JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 10, No. 10, October 2008, p. 2588 - 2591

Optically transparent colloidal suspensions of single crystalline ZnO quantum dots prepared by simple wet-chemistry

M. K. PATRA, K. MANZOOR[a], M. MANOTH, V. S. CHOUDHRY, S. R. VADERA, N. KUMAR*
Defence Laboratory, Jodhpur-342011, India
[a]Amrita Center for Nanosciences, AIMS Campus, Cochin-682 026, India

Highly stable and optically transparent colloidal ZnO QDs have been synthesized at room temperature without using any surface capping agent. The as synthesized QDs show phase singularity of ZnO particles having wurzite (hexagonal) structure. TEM as well as AFM studies indicate that the average crystalline size of QDs is ~ 7nm. Further, high resolution TEM image shows formation of hexagonal shape particles having lattice fringes along (001) plane of wurzite phase. Photoluminescence (PL) studies show bright luminescence with peak maximum at 530nm due to oxygen vacancy centers (V_o) present in QDs. The optical transmission spectrum of colloidal QDs of ZnO shows sharp absorption at 3.48eV which is blue shifted as compared to bulk ZnO (3.36eV) due to the quantum confinement effect. The band gap energy observed in QDs of ZnO is consistent with the energy calculated by using effective mass approximation model of Brus.

(Received March 31, 2008; accepted August 14, 2008)

Keywords: Semiconductor, Chemical synthesis, Luminescence, ZnO, Quantum dot

1. Introduction

Quantum dots (QDs) are considered to be highly important technological materials due to their unique optical and electro-optical properties owing to the strong quantum confinement effects at nanometer scale. Among various types of QD materials, ZnO QDs have attracted attention of scientific community due to their two most important properties i.e. wide-band gap value of ~ 3.36eV and high value (60meV) exciton binding energy [1]. These properties together with other important attributes such as long term environmental stability, bio- compatibility and low cost render ZnO an ideal material for a number of technological applications such as transparent electrodes for photovoltaic and electroluminescent devices, transparent UV filter, UV light emitting diodes, UV-lasers, sensors, etc.[2-5]. Recently, the interest in experimental and theoretical research on ZnO QDs has grown as these materials provide greater opportunities for tailoring of physical and optical properties. For example, ZnO QDs show enhanced UV photoluminescence properties [6]. Similarly, self assembled ZnO QDs show tunable optical properties [7]. Further, high luminescence colloidal ZnO QDs have shown potential for their applications in the area of bio- imaging[8].

There are several reports on the chemical synthesis of colloidal ZnO QDs. Important among these includes sol-gel [9], double-jet precipitation [10], chemical precipitation [11], etc. The majority of them deal with precipitation of zinc salts with alkali hydroxide to give $Zn(OH)_2$ which is then dehydrated in the presence of an alcohol. These ZnO colloids are stabilized by using various surface capping agents viz. long chain aliphatic thiols, amines, polyvinyalpyrolidone (PVP), hexametaphosphates, propionic acid, etc [12-15]. The colloids in most of these processes generally aggregate together and result into either turbid suspensions or precipitates. For many of the optical and electro-optical applications, there is requirement of optically transparent QD solutions. Recently, Huang et al.[16] reported preparation of surface- modified stable transparent ZnO QDs in absolute ethanol medium with 3-(Trimetoxysilyl) propyal methacrylate as the stabilizing agent. In a very recent report, D. Sun [17] has prepared transparent PMMA/ZnO nanocomposite films by using 5nm size colloidal ZnO QDs. In almost all reported chemical synthesis methods the aggregation of ZnO QDs has been arrested by way of surface modifications. In this paper, we report simple wet chemical synthesis of stable transparent colloidal ZnO QDs at room temperature without any surface modification.

2. Experimental details

In the present synthesis, we have used substituted alcohol viz. 2-ethoxy ethanol as medium for reaction. In a typical synthesis, 0.1 M of zinc acetate solution was prepared in 2-ethoxy ethanol. For dissolving the zinc salt, the solution was stirred continuously for 2hrs. Similarly, 0.1M solution of potassium hydroxide (KOH) was also prepared in 2-ethoxy ethanol. The reaction was carried out at room temperature by drop wise addition of KOH solution in to zinc acetate solution with constant stirring. Final pH of the solution was maintained at ~7. The resulting solution was homogenized by stirring continuously for 3hrs with a magnetic stirrer and finally filtered through wattmann filter paper to remove any insoluble precipitates The solution thus obtained was found to show bright luminescence under UV excitation, thereby indicating formation of ZnO particles. The luminescence intensity was found to increase when the freshly prepared colloidal solution was kept for ~3hrs, thus suggesting nucleation and growth of QDs. However, it is quite interestingly to note that the solution remains clear and transparent without any precipitate even after 3-4 months. Moreover, the luminescence property of the solution is maintained. The colloidal solution has been characterized for its structural, microscopic and optical properties.

