synthesis procedure, in this technique 0.1M of Zinc nitrate hexahydrate was dissolved completely in 50ml water, an aqueous solution of NaOH was added in the above prepared aqueous solution of zinc nitrate hexahydrate. Prepared solution get stirred for 15min. at 50-60^{R}C. The solution was kept in a temperature controlled oven at 90-100$^{æ\%}$C for 1 hr. The influence of temperature and time-period of heating process was then investigated.

Hydrothermal growth of ZnO micro/nano-rods coated with surfactants

For the synthesis of ZnO micro/nano-rods, an equimolar aqueous solution of (Zn $(NO_3)_2 \cdot 6H_2O$) and surfactant (HMT or TOAB) was pre-pared at room temperature. In 50 ml water, 0.1M Zn $(NO_3)_2 \cdot 6H_2O$ was dissolved, an aqueous solution of 0.1M of specific surfactant was added into the above prepared solution followed by the addition of NaOH as described above.

The system was allowed to cool down to room temperature. The powder was then taken out by centrifugation from the solution after 1 h, thoroughly washed with distilled water to eliminate residual salts, and dried at room temperature.

Analytical measurements

For structural studies, the prepared samples were characterized by using scanning electron microscopy (JEOL-JSM-6390). The samples were characterized for optical properties through photoluminescence (PL) spectra at room temperature and the data were recorded using

fluorescence spectrometer (F-7000 Hitachi) exiting with its xenon lamp.

RESULTS AND DISCUSSION

Scanning electron microscopy

`The morphology and microstructures of our samples were investigated by the images taken from scanning electron microscope. Tetraoctylammonium bromide (TOAB or TOABr) is a quaternary ammonium compound with the chemical formula: $[CH_3(CH_2)_7]_4N$ Br. It is generally used as a phase transfer catalyst between an aqueous solution and an organic solution. Quaternary ammonium compounds (QACs) are cationic surfactants. They are synthetic organically tetra-substituted ammonium compounds, where the R substituents are alkyl or heterocyclic radicals.

A common characteristic of these synthetic compounds is that one of the R's is a long-chain hydrophobic aliphatic residue. Herein we found a simple synthetic approach to build ZnO nanostructures from nanoparticles at 90-100ᴿᵒC by using $(Zn\ (NO_3)_2 \cdot 6H_2O)$ as an inorganic precursor and sodium hydroxide as a basic source in the presence of tetraoctylammonium bromide (TOAB) and hexamethylenetetramine in aqueous medium. Fig. 1 a and b shows the SEM morphologies of ZnO capped with tetraoctylammonium bromide. As
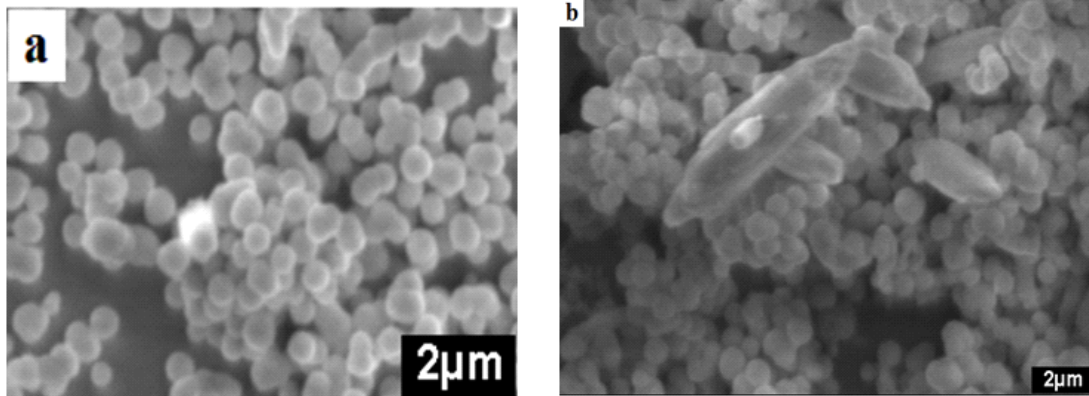

