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ARTICLE

Green Synthesis of High Quality CdSe Quantum Dots: High Luminescence in Green to Red Region

Anil K. Malik✉

Author affiliations:

Department of Physics, Mulatnimalmodi College, Modinagar-201 204, India

✉To whom correspondence to be addressed:

E-mail: anilmalikiitd@gmail.com

ABSTRACT

Cadmium precursors *viz.* cadmium(II) acetate and acetylacetonate, less toxic than Me_2Cd give in one-step synthesis procedure comparable CdSe quantum dots (QDs) which show photoluminescence over a wide frequency range from green to red region of electromagnetic spectrum. The FWHM values of sharp photoluminescence spectra of quantum dots prepared from cadmium(II) acetylacetonate and cadmium(II) acetate are 23 ± 2 nm and 14 ± 2 nm, respectively, indicating that absorption occurs in a very narrow range of wavelengths. The band gaps of CdSe quantum dots prepared using cadmium(II) acetylacetonate and cadmium(II) acetate precursors are 2.08 and 2.13 eV, respectively. Powder X-ray diffraction shows hexagonal structure of quantum dots. TEM and HRTEM images of quantum dots revealed that they are almost mono disperse and of size ≤ 4 nm. The precursor and reaction time affect size, absorption and photoluminescence properties of the quantum dots. The temporal growth was monitored by UV-visible spectroscopy (up to 20 min). The size of quantum dots increases with reaction time and photoluminescence peak shifts to higher wavelength with increasing reaction time.

KEYWORDS

Photoluminescence, CdSe quantum dots, Cadmium acetylacetonate, Cadmium acetate.

INTRODUCTION

Monodispersed II-VI group semiconducting nanoparticles have attracted much attention of researchers due to their potential applications as non-linear optical materials [1], in devices for biomedical imaging [2] and as photovoltaics [3]. The band gap of these semiconducting nanoparticles depends on their size and shape. Therefore by controlling them, nanoparticles that can absorb and emit light in the desired frequency range of electromagnetic spectrum can be designed. Thus tailoring of such properties in nanoparticles continues as a current interest. Chemical routes for this purpose are widely used, as size, shape and morphology of nanoparticles can be easily controlled by changing conditions of synthesis and reagents. Such a control is difficult in physical methods like epitaxial growth and sputtering. Apart from an advantage of both size and shape [4-8] control over physical methods, the production of nanoparticles in large quantities is an additional

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advantage of chemical methods. In chemical method, the size of nanoparticles formed is dependent on the nucleation step (key parameter), which can be separated from their growth by adding a hot surfactant solution, which leads to a narrow distribution of size of nanoparticles. The final shape of the nanoparticles is, moreover, determined by the crystalline structure of the particles during nucleation, provided no structural phase transitions occur during growth. The nanoparticles of CdSe exist in two crystalline structures: Wurtzite (W, hexagonal) and zinc blende (ZB, cubic) [9]. The reaction conditions and precursors of cadmium used for their synthesis of control the structure. The mild one gives zinc blende and harsh one W structure.

Cadmium selenide nanoparticles, produced by chemical methods, are most popular among cadmium chalcogenides nanoparticles [10] due to their unique optical and electrical properties. There are many studies which have reported chemical synthesis of CdSe nanoparticles [4,11-13]. Some of these reports are on preparation of such CdSe nanoparticles, which give photoluminescence in the green to orange region of the solar spectrum. Photoluminescence in violet-green region of visible spectrum by CdSe quantum dots has also been reported by Shukla and Nigra [14] Some investigations on CdSe nanoparticles coated with shells of ZnSe or ZnS [15-19] have also been reported. They show photoluminescence in the blue region of the solar spectrum. We have observed that quantum dots of CdSe showing sharp photoluminescence (very low FWHM) in a wide range of frequency from green to red and having size in narrow range can be synthesized from cadmium(II) acetate and cadmium(II) acetylacetonate by a one pot synthesis. The improvement in the photoluminescence properties (emission wavelength range and FWHM) and dispersity is considerable. The temporal evolution of CdSe quantum dots using two different cadmium precursors and its effect on size and photoluminescence properties have been studied. The addition of octadecylamine narrows the size distribution of CdSe quantum dots during their growth which probably results improvement in their photoluminescence properties [20,21].