For structural characterization, the solution of ZnO QDs was spray coated on glass substrate. The sample was studied by using powder X-ray diffractometer, Philips Xpert-PRO fitted with Cu K_α souce. Transmission electron microscope (TEM), JEOl-JEM-200LX and Atomic Force Microscope (AFM), NT-MDT Solver TS 150, in semi-contact mode, have been used to determine the size of ZnO QDs. Further, high resolution images of the particle have been recorded by using high resolution transmission electron microscope (HRTEM), JEOL2010. A drop of solution was placed on to carbon coated copper grid for TEM analysis and the solution was fine sprayed on polished mica substrate for AFM studies. Optical studies of the transparent solution was carried out by using Lambda 600 Perkin Elmera UV-VIS spectrophotometer. Photoluminescence (PL) emission and excitation spectra at room temperature were recorded by using JASCO-FP-6500 spectroflurometer.

3. Results and discussion

Fig.1 shows X-ray diffraction (XRD) pattern of the sample. The diffraction peaks corresponding to (100), (002), (101), (102) (110), (103) and (200) planes indicate the hexagonal structure of ZnO QDs. Further, the line broadening of these peaks suggest that the particles are in nanometer size. From the XRD line width, by using Debey Scherrer formula, the average size of crystalline ZnO crystals is estimated to be around ~7nm. TEM image of the ZnO QDs, shown in Fig.2(a), also indicates ~ 7nm size of particles. HRTEM image (Fig.2(b)) shows particles are hexagonal in shape with lattice fringes having spacing of ~ 0.26nm matching very well with the (001) lattice plane of the wurzite phase of ZnO. From AFM image of the QDs, shown in Fig.3, the height of QDs is estimated ~3.7nm and diameter ~ 7nm, which is well agreement with the XRD and TEM results. The above results therefore clearly suggest the formation of single crystalline ZnO QDs.

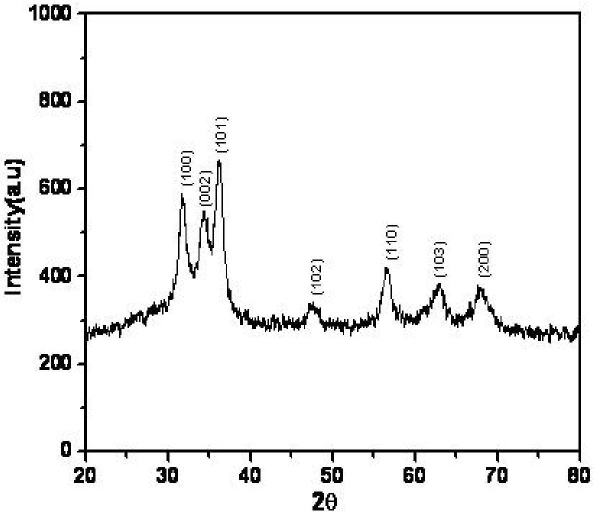

Fig.1 XRD spectra of as prepared ZnO QDs sprayed on glass substrate.