Fig. 1: (a and b) Nucleation and growth of ZnO micro-seeds prepared at100˚%C for 1 hr using TOAB as capping agent
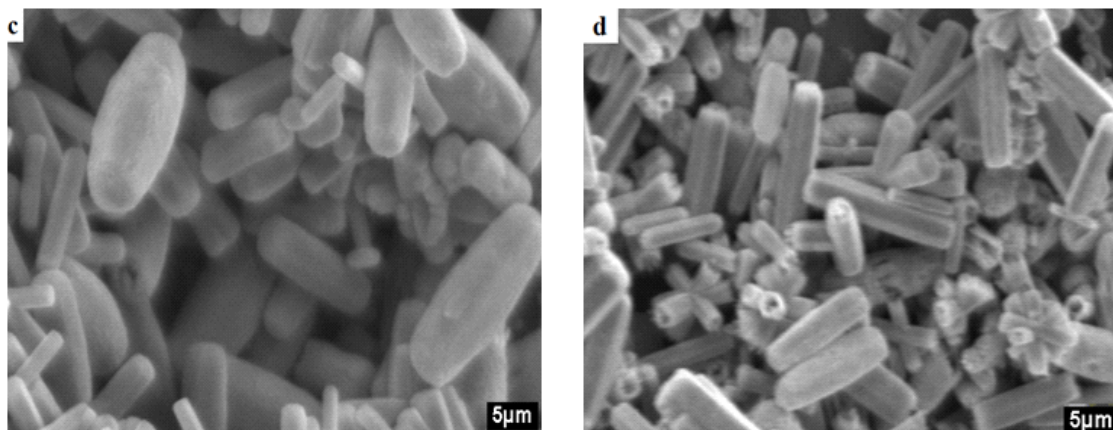

Fig. 2: SEM images of prepared ZnO micro-rods with regular hexagonal shape using Hexamine as capping agent

shown in figures ZnO nanoparticles were obtained by using H_2O as the solvent.

HMT is hydroxide anion-generating agent and in our study, hydroxide anions are provided by hydration of hexamethylenetetramine (HMT). In the first stage OH^- ions are formed as a result of the reaction of H_2O with HMT and subsequently ZnO nuclei are formed. In the second stage the formed ZnO nuclei grow preferentially, resulting in the formation of hexagonal ZnO micro/nanorods. Following the above experimental technique, we observed ZnO micro-rods at lower temperature with regular hexagonal shape using Hexamine as capping agent. Fig. 2 a and b shows the SEM morphologies of ZnO capped with hexamethylenetetramine (HMT) as capping agent.

Photoluminescence spectroscopy

In the photoluminescence (PL) spectra of ZnO, in general there are emission bands in the UV and visible regions. The UV peak is usually considered as the characteristic emission of ZnO and attributed to the band edge emission or the exciton transition. In many reports, the characteristic emission of ZnO was absent in their luminescence spectra. Generally the UV emission in ZnO disappears in two cases. First, if the excitation energy is considerably lower that its band gap energy and second, if the intensity of visible emission is much higher due to increased defect density. In our case also, UV emission is absent as

the excitation wavelength is 325 nm. If we excite the specimens at wavelength of 300 nm or less there would be UV emission in the PL spectrum.

Since, ZnO film included oxygen vacancy (V_O), zinc vacancy (V_{Zn}), interstitial zinc (Zn_i), interstitial oxygen (O_i) and antisite oxygen (O_{Zn}), it is thought that the deep-level emission was caused by different intrinsic defects in ZnO film, such as V_O, V_{Zn}, Zn_i and O_i[34]. Because the deep-level emission center (2.50 eV) is smaller than the band gap energy of ZnO (3.37 eV), the deep-level emission must be related to the defect level in band gap [35, 36]. Fig. 3 shows the room temperature photoluminescence (PL) spectrum of the three samples, excited at 325 nm. The excitation energy was chosen from photoluminescence excitation (PLE) spectra of the specimens which showed an intense peak at 325 nm. In all the samples, two bands are observed around 416 nm (violet band 1) and (blue band) at 460 nm.

The violet emission at about 416 nm confirms the excess of oxygen rich condition and attributed the PL to the possible existence of cubic ZnO. In ZnO, Zn_{3d} electron strongly interacts with the O_{2p} electron i.e. oxygen has tightly bound 2p electrons and Zn has tightly bound 3d electrons, which sense the nuclear attraction efficiently. From theoretical band calculations it reveals that vacant Zn (V_{Zn}) and interstitial O (O_i) produce shallow acceptor levels at 0.3 eV and 0.4 eV above the top
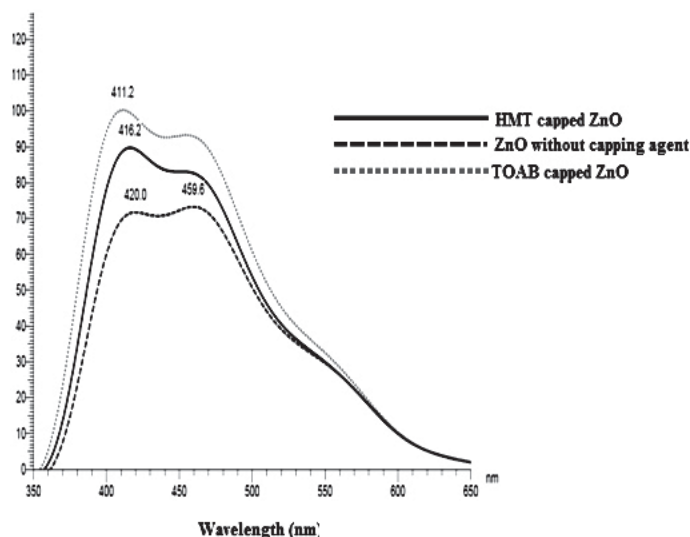

