

Wurtzite ZnSe quantum dots: Synthesis, characterization and PL properties

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One-pot, facile solution phase approach is explored for the fabrication of uniform and nearly monodispersed colloidal ZnSe semiconductor quantum dots (QDs). ZnSe QDs have been synthesized by wet chemical, template free process by Zinc acetate and elemental Selenium powder in presence of ethylene glycol, hydrazine hydrate and a defined amount of water at 70°C. The product was in strong quantum confinement regime, having yield as high as 80%. The phase analysis, purity and morphology of the product has been well studied by X-ray diffraction (XRD), UV-Vis spectroscopy, Photo-luminescent spectroscopy (PL), Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM) and Atomic force microscopy (AFM) techniques to show that we obtain nearly monodispersed size distribution. X-ray diffraction pattern indicates that ZnSe QDs possess Wurtzite (Hexagonal) structure. Transmission electron microscopy images showed that the diameters are in the range of 1 nm. Due to their high refractive index and absence of absorption in the visible region, the monodispersed ZnSe QDs could be potential building blocks to construct functional devices and photonic band gap crystals.

Keywords: Blue Shift, Quantum confinement, Quantum dot, Semiconductor, Wurtzite structure, ZnSe.

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1. Introduction

The recognition of strongly size and shape dependent physical/chemical properties of nanostructure materials has stimulated efforts towards the fabrication of nanocrystals in a systematic and controlled way [1-10]. Chemically synthesized nanostructures and their assembly are of fundamental importance due to their unique dimension dependent properties and their potential applications as building blocks in nanoelectronics, nano-optonics, nanosensors & actuators, and in biology [11-15]. Recently much interest has been aroused in the preparation and assembly of semiconductor QDs due to their narrow and intensive emission spectra, continuous absorption band, high chemical and photo bleaching stability, processability and surface functionality. There is a wide range of very efficient light emitting QDs, which can be synthesized both in organic or as aqueous solutions [16-24]. ZnSe an important II-VI, n-type, direct band gap semiconductor has attracted considerable attention due to its applications in light-emitting diodes, photo-detectors and full color display [25-28]. The wide band gap (bulk band gap 2.7 eV) of ZnSe and significantly large binding energy (21meV) [29], make this an ideal choice as an inorganic passivation shell for a variety of semiconductor core/shell nanocrystals, in order to improve the

stability and emission properties of the semiconductor core nanocrystals with relatively narrow band gap and for efficient room temperature exciton devices with improve temperature characteristics [30-33]. ZnSe is also attractive host for the formation of doped nanocrystals [34-36]. Several novel applications have been presented which require size, shape and phase control of ZnSe nanostructured materials [37-40]. There are several reports describing various synthesis route for ZnSe nanoparticles [41-51], most of the reports yielded the cubic (Zinc blende) structure of ZnSe with a less amount of hexagonal (Wurtzite) structure. So far, various ZnSe nanostructures including quantum dots [43, 52-55] nanowires [49, 56-60] and nanoribbons [47, 59] have been synthesized. Herein, we demonstrate the successful synthesis of the uniform, nearly monodispersed; hexagonal wurtzite ZnSe QDs by a relatively cheaper, less hazardous wet chemical method. Less hazardous elemental selenium and zinc acetate being used as precursor. The paper deals with preparation, characterization, absorption and photoluminescence properties of wurtzite ZnSe QDs. The absorption analysis displays a large 'blue shift'.

2. Experimental details

2.1. Material preparation

A typical procedure for synthesis of ZnSe QDs is as follows. Highly pure Zinc acetate (99.9%) and Selenium (99.999%) purchased from Alfa, used without further purification. Ethylene glycol and Hydrazine hydrate of analytical grade purchased from Merk, Germany and used as received. In synthesis (0.6g) Zinc acetate and (0.409g) Elemental Selenium was taken with deionized water, ethylene glycol and hydrazine hydrate in the volume ratio of 6:3:1 respectively in a 200 ml capacity conical flask. Then the solution was refluxed under vigorous stirring at 70°C for 8 hrs. Finally, the yellowish precipitates were collected and washed with anhydrous ethanol and hot distilled water for several times, then dried in vacuum at 50°C for 6 hrs.

