

Synthesis and characterization of CdTe/CdSe core/shell nanoparticles with high emission from 570 to 610 nm

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Abstract. The paper presents the advance process of synthesis of CdTe/CdSe core/shell Quantum Dots (QDs) with emission wavelength from 570 to 610 nm. This synthesis was performed using modified Hot-Injection method. The CdTe/CdSe core-shell QDs have been characterized by the transmission electron microscopy (TEM) with the aim to control the QDs shape and the average size. The optical absorption and photoluminescence (PL) spectra are investigated in four samples obtained at different reaction times (5, 10, 15 and 20 s) of core growth after the CdSe passivation of the CdTe cores. Obtained results have shown that synthesized QDs have a good crystallinity, spherical shape and bright emission at 610 nm. The reaction time enlargement permits increasing the average size of CdTe/CdSe core-shell QDs, together with “red” shifting the PL wavelength and increasing the PL intensity. The advantages of synthesized CdTe/CdSe core/shell QDs are discussed.

1. Introduction

To date, QDs have various nanostructured configurations, typically as core/shell heterostructure QDs, where two different semiconductors are incorporated into a single colloidal QD. The CdTe/CdSe core/shell QDs, have been synthesized via colloidal chemical routine [1-5] and studied intensively owing to the quantum confinement effects, size-dependent photoemission, narrow emission spectrum and high-quantum yield photoluminescence (up to 75%) [6-7]. These QDs were applied as well for biomedical imaging, in photovoltaic devices, for the bioconjugation to antibodies [8-9] and in the early detection of a set of important diseases including cancer. Band gap engineering in CdTe/CdSe core/shell QDs can open a new window for the various QD material choices. In these core/shell heterostructured nanoparticles one of carriers is mostly confined in the core of QDs, while other one remains in the shell, giving a significant increase in the exciton lifetime [10]. For CdTe/ CdSe QDs the hole is mostly confined to the CdTe core, while the electron is located mostly in the CdSe shell.

2. Experimental details

2.1. Materials

All the following material were purchased from Aldrich[®]: Cadmium acetate hydrate ((C₂H₃O₂)₂Cd xH₂O, 99.99%), tellurium (Te, 99.99%), selenium (Se, 99.99%), tri-n-octylphosphine (C₂₄H₅₁P, 97.00%) (TOP), tri-n-octylphosphine oxide (C₂₄H₅₁PO, 90.00%) (TOPO), 1-octadecene (C₁₈H₃₆, 95%)



(ODE) and oleic acid ($C_{18}H_{34}O_2$, 90%). All materials were used directly without any further purification.

2.2. Synthesis of CdTe core

The CdTe-core was prepared via a modified Hot-Injection method published earlier in [11]. Cadmium precursor were prepared by dissolving 40 mg of Cadmium acetate hydrate, 0.8 g of TOPO, 8 ml of TOP, 0.6 ml of oleic acid and 10 ml of octadecene in a flask. The mixture was heated at 350 °C during 90 minutes and shaken vigorously. The tellurium precursor was prepared by mixing 26 mg of tellurium powder, 3 ml of TOP at temperature of 200 °C during 2 hours and shaken vigorously. The CdTe-core solution was produced by injecting 1 ml room-temperature tellurium precursor into the cadmium precursor at 350 °C. The nucleation of CdTe immediately started and the aliquots amount of reaction solution were extracted every 10 seconds, namely 10, 20, 30 and 40 s in order to get variation in the size core. The reactions of aliquots amount were quenched by introducing them into 50 ml of liquid nitrogen. All steps in the reaction were carried out under N_2 atmosphere

2.3. Synthesis of CdTe/CdSe core/shell

After the CdTe-core solution was produced, the CdSe-shell was grown on the CdTe-core surface using the selenium precursor which was prepared mixing 26 mg of selenium powder, 3 ml of TOP at temperature of 200 °C during 2 hours and shaken vigorously. To produce CdTe/CdSe core/shell, 1 ml of the CdTe-core solution and 1 ml of selenium precursor were injected at the same time into hot solution (350 °C) of cadmium precursor. The formation of CdSe-shell immediately started and one aliquots amount of reaction solution was extracted after 20s. The reaction of the aliquot amount was quenched by introducing it into 50 ml of liquid nitrogen. The reaction was carried out under N_2 atmosphere. For further purification, 1 ml of $CHCl_3$ and 5 ml of CH_3OH were added to 2 ml of CdTe/CdSe core/shell solution, this mixture was shaken during 15 min. The $CHCl_3$ and CH_3OH were used as solvent to separate CdTe/CdSe core/shell nanocrystals from byproducts and unreacted precursors.

