

Preparation and characterization of Core/shell CdSe/CdS QDs

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Abstract- In the present study we have focussed on preparation of core/shell CdSe/CdS quantum dots (QDs). CdSe and Core/shell CdSe/CdS QDs were prepared via colloidal synthesis in aqueous medium. CdSe and Core/shell CdSe/CdS QDs optical properties and size were characterized by ultraviolet-visible (UV-vis) absorption spectra, Photoluminescence spectra and DLS measurement. The result showed that the absorption spectra clearly indicate the absorption peak shift from 500 nm to 650 nm on increasing; the emission maximum of CdSe/CdS is at 598 nm and the particle size average diameter of the core/shell CdSe/CdS quantum dot is reported as 13.36nm.

Index Terms: Quantumdots, cadmium selenide, cadmium sulphide, ultraviolet-visible, Photoluminescence, dynamic light scattering

1 INTRODUCTION

High quality quantum dots have been prepared with advances in the modern colloid chemistry[1]. Because of the interest in size-tailored photoluminescence and strong resistance against photochemical reaction in solution, quantum dots have been widely used as bio-labels[2-3]. However, it is still an interest of researchers to boost the quantum yield (defined as the ratio of emission to absorption photons) and, thus, reduce the number of the quantum dots needed in the experiment. The atoms on the surface of a quantum dot act as defects since they are not fully bonded. Many of these defects are removed by being passivated with organic surfactants during certain synthesis process. Although up to 10% quantum yield (at room temperature) of these capped dots has been reported[4], it remains as a challenge to passivate both anionic and cationic sites on the surface with organic ligands. An alternative method to the use of organic molecules as surface passivation is to coat the surface with higher band gap inorganic semiconductor to form a core/shell structure. Not only are the dangling bonds of the core fixed by the shell, but the electron-hole pairs are more confined by the higher potential barriers as well.

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A variety of such core/shell nanostructure, CdSe/ZnS[5], CdSe/ZnSe[6], and CdSe/CdS[7] have been fabricated and improved photoluminescence quantum

yield (up to 85%) has been reported. Both ZnSe (2.72 eV) and CdS (2.42 eV) have higher band gap than that of CdSe (1.76 eV) and thus makes them good candidates as shell material. However, the larger lattice mismatch between ZnSe and CdSe (6.3%) makes CdS (3.9%) a better choice to be the capping agent around the CdSe quantum dots. In this chapter, a description of the results obtained when CdSe/CdS core/shell QDs were synthesized. A thin layer of CdS crystal was grown on CdSe quantum dots, the latter were synthesized according to the description, to form CdSe/CdS core/shell quantum dots. Both UV-Vis absorption and photoluminescence spectra of the CdSe/CdS solution were measured to characterize the core/shell system

2. EXPERIMENTAL SECTION

2.1. MATERIALS USED

The materials used were of the purest quality commercially available and used as received. Cadmium oxide (99.998%) and Sulphur was purchased from Nice chemicals, Trioctylphosphine (90%), Trioctylphosphine oxide (90%), Octadecene and selenium powder (Se, 99.99%) were bought from Aldrich Chem. Co., and oleic acid was purchased from Aldrich Chemical Company.

2.2. PREPARATION OF COLLOIDAL CdSe QUANTUM DOTS

CdSe nanocrystals are synthesized from CdO and elemental Se using a kinetic growth method[8-12] where particle size depends on reaction time. A stock solution of Se precursor may be prepared ahead of time by combining 30 mg of Se and 5 ml of 1-octadecene (tech., 90%) in a 10-mL round-bottom flask clamped over a stirrer hot plate. A syringe is used to measure 0.4 mL of trioctylphosphine from its Sure-Seal bottle to the same 10- ml flask. A magnetic stir bar is added and the solution is stirred for 30 min. It is heated at 60 deg C to speed the dissolution of Se. The stock solution is stored at room temperature in a sealed container and has enough Se precursors for the preparations.