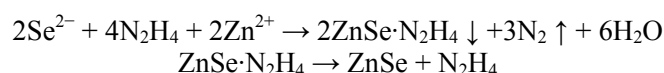
2.2. Characterization techniques

The X-ray diffraction pattern of as-synthesized freshly dried ZnSe sample was recorded by a Rigaku Rotoflux diffractometer (operating at 40 kV, 100 mA) with Cu-K α ($\lambda = 1.54056 \text{ \AA}$) radiation. UV-Visible spectra was recorded by UV-Vis160 Spectrophotometer (Shimadzu, Japan) in the spectral range between 250 and 800 nm using a spectral bandwidth of 1nm, absorption experiments were preformed at room temperature. Global photoluminescence spectra of ZnSe QDs were recorded with the help of a computer controlled rationing luminescence spectrometer (LS55-Perkin Elmer Instruments, UK) with accuracy = $\pm 1.0 \text{ nm}$ and reproducibility = $\pm 0.5 \text{ nm}$. A tunable 2 kW pulse $< 10 \mu\text{s}$ from a xenon discharge lamp was used as the excitation source. A gated photomultiplier tube was used as a detector. Before the PL experiments, the signal to noise ratio was adjusted to 500:1 using the Raman band of water with excitation in the range 250 nm depending on particle size. AFM measurements were conducted using Molecular Imaging, USA make AFM equipment in non-contact, acoustic AC (AAC) mode. An advantage of AAC mode is that besides the topography image phase image is also obtained. Thin film samples were exposed to white light using a 50 watt quartz tungsten halogen (QTH) lamp (with a spectral range of 450 to 850 nm), from a distance of 10 cm for few hrs at room temperature. In order to obtain unbiased structural characterization data measurements were done under ambient conditions (20°C/ 40% RH) using a micro cantilever probe, tip radius and probe spring constant are in the ranges of 5-10 nm and 4-5 N/m, respectively. TEM investigations were carried out using a Techni 20G²- TEM, typical e-beam voltage employed was 200 kV. The as-prepared ZnSe was coated on formvar coated copper grids. FTIR spectrum was measured by using Jasco-5300 Fourier transform infrared spectrometer at room temperature with the sample milled in KBr.

3. Results and discussion

3.1. Possible reaction mechanism

In the present work, Se source was derived from the reduction of Se by N_2H_4 . These highly reactive Se can be easily converted into Se^{2-} , which results in a high monomer concentration. In the initial step, hydrazine hydrate complexes with metallic Zn^{2+} and forms the transparent soluble complexes solution, which effectively decreases the concentration of Zn^{2+} and avoids the precipitation of ZnSeO_3 , thus providing a more homogenous solution environment for the reaction. Se^{2-} is released slowly and interacts with surplus N_2H_4 to form the molecular precursor immediately. The reaction could be described as follows:



Decomposition of precursor can proceed thoroughly under present condition. The application of N_2H_4 as the coordination agent is determinative for the phase of the products. ZnSe has two types of crystal phase, cubic (blende) and hexagonal (wurtzite) phase. Many wet chemical methods applied to synthesize ZnSe can only obtain cubic blende structure [61–64]. So it can be drawn that the complexing ability of groups containing atom N (such as NH_2 or NH_3) can effectively determine the final phase of the products. Peng et al. [65] also found similar phenomena during preparing CdSe using $\text{NH}_3\cdot\text{H}_2\text{O}$ as complexing agent, and the exact mechanism was not fully understood. However, because NH_3 could not take the role of molecular template, all the products were QDs. All the above results reveal that $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, as solvent, favors the formation of wurtzite ZnSe nanostructure.

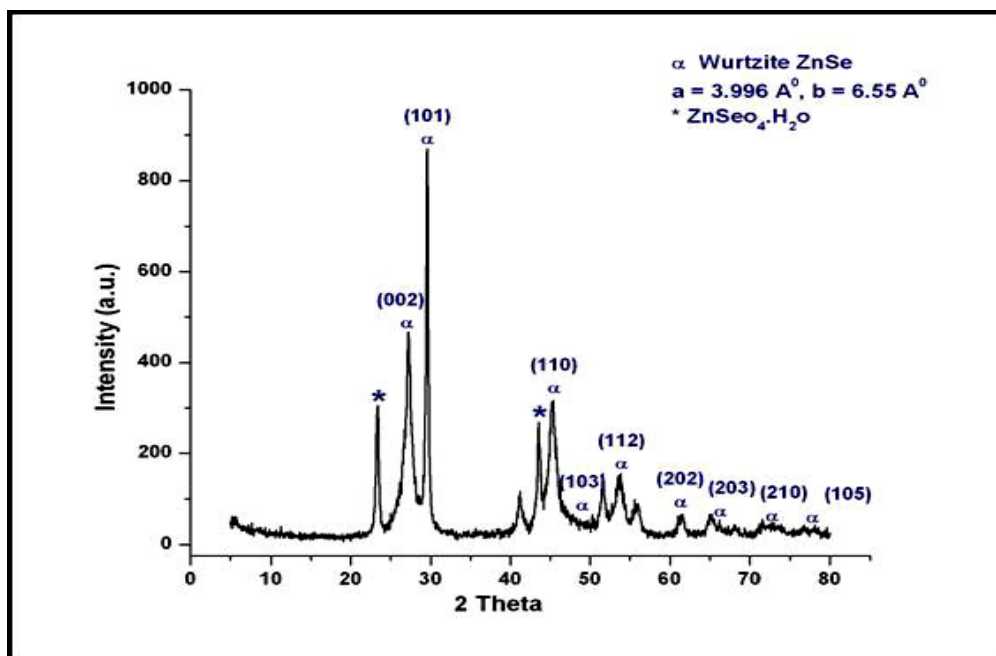


Figure 1. X-ray diffraction pattern of ZnSe Sample.

