Preparation of cadmium selenide colloidal quantum dots in non-coordinating solvent octadecene

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Abstract. Nearly monodisperse cadmium selenide quantum dots (QDs) were synthesized in non-coordinating solvent octadecene through phosphine-free method using oleic acid as surfactant. Selenium powder suspension in octadecene obtained by ultrasound processing was used as one of precursor solutions. Influence of multiple selenium precursor injections on nanocrystal growth process was investigated. Nanoparticles were characterized by means of absorption and photoluminescence spectroscopies.

1. Introduction
Extensive development of colloidal semiconductor QDs field is caused by their important features (tunable absorption and emission spectra, high luminescence quantum yield, processibility) which give way to wide range of prospective applications in light emitting devices, photovoltaic cells, photodetectors. Facility of nanocrystal surface processing and higher stability against photodegradation in comparison with conventional organic fluorophores stimulates application of colloidal QDs in biological and medical detection [1, 2]. Cadmium selenide (CdSe) is semiconductor with band gap of 1.7 eV which is widely used as a QDs material for visible spectrum.

Classical hot-injection method introduced in the beginning of 1990s [3] allowed preparation of nearly monodisperse colloidal nanocrystals of AIIBVI semiconductors. Using rapid injection of precursors at elevated temperatures it enabled separation of nucleation and growth stages making synthesis procedure more controllable. One of its major drawbacks however was high toxicity and pyrophoricity of the components being used (namely, dimethyl cadmium as cadmium precursor, mixture of trioctylphosphine and trioctylphosphine oxide as coordinating solvent) which necessitates employing of air free techniques. In this respect one of the options of medium for colloidal QDs production is water [4, 5]. However as a rule these methods yield nanoparticles of poorer quality and size distribution.

Later less hazardous compounds were proposed as immediate sources of cadmium and selenium species such as cadmium – fatty acid complexes and elemental selenium, fatty acids and long-chained alkylamines might be used as stabilizing agents [6, 7]. Due to low toxicity and cost non-coordinating solvent octadecene proves to be a good alternative to coordinating phosphate-based solvents. Its boiling point is high enough (317 °C) and its melting point is below room temperature making it convenient to use. Moreover being non-coordinating compound octadecene doesn’t participate in nanoparticle stabilization making synthesis procedure more controllable.

2. Materials and methods
Cadmium oxide (CdO), elemental selenium (powder), Octadecene 90% technical grade (ODE), oleic acid (OA), acetone were used without additional purification.

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.

Mean size of nanoparticles was determined using polynomial equation from the work [8]:
\[ a = \left(1.6122 \cdot 10^{-9}\right)\lambda^2 - \left(2.6575 \cdot 10^{-6}\right)\lambda^3 + \left(1.6242 \cdot 10^{-3}\right)\lambda^2 - 0.4277\lambda + 41.57, \]  

(1)

where \( a \) is average size of particles, \( \lambda \) is a wavelength of the first excitonic peak. Derived from experimental data acquired by means of TEM studies this equation supposedly is more reliable than effective mass approximation model for smaller nanoparticles.

3. Experiment and results

For the first CdSe QDs synthesis two precursor solutions were prepared. Firstly 1 mmol of CdO, 20 mmol of OA and 40 ml of ODE were loaded into 100 ml three neck flask and heated to 160 °C under nitrogen flow to obtain clear yellowish solution of cadmium oleate in ODE. For preparation of selenium precursor solution 0.5 mmol of selenium powder, 10 mmol of OA and 3.4 ml of ODE were treated in ultrasound bath at room temperature to form homogeneous suspension. Cadmium precursor solution was heated further up to 240 °C and selenium suspension was rapidly injected which resulted in immediate nucleation. To monitor nanoparticle growth aliquots were taken in 10 seconds, 40 seconds, 2, 16 and 120 minutes after injection. Nanocrystals were further precipitated from crude solution by addition of certain amount of acetone with subsequent centrifugation and were redissolved in hexane. Due to hydrophobic surface thus prepared nanocrystals are soluble in other common non-polar solvents of choice such as toluene and chloroform. Figures 1 and 2 show absorption and photoluminescence spectra.