The Cd precursor is prepared by adding 65 mg of CdO to a 250-mL round-bottom flask clamped in a heating mantle. To the same flask 3 ml of oleic acid and 50 ml of octadecene are added. A thermometer capable of measuring 2250C is inserted, the temperature to which the flask is then heated. When the temperature reaches 2250C, 5 mL of the room-temperature selenium solution is transferred to the 2250C cadmium solution. Because the characteristics of the products depend on reaction time, one should begin timing when the selenium solution is added. A 9-inch Pasteur pipet is used to remove and quench approximately 2 ml samples at frequent time intervals (0mins, 2mins, 4mins and 6mins) as quickly as possible in the beginning and when noticeable color change is detected at later times. The set of CdSe quantum dots are shown in Fig. The samples were pipetted out within six minutes and also we can see four different colors which indicate that different sizes of CdSe quantum dots.



Fig2.2: Colloidal suspension of CdSe quantum dots of increasing size

2.3. SYNTHESIS OF COLLOIDAL CORE/SHELL CdSe/CdS QUANTUM DOTS

Highly fluorescent CdSe/CdS QDs were synthesized using following procedures with slight modifications and solvent change[12-17]. In a Schlenk flask, mixture of 0.2mmol of CdO and 0.8mmol of stearic acid were heated to 150 °C until they become a colorless solution. After the solution was cooled to room temperature, ODE (1.5 g) and TOPO (0.5 g) were added to the solution. This solution was then reheated to 200 °C under nitrogen protection. Subsequently, a selenium solution (made by dissolving 0.2mmol of Se in 2.0 g of TOP) was injected quickly. The reaction is continued until yellow green fluorescence can be observed under an UV lamp. To grow the shell structure, we first mixed 0.42 mol of sulfur, 1.0 g TOP and 1.0 g TOPO together and heated the mixture to 150 °C to get a clear solution (solution 1). Next, 0.2mmol of Se and 2.0 g of TOP

were mixed together and heated to 150 °C to get another clear solution (solution 2). Solutions 1 and 2 were injected into the reaction mixture mentioned above, and the growth of CdSe/CdS QDs was monitored continuously by checking the fluorescence of the solution. The heater was removed when the solution appears brownish color. The unit of concentration reported here is optical density of a solution at 570nm (OD570), which was determined by using a UV-vis spectrometer and checked its photoluminescence by PL-Spectroscopy.

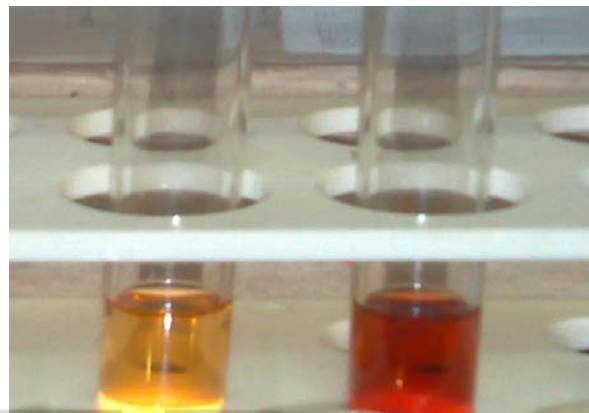


Fig2.3: Colloidal suspension of CdSe/CdS Core/Shell quantum dots (diluted & non-diluted)

3. RESULT AND DISCUSSION

A major challenge in nanocrystal synthesis is the production of monodisperse particles. Monodisperse means the particles exhibit a relatively narrow size distribution, resulting in narrow absorbance and emission peaks. The growth of CdSe quantum dots and CdSe/CdS core/shell quantum dots could be identified by the color change in the UV-Vis spectra. DLS measurement also gives the size distribution and the average size of the prepared sample. The results obtained from the various measurements are discussed below. Prepared nanofibers were characterized by using Scanning Electron Microscope technique.

3.1. OPTICAL ABSORPTION

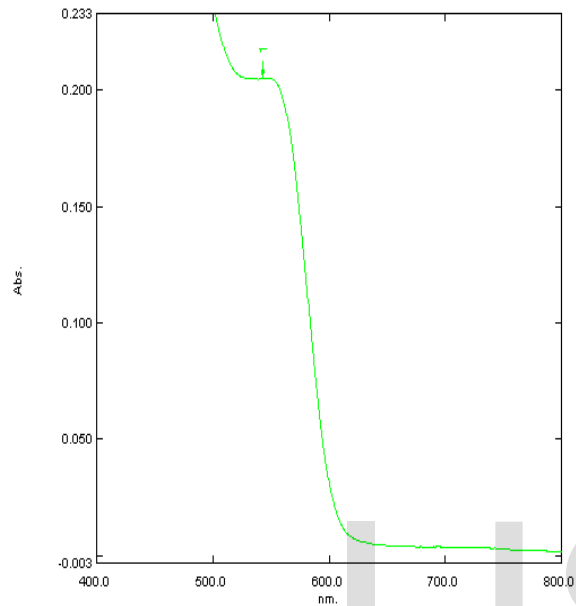
3.1.1. UV SPECTRUM FOR CdSE QUANTUM DOTS