3.2. Structural Characterization

X-ray diffraction pattern of the as prepared ZnSe sample is shown in Fig. 1. All the diffraction peaks in this pattern can be indexed to Wurtzite (hexagonal) structure. Which is in very good accordance with the JCPDS card no.15-0105 for ZnSe ($a = b = 3.996 \text{ \AA}$, $c = 6.55 \text{ \AA}$). The several peaks of hexagonal phase of ZnSe have been obtained due to diffraction from (0 0 2), (1 0 1), (1 1 0), (1 0 3), (1 1 2), (2 0 2), (2 0 3), (2 1 0) and (1 0 5) planes of ZnSe. Two peaks of $\text{ZnSeO}_4 \cdot \text{H}_2\text{O}$ have also been obtained in the diffraction data. The information on the particle size (A) of ZnSe QDs has been obtained from the following Scherrer relations:

$$A = 0.9 \lambda / \beta \cos \theta \quad (1)$$

where β is the full-widths-at-half-maximum (FWHM) of the diffraction peaks.

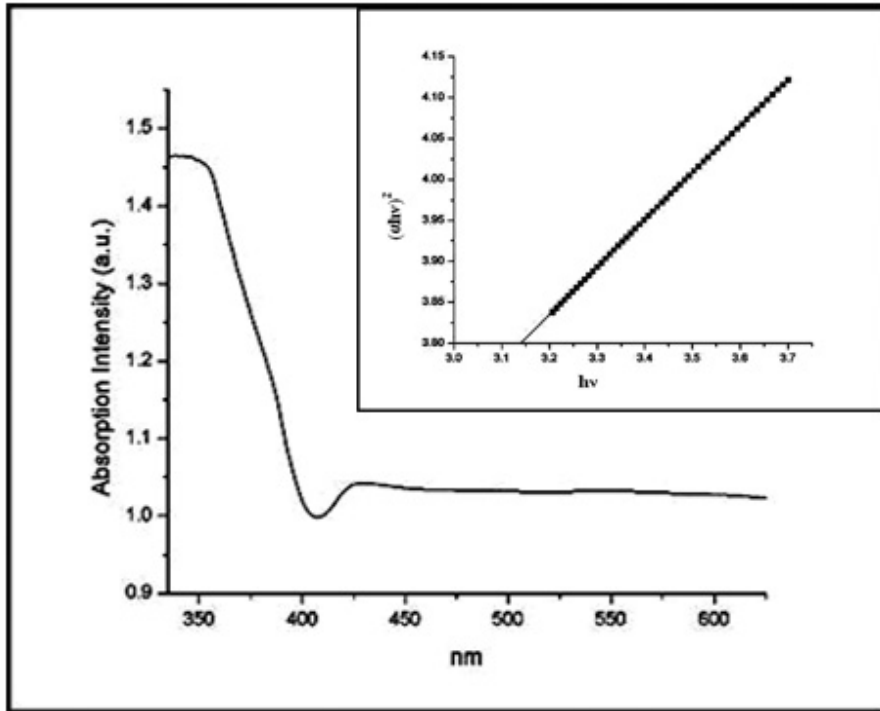


Figure 2. Absorption spectra of ZnSe Sample. The variation of $(\alpha h\nu)^2$ versus $h\nu$ of ZnSe (inset Figure. 2(A)) at room temperature.

3.3. Optical studies

The optical properties of ZnSe QDs are dependent on the size and the shape of the QDs. The optical properties of ZnSe QDs were characterized by UV–Vis absorption and the result is shown in Fig. 2. There is a obvious shoulder peaks in the UV–Vis absorption spectrum, and the

corresponding onset at 330 nm which can be assigned to the band gap and the second excited state within each crystallite, respectively [66]. The absorption spectra of ZnSe QDs were studied without taking into account the reflection and transmission losses. The absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors.

$$\alpha = \frac{k (h\nu - E_g)^{n/2}}{h\nu} \quad (2)$$

where k is a constant, E_g the optical band gap and n is a constant equal to 1 for direct gap semiconductors and 4 for indirect gap semiconductor materials. The variation of $(\alpha h\nu)^2$ versus $h\nu$ is linear at the absorption edge which confirmed direct band gap transition in ZnSe. Extrapolating the straight-line portion of the plot $(\alpha h\nu)^2$ versus $h\nu$ for zero absorption coefficient value gives the, E_g , which are shown in inset in Fig. 2(A). The band gap energy, E_g , of ZnSe QDs was found to be 3.14 eV that showed the 'blue shift' of 0.44 eV from standard bulk band gap at room temperature ($E_g = 2.7$ eV). It is well-known that the reaction conditions such as heating time, temperature, kinds and amount of reagents have effect on the morphology and size of the products in the processes.

