Influence of Cd:Se precursor ratio on optical properties of colloidal CdSe tetrapods prepared in octadecene

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Abstract. Colloidal CdSe tetrapods were synthesized by chemical method in octadecene with the initial Cd:Se precursor ratios from 6:1 to 1:10 and the different monomer concentrations. Their stoichiometry and optical properties were investigated using the energy dispersion X-ray, absorption and photoluminescence spectroscopy. It was found that the CdSe tetrapods are Cd rich for all of the obtained sizes. Their stoichiometry was almost not changed during the growth and depends on the initial precursor ratio. The double-peak structure corresponding to the optical transitions in the core and arms of CdSe tetrapods was observed clearly in both the optical absorption and photoluminescence spectra for the Cd:Se precursor ratios from 2:1 to 1:2. The influence of the initial Cd:Se precursor ratio and monomer concentration on the growth of CdSe tetrapods and their optical properties has been analysed and discussed.

Keyword: CdSe tetrapods, Cd:Se precursor ratio, optical properties, monomer concentration.

1. Introduction
Semiconductor nanocrystals (NCs) have attracted great interest over the past years because their properties can be tailored by a judicious control of particle composition, size, and surface [1-2]. These characteristics arise from several phenomena (quantum confinement of charge carriers, surface effects, and geometrical confinement of phonons) and have turned semiconductor NCs into promising materials for many applications, such as light emitting diodes [3], lasers [4], and biomedical tags for fluoroimmunoassays, nanosensors, and biological imaging [5].

The high surface-to-volume ratio of small NCs suggests that the surface properties should have significant effects on their structural and optical properties. It is well-known that the emission efficiency, spectrum, and time evolution are very strongly affected by the surface. This is generally understood as being due to the presence of gap surface states arising from surface nonstoichiometry, unsaturated bond, etc. Control of the surface is in particular the key to highly luminescent NCs.

To realize this wide range of potential applications the luminescent properties (emission colour, photoluminescence quantum yield (PL QY), luminescence lifetime, and stability) of semiconductor NCs must be strictly controlled. At present, the control and reproducibility of the PL QY has remained an elusive issue, only recently some of the factors determining the PL efficiency of NCs have been properly addressed [6-8]. The influence of the initial ratio between the Cd and the Se precursor on the temporal evolution of the ensemble PL QY of CdSe NCs during their growth at 290°C in a coordinating solvent has been investigated by Qu and Peng [6]. The position and temporal width of the
“bright point”, the highest QY, the growth kinetics, and the sharpness of the PL peak were all reported to be strongly dependent on the initial Cd:Se ratio. The existence of the “bright point” was interpreted as a signature of an optimal surface structure/reconstruction of the NCs grown under a given set of initial conditions.

Although the crucial role of the surface is clearly demonstrated, but the mechanisms underlying the correlation between the surface quality and the growth conditions have yet to be determined. Most importantly, a comprehensive investigation of several parameters (for example, the initial Cd:Se precursor ratio) in a single synthetic system is still lacking. In this work, we report on the influence of initial Cd:Se precursor ratio on the optical properties as well as the growth of colloidal CdSe tetrapods (TPs) prepared in octadecene – a noncoordinating solvent.

2. Experimental

Chemicals: Cadmium oxide (CdO), oleic acid (OA), selenium (Se), trioctylphosphine (TOP), octadecene (ODE).

Preparation: To prepare the stock Se injection solution, Se powder was reacted with TOP, the resulting colorless solution was dispersed in ODE to give a final stock solution and was loaded into a syringe. Meanwhile, a mixture of CdO, OA and ODE was loaded into a three-neck flask, stirred and heated to 200°C under nitrogen gas flow to form an optical clear solution. At this temperature, the TOPSe solution was rapidly injected into the vigorously stirred reaction flask to grow CdSe TPs. The influence of the initial Cd:Se precursor molar ratio was investigated for the different values (6:1, 4:1, 2:1, 1:1, 1:2, 1:4, 1:6, 1:8 and 1:10) chosen to cover the limits from a large excess of Cd precursor to a large excess of Se precursor. The OA:Cd and TOP:Se molar ratio of 6:1 and 4.5:1, respectively, were kept for all of our experiments. At various time intervals, aliquots of the reaction mixture were removed for the further optical measurements. A centrifugation procedure was used to purify the CdSe TPs from unreacted precursors and side products, and then the CdSe TPs were dispersed in toluene.

