

Cadmium selenide and zinc sulfide nanoparticles – challenges in synthesis revealed through optical properties

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Abstract—Semiconductor nanoparticles, also called quantum dots (QDs), are emerging as the new class of fluorescent labeling materials in biological applications. In comparison with fluorescent dyes, QDs have unique optical and electronic properties: size-tunable light emission, high brightness, broad excitation with possible simultaneous excitation of multiple fluorescent colors. One of the key challenges for synthesis chemistry is to produce small size and monodisperse (single color) QDs with high reproducibility. In this report we describe synthesis and characterization of CdSe and ZnS QDs using two different synthesis approaches. The first is carried out at high temperature in Trioctyl-Phosphine Oxide (TOPO) as a coordinating solvent, while the second synthesis is carried out at lower temperature in ethylene glycol. We present the challenges in nanoparticle synthesis and show ways, in which these could be overcome.

Keywords-quantum qots, fluorescent labelling

I. INTRODUCTION

Semiconductor quantum dots (QDs) have captivated scientists and engineers over the past two decades owing to their fascinating optical and electronic properties, which are different from either isolated molecules or bulk materials [1]. Such zero-dimensional semiconductors may be used in a wide array of fields in applications such as electro-optical devices, spectral bar coding, light filtering and others. Recent research has stimulated considerable interest in developing these quantum-confined nanocrystals as fluorescent probes for biological applications. Compared with fluorescent dyes, semiconductor nanocrystals offer several significant advantages such as size- and composition-tunable emission wavelengths, broad excitation characteristics, narrow emission lines desirable in multiplex labeling applications, and very high level of brightness and photostability. As a result QDs have found applications in biological staining and diagnostics [2] and more recently in *in vivo* cancer targeting and imaging [3], and an extensive review on these two topics was given in Reference [4]. Application of QDs for fluorescence resonance energy transfer (FRET) and bio-sensing was signaled briefly [5]. Topics on QDs as cellular probes were reviewed by Alivisatos and co-workers [6] and a full review of the biological applications of QDs can be found in [7].

A large number of methods have been developed to produce high quality QDs since two decades ago [8, 9], but the process is still experimentally quite challenging. Synthesis of monodisperse and small, well-controlled size QDs is difficult because most of the methods are very sensitive to the initial conditions and small variations at early stages of the nucleation process cause significant differences in nanocrystals size distributions. The dynamics of the process matters too, as the nanocrystals undergo growth and Oswald ripening as the synthesis progresses in time. In order to control nanocrystal size different coordinating solvents can be used to prevent the growth and agglomeration of QDs and provide passivation of surface states. These processes are difficult to control, however it is possible to suggest growth protocols that self-terminate at a desired size.

II. EXPERIMENTS

CdSe QDs were synthesized according to the method based on Reference [10]. In this synthesis, cadmium oxide or cadmium acetate is dissolved in TOPO as the high boiling point and coordinating solvent. In the next step selenium precursor in a form of Trioctyl-Phosphine Selenide (TOPSe) is rapidly injected into the hot TOPO/Cd precursor at a defined initial temperature, in this case: 300, 310, 320 and 330°C in typical air-less synthesis setup. After injection the temperature drops down rapidly (about 30°C) and maintaining it afterwards at constant level is critical for controllable nucleation and subsequent growth of CdSe nanocrystals. Extracting the aliquots at different refluxing times, ranging from 10 to 120 seconds from the injection was used to monitor the growth process. In each case a reaction vessel was removed from a heating mantle after 120 seconds and the final aliquot refers to the nanoparticles remained in the vessel and cooled down to room temperature. The sample aliquots were diluted with toluene for spectroscopic measurements.

ZnS QDs were synthesized by the colloidal method according to the work of Zhao et al [11]. In this method the zinc precursor is prepared by dissolving ZnCl₂ with tetramethylammonium hydroxide (TMAH) in ethylene glycol (EG) as a solvent. During the synthesis a second solution containing thiourea dissolved in EG is rapidly injected into zinc containing mixture heated to 100°C. After injection the

temperature is raised to 150°C to carry the reaction and aliquots after 20 minutes, 1, 3 and 5 hours of the synthesis process are collected. The nanocrystals are isolated from the solution by the centrifugation, washed with acetone and ethanol, and redispersed in ethanol for measurements.

The absorption spectra were measured on Cary 5000 UV-Vis-NIR Spectrophotometer from Varian. The photoluminescence (PL) spectra were collected on Fluorolog Tau 3 system from Jobin-Yvon-Horiba with 450 W Xe lamp excitation. Its spectral width was set to 2 nm. All spectra were corrected for system response and all data were collected at room temperature.

