Synthesis of cadmium selenide colloidal quantum dots in aquatic medium

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Abstract. Cadmium selenide nanocrystals were prepared in water phase through facile wet chemistry technique with thioglycolic acid (TGA) acting as capping agent. Structures were characterized using X-ray diffraction (XRD), UV-vis absorption and photoluminescence spectroscopies. Depending on synthesis conditions nanoparticles exhibit photoluminescence with maximum in the region of 580 – 680 nm. Influence of technological parameters and component concentrations on nanocrystals average size and properties was studied.

1. Introduction
Semiconductor quantum dots (QDs) have recently attracted much attention because of their application prospects in the variety of optoelectronic devices such as light-emitting diodes, photodetectors, solar cells and lasers. By virtue of technological procedure facility QDs are suitable material for flexible electronics, particularly for conductive polymers based structures. Another area where QDs may be widely used is biological and medical detecting [1,2]. In comparison with organic fluorophores semiconductor nanocrystals are much more stable to photodegradation. Absorption band wideness and variety of available emission colors make it possible to excite plurality of QDs with different sizes by means of the same radiation source, thus allowing detecting signals from different targets simultaneously. Cadmium selenide nanocrystals exhibit strong quantum confinement and by regulating their size one can obtain emission in almost entire visible range.

The hot-injection method proposed in early nineties [3] had instigated activity in the field of metal chalcogenide nanoparticles synthesis. It allowed to obtain highly luminescent crystals with good monodispersity but has certain disadvantages connected with expensive and hazardous pyrophoric reactives being used. Plenty of adaptations of original technology have been developed since then [4,5]. One of the natural choices of medium for QDs preparation might be polar solvents, for example water. Despite poorer crystallinity and therefore generally inferior optical properties as compared to nanoparticles synthesized in non-polar media these methods are considered to be more environmentally benign and provide nanocrystals compatibility with biological tissues eliminating necessity for ligand exchange operations. Suitable precursors in this case may include water-soluble metal and chalcogenide salts as sources of metal and chalcogenide ions respectively while thiols might be used for surface passivation.

2. Materials and methods
Commercially purchased NaBH₄, CdCl₂·2.5H₂O, elemental Se (powder), thioglycolic acid (TGA, 80%), KOH (6M), propanol-2 (anhydrous) were used without any further purification. Distilled water was used as synthesis medium.

Absorption spectra were acquired on a PE-5400UV UV-vis spectrophotometer (LLC “Ekohim”). Photoluminescence measurements were carried out on equipment based on fast scanning spectrometer Ocean Optics USB-4000 using laser excitation on λ = 445 nm. XRD analysis was performed with diffractometer DRN “Farad” using CuKα radiation.
Average size of nanocrystals might be estimated via polynomial expression from the work [6]:

\[
a = \left(1.6122 \times 10^{-9}\right) \lambda^4 - \left(2.6575 \times 10^{-6}\right) \lambda^3 + \left(1.6242 \times 10^{-3}\right) \lambda^2 - 0.4277 \lambda + 41.57, \tag{1}
\]

where \(a\) is average size of particles, \(\lambda\) is a wavelength of the first excitonic peak. This equation was derived from various experimental data acquired through TEM studies and supposedly gives more reliable values for relatively small particles than effective mass approximation model.

3. Experiment and results

Typical synthesis procedure was adapted from reference [7] with several modifications and included following steps. Sodium hydroselenide solution was prepared by dissolving NaBH\(_4\) and Se powder in distilled water in a glass vial. It resulted in vigorous reaction accompanied with intensive hydrogen gassing. The reaction might be described as follows:

\[
4\text{NaBH}_4 + 2\text{Se} + 7\text{H}_2\text{O} \rightarrow 2\text{NaHSe} + \text{Na}_2\text{B}_4\text{O}_7 + 14\text{H}_2
\]

To obtain cadmium precursor solution cadmium chloride hydrate was dissolved in distilled water and certain amount of TGA was added so that the mixture became turbid. By dropwise addition of KOH (6M) acidity of the solution was brought up to approximate value \(\text{pH} = 11\) and it cleared. It is suggested that moderately alkaline environment facilitates formation of \(\text{Cd}^{2+}\)-TGA complexes which act as immediate reactant [8].