Measurements: The optical absorption spectra of CdSe TPs were recorded by Jasco V670 UV-Vis-NIR spectrometer. The PL spectra were collected on LABRAM-1B spectrometer, fitted with the Argon ion laser of wavelength 488 nm. To determine the stoichiometry of CdSe TPs the energy dispersion X-ray spectroscopy (EDXS) was performed using Hitachi FE-SEM S4800 at the beam voltage of 20 kV. The elemental analysis was carried out at different places of area 2 mm × 2 mm on the surface of solid samples. For EDXS measurements, the purification procedure was repeated 3 times. Transmission electron microscopy (TEM) was carried out using a JEM 1010 microscope fitted with an acceleration voltage of 80 kV.

3. Results and discussion

It is known that the injection of the TOPSe at high temperatures leads to the creation of CdSe TPs. Figure 1 is a TEM image of the CdSe TPs prepared with the Cd:Se precursor ratio of 2:1 and the reaction time of 180 min.

![Figure 1. TEM image of CdSe TPs prepared with the initial Cd:Se precursor ratio of 2:1 and the reaction time of 180 min.](image-url)
The Cd:Se stoichiometry of CdSe TPs with the arm diameters ranging from 4.6 to 5.7 nm is presented in figure 2. Surprising, all of the CdSe TPs are Cd rich for the initial Cd:Se precursor ratios from 6:1 to 1:10. Figure 3 displays the stoichiometry of CdSe TPs prepared with the initial Cd:Se precursor ratios ranging from 6:1 to 1:10 and the reaction time of 20 min. It can be seen that the Cd:Se ratio of CdSe TPs increases with increasing the initial Cd:Se precursor ratio. It is possible that the metallic cadmium was formatted in our preparation conditions. Donega et al. noted that the injection of Cd(CH_{3})_{2} in hot TOPO – HAD (hexadecylamine) under strictly water and oxygen – free conditions leads to the formation of metallic cadmium [9].

Recent experiments have shown that colloidal NCs can be nonstoichiometric. In this case of CdSe NCs, the Cd:Se stoichiometry of the resulting particles are always found to be between 1 and 1.2 [10-11]. Jasieniak et al. have manipulated the CdSe NCs surface, yielding nonstoichiometric quantum dots with a surface enriched in Cd or Se [11]. Guzelian et al. have determined an In:P ratio of 0.86:1 for InP NCs [12]. Recently, Moreels et al. also have shown that PbSe quantum dots prepared in OA-TOP-DPE (diphenil ether) reaction system are nonstoichiometric, consisting of a quasi-stoichiometric core terminated by a Pb surface shell [13].

![Figure 2](image1.png)

**Figure 2.** Cd:Se stoichiometry of CdSe TPs prepared with the different initial Cd:Se precursor ratios vs. the arm diameters.

![Figure 3](image2.png)

**Figure 3.** Cd:Se stoichiometry of CdSe TPs drawn at the reaction time of 20 min vs. the initial Cd:Se precursor ratios.

Figure 4 displays the temporal evolution of the optical absorption and PL spectra of CdSe TPs prepared with the initial Cd:Se precursor ratios of 4:1, 1:1 and 1:4. The first absorption peaks and the emission peaks were normalized in the intensity. The growth of the TPs is clearly evidenced in Figure 4 by the shift of both the absorption and PL spectra to long wavelength. It can be seen that the TP size quickly increases at the initial stages of the synthesis. Especially, the appearance of a new emission peak during the first reaction minutes is observed clearly for the initial precursor ratio of 1:1. The long-wavelength peak is attributed to the emission of TP core, and the short-wavelength peak to the emission from TP arms. These two emission peaks are separated gradually and the emission intensity of the arms increases in comparison with that of the core as the TP size increases.

It seems that the PL spectra exhibit a one-peak structure for the initial precursor ratios of 4:1 and 1:4. However, the second derivative spectra of absorbance confirm the formation of CdSe TPs in these cases. Although the PL spectra of CdSe TPs prepared with the Cd:Se precursor ratios of 4:1 and 1:4 exhibit one-peak structure, but we believe that the broad of PL spectra to long wavelength is due to the contribution of the emission from TP core. It should be noted that the previous reports on their optical properties of CdSe TPs are very different. The double-peak structure was observed clearly only in the absorption spectra [14], or in the PL spectra [15], even this double-peak structure was not observed in both the absorption spectra and the PL spectra [16]. Our experimental results show that the emission...
peak of TP core is separated gradually from that of the arms and quenched rapidly with increasing the TP size. It is possible that the appearance of the double-peak structure relates to the surface chemistry of colloidal CdSe TPs, namely, to the initial Cd:Se precursor ratio.

Figure 4. Temporal evolution of the absorption and PL spectra of CdSe TPs prepared with the initial Cd:Se precursor ratios of 4:1, 1:1, and 1:4.