EXPERIMENTAL

The reagent grade cadmium(II) acetate hydrate (99.99 %), cadmium(II) acetylacetonate (99.99 %), selenium (99.5 %, 100 mesh), trioctyl phosphine oxide (TOPO), trioctyl phosphine (TOP), 1-octadecene (ODE), oleic acid (OA), octadecylamine (ODA) were procured from Aldrich (USA) and used as received. All organic solvents (HPLC grade) were obtained from Merck (India). Other chemicals were procured locally.

The synthesis of CdSe quantum dots was conducted in a moisture and oxygen-free atmosphere. CdSe quantum dots were synthesized using a one-step process involving reduction of cadmium(II) acetylacetonate or acetate. A 0.1 mmol of Se was dissolved in 1 mL of tri-*n*-octylphosphine (TOP) and kept in a syringe as TOPSe. A 0.1 mmol of cadmium precursor (cadmium(II) acetylacetonate or cadmium(II) acetate) and 0.4 mmol of oleic acid were added to 4 mL of 1-octadecene and heated to 240 °C with continuous stirring under an N_2 atmosphere until a colourless solution was obtained. The temperature was lowered to room temperature and 1.5 g of octadecylamine and 1.5 g of tri-*n*-octylphosphine were added to the mixture, which was further heated to 300 °C under N_2 atmosphere with continuous stirring. After attaining a constant temperature, TOPSe solution was injected swiftly in the reaction mixture. The temperature fell down to 270 °C and the reaction mixture was allowed to reflux. Aliquots of the reaction mixture were withdrawn at various intervals. They were diluted with hexane and subjected to photoluminescence and UV absorption spectral studies to understand the formation and size of the quantum dots. The reaction mixture was cooled down and washed thrice with a 1:1 mixture of hexane and methanol, allowing separation of the quantum dots in hexane and the unreacted precursors. Finally, the quantum dots were precipitated by adding ethanol to the hexane layer, separated by centrifugation and redissolved in hexane.

UV-visible spectra (200-800) were recorded at room temperature with a Lambda Bio 20 (Perkin Elmer) UV-visible spectrophotometer. The photoluminescence spectra were taken on a Horiba Scientific, Fluoromax-4 spectrofluorometer fitted with a PMT emission detector with 5 nm excitation and emission slits. The excitation wavelength was kept at 400 nm for all of the measurements reported here. The same sample was used for absorption and photoluminescence measurements and the concentration was kept low so as to get an absorbance below 0.1. The scan range chosen for each sample was 200-800 nm using a 0.5 s integration time. The diluted solution was placed in a quartz fluorescence cell with 10 mm path length. The powder XRD measurements were made on a Bruker D8 advanced powder X-ray diffractometer with 2θ range 10 to 70° with the step size of 0.05° and step time 1 s. A Cu radiation source was used along with a polycapillary lens and a Ni filter to provide the incident beam. The power settings on the X-ray generator were 45 kV and 40 mA. The samples of CdSe used for the powder XRD measurements were prepared by placing a colloidal solution of CdSe quantum dots on a glass slide and the solvent was removed by drying in a vacuum oven at 30 °C for several hours. TEM images were recorded on a Philips instrument model CM-12 operated at an accelerating voltage of 100 kV and high resolution TEM on an instrument model FEI Technai G220 with accelerating voltage of 200 kV. Samples were prepared on 200-mesh carbon coated Cu grids by dropping 10 μL of solutions the quantum dots in hexane and allowing the solvent to evaporate.