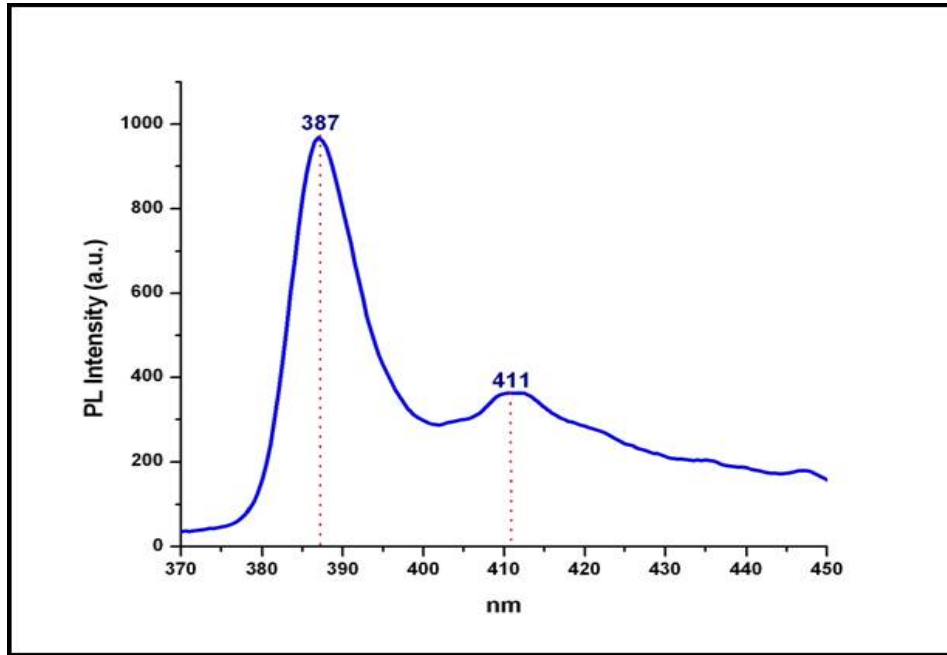


Figure 3. Photoluminescence spectra of the ZnSe Sample at room temperature.

The room temperature PL spectrum centered at 387 nm of as prepared ZnSe QDs excited at 230 nm is shown in Fig. 3, which is attributed to the recombination of excitons and the UV- blue emissions at about 410 nm which results from the recombination of a photon-generated hole with a charge state of the specific defect.

3.4. Topological and Morphological Studies

For topological studies ZnSe QDs were deposited in the form of film on a (1 x 1 inch and 1 mm thick) mica sheet by dispersing the ZnSe QDs powder in methanol.

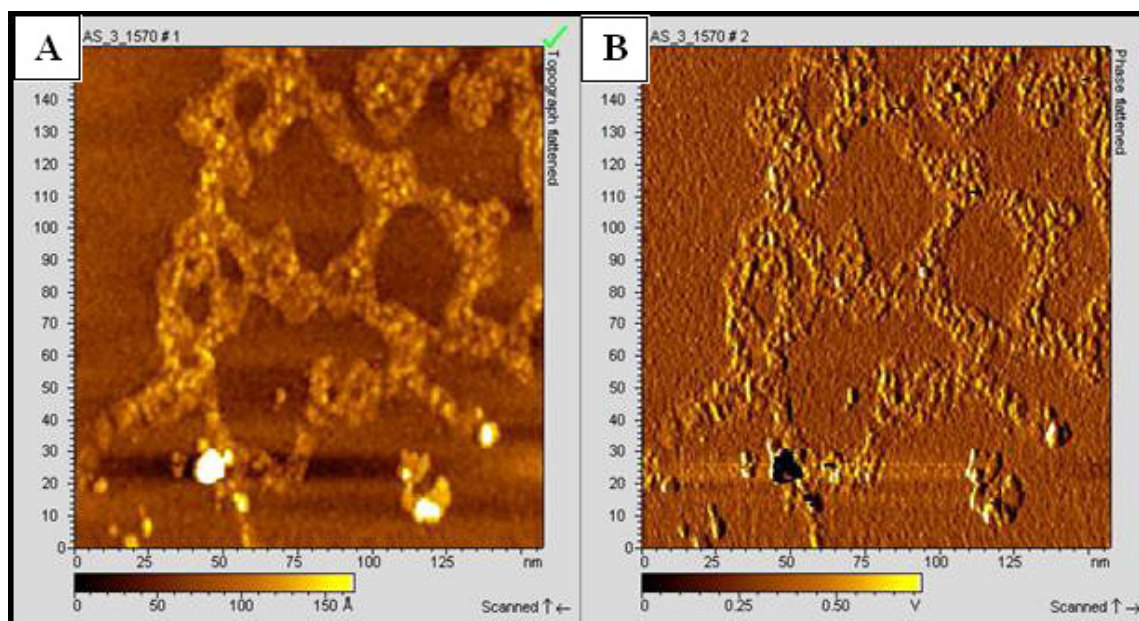


Figure 4 (A-B). Topographical and Phase Modulated AFM images in $(150 \text{ nm})^2$ scan area of ZnSe sample.

Figure 4 (A-B) shows Topographical and Phase Modulated AFM images of as-deposited ZnSe thin film. The topology of as-deposited ZnSe QDs film surface is viewed two-dimensionally. The samples were imaged using a $150 \text{ nm} \times 150 \text{ nm}$ area. Before each sample observation, the condition of the cantilever was cross-examined by taking images of the freshly cleaved mica surface. The AFM morphology clearly revealed that the deposition of ZnSe film took place via aggregations of QDs i.e. non-homogeneous precipitation on the solution on mica sheet. The AFM image clearly shows the formation of ZnSe QDs of nearly equal size.