In one implementation component molar ratio was adjusted to \([\text{Cd}^{2+}] : [\text{Se}^{2-}] : [\text{TGA}] = 1:0.5:2.4\). Selenium precursor solution was swiftly injected in solution containing cadmium ions under vigorous stirring at room temperature, followed by rapid heating. The first aliquot was withdrawn from the reaction volume immediately. The rest of samples were taken at 35 °C, 50 °C and 70 °C respectively. Absorption and photoluminescence spectra of this series are represented in the figures 1 and 2.

As might be seen from the figure 1 absorption onset shifts towards long wavelengths in the course of the reaction which points at nanocrystals growth. At the same time the first excitonic peak becomes lower and less distinct. Supposedly it indicates that the particle monodispersity somewhat worsens. Photoluminescence spectra almost don’t change their position and feature broad peaks with large Stokes shift. It probably means that radiative recombination occurs via trap states on the surface of nanocrystals due to insufficient surface passivation.
In another implementation molar ratio $[\text{Cd}^{2+}] : [\text{Se}^{2-}] : [\text{TGA}] = 1:0.25:1.2$ was used. Precursor solutions were prepared as described above and NaHSe solution was injected at 45 °C. Temperature was raised gradually throughout experiment and aliquots were taken from the reaction flask in the following order: 2-1 – 0.5 min (50 °C), 2-2 – 6 min (51 °C), 2-3 – 22 min (58 °C), 2-4 – 60 min (63 °C), 2-5 – 90 min (64 °C), 2-6 – 125 min (95 °C). Resulting spectra are shown in the figures 3 and 4.

![Figure 3](image1)

**Figure 3.** Absorption spectra of CdSe nanoparticles prepared with molar ratio $[\text{Cd}^{2+}] : [\text{Se}^{2-}] : [\text{TGA}] = 1:0.25:1.2$.

![Figure 4](image2)

**Figure 4.** Photoluminescence spectra of CdSe nanoparticles prepared with molar ratio $[\text{Cd}^{2+}] : [\text{Se}^{2-}] : [\text{TGA}] = 1:0.25:1.2$.

It is notable that in this case smaller nanoparticles were formed so that according to equation (1) approximate average size for the last sample was less than 1.6 nm. Absorption curves retain first excitonic transition maximum prompting uniform growth and relatively stable monodispersity in the course of the reaction. Corresponding emission band peak shifts from 580 to 640 nm.

In order to reveal influence of higher injection temperature precursors were mixed at 97 °C and temperature was maintained constant. Samples were consequently acquired in 0.5; 6; 25; 60 and 90 minutes after start of the reaction. Molar ratio was $[\text{Cd}^{2+}] : [\text{Se}^{2-}] : [\text{TGA}] = 1:0.6:1.4$.

![Figure 5](image3)

**Figure 5.** Absorption spectra of CdSe nanoparticles prepared at 97 °C.

![Figure 6](image4)

**Figure 6.** Photoluminescence spectra of CdSe nanoparticles prepared at 97 °C.

As can be seen from absorption spectra in the figure 5 larger nanocrystals were formed at nucleation stage. In 25 minutes crystal growth noticeably slowed down which is reflected on
photoluminescence spectra either. Photoluminescence peak maximum (figure 6) shifts from 615 to 683 nm. The mean size of thus obtained nanoparticles was estimated less than 2.2 nm (for the last sample).

In order to confirm crystallinity of nanoparticles X – ray diffraction analysis was performed on the powder sample. For this fourth sample of the second series (2-4) was precipitated by means of propanol – 2 addition with subsequent centrifugation. X-ray analysis showed that nanocrystals are characterised by hexagonal wurzite structure rather than zinc blend which is not typical for CdSe nanoparticles synthesized in aqueous solutions [7–10]. Nevertheless possibility of two phase coexistence cannot be excluded particularly considering such a small average size of the QDs.

4. Conclusion
As a result of this work several series of CdSe QDs stabilized with TGA were synthesised in water phase. Depending on temperature regime and molar ratio of the components current method yields nanoparticles with mean size less than 2.2 nm. Particles exhibit photoluminescence in the range of 580 – 680 nm. Their emission that is characterized by wide peaks and large Stokes shift should be accounted for recombination via surface trap states. It was showed that higher precursor injection temperatures allow obtaining larger nanoparticles on nucleation stage while raising temperature along the course of the reaction results in higher growth rates. Application of higher molar ratio [Cd\(^{2+}\)]:[Se\(^{2-}\)] facilitated formation of comparatively small nanocrystals (average size less than 1.6 nm). XRD analysis shows that thus prepared crystallites pertain to hexagonal wurzite structure.

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