RESULTS AND DISCUSSION

The quality of CdSe quantum dots synthesized by present procedure in a non-coordinating solvent [22] octadecene, was found good with nearly monodisperse size and shape. The temporal study was undertaken to investigate the crystal growth of CdSe quantum dots. For these studies (i) the ratio of cadmium precursor cadmium(II) acetylacetonate or cadmium(II) acetate to selenium, (ii) the moles of (trioctyl phosphine oxide) and octadecylamine and (iii) the temperature of the reaction mixture over a 20 min time period were kept constant. From reaction mixture aliquots were taken and quenched in hexane at time intervals of 1, 3, 5, 10, 15 and 20 min from the start. The progress of CdSe crystal growth in each aliquot was monitored by taking their UV-visible and photoluminescence spectra. The results are shown in Figs. 1 and 2. The changes observed in quantum dots were insignificant when reaction time was greater than 20 min. The sizes were calculated from UV-visible spectra [23] and were found in the range 4.32 and 3.88 nm respectively when cadmium(II) acetylacetonate and cadmium(II) acetate were used. It is worth noting that the quantum dots obtained from two precursors under identical reaction conditions differ only marginally in size.The photoluminescence spectra reveal that the value of full width at half maximum (FWHM) of the photoluminescence peaks of quantum dots obtained after 20 min from cadmium(II) acetylacetonate is 23 ± 2 nm and is significantly higher than that of quantum dots (14 ± 2 nm) obtained from cadmium(II) acetate. Our values are lower than those, reported earlier [14] (about 30 nm) for CdSe quantum dots obtained from cadmium(II) acetylacetonate precursor. The sharpness of photoluminescence peaks is more for quantum dots obtained from cadmium(II) acetate. Thus photoluminescence properties of quantum dots prepared by present procedure are superior to those reported earlier [14]. A red shift (colour changed from green to wine red) in photoluminescence peaks of quantum dots with increasing reaction time of their synthesis, was observed for both the cadmium precursors indicating the dependence of their size on reaction time. In Figs. 1 and 2, photoluminescence spectra recorded for varying reaction time are exhibited. A systematic increase in peak wavelength from 579 to 601 nm in case of cadmium(II) acetyl-acetonate precursor was observed while in case of cadmium(II) acetate, the change in wavelength was not systematic and varied over a very narrow range (from 570 to 573.5 nm) for a similar period of reaction. The small value of red shift indicates that growth process in case of cadmium(II) acetate is much faster than the one in case of cadmium(II) acetylacetonate. The red shifts were also observed in case of absorption spectra with increase in reaction time. The band gaps of CdSe quantum dots obtained after 20 min reaction time using cadmium(II) acetylacetonate and cadmium(II) acetate precursors are 2.08 and 2.13 eV respectively. Figs. 1 and 2 also show that wavelength of maximum absorption in UV-visible spectra of quantum dots increases with reaction time.

The powder-XRD patterns obtained for quantum dots prepared from cadmium(II) acetylacetonate and cadmium(II) acetate are shown in Fig. 3. They suggest that CdSe quantum dots have wurtzite structure in both cases. The wurtzite structure is commonly formed in high temperature (≥ 270 °C) synthesis [24] of CdSe quantum dots carried in TOPO (containing amine). This is consistent with our results. The low or room temperature synthesis results in zinc blende structure which sometimes also has faults [25]. Peng and Reng [26] synthesized wurtzite structure