The optical absorption wavelength was measured by using UV spectrometer and spectrum was taken for CdSe samples. The absorbance spectra of samples pipetted at different reaction times of 2mins and 6mins after injection of Se precursor is given in fig . The absorption spectrum shows striking excitonic features around 520 nm to 590 nm in the visible range. The absorption spectra clearly indicates that the absorption peak shift from 520 nm to 590 nm on increasing the particle size. It should be noted that such pronounced absorption spectrum predicts good

crystallinity in the sample and also confirms that the material is a semiconductor.

LIGHT BROWNISH (2MINS):

Size -**543.1nm** & absorption -**0.210**



BROWNISH (6MINS):

Size -**577nm** & absorption -**0.137**

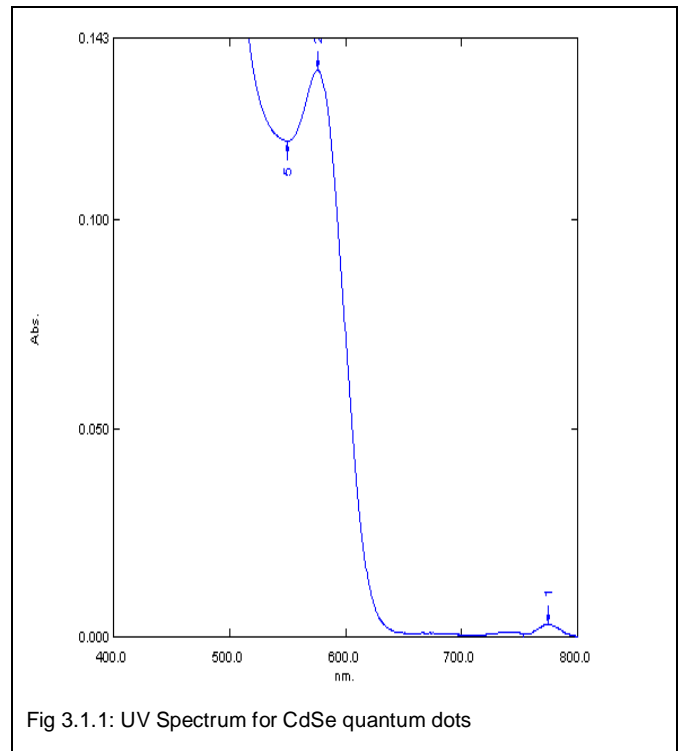
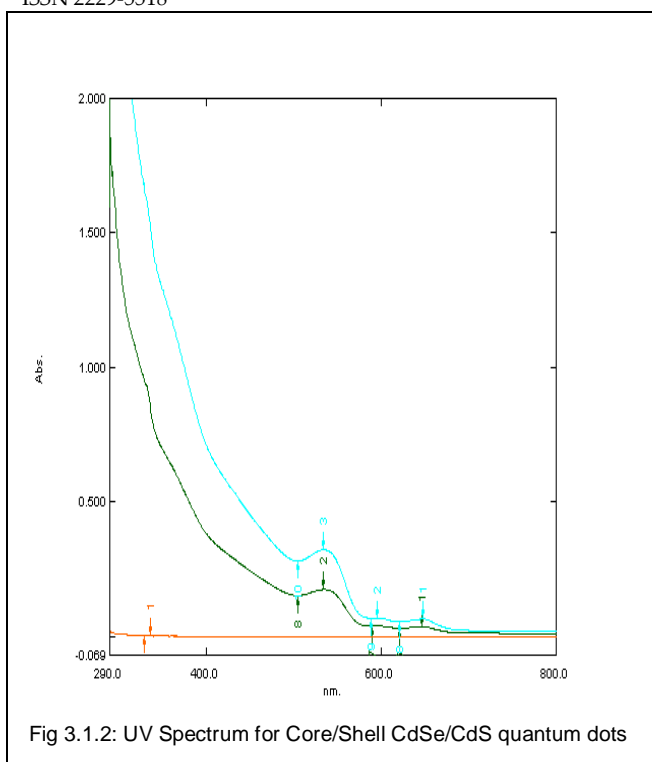