Fig. 3: Room-temperature photoluminescence spectrum of pure ZnO, capped with HMT and TOAB at 100°C

of the valance band (VB), and that interstitial Zn (Zn_i) produces a shallow donor level at 0.5 eV below the bottom of CB. As shown in Fig. 3, violet luminescence in band 1 at ~411.2-420 nm (2.94 Ev) is attributed to the transition from conduction band to the deep holes trapped levels like interstitial zinc (Zn_i). The broad emission peak in blue band at 459 nm (2.7 eV) might be related to the surface defect in ZnO thin films.

It can be seen that the ZnO sample without capping agent shows lowest visible emission among all the ZnO samples capped with surfactants. TOAB contains four long hydrocarbon chains of equal length, which may hinder the interaction with other TOAB molecules due to steric effect. This result in the increase of core size, hence the particle size may be still large.

CONCLUSIONS

In summary, we have prepared ZnO nanoparticles capped with hexamine and tetraoctylammonium bromide surfactants, and their optical properties were investigated using fluorescence technique. It is concluded that pure hexagonal-phase ZnO structures were synthesized through this fast and simple irradiation method from the solution comprising zinc nitrate and hexamine at lower temperature. Whereas seeded nanostructures were observed in case of TOAB as capping agent. Evolution of different morphological structures of ZnO has been realized. The fabricated structure shows a strong photoluminescence in the violet region.

REFERENCES

1. P.X. Gao, Z.L. Wang, Nanopropeller arrays of zinc oxides, *Appl. Phys. Lett.* **84**: 2883–2885 (2004).

2. T.L. Sounart, J. Liu, J.A. Voigt, M. Huo, E.D. Spoerke, B. Mckenzie, Secondary nucleation and growth of ZnO, *J. Am. Chem. Soc.* **129** 15786–15793 (2007).

3. L.F. Xu, Q.W. Chen, D.S. Xu, Hierarchical ZnO nanostructures obtained by electrode position, *J. Phys. Chem.* C **111:** 11560–11565(2007).

4. Y. Baek, Y. Song, K. Yong, A novel heteronanostructure system: hierarchical W nanothorn arrays on WO3 nanowhiskers, *Adv. Mater.* **18:** 3105–3110 (2006).

5. C. Ye, L. Zhang, X. Fang, Y. Wang, P. Yan, J. Zhao, Hierarchical structure: silicon nanowires standing on silica microwires, *Adv. Mater.* **16**: 1019–10233 (2004).

6. X.J. Mao, S.W. Wang, S.Z. Shimai, Porous ceramics with Tri-modal pores prepared by foaming and starch consolidation, *Ceram. Int.* **34:** 107–112 (2008).

7. S. Komarneni, M. Bruno, E. Mariani, Synthesis of ZnO with and without microwaves, *Mater. Res. Bull.* **35** 1843–1847 (2000).

8. T. Zhang, W. Dong, M.K. Brewer, S. Konar, R.N. Njabon, Z.R. Tian, Site-specific nucleation and growth kinetics in hierarchical nanosyntheses of branched ZnO crystallites, J. Am. Chem. Soc. **128**: 10960–10968 (2006).

9. Z. Gao, Y. Gu, Y. Zhang, First-principles studies on the structural transition of ZnO nanowires at high pressure, *J. Nanomater.* 5 (2010).

10. X. Wang, J. Song, J. Liu, Z.L. Wang, Direct-current nanogenerator driven by ultrasonic waves, Science **316** (5821) 102–105 (2007).

11. Y. Xi, J. Song, S. Xu, et al., Growth of ZnO nanotube arrays and nanotube based piezoelectric nanogenerators, *J. Mater. Chem.* **19**(48): 9260-9264 (2009).

12. Z.L. Wang, J. Song, Piezoelectric nanogenerators based on zinc oxide nanowires arrays, *Science* **312** (5771): 243–246 (2006).

13. A.B. Djurisic, A.M.C. Ng, X.Y. Chen, ZnO nanostructures for optoelectronics: material properties and device applications, *Prog. Quant. Electron.* 34 (4): 191–259 (2010).

14. F. Tuomisto, Vacancy profiles and clustering in light-ion-implanted GaN and ZnO, *Appl. Surf. Sci.* **255**(1): 54–57 (2008).

15. U. Pal, J.G. Serrano, P. Santiago, G. Xiong,

K.B. Ucer, R.T. Williams, Synthesis and optical properties of ZnO nanostructures with different morphologies, *Opt. Mater.* **29**(1): 65–69 (2006).