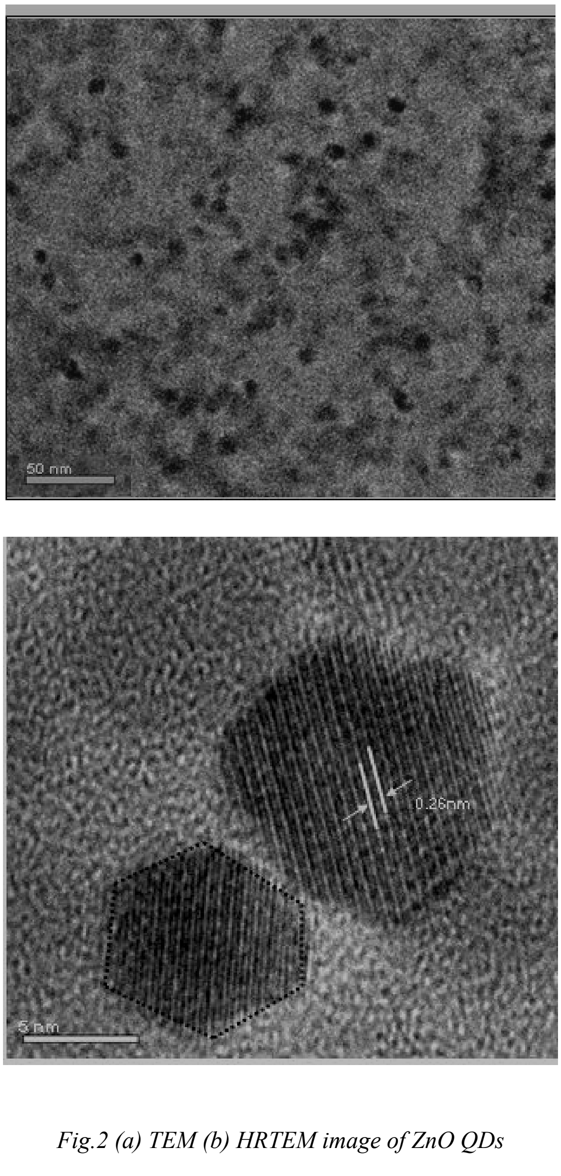

Fig.2 (a) TEM (b) HRTEM image of ZnO QDs

Optical transmission spectrum of ZnO QDs solution measured at room temperature is shown in Fig.4. Spectrum shows more than 97% transmission in optical regime (400-700nm). The sharp band edge absorption observed at ~ 356nm corresponds to the direct band gap of ZnO (3.48eV). The value of band gap is higher as compared to bulk ZnO band gap of ~3.36eV and is the result of quantum confinement effects in ZnO QDs. The inset figure (a) shows clear solution of as prepared ZnO QDs placed in quartz vial showing bright luminescence under UV excitation (inset fig.(b)).

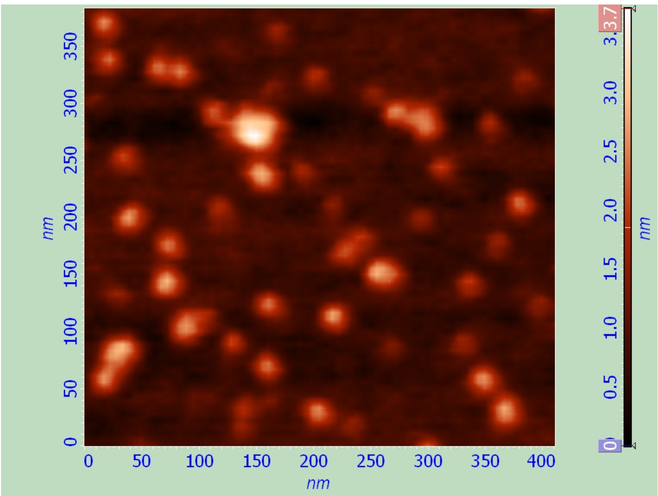

Fig.3 AFM image of as prepared ZnO QDs.

The PL emission and excitation spectra of ZnO QDs recorded at room temperature, are shown in Fig. 5. The emission spectrum shows a broad emission with peak maximum at 530nm and the corresponding excitation spectrum shows peak maximum at 357nm indicating band-to- band excitation of ZnO. Extensive investigations have been reported world over on the origin of broad green emission from the ZnO QDs in the visible region. It is commonly believed that the green emission from ZnO originates from oxygen vacancies (V_O) [18-20]. Vanheusden et al.[21] further suggest that the green emission in ZnO is due to the recombination of electrons in singly occupied oxygen vacancies with photoexcited hole in the valence band. The first principle calculations by Zhang et al.[22] support this identification and show that V_O defects have low formation enthalpy and hence are readily formed. The photogenerated electrons can be trapped into oxygen vacancies through a nonradiative decay and then recombine with holes in the valence band. Yang et al. [6] observed green emission from ZnO QDs grown by chemical methods and attributed it to the presence of oxygen vacancy centers. On the similar lines the observed visible emission at 530nm in the present studies can also be attributed to the oxygen vacancy centers in QDs. The band gap energy (E_g) for ~7nm sized ZnO particle of wurzite structure has been calculated by using Eq.(1), given by effective mass approximation model of Brus [23].