Fig 3.1.1: UV Spectrum for CdSe quantum dots

3.1.2. UV SPECTRUM FOR CORE/SHELL CdSe/CdS QUANTUM DOTS

The optical absorption wavelength was measured by using UV spectrometer and spectrum was taken for Core/Shell CdSe/CdS sample. The absorbance spectra of sample is given in fig3.1.2. The absorption spectrum shows the striking excitonic features around 500 nm to 650 nm in the visible. The absorption spectra clearly indicate the absorption peak shift from 500 nm to 650 nm on increasing the particle size. The observed absorption spectrum predicts good crystallinity in the sample and also confirms the material is a semiconductor.

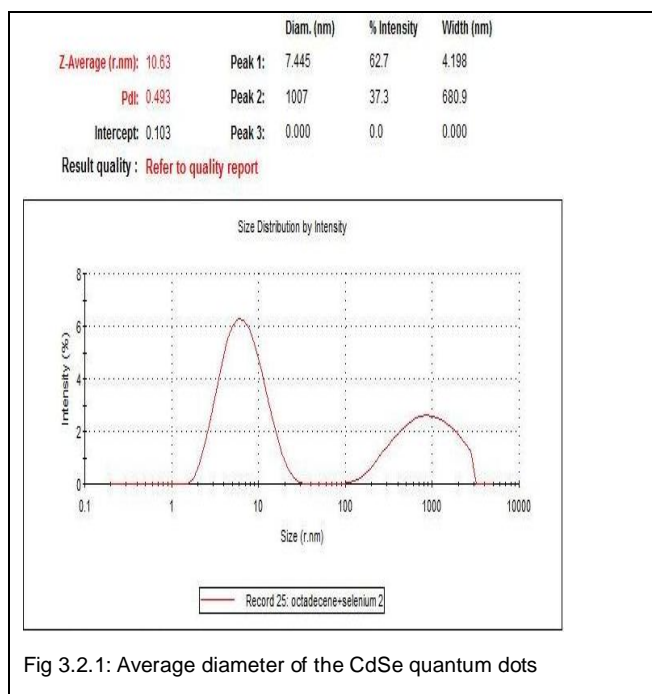


3.2. DLS(DYNAMIC LIGHT SCATTERING) MEASUREMENT

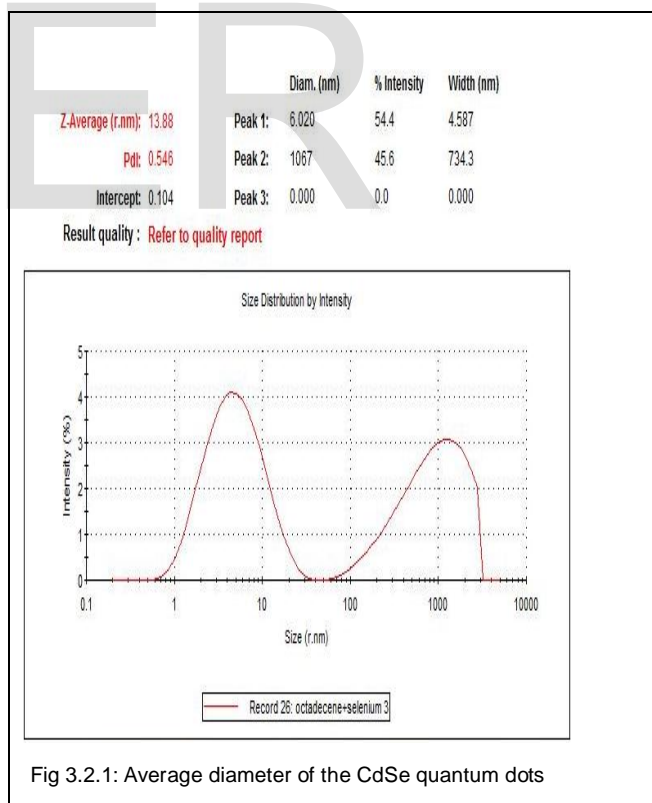
3.2.1. PARTICLE SIZE FOR CdSe QUANTUM DOTS