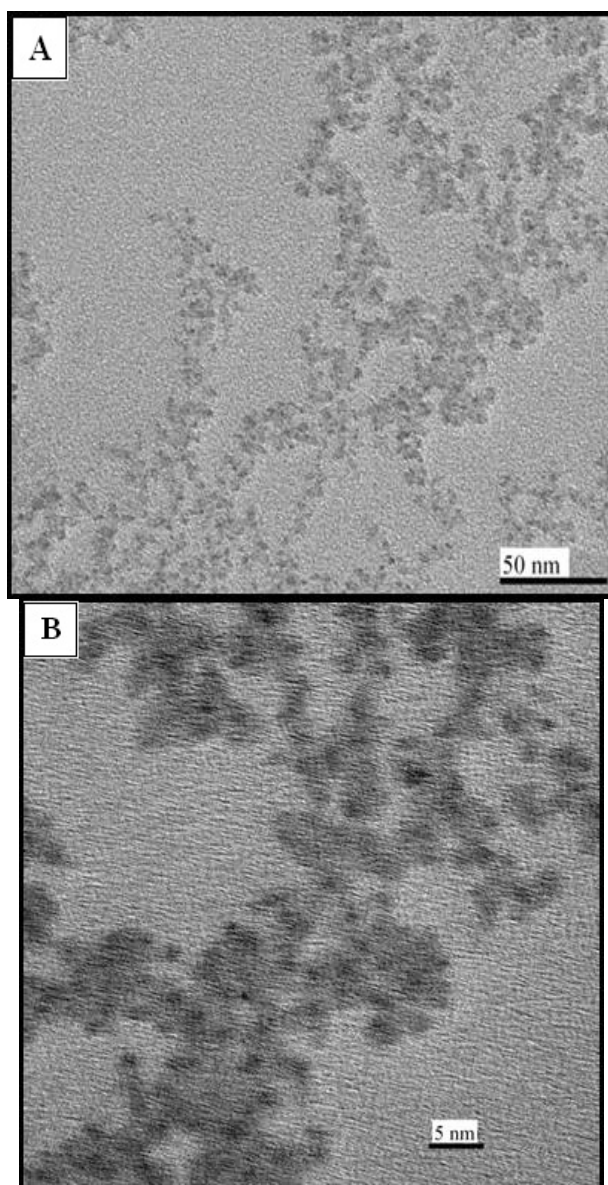


Figure 5. (A-B) TEM Micrographs of ZnSe QDs.

Fig. 5 (A-B) shows transmission electron micrographs of ZnSe QDS with different magnifications.

It is revealed from figures that the QDs with an average diameter of 1 nm are nearly mono dispersed without aggregation. The TEM micrograph revealed a nearly monodispersed ZnSe QDs which is in well agreements with the values observed from AFM morphological studies. It also revealed the ZnSe QDs are distinguishable from each other.

4. IR spectroscopy and proposed mechanism

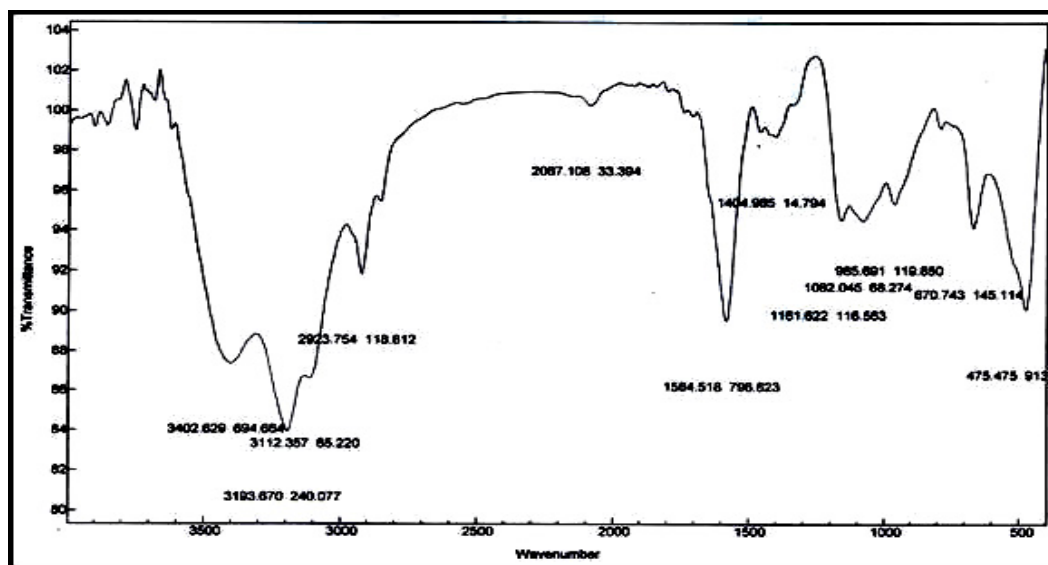


Figure 6. FT-IR spectrum of ZnSe sample milled in KBr at room temperature.