2.4. Characterization

The photoluminescence signal was dispersed by a spex 500M monochromator with focal length 0.5 m and detected by Hamamatsu GaAs photomultiplier tube (PMT) model R943-02 at room temperature. A He-Cd laser 325 nm with 50 mW power was used for PL excitation. To control the shape and size of nanocrystals a JOEL JEM 6300 transmission electron microscope was used. The optical absorptions were measured using a Perkin Elmer UV-Vis/ lambda 24/deuterium lamp spectrometer.

3. Experimental results and discussion

The first step in the nanocrystal growth is the nucleation in a solution at constant temperature and pressure. This process is driven by the difference in the free energy between the crystalline phase and the solution phase. The synthesis of monodisperse colloids via homogeneous nucleation requires a temporal separation of nucleation and growth of the seeds. Initially the concentration of monomers constantly increases by addition from exterior. In stage I no nucleation occurs even in supersaturated solution ($S>1$), due to the high energy barrier for spontaneous homogeneous nucleation. The latter is overcome in stage II for a yet higher degree of supersaturation ($S>S_c$), where nucleation and formation of stable nuclei take place. As the rate of monomer supply, the monomer concentration and hence the supersaturation decrease below S_c , the level at which the nucleation rate becomes zero. In the following stage III, the particle growth continues under further monomer consumption as long as the system is in the supersaturated regime. When the formation of the CdTe core was achieved, the CdSe-shell was grown on the CdTe-core surface. The mismatch (7.1%) of the lattice constant between the core (CdTe) and shell (CdSe) facilitates the epitaxial growth of the CdSe shell around the CdTe core. Using the hot-injection synthesis method, it is possible to obtain samples with very low standard deviation from the mean size as shown in TEM images of the as-prepared CdTe/CdSe nanocrystal

(figure 1) from aliquots (namely 10, 20, 30 and 40 s) and its analysis presented in the histogram of particle size distribution in figure 2 where QDs average size increase from 3 to 6 nm.

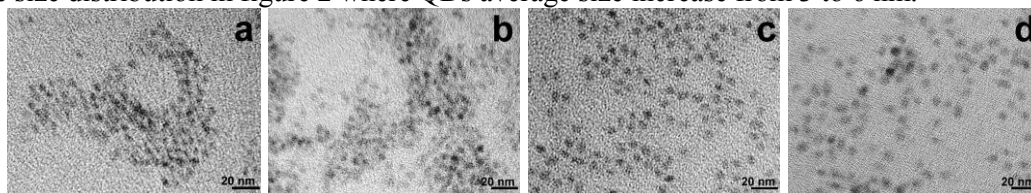


Figure 1. TEM images of the CdTe/CdSe core-shell nanocrystals prepared at the reaction time a) 10s, b) 20s, c) 30s, and d) 40s.

Simultaneously the CdSe shell growth reduces the number of dangling bonds on the CdTe surface, which can act as a trap states for charge carriers and reduce fluorescence Quantum Yield. The CdTe/CdSe nanocrystals are interesting owing to the type II QDs: the conduction band edge of the CdSe shell is located in the band gap of the CdTe core as it is shown in figure 3 for the bulk materials.

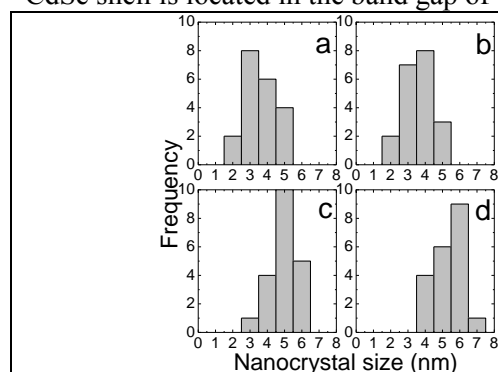


Figure 2. The histogram of nanocrystal size distribution obtained from TEM images in Fig. 1

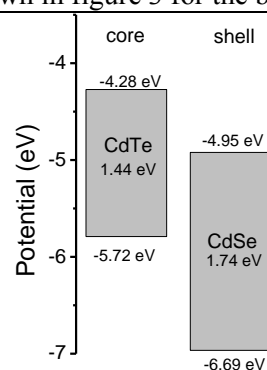


Figure 3. Plot illustrating the CdTe and CdSe band offset alignment in the energy diagram (the bulk values energies were taken from literature).