Dynamic Laser Light Scattering experiments were carried out for measuring the Size of the prepared CdSe quantum dots. The average Size Distribution Report of the CdSe quantum dots samples dispersed in an organic solvent-octadecene and pipetted at different reaction times of 2mins and 6mins after injection of Se precursor is shown in the below Fig4.2.1. The average diameters of the CdSe quantum dots are reported as 10.63nm for light brownish color(2mis) and 13.88nm for brownish color sample (6mins).

LIGHT BROWNISH (2MINS):



BROWNISH (6MINS):



3.2.2. PARTICLE SIZE FOR CORE/SHELL CdSe/CdS QUANTUM DOTS

Dynamic Laser Light Scattering experiments were carried out for measuring the Size of the prepared Core /Shell

CdSe/CdS quantum dots. The average Size Distribution Report of Core/Shell CdSe/CdS quantum dots prepared in an organic solvent-octadecene is shown in the below Fig 3.2.2. The average diameter of the core/shell CdSe/CdS quantum dot is reported as 13.36nm.

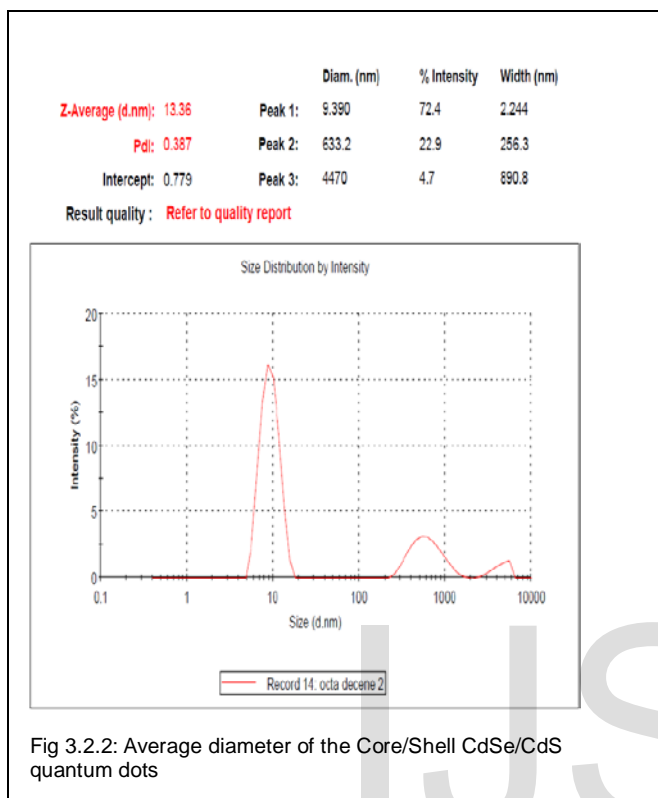
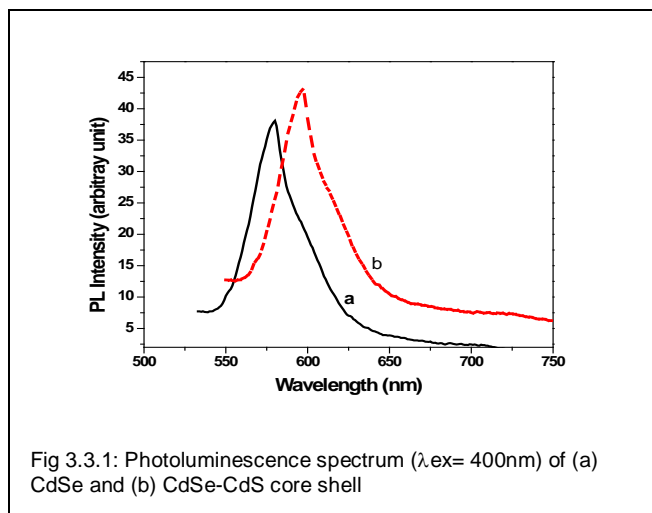