As prepared sample was characterized by FTIR analysis and the corresponding spectrum is shown in Fig.6. The broad peak at 3402 cm^{-1} and the weak peak at 1584 cm^{-1} are assigned to O-H characteristic vibrations resulting from all small quantity of H_2O on the sample. The sharp peak at 3112 cm^{-1} corresponds to N-H stretching vibration band and the shift toward lower frequency compared with hydrazine may result from the interaction of N_2H_4 with zinc ion and regular periodic structure of molecular precursor. The NH_2 scissor and twist band appears at 1584 cm^{-1} and 11561 cm^{-1} , respectively. Sharper and stronger peaks indicate weaker interaction ordered arrangements of hydrazine molecules existing in the precursors. All IR characteristic indicates that the N_2H_4 molecular has intercalated into the complex and formed a molecular precursor.

Based on these observations, a growth mechanism of ZnSe QDs is proposed. In the reaction, EN is a bidentate ligand and can coordinate with Zn^{+2} to form a relatively stable Zn^{+2} complexes. In the reaction system, Se is reduced by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to form Se^{2-} , and Se^{2-} ions will react than with above complex to form ZnSe which is similar to the structure shown in schematic representation in Fig. 7. EN would be removed by washing several times with methanol and hot distilled water and than after heating the sample at 50°C in vacuum for 6 hrs.

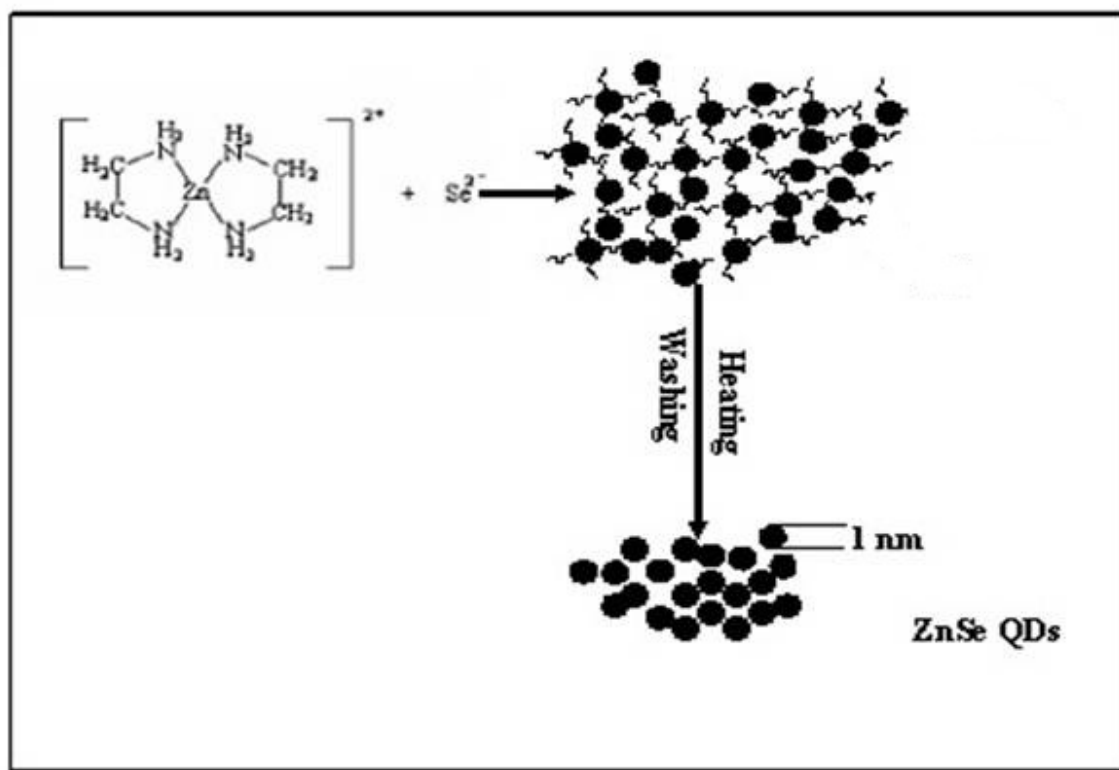


Figure 7. Schematic representation of the formation of ZnSe (en) and ZnSe QDs.

5. Conclusions

In summary, highly luminescent, nearly monodispersed wurtzite ZnSe QDs has been prepared in aqueous solution of Hydrazine hydrate and Ethylene glycol at 70°C within 8 hrs, free from any hazardous element and surfactant or template. Strong ‘blue-shifts’ was observed in UV-Vis (0.44eV from bulk value) analysis recorded of the sample, yield of the product found as high as 80%. Ethylene glycol, hydrazine hydrate and a defined amount of water play important role in the formation of ZnSe QDs. Hydrazine hydrate played multiple roles in the formation of ZnSe QDs it served not only as reduction agent which helps to dissolve Se in the mix solvent but also as a complexing agent, reaction and shape controller, molecular template and as the stabilizing agent.