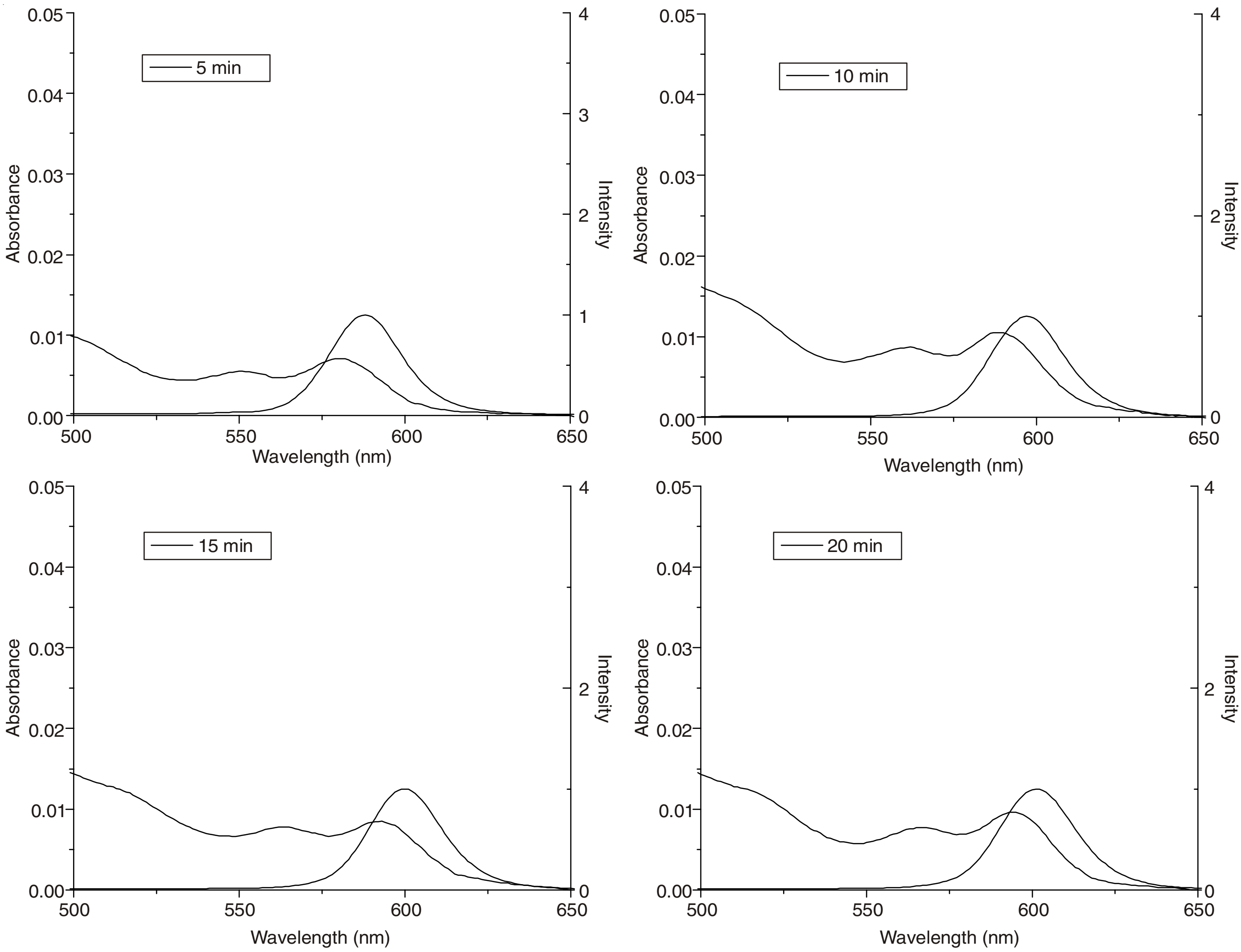

Fig. 1. UV-visible and photoluminescence spectra of CdSe quantum dots synthesized from cadmium(II) acetylacetonate