Fig 3.2.2: Average diameter of the Core/Shell CdSe/CdS quantum dots

3.3. PHOTOLUMINESCENCE

3.3.1. PL SPECTRUM FOR CdSe QD'S & CORE/SHELL CdSe/CdS QD'S

The photoluminescence spectra ($\lambda_{ex}=400$ nm) of CdSe/CdS shows emission close to the absorption band edge. The emission maximum of CdSe/CdS is at 598 nm. The emission maxima of the core/shell materials shows red shifts in relation to the emission maximum of CdSe is at 550nm, consistent with the red shifts visible in the absorption spectra. More importantly, the intensity of the emission maximum, which is normalized to the absorption spectrum, is considerably increased in the core/shell structure as compared to the parent materials (CdSe).



4. CONCLUSIONS

CdSe/CdS, core/shell structure has been synthesized from Cadmium oxide, Sulphur, Trioctylphosphine, Trioctylphosphineoxide, Octadecene, stearic acid and selenium powder precursors and their optical properties discussed. The absorption and emission spectra of core/shell structures show red shifts as compared to the parent materials which indicate the formation of core/shell structures. More importantly, the intensity of the emission maximum, which is normalized to the absorption spectrum, is considerably increased in the core/shell structure as compared to the parent materials. Particle Size Analyzer value shows prepared quantum dots are 10nm to 14nm.

REFERENCE

- [1] Murray, C. B., C. R. Kagan, et al. (2000). UAnnu. Rev. Mater. Sci.U 30: 545.
- [2] Bruchez, M. P., M. Moronne, et al. (1998). UScienceU 281: 2013.
- [3] Chan, W. C. W. and S. Nie (1998). "Quantum Dot Bioconjugates for Ultrasensitive Nonisotopic Detection." UScienceU 281: 2016.
- [4] Michalet, X., F. F. Pinaud, et al. (2005). "Quantum dots for live cells, in vivo imaging and diagnostics." UScienceU 307: 583
- [5] Dabbousi, B. O., J. Rodriguez-Viejo, et al. (1997). "(CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites." UJ Phys Chem BU 101: 9463.
- [6] Reiss P., J. Bleuse, et al. (2002). "Highly Luminescent CdSe/ZnSe Core/Shell Nanocrystals of Low Size Dispersion." UNano Lett.U 2: 781-784.
- [7] Peng, X., M. C. Schlamp, et al. (1997). "Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility." 119: 7019.
- [8] Guo W., Li JJ., Wang YA., Peng X., Conjugation chemistry and bioapplications of semiconductor box nanocrystals

- prepared vis dendrimer bridging, Chem. Mater. 15 (2003) 3125–3133.
- [9] Elizabeth M, Boatman and George C.Lisensky (2005) 'A safer, Easier, Faster Synthesis for CdSe quantum dot Nanocrystals' journal of chemical education vol.82 pp.1697.
- [10] Jeaho park, Kwan Hyi Lee, Justin F.Galloway, and Peter C.Searson (2008) 'Synthesis of Cadmium selenide Quantum Dots from non-coordinating solvent: Growth Kinetics and particle size distribution' J.phys.chem. Vol.112 pp.17849-17854.
- [11] Seoudi R, Elokr M.M., Shabaka A.A., Sobhi.A. (2008) 'Synthesis, characterization and electrical properties studies of Cadmium Selenide nanoparticle' Physica B., Vol. 403 Pp.152-158.
- [12] Yang Z., Cingarapu S., Klabunde K.J., (2009) 'An unusual fluorescence evolution of cadmium selenide (CdSe) nanoparticles generated from a cadmium oxide/trioctylphosphine selenide/trioctylphosphine heterogeneous system', Chemical Physics Letters.
- [13] Peng X., Schlamp MC., Kadavanich AV., Alivisatos AP., Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility, J. Am. Chem. Soc. 119 (1997) 7019–7029.
- [14] Li J., Wang YA., Guo WZ., Keay JC., Mishima TD., Johnson MB., Peng X., Largescale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction, J. Am. Chem. Soc. 125 (2003) 12567–12575.
- [15] Qu L., Peng X., Control of photoluminescence properties of CdSe nanocrystals in growth, J. Am. Chem. Soc. 124 (2002) 2049–2055.
- [16] Malik MA., Brien PO., Revaprasadu N., A Simple route to the synthesis of core/shell.

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