III. RESULTS

Figure 1 and Figure 2 show the absorption and photoluminescence (PL) spectra, respectively, for CdSe QDs aliquots extracted at different times for synthesis G330 (see Figure 3) with the injection temperature of 330°C. The peak positions in these spectra reflect the nanoparticle size changes as due to quantum confinement effect, the higher energy features characterize the smaller nanoparticles. A diameter of the QDs was calculated using the empirical fitting functions from Ref [12] and the results for synthesis G330 are listed in TABLE I. The diameter of the QD's grows almost linearly for entire heating period between 10 and 120 s. The same method of assessing diameter is also used in Figure 3 and shows the same trend for other syntheses. As the time after injection increases the QDs grow and therefore the main peaks in absorption and photoluminescence show a red shift. The size distribution also becomes broader, which is indicated by the width of the main peaks. Samples from shorter refluxing time (less than 60 s) show sharper main peaks as well as a tail near 610 nm, which is likely to be due to the surface defects.

We repeated growth experiments a number of times at varying temperatures and otherwise under identical conditions to estimate reproducibility, and the results are presented in Figure 3. For the injection temperatures above 300°C, the nanoparticle quality was good, judged from the Gaussian shape of a band gap - dominated PL, its high intensity and narrow FWHM. However, refluxing during each of these processes shows that the nanoparticle size evolution was different even when identical injecting temperature was maintained. The overall trend in the evolution of size offers some opportunities to control the particle size, but more complex than simply the control of refluxing time and temperature.

Figure 4 shows that the QDs are stable after about two months and further ripening at room temperature does not occur. It should be noted that the FWHM of the main emission peak reduces from 21 nm to 19 nm and the tail attributed to surface defects decreases considerably.

Figure 5 and Figure 6 shows the absorption and the photoluminescence (PL) spectra of ZnS QDs, respectively. The low temperature synthesis produces larger QDs with broader absorption and PL. In EG, non-coordinating solvent, smaller average size of particles were obtained after longer refluxing time. At the same time, the size variation became large and spectra are dominated by defect luminescence indicating poor passivation of surface states. Gaussian fitting shows that as a

result photoluminescence spectrum consist of four peaks (Figure 6).

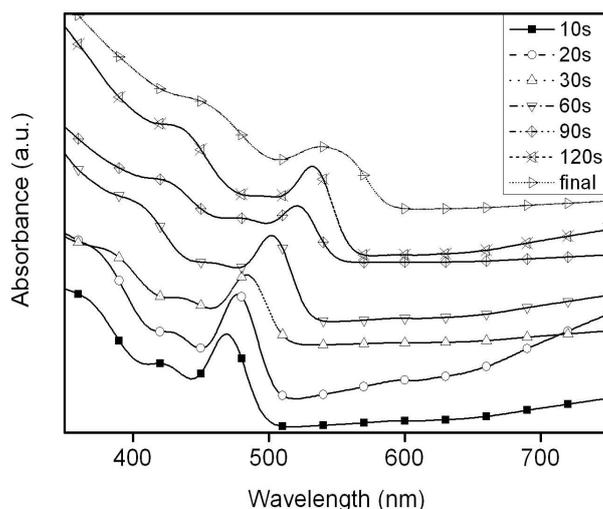


Figure 1. Absorption spectra of CdSe QDs after various refluxing times. The final sample is taken by the time when QDs are stable enough and will not grow any longer. Normally, samples of shorter refluxing times show sharper main peaks as well as the minor ones. The FWHM indicates the size distribution of particles. The spectrum is collected with 1 nm resolution.

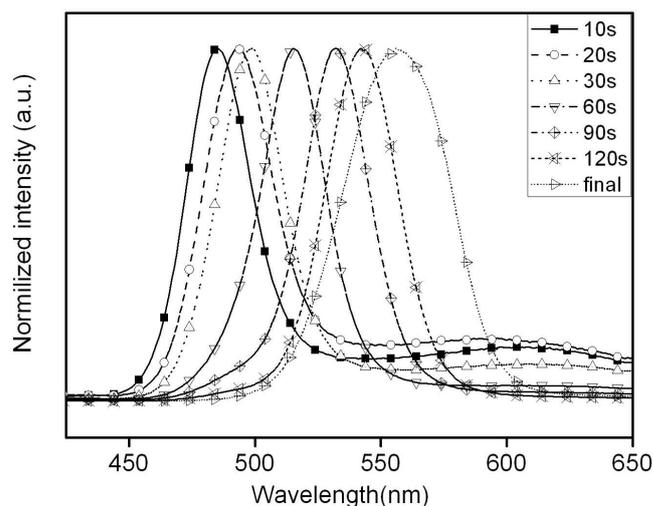


Figure 2. Emission spectra of CdSe QDs after various refluxing times. The excitation wavelength is 350 nm. The minor peaks at the longer wavelength indicate a surface defect. The spectrum is collected with 2 nm slit size.