Remarkably, the temporal evolution of the PL spectra of CdSe TPs prepared with the initial precursor ratio of 1:4 is relatively regular. Meanwhile, the temporal evolution of their absorption spectra is unusual. The absorption peak shifts to short wavelength at the reaction time of 0.5, 30, 60, and 180 min. After 6 min from the moment of the TOPSe-solution injection into the reaction flask the temperature in the reaction mixture is stable at 200 ± 3°C. Therefore, it is possible that the unusual temporal evolution of the absorption spectra is due to the unstable growth of CdSe TPs. The unstable growth of CdSe TPs also is observed for the Cd:Se precursor ratios of 6:1, 1:6, 1:8, and 1:10. It is well-known that only a limited amount of Cd monomer is stable under the conditions prevalent during the synthesis. A large excess of Cd precursor can lead to uncontrolled growth of large CdSe NCs [9]. The preparation of CdSe NCs in trioctylphosphine oxide (TOPO), in which the particles were grown stably with the Cd:Se precursor ratios from 2:1 to 1:10, was reported in [6]. However, our experiments
show that the growth of CdSe TPs in ODE is more stable only for the initial precursor ratios ranging from 2:1 to 1:2, indicating the important role of the reaction media.

In order to determine the influence of monomer concentration on the optical properties of CdSe TPs, we prepared the CdSe TPs with the initial Cd:Se ratio of 2:1 and Cd monomer concentrations in ODE of 0.033, 0.017, and 0.011 M. The temporal evolution of the absorption and PL spectra of CdSe TPs is presented in figure 5. The double-peak structure was observed clearly in both the absorption and PL spectra of the sample series. The temporal evolution of the absorption and PL spectra is similar to that in the case of the Cd:Se ratio of 1:1. It can be seen that the monomer concentrations almost do not change the spectroscopic characteristics of the CdSe TPs.

Figure 5. Temporal evolution of the absorption and PL spectra of CdSe TPs prepared with the initial Cd:Se ratio of 2:1 and Cd monomer concentrations in ODE of 0.033, 0.017, and 0.011 M.

Figure 6 presents the temporal evolution of the TP size during the growth. The diameters of the spherical core and columnar arms are estimated according to Brus expression [17] and the method of Gu et al. [18], respectively. The positions of the first two exciton peaks are determined from the second derivative spectra of absorbance with respect to the energy. It should be noted that: (i) the diameter of TP core is larger than that of the arm; (ii) the core size increases more quickly in comparison with the arm diameter; and (iii) the low monomer concentration leads to the decrease in the diameter of core and arms.
The PL spectra of CdSe TPs prepared with three different monomer concentrations and drawn at the same reaction time are compared in figure 7. It can be seen that the low monomer concentrations lead to the rapid quenching of the luminescence from the TP core, and therefore the spectral shape becomes more symmetric.

Figure 8 shows the temporal evolution of PL spectra of CdSe TPs prepared with the Cd monomer concentration of 0.017 M in the wavelength region from 500 to 830 nm. The growth of CdSe TPs during the first reaction minutes leads to not only the appearance of a second peak, but also increase in the intensity of the emission band at ~ 750 nm. The intensities of both the emission from TP core and long wavelength band decrease in the next reaction time, and then they disappear.

Figure 6. Temporal evolution of the size of CdSe TPs prepared with the initial Cd:Se ratio of 2:1 and Cd monomer concentration of 0.033, 0.017 and 0.011 M.

Figure 7. PL spectra of CdSe TPs prepared with the Cd monomer concentrations of 0.033, 0.017, and 0.011 M. The samples were drawn at the reaction time of 100 min.

Figure 8. Temporal evolution of PL spectra of CdSe TPs prepared with the Cd monomer concentration of 0.017 M.
4. Conclusions
Colloidal CdSe TPs were synthesized by chemical method in ODE with the initial Cd:Se precursor ratios from 6:1 to 1:10 and different monomer concentrations. It was found that the CdSe TPs are Cd rich for all of the obtained sizes. Their stoichiometry depends on the initial precursor ratio.

The double-peak structure corresponding to the optical transitions in the core and arms of CdSe TPs was observed clearly in both the optical absorption and PL spectra for the Cd:Se precursor ratios from 2:1 to 1:2. These two emission peaks are separated gradually and the emission intensity of the arms increases in comparison with that of the core as the TP size increases. The rapid decrease in the emission intensity of the TP core with increasing its size is unclear. The temporal evolution of the optical absorption spectra shows that the growth of CdSe TPs in ODE is stable only for the initial precursor ratios ranging from 2:1 to 1:2. Moreover, the Cd monomer concentration in the range of 0.011 – 0.033 M almost does not change the spectroscopic characteristics of the CdSe TPs.

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