$$E_g(\text{Quantumdot}) = E_g(\text{Bulk}) + \left(\frac{h^2}{8R^2}\right)(1/m_h + 1/m_e) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r R} \qquad (1)$$

Where h is the Planck's constant, R is the radius of quantum dot (QD), ε_r the dielectric constant of the material and m_h and m_e are the effective masses of hole and electron respectively. We have taken $m_e \approx 0.26\ m_0$ and $m_h \approx 0.59m_0$, $\varepsilon_r = 8.5$ for ZnO [24]. The calculation gives the band gap energy of 3.446eV for QD. The results thus suggest that the excitation at 357nm (3.46eV) arises from the band- to- band transition of electrons in ZnO QDs. The calculated energy for ZnO QDs is quite in agreement with the experimentally obtained band gap energy from optical studies.

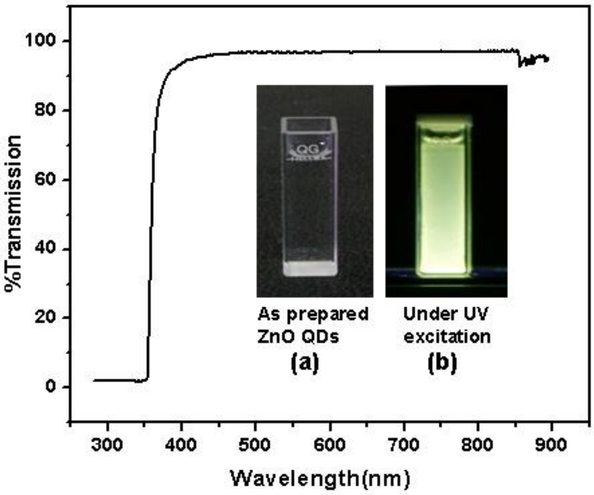

Fig.4 Transmission spectra of ZnO QDs measured at room temperature. Inset Figure (a) shows transparent solution of as prepared QDs and (b) luminescence under UV excitation.

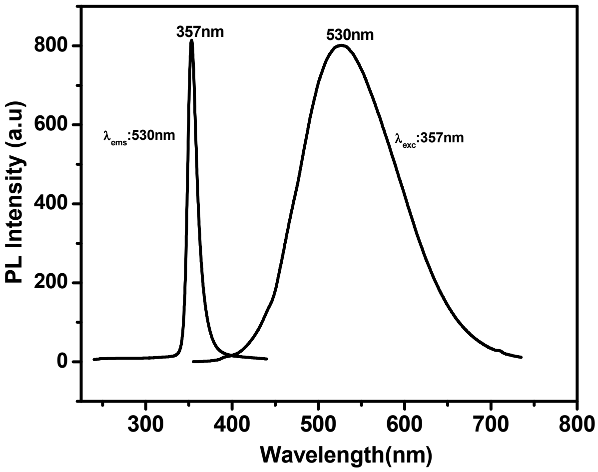

Fig.5 Room temperature PL spectra of ZnO QDs.

It is very interesting to note that use of substituted alcohol viz. 2-ethoxy ethanol as reaction medium together with control of pH has helped in preventing the aggregation of nanoparticles. In general, the preparation of ZnO nanoparticles in alcoholic solution depends on the dehydration property of alcohol. This dehydrating ability of unsubstituted alcohols plays an important role in the removal of coordinated water from the precursors compound (basic zinc acetate) that promotes the formation of anhydrous oxide structure at room temperature. But once ZnO particle nucleates, the growth process continues with time and the size of crystallites depends on a variety of factors such as Zn and OH ions concentrations, reaction medium, availability of oxygen in the medium and temperature. To obtain stable colloids, the all above factors should be properly controlled during synthesis. In the present synthesis the pH of the solution was kept ~7. Faster growth of ZnO particles was observed at pH value >7 resulting into a turbid solution. It is reported that the fresh ZnO nanoparticles prepared from zinc acetate dihydrate in ethanol solution are elctrostatically stabilized by negatively-charged repulsion between carboxylic acid groups on the nanoparticle surfaces [25]. Hence use of zinc acetate salt in our synthesis work might also be one of the contributing factors in controlling the size of ZnO nanoparticles. In addition, the presence of bulky group (ethoxy ethanol) in the solution provides steric effect around QDs preventing aggregration of particles. Therefore both carboxylic group on surface and the ethoxy ethanol medium help to control the growth of ZnO QDs to obtain transparent colloidal solution.