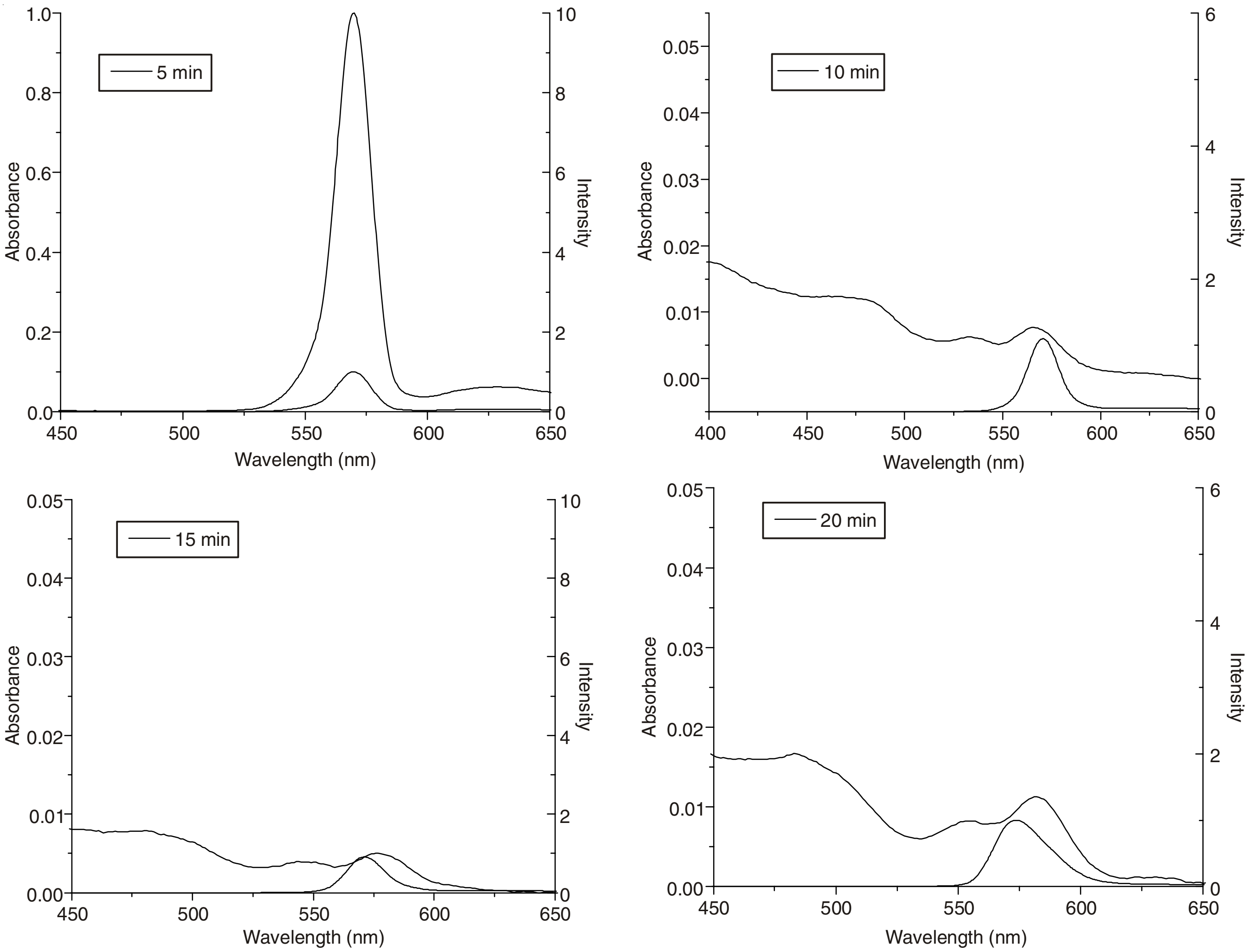

Fig. 2. UV-visible and photoluminescence spectra of CdSe quantum dots synthesized from cadmium(II) acetate

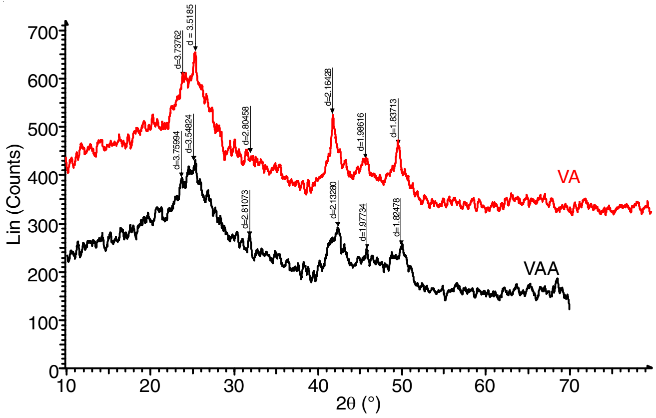

Fig. 3. X-Ray diffraction pattern of CdSe quantum dots obtained from cadmium acetylacetonate (VAA-bottom) and cadmium(II) acetate (VA-top) precursor respectively

(hexagonal) of CdSe in TOPO at 300 °C. However in some other solvents different results have been reported. Sasamoto *et al*. [27] reported that CdSe synthesized at 60 °C gave cubic particles and hexagonal at 80 °C when sodium sulphite was used as a stabilizing agent and sodium dicarboxylate as a complexing agent. Palchik *et al*. [28] observed formation of cubic CdSe at 287 °C when the solvent used was triethylene glycol and formation of hexagonal CdSe at 196 °C in ethylene glycol. The small size of presently prepared CdSe quantum dots is indicated by broad nature of X-ray diffraction peaks (Fig. 3). The average diameter of these quantum dots by Scherrer's formula [29] has been found to be 4.02 and 3.64 nm when particles were obtained from cadmium(II) acetylacetonate and acetate respectively.