16. J.H. Yu, G.M. Choi, Selective CO gas detection of CuO and ZnO-doped SnO$_2$ gas sensor, *Sens. Actuators,* B **75**(1–2): 56–61 (2000).

17. A.Z. Sadek, W. Wlodarski, Y.X. Li, et al., A ZnO nanorod based layered ZnO/64°C YX-LiNbO3 SAW hydrogen gas sensor, *Thin Solid Films* **515** (24): 8705–8708 (2007).

18. J. Xu, Y. Zhang, Y. Chen, Q. Xiang, Q. Pan, L. Shi, Uniform ZnO nanorods can be used to improve the response of ZnO gas sensor, *Mater. Sci. Eng.* B **150**(1): 55–60 (2008).

19. H. Zhang, N. Du, B. Chen, D. Li, D. Yang, Carbon nanotube-ZnO nanosphere heterostructures: low-temperature chemical reaction synthesis, photolumi-nescence, and their application for room temperature NH3 gas sensor, *Sci. Adv. Mater.* **1**: 13–17 (2009).

20. X. Xu, X. Fang, H. Zeng, T. Zhai, Y. Bando, D. Golberg, One-dimensional nanos-tructures in porous anodic alumina membranes, *Sci. Adv. Mater.* **2**(3): 273–294 (2010).

21. H. Zeng, J. Cui, B. Cas, U. Gibson, Y. Bando, D. Golberg, Electrochemical deposition of ZnO nanowire arrays: organization, doping, and properties, *Sci. Adv. Mater.* **2**(3): 336–358 (2010).

22. G. Shen, D. Chen, 1-D hetero-nanostructures: from growth to devices, *Sci. Adv. Mater.* **1** 213–226 (2009).

23. S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, Z.L. Wang, Self-powered nanowires devices, *Nat. Nanotechnol.* **5**: 366-373 (2010).

24. Z.L. Wang, ZnO nanowires and nanobelt platform for nanotechnology, *Mater. Sci. Eng.* **64**(3-4): 33–71 (2009).

25. R.A. Rosenberg, M. Abu Haija, K. Vijayalakshmi, J. Zhou, S. Xu, Z.L. Wang, Depth resolved luminescence from oriented ZnO nanowires, *Appl. Phys. Lett.* **95**(24): 3 (2009).

26. M. Lucas, Z.L. Wang, E. Riedo, Growth direction and morphology of ZnO nanobelts revealed by combining in situ atomic force microscopy and polarized Raman spectroscopy, *Phys. Rev.* B **81**: 5 (2010).

27. M. Lucas, Z.L. Wang, E. Riedo, Combined polarized Raman and atomic force microscopy: in situ study of point defects and mechanical properties in individual ZnO nanobelts, *Appl. Phys. Lett.* **95**(5) (2009).

28. S. Xu, Y. Wei, M. Kirham, et al., Patterned growth of vertically aligned ZnO nanowire arrays on inorganic substrates at low temperature without catalyst, *J. Am. Chem. Soc.* **130**(45): 14958–14959 (2008).

29. S. Xu, C. Lao, B. Weintraub, Z.L. Wang, Density controlled growth of aligned ZnO nanowires arrays by seedless chemical approach on smooth surfaces, *J. Mater. Res.* **23** (8): 2072–2077 (2008).

30. C. Lui, Y. Masuda, Y. Wu, et al., A simple route for growing thin films of uniform ZnO nanorod arrays on functionalized Si surface, *Thin Solid Films* **503**: 110–114 (2006).

31. L. Vayssieres, Growth of arrayed nanorods and nanowires of ZnO from aqueous solution, *J. Adv. Mater.* **15**: 464–466 (2003).

32. N. Saito, H. Haneda, W.S. Seo, et al., Low-temperature fabrication of light-emitting zinc oxide micro patterns using self-assembled monolayers, *J. Langmuir* **17**: 1461–2146 (2001).

33. A. Sugunan, H.C. Warad, M. Boman, J. Dutta, *J. Sol–Gel Sci. Technol.* **39** 4 (2006).

34. K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, J.A. Voiget, *Appl. Phys. Lett.* **68**: 403 (1996).

35. Tapas Kumar Kundu, Nantu Karak, Puspendu Barik, Satyajit Saha, Optical properties of ZnO nanoparticles prepared by chemical method using poly (vinylalcohol) (PVA) as capping agent, *Int. J. Soft Comp. Eng.* **1**: 19–24 (2011).

36. Padmini Pandey, Neha Singh, Fozia Z. Haque, Development and optical study of hexagonal multi-linked ZnO micro-rods grown using hexamine as capping agent, doi:**10**.1016/j.ijleo.2012.03.007, (2012) in press.