4. Conclusions

In summary, we have successfully synthesized stable transparent colloidal ZnO QDs just by replacing alcohol with a substituted alcohol and optimization of pH of the reaction medium without using any capping agent. The solution exhibits more than 97% transparency in optical regime. XRD studies confirm the formation of pure hexagonal crystal phase of ZnO. TEM and AFM studies reveal formation of ~ 7nm size particles. Quantum confinement effect is evident from the optical studies and is consistent with the band gap energy calculated by using Brus equation. Photoluminescence studies show visible emission with peak maximum at 530nm which attributed to the presence of oxygen vacancy centers in QDs.

Acknowledgements

The authors are thankful to Director I IT, Chennai for extending the TEM facilities

References

[1] U. Özgur, Y. I. Alivov, C. Liu, A. Take, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Markoc, J. Appl. Phys. **98**, 041301 (2005).

[2] K. Westermark, H. Rensmo, A.C. Lees, J. G. Vos and H. Siegbahn, J. Phys. Chem. B **106**, 10108 (2002).

[3] C. H.Liu, J.A. Zapien, Y. Yao, X. M. Meng, C. S. Lee,S.S. Fan, Y. Lifshitz, S. T. Lee, Adv. Mater. **15**, 838 (2003).

[4] X. L. Cheng, H. Zhao, L. H. Huo, S. Gao, J.G. Zhao, Sens. Actuator B **102**, 248 (2004).

[5] Z. K. Tang, G.K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).

[6] C. L. Yang, J. N. Wang, W.K. Ge, L. Guo, S.H. Yang, D.Z. Shen, J. Appl. Phys. **90**, 4489 (2001).

[7] J. G. Lu, Z. Z. Ye, Y. Z. Zhang, Q. L. Liang, Sz Fujita, Z. L. Wang, Appl. Phys. Lett., **89**, 023122 (2006).

[8] Y. L. Wu, C. S. Lim, S. Fu, A. I. Y Tok, H. M. Lau, F. Y. C. Boey, X. T. Zeng, Nanotecnology, **18**, 215604 (2007).

[9] S. Sakohara, L. K. Ticknanen and M. A. Anderson, J. Phys. Chem. **96**, 11086 (1992).

[10] Q. Zhong and E. Matijevic, J. Mater. Chem. **6**, 443 (1996).

[11] A. Chittofrati and E. Matijevic, Colloids Surf. **48**, 65 (1990).

[12] C. Li and N. Murase, Langmuir **20**, 1-4 (2004).

[13] H. Zhang, Z. Cui, Y. Wang, K. Zhang, X. Ji, C. Lu, B. Yang, M. Gao, Adv. Mater. **15**, 777 (2003).

[14] K. Borgohain and S. Mahamuni, Semicond. Sci. Technol. **13**, 1154 (1998).

[15] U. Koch, A. Fojtik, H. Weller and A. Hanglein, Chem. Phys. Lett. **122**, 507 (1985).

[16] C.-H. Huang and W.-T. Whang, J. Mater. Chem. **15**, 267 (2005).

[17] D. Sun, Nanotecnology **18**, 215606 (2007).

[18] L. Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge and G. K. L. Wang, Appl. Phys. Lett. **76**, 2901 (2000).

[19] S. Mahamuni, K. Borgohain, B. S. Bendre, V. J. Leppert ,S. H. Risbud, J. Appl. Phys. **85**, 2861 (1999).

[20] S. A. Studenikin, N. Golego and M. Cociverra, J. Appl. Phys. **84**, 2287 (1998).

[21] K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Vogit and B. E.Gnade, J. Appl. Phys. **79**,7983 (1996).

[22] S.B. Zhang, S.-H. Wei and A. Zunger, Phys. Rev. B **63**,075205 (2001).

[23] L. E. Brus, J. Chem. Phys., **80**, 4403 (1984).

[24] E. M. Wong, P. G. Hoertz, C.J. Liang, B.-M. Shi, G.J. Meyer and P. C. Searson, Langmuir, **17**, 8362 (2001).

[25] S. Sakohara, M. Ishida, M. A. Anderson, J. Phys. Chem. B **102**, 10169 (1998).

---

[*] Corresponding author: nkjainjd@yahoo.com