TABLE I. DIAMETER ASSESSMENT BASED ON THE FIRST EXCITONIC ABSORPTION PEAK POSITION

Fluxing time(s)	10	20	30	60	90	120	final
First excitonic absorption peak (nm)	469	477	483	501	521	531	537
Mean diameter of the QD (nm)	2.09	2.15	2.20	2.35	2.57	2.71	2.80

IV. DISCUSSION

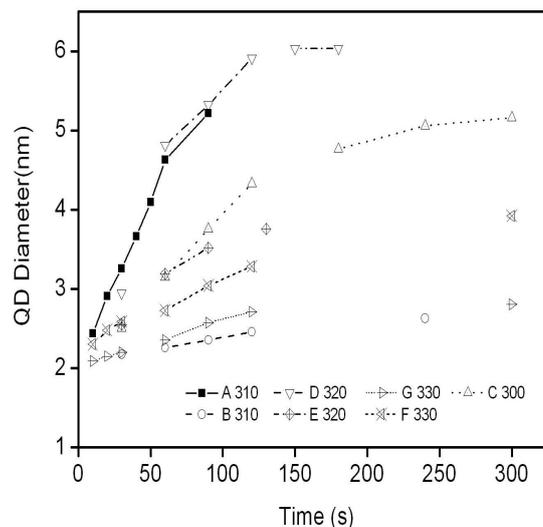
All QDs discussed here were obtained through the colloidal chemical synthesis route. The nucleation and growth of CdSe QDs were carried out by injecting rapidly the selenium source into the cadmium precursor above 300°C in TOPO coordinating solvent, following Peng et al [13]. Based on the observed optical properties, the hot injection method was able to produce good quality CdSe QDs with bright PL emission. The sample QDs directly collected after high temperature synthesis in TOPO and redispersed in toluene, were stable enough for practical applications. However, the reproducibility of the procedure was not precise and produced nanoparticles with varying size distributions. The relatively low temperature synthesis of ZnS QDs in EG, non-coordinating solvent, produced luminescent nanoparticles but with much broader PL and emission strongly affected by internal and surface defects. The ripening after the synthesis was also pronounced for this synthesis.

According to the optical characteristics shown in Figure 1 and 2, CdSe nanoparticles in aliquots extracted earlier yielded brighter PL and had smaller and more homogeneous sizes but a stronger contribution of surface defects. This is because during the growth, small QDs are first to appear during nucleation process, and evolve very quickly, as shown in Figure 3. At this stage the ratio of surface to internal atoms in formed nanocrystals is the highest. Shortly after nucleation the average diameter of QDs experience linear growth for the entire 120 s heating period investigated here. The fastest and the slowest growth for that period both happened in the synthesis with injection at 310°C, which were 0.035 and 0.003 nm/s (reference to TABLE II). This pronounced variation proves the poor reproducibility.

After removing the heating mantle at 120 s, the growth speed slows down. Due to the short growing time, initially formed, small QDs often have significant surface defects as they did not have time to become stabilized. In this phase, there is no significant Ostwald ripening effect, so the size distribution in first aliquots is very small. As the growth of nanoparticles progresses the surface defects have the time to evolve and many annihilate leading to the reduced contribution of surface defects, observed in PL. Also noticeably Ostwald ripening increases in the final stages of the synthesis and as a result the size distribution becomes broader. Aging experiment showed that there is no further Ostwald ripening effect inside a QD solution stored at room temperature for more than two months. We also note that toluene/TOPO solution at RT helps the QDs to remove surface defects and narrow the size distribution, which is referred to as the effect of focusing in Reference[13]. As a side issue we note that in Figure 3, the main emission peak blue shifted by about 3 nm, which is an indication of particle size shrink. This shows a clue for QD post treatment to remove the surface defects and narrow size distribution.

Unlike the CdSe, ZnS QDs show a different evolution as shown in Figure 5. Here, longer refluxing time does not enlarge the average size but reduces it. The longer refluxing times are required to decompose thiourea, which is a source of sulfur ions and also plays an active role to passivate the surface

defects in ZnS QDs. At the same time Ostwald ripening is increasing the size variation. The main emission peak in Figure 6 shows very wide FWHM, and it appears due to broad size distribution and several types of defects. The Gaussian fitting clearly indicates that there are four minor peaks under the main



curve.