The staggered band alignment leads to a smaller “effective band gap” than the energy band gap of core and shell materials, that permits obtaining a significant red shift of the emission wavelength. The absorption spectra of four samples are shown in figure 4. The temporal evolution of the UV/Vis absorption spectra of the CdTe core was monitored in as-prepared CdTe/CdSe nanocrystals. This figure shows a continuous red shift in absorption with increasing reaction time at the creation of the CdTe core

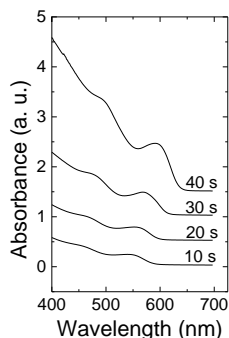


Figure 4. UV-vis absorption spectra for the four studied samples

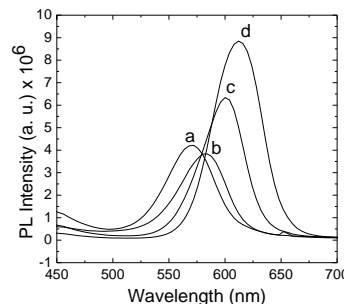


Figure 5. PL spectra corresponding to the samples prepared at the times 10, 20, 30 and 40 s presented from left to right.

The first excitonic absorption peaks in samples under study are summarized in table 1. PL spectra of the CdTe/CdSe nanocrystals are presented in figure 5. In the PL spectra we have seen emissions

energy maximum localized in 2.17, 2.12, 2.06 and 2.03 eV, in the different four samples, which are higher than the “effective band gap” of the bulk core/shell materials due to the quantum confinement effect. Thus the band gaps of both core and shell increase leading to increasing the “effective band gap” of the CdTe/CdSe nanocrystal. In this case the change of the PL peak position from 570 to 610 nm is related to the enlargement of the nanoparticles size. Note that studied CdTe/CdSe nanocrystal have a size between 3-6 nm that is lower than Borh radii in CdTe equal to 7 nm. The PL intensity rises when the particle size increases, probably, owing to increasing at the same time the concentration of nanocrystals with raising the reaction time. The FWHM values of PL bands are reported in table 1 as well. It is clear that we have obtained a very small FWHM that means that the high-quality CdTe/CdSe core/shell nanocrystals have been produced. Thus using modified hot injection synthesis method, it is possible to obtain samples with 5-10% standard deviation from the mean size.

Table 1

Reaction time (s)	PL peak position (nm)	FEAP* (nm)	Average size (nm)	FWHM (nm)
10	570	540	3	50
20	584	552	4	48
30	600	568	5	46
40	610	591	6	42

*First excitonic absorption peak

4. Conclusions

We have successfully synthesized CdTe/CdSe core/shell QDs with strongly emission from 570 to 610 nm using a modified hot-injection method. This emission can be tuned in the mentioned range in dependence of the reaction time. The presented results show low energy shift and rise of PL intensity with increasing the QD size. An effective suppression on the non-radiative recombination of electrons and holes at the surface of the core has successfully achieved. Obtained core/shell QDS are characterized by the high emission intensity and small size dispersion.

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References

- [1] S. Kim, B. Fisher, HJ Eisler, M. Bawendi, J Am. Chem. Soc. 125 (2003) 11466
- [2] X. Peng, M. C. Schlamp, A. V. Kadavanich,; A. P. Alivisatos, J. Am. Chem. Soc. 119 (1997) 7019.
- [3] LM. Sai and X. Y. Kong, Nanoscale Research Letters 6 (2011) 399.
- [4] H. Zhong, Y. Zhou, Y. Yang, C. Yang, Y. Li, J. Phys. Chem. C 111 (2007) 6538.
- [5] Y.S. Xia, C.Q. Zhu, Analyst 133 (2008) 928.
- [6] M. Kuno, D.P. Fromm, H.F. Hamann, A. Gallagher, D.J. Nesbitt, J. Phys. Chem. 115 (2001) 1028.
- [7] T.V. Torchynska, Nanotechnology 20 (2009) 095401.
- [8] N. Tessler, V. Medvedev, M. Kazes, S.H. Kan, U. Banin, Science 295 (2002) 1506.
- [9] T.V. Torchynska, J.L. Casas Espinola, J.A. Jaramillo Gómez, J. Douda, K. Gazarian, Physica E 51 (2013) 55
- [10] (2013) 60
- [11] S. Kim, Y. T.Lim, E. G. Soltesz, A. M. De Grand, J. Lee, A. Nakayama, J. A. Parker, T. Mihaljevic, R. G. Laurence, D. M. Dor, L. H. Cohn, M. G. Bawendi, J. V Frangioni, Nat. Biotechnol. 22 (2004) 93.