The TEM and HRTEM images of the quantum dots are given in Fig. 4. The average diameter of quantum dots from TEM has also been found to be 4.12 and 3.89 nm for cadmium sources, cadmium(II) acetylacetonate and cadmium(II) acetate respectively. These results about size are consistent with those obtained from powder XRD and absorption spectra. The TEM images suggest that quantum dots are nearly spherical and monodisperse. The HRTEM images also reveal the high crystallinity of the quantum dots and their size of the order ≤ 4 nm.

Conclusion

The similar hexagonal CdSe quantum dots of good dispersity and small size of the order ≤ 4 nm have been prepared from two precursors cadmium(II) acetylacetonate and cadmium(II) acetate. Their photoluminescence properties are better than those reported earlier [18-23] in terms of narrow wavelength range as revealed by FWHM values (23 ± 2 and 14 ± 2 nm). The other advantages of the present route are: (i) the precursors, cadmium(II) acetylacetonate and cadmium(II) acetate used are

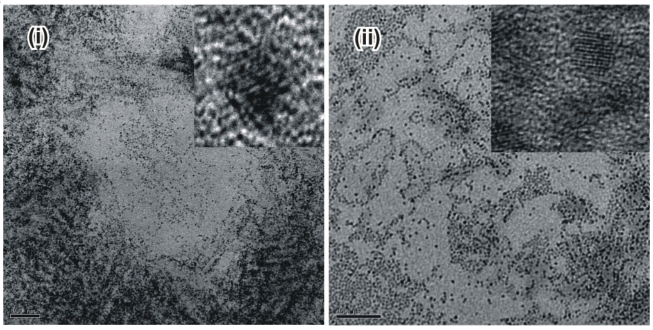

Fig. 4. TEM (100 nm scale) and HRTEM (at corner, 5 nm scale) images of CdSe nanoparticles synthesized from (i) cadmium acetylacetonate and (ii) cadmium acetate

less toxic, more stable and crystalline and (ii) solvents used are not expensive.