Figure 3. QD diameter vs refluxing time for seven syntheses. The curves were obtained for different injection temperatures: 300, 310, 320 and 330°C. The heater was removed at 120 s. The diameter growth speed is listed in TABLE II.

TABLE II. AVERAGE DIAMETER GROWTH SPEED IN SEVEN BATCH OF SYNTHESIS UNDER DIFFERENT INJECTION TEMPERATURE

Synthesis	A310	B310	C300	D320	E320	F330	G330
Diameter Growth (nm/s)	0.035	0.003	0.020	0.033	0.016	0.009	0.006

The average growth speed is calculated before 120 s when the mantle was removed at that time.

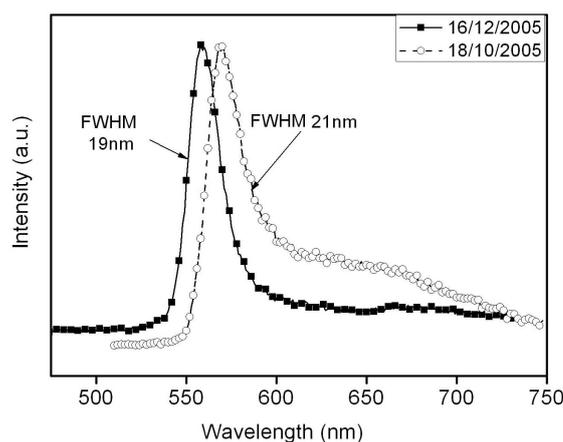


Figure 4. Aging effect of CdSe QDs in toluene/TOPO solution stored at room temperature for two months. The PL intensity does not change while the FWHM become narrower. The spectrum collected with 2 nm slit width.

V. CONCLUSIONS

Indeed the colloidal chemical synthesis is an effective method to fabricate QD, however, despite apparent simplicity the technology is quite complex. The CdSe synthesis in high boiling temperature/coordinating solvent TOPO produced small nanoparticles in 2-6 nm size range, which can be separated into narrower size distribution fractions simply by collecting aliquots at different stages of the synthesis. The repeatability of the process is relatively poor. For example, at the same injecting temperature, every batch of CdSe QDs shows a different growth rate. The difference of the peak emission wavelength, obtained for the same time and temperature, can reach 120 nm in two separate batches. In low temperature synthesis of ZnS QDs the growth rate of nanoparticles is lower but it generally produces large QDs and the ripening continues at room temperature. There is an opportunity to use solvents to reduce the average particle size and simultaneously control the final size distribution.

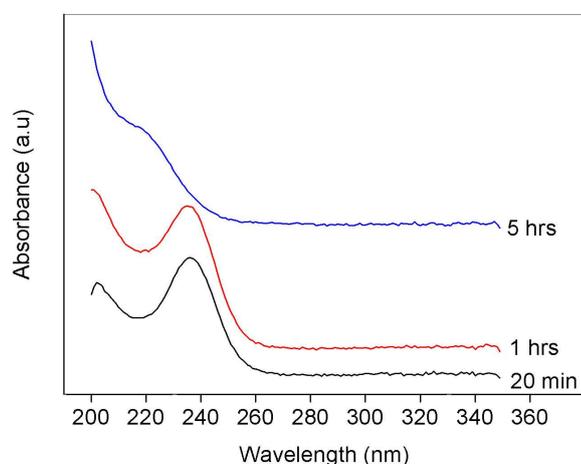


Figure 5. The absorption spectra of ZnS QDs after 20 mins, 1 hr and 5 hr of the refluxing time. The ripening process do not stop after removal of the heat. Spectrum collected with 1 nm resolution.

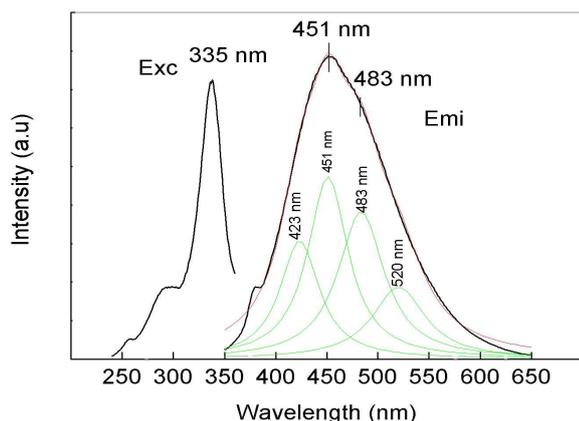


Figure 6. The excitation and emission spectra of ZnS QDs with refluxing time of 3 hours at 160°C. Curve fitting shows there are at least 4 minor peaks contributing to emission. Spectrum collected with 5 nm slit width.

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