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References

- [1] B. Gates, B. Mayers, B. Cattle, Y. Xia, *Adv. Func. Mater.*, **12**, 219 (2002).
- [2] C.J. Barrelet, Y. Wu, D.C. Bell, C.M. Lieber, *J. Am. Chem. Soc.*, **125**, 11498 (2003).
- [3] S. Kan, T. Mokari, E. Rothenberg, U. Banin, *Nature Mater.*, **2**, 155 (2003).
- [4] M.P. Zach, K.H. Nag, R.M. Penner, *Science*, **290**, 2120 (2000).
- [5] Z. Zhang, N.A. Kotov, M. Giersig, *Science*, **297**, 237 (2002).
- [6] S.M. Le, S.N. Cho, J. Cheon, *Adv. Mater.*, **15**, 441 (2003).
- [7] T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-Sayed, *Science*, **272**, 1924 (1996).
- [8] M. Monge, M.L. Kahn, A. Maisonnat, B. Chaudret *Angew. Chem. Int. Ed.*, **115**, 5749 (2003).
- [9] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature*, **404**, 59 (2000).
- [10] L. Manna, D.J. Milliron, A. Meisel, E.C. Scher, A.P. Alivisatos, *Nature Mater.*, **2**, 382 (2003).
- [11] J.F. Wang, M.S. Gudiksen, X.F. Duan, Y. Cui, C.M. Lieber, *Science*, **293**, 1455 (2001).
- [12] J. Hu, L. Li, W. Yang, L. Manna, L. Wang, A.P. Alivisatos, *Science*, **292**, 2060 (2001).
- [13] R.S. Friedman, M.C. McAlpine, D.S. Ricketts, D. Ham, C.M. Lieber, *Nature*, **434**, 1085 (2005).
- [14] W.C.W. Chan, S. Nie, *Science*, **281**, 2016 (1998).
- [15] M. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, *Science*, **281**, 2013 (1998).
- [16] A.P. Alivisatos, *J. Phys. Chem.*, **100**, 13226 (1996).
- [17] C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.*, **115**, 8706 (1993).
- [18] O.I. Micic, J. Sprague, Z. Lu, A.J. Nozik, *Appl. Phys. Lett.*, **68**, 3150 (1996).
- [19] N. Gaponik, D.V. Talapin, A.L. Rogach, K. Hoppe, E.V. Shevchenko, A. Kornowski, A. Eychmüller, H. Weller, *J. Phys. Chem.*, **106**, 7177 (2002).
- [20] B.L. Wehrenberg, C. Wang, P. Guyot-Sionnest, *J. Phys. Chem. B*, **106**, 10634 (2002).
- [21] H. Du, C. Chen, R. Krishnan, T.D. Krauss, J.M. Harbold, F.W. Wise, M.G. Thomas, J. Silcox, *Nano Lett.*, **2**, 1321 (2002).
- [22] A. Rogach, S. Kershaw, M. Burt, M. Harrison, A. Kornowski, A. Eychmüller, H. Weller, *Adv. Mater.*, **11**, 552 (1999).
- [23] Y.W. Cao, U. Banin, *J. Am. Chem. Soc.*, **122**, 9692 (2000).
- [24] L. Spanhel, M. Haase, H. Weller, A. Henglein, *J. Am. Chem. Soc.*, **109**, 5649 (1987).
- [25] T. Matasuoka, *Adv. Mater.*, **8**, 469 (1996).
- [26] J. Wang, D.C. Hutchings, A. Miller, E.W. Van Stryland, K.R. Welford, I.T. Muirhead, K.L. Lewis, *J. Appl. Phys.*, **73**, 4746 (1993).
- [27] S.K. Hong, E. Kurts, J.H. Chang, T. Hanada, M. Oku, T. Yao, *Appl. Phys. Lett.*, **78**, 165 (2001).
- [28] H. Jeon, J. Ding, W. Patterson, A.V. Nurmikko, W. Xie, D.C. Grillo, M. Kobayashi, R.L. Gunshor, *Appl. Phys. Lett.*, **59**, 3619 (1991).
- [29] Z.M. Zhu, N.Z. Liu, G.H. Li, H.X. Han, Z.P. Wang, S.Z. Wang, L. He, R.B. Ji, Y. Wu, *J. Infrared Millimeter Waves*, **18**, 13 (1999).
- [30] M.A. Hines, Guyot-Sionnest, *J. Phys. Chem.*, **100**, 468 (1996).
- [31] Y. Cao, U. Banin, *J. Am. Chem. Soc.*, **122**, 9692 (2000).
- [32] P. Reiss, J. Bleuse, A. Pron, *Nano Lett.*, **2**, 781 (2002).
- [33] R. Rujkorakarmn, A.J. Nelson, *J. Appl. Phys.*, **87**, 8557 (2000).
- [34] D.J. Norris, N. Yao, F.T. Charnock, T.A. Kennedy, *Nano Lett.*, **1**, 3 (2001).
- [35] M.A. Malik, P. O'Brien, N. Revaprasadu, *J. Mater. Chem.*, **11**, 2382 (2001).
- [36] T.J. Jr. Norman, D. Magana, T. Wilson, C. Burns, J.Z. Zhang, D. Cao, F. Bridges, *J. Phys. Chem. B*, **107**, 6309 (2003).
- [37] C.M. Lieber, *Nano Lett.*, **2**, 82 (2002).