As can be seen from absorption spectra nanocrystal growth almost stopped in 16 minutes after injection of selenium precursor solution. Photoluminescence spectra feature two distinctive bands. The left one corresponds to interband radiative recombination and its form reflects nanocrystal size distribution. Presence of wider band on longer wavelengths may be explained by insufficient passivation of nanoparticle surface by stabilizer molecules that causes radiative recombination via trap states inside band gap. Interband photoluminescence peak full width on half maximum parameter (FWHM) decreased at the first stage of the reaction from 38 nm (10 sec) to 31 nm (40 sec and 2 min). Samples obtained in 16 minutes and 120 minutes are characterized by larger FWHM of 39 nm and 53 nm. An explanation to this might be given as follows: depletion of free monomers in reaction volume shifts thermodynamic equilibrium towards growth of larger nanocrystals at the expense of smaller ones which leads to nanoparticles size distribution broadening. This effect is known as Ostwald ripening.
The same synthesis was repeated with smaller amount of stabilizer being used. 1 mmol of CdO, 5 mmol of OA and 40 ml of ODE were used for cadmium precursor solution preparation. Selenium suspension consisted of 0.5 mmol of Se and 1 mmol of OA in 5 ml of ODE.

The first excitonic peak of the sample obtained in 2 minutes (figure 3) after injection is positioned at 490 nm which indicates that in comparison with previous implementation smaller nanoparticles were formed at initial stage of the reaction. As in the previous case growth rate was rather slow but nanoparticle size distribution stayed narrow throughout whole experiment. For 60 minutes of reaction photoluminescence FWHM (figure 4) increased from 25 nm to 28 nm only. It’s also should be noted that nanocrystals which were formed right after nucleation likely had surface of low quality.

Figure 3. Absorption spectra of CdSe QDs.

Figure 4. Photoluminescence spectra of CdSe QDs.

The next experiment was based on the first one with only one difference that selenium precursor solution was divided into two equal batches. One half of the solution (0.25 mmol of selenium) was injected as described earlier and the second half was used in the course of the reaction so that initial molar ratio between cadmium and selenium species upon nucleation was [Cd]:[Se] = 4:1. Absorption and photoluminescence spectra are shown in figures 5 and 6.

Figure 5. Absorption spectra of CdSe QDs prepared with use of Se precursor multiple injections.

Figure 6. Photoluminescence spectra of CdSe QDs prepared with use of Se precursor multiple injections.
As can be well seen on absorption spectra (figure 5) similar to the previous case growth slows
down considerably in 10 minutes after initial selenium injection. Additional injections were performed
on 12th and 22nd minutes using two approximately equal parts of the second half of the suspension. It is
noticeable that precursor addition resulted in growth resumption as wavelength distance between first
excitonic peaks of the third (10 minutes) and forth (14 minutes) samples is about 25 nm.
Photoluminescence FWHM (figure 6) gradually decreased from the start of the reaction from 31 to 41
nm for the first three samples. Second injection of selenium suspension resulted in focusing of
nanoparticle size distribution so that FWHM after 14 minutes of growth was about 34 nm and it didn’t
change considerably till the last aliquot was taken on 37th minute. The average size of nanocrystals as
calculated from equation (1) ranges from 2.1 to 2.8 nm.

4. Conclusion
As a result colloidal QDs of CdSe were synthesized via phosphine-free hot-injection method using
suspension of selenium in ODE as one of precursor solutions. Implementation with relatively high
concentration of stabilizing agent is characterized by fast slowing down of growth with subsequent
nanoparticle size distribution broadening via Ostwald ripening. Multiple injection of selenium
precursor promoted further growth of nanoparticles without substantial deterioration of
monodispersity of the system. Synthesis with lower amount of stabilizing oleic acid yielded
nanoparticles with better monodispersity and as consequence lower photoluminescence FWHM
(corresponding to interband transition (less than 30 nm). The average size of prepared CdSe QDs lies
between 2 and 3 nm.

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