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REFERENCES

1. K.L. Moran, W.T.A. Harrison, I. Kamber, T.E. Gier, X.H. Bu, D. Herren, P. Behrens, H. Eckert and G.D. Stucky, *Chem. Mater.*, **8**, 1930 (1996); http://dx.doi.org/10.1021/cm960168c.
2. A.H. Fu, W.W. Gu, C. Larabell and A.P. Alivisatos, *Curr. Opin. Neurobiol.*, **15**, 568 (2005); http://dx.doi.org/10.1016/j.conb.2005.08.004.
3. Y. Liu, L. Wang and Y. Cao, *Front. Chem. China*, **2**, 383 (2007); http://dx.doi.org/10.1007/s11458-007-0072-x.
4. A.P. Alivisatos, X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher and A. Kadavanich, *Nature*, **404**, 59 (2000); http://dx.doi.org/10.1038/35003535.
5. X.G. Peng, *Adv. Mater.*, **15**, 459 (2003); http://dx.doi.org/10.1002/adma.200390107.
6. Y.W. Jun, Y.Y. Jung and J.J. Cheon, *J. Am. Chem. Soc.*, **124**, 615 (2002); http://dx.doi.org/10.1021/ja016887w.
7. E.C. Scher, L. Manna and A.P. Alivisatos, *Philos. Trans. R. Soc. London, Ser. A*, **361**, 241 (2003); http://dx.doi.org/10.1098/rsta.2002.1126.
8. L. Manna, E.C. Scher and A.P. Alivisatos, *J. Am. Chem. Soc.*, **122**, 12700 (2000); http://dx.doi.org/10.1021/ja003055+.
9. V.A. Fedorov, V.A. Ganshin and Y.N. Korkishko, *Phy. Status. Solidi. A*, **126**, K5 (1991); http://dx.doi.org/10.1002/pssa.2211260133.
10. C.B. Murray, D.J. Norris and M.G. Bawendi, *J. Am. Chem. Soc.*, **115**, 8706 (1993); http://dx.doi.org/10.1021/ja00072a025.
11. S.D. Bunge, K.M. Krueger, T.J. Boyle, M.A. Rodriguez, T.J. Headley and V.L. Colvin, *J. Mater. Chem.*, **13**, 1705 (2003); http://dx.doi.org/10.1039/b302294c.
12. J. Hambrock, A. Birkner and R.A. Fischer, *J. Mater. Chem.*, **11**, 3197 (2001); http://dx.doi.org/10.1039/b104231a.
13. X.C. Jiang, B. Mayers, T. Herricks and Y.N. Xia, *Adv. Mater.*, **15**, 1740 (2003); http://dx.doi.org/10.1002/adma.200305737.
14. N. Shukla and M.M. Nigra, *Luminescence*, **25**, 14 (2010); http://dx.doi.org/10.1002/bio.1134.
15. J.S. Steckel, J.P. Zimmer, S. Coe-Sullivan, N.E. Stott, V. Bulovic and M.G. Bawendi, *Angew. Chem. Int. Ed.*, **43**, 2154 (2004); http://dx.doi.org/10.1002/anie.200453728.
16. B.O. Dabbousi, J.R. Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, and M.G. Bawendi, *J. Phy. Chem. Br.*, **101**, 9463 (1997); http://dx.doi.org/10.1021/jp971091y.
17. P. Reiss, J. Bleuse and A. Pron, *Nano Lett.*, **2**, 781 (2002); http://dx.doi.org/10.1021/nl025596y.
18. D.C. Pan, Q. Wang, S.C. Jiang, X.L. Ji and L.J. An, *Adv. Mater.*, **17**, 176 (2005); http://dx.doi.org/10.1002/adma.200401425.
19. W.X. Zhang, C. Wang, L. Zhang, X.M. Zhang, X.M. Liu, K.B. Tang and Y.T. Qian, *J. Solid State Chem.*, **151**, 241 (2000); http://dx.doi.org/10.1006/jssc.2000.8646.
20. D. Tonti, F. van Mourik and M. Chergui, *Nano Lett.*, **4**, 2483 (2004); http://dx.doi.org/10.1021/nl0486057.
21. X. Chen, J.L. Hutchison, P.J. Dobson and G.J. Wakefield, *Mater. Sci.*, **44**, 285 (2009); http://dx.doi.org/10.1007/s10853-008-3055-6.
22. X.G. Peng, *Chem. Eur. J.*, **8**, 334 (2002); http://dx.doi.org/10.1002/1521-3765(20020118)8:2<334::AID-CHEM334>3.0.CO;2-T.
23. W.W. Yu, L. Qu, W. Guo and X.G. Peng, *Chem. Mater.*, **15**, 2854 (2003); http://dx.doi.org/10.1021/cm034081k.
24. L. Qu and X. Peng, *J. Am. Chem. Soc.*, **124**, 2049 (2002); http://dx.doi.org/10.1021/ja017002j.
25. J.-Y. Zhang, X.-Y. Wang, M. Xiao, L. Qu and X. Peng, *Appl. Phys. Lett.*, **81**, 2076 (2002); http://dx.doi.org/10.1063/1.1507613.
26. Z.A. Peng and X.G. Peng, *J. Am. Chem. Soc.*, **123**, 183 (2001); http://dx.doi.org/10.1021/ja003633m.
27. O. Yamamoto, T. Sasamoto and M. Inagaki, *J. Mater. Res.*, **13**, 3394 (1998); http://dx.doi.org/10.1557/JMR.1998.0462.
28. O. Palchik, R. Kerner, A. Gedanken, A.M. Weiss, M.A. Slifkin and V. Palchik, *J. Mater. Chem.*, **11**, 874 (2001); http://dx.doi.org/10.1039/b008088h.
29. A.L. Washington II and G.F. Strouse, *Chem. Mater.*, **21**, 3586 (2009); http://dx.doi.org/10.1021/cm900624z.