- [38] M.S. Gudiksen, L.J. Lauhon, J.F. Wang, D.C. Smith, C.M. Lieber, *Nature*, **415**, 617 (2002).
- [39] Y. Wu, R. Fan, P. Yang, *Nano Lett.*, **2**, 83 (2002).
- [40] Y. Jiang, X.M. Meng, J. Liu, Z.R. Hong, C.S. Lee, S.T. Lee, *Adv. Mater.*, **15**, 1195 (2003).
- [41] M.A. Hines, P. Guyot-Sionnest, *J. Phys. Chem. B*, **102**, 3655 (1998).
- [42] M. Revaprasadu, M.A. Malik, P. O'Brien, M.M. Zulu, G. Wakefield, *J. Mater. Chem.*, **8**, 1885 (1998).
- [43] C.A. Smith, H.W.H. Lee, V.J. Leppert, S.H. Risbud, *Appl. Phys. Lett.*, **75**, 1688 (1999).
- [44] P.D. Cozzoli, L. Manna, M.L. Curri, S. Kudera, C. Giannini, M. Striccoli, A. Agostiano, *Chem. Mater.*, **17**, 1296 (2005).
- [45] Y.C. Zhu, Y. Bando, *Chem. Phys. Lett.*, **377**, 367 (2003).
- [46] Y. Dong, Q. Peng, Y. Li, *Inorg. Chem. Commun.*, **7**, 370 (2004).
- [47] Y. Jiang, X.M. Meng, W.C. Yiu, J. Liu, J.X. Ding, C.S. Lee, S.T. Lee, *J. Phys. Chem. B*, **108**, 2784 (2004).
- [48] R. Solanki, J. Huo, J.L. Freeouf, B. Miner, *Appl. Phys. Lett.*, **81**, 3864 (2002).
- [49] X.F. Duan, C.M. Lieber, *Adv. Mater.*, **12**, 298 (2000).
- [50] W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie, Y. Qian, *Inorg. Chem. Commun.*, **2**, 83 (1999).
- [51] A. Govindaraj, F.L. Deepak, N.A. Gunari, C.N.R. Rao, *Isr. J. Chem.*, **41**, 23 (2001).
- [52] Z.H. Ma, W.D. Sun, I.K. Sou, G.K.L. Wong, *Appl. Phys. Lett.*, **73**, 1340 (1998).
- [53] D. Sarigiannis, J.D. Peck, G. Kioseoglou, A. Petrou, T.J. Mountziaris, *Appl. Phys. Lett.*, **80**, 4024 (2002).
- [54] T. Tawara, S. Tanaka, H. Kumano, I. Suemune, *Appl. Phys. Lett.*, **75**, 235 (1999).
- [55] H. Rho, H.E. Jackson, S. Lee, M. Dobrowolska, J.K. Furdyna, *Phys. Rev. B*, **61**, 15641 (2000).
- [56] Y.F. Chan, X.F. Duan, S.K. Chan, I.K. Sou, X.X. Zhang, N. Wang, *Appl. Phys. Lett.*, **83**, 2665 (2003).
- [57] B. Xiang, H.Z. Zhang, G.H. Li, F.H. Yang, F.H. Su, R.M. Wang, J. Xu, G.W. Lu, X.C. Sun, Q. Zhao, D.P. Yu, *Appl. Phys. Lett.*, **82**, 3330 (2003).
- [58] X.T. Zhang, Z. Liu, Y.P. Leung, Q. Li, S.K. Hark, *Appl. Phys. Lett.*, **83**, 5533 (2003).
- [59] X.T. Zhang, K.M. Ip, Z. Liu, Y.P. Leung, Q. Li, S.K. Hark, *Appl. Phys. Lett.*, **84**, 2641 (2004).
- [60] J. Zhu, Y. Koltypin, A. Gedanken, *Chem. Mater.*, **12**, 73 (2000).
- [61] F.T. Quinlan, J. Kuther, W. Tremel, W. Knoll, S. Risbud, P. Stroeve, *Langmuir*, **16**, 4049 (2000).
- [62] R.T. Lv, C.B. Cao, H.Z. Zhai, D.Z. Wang, S.Y. Liu, H.S. Zhu, *Solid State Commun.*, **130**, 241 (2004).
- [63] Y.D. Li, Y. Ding, Y.T. Qian, Y. Zhang, L. Yang, *Inorg. Chem.*, **37**, 2844 (1998).
- [64] Y.J. Dong, Q. Peng, Y.D. Li, *Inorg. Chem. Commun.*, **7**, 370 (2004).
- [65] Q. Peng, Y.J. Dong, Z.X. Deng, Y.D. Li, *Inorg. Chem.*, **41**, 5249 (2002).
- [66] J.H. Zhan, X.G. Yang, W.X. Zhang, D.W. Wang, Y. Xie, Y.T. Qian, *J. Mater. Res.*, **15**, 629 (2000).

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