Synthesis and optical properties of CdTe nanocrystals with improved optical properties

Kiran Jain*, Vibha Srivastava & Abhilasha Chouksey
Electronic Materials Division, National Physical Laboratory, Dr K S Krishnan Marg, New Delhi 110 012, India

Received 24 February 2009; 29 April 2009

CdTe nanocrystals are prepared by hydrothermal route using the reaction between Cd\textsuperscript{2+} and KHTe in the presence of thioglycolic acid as the stabilizing agent. Hydrothermal synthesis under optimum conditions resulted in a rapid growth. CdTe nanocrystals with high PL intensity and narrow PL spectra are obtained in less time. The growth mechanism of CdTe nanocrystals is investigated. The growth rate in the initial stage of synthesis is higher in hydrothermal synthesis resulting in an increased growth in diffusion controlled focused region.

Keywords: CdTe, Nanostructures, Hydrothermal, Luminescence

CdTe is a semiconductor material with band gap energy of 1.56 eV and found application in different research areas ranging from microelectronics to fluorescent bio-labeling. This is due to the great tunability of its electro-optical properties, which is achieved by size, surface, and morphological control of the particles in the quantum confinement regime\textsuperscript{1-3}. The investigation and optimization of semiconductor nanoparticles synthesis is an important problem. Photoluminescence (PL) quantum efficiency near to 65% is achieved at room temperature in CdTe nanocrystals (NCs) synthesized by metal-organic technologies\textsuperscript{4}. Water based routes offer advantages due to simplicity, use of nontoxic solvents and low reaction temperatures, stability of PL properties and the possibility of NC size tunability\textsuperscript{5-20}. Moreover, small sized nanocrystals are possible. The width of emission peaks is somewhat narrower than that of the nano-crystals produced by other routes. Effective passivation by the formation of cadmium thiol complexes at the surface was found to be the origin of high PL quantum efficiency\textsuperscript{11}. The thiol capped CdTe were reported to yield Quantum yield as high as 80%\textsuperscript{12}. Aqueous CdTe NCs have been successfully synthesized by using refluxing\textsuperscript{5,6} hydrothermally (in an autoclave)\textsuperscript{7} as well as a microwave irradiated vessel\textsuperscript{8,9}. Hydrothermal synthesis is a low cost synthesis route and highly crystalline product with narrow grain size distribution and high purity without post heat treatment could be obtained. The PL can be tuned in a wide spectral range using hydrothermal synthesis\textsuperscript{11-16}.

In the present work, the optical properties of hydrothermally synthesized CdTe nanocrystals prepared by aqueous route were investigated. The associated change in size, emission peak position, intensity with increasing reaction time and temperature were studied. Effect of increasing the hydrothermal synthesis temperature and time resulted in luminescence peak shift, which can be correlated to particles growth. Further, the growth kinetics of CdTe nanocrystals was investigated in thiol stabilized aqueous medium under different experimental conditions.

Experimental Procedure

The thiol capped CdTe NCs were prepared by the hydrothermal route at different temperatures. First KHTe was generated from the reaction of Te powder with KBH\textsubscript{4} in the presence of N\textsubscript{2} gas. Precursor solution of CdTe nanocrystals was prepared by adding KHTe solution to (CH\textsubscript{3}COO)\textsubscript{2}.2H\textsubscript{2}O and thioglycolic acid in the presence of N\textsubscript{2}. The molar ratio of Cd: Te: thiol was fixed at 4:1:5. The concentration of the precursor solution was kept as Cd = 2 mmol, pH value was fixed at 11. The CdTe precursor solution was put into Teflon lined stainless steel Autoclave. Different particle sizes were obtained by heating at 120°C, 140°C and 170°C for different duration. Another batch of CdTe nanoparticles was similarly prepared by refluxing the precursor solution for different duration at 100°C. The CdTe precursor solution was put into a refluxed vessel. Different particle sizes were obtained by heating at 120°C, 140°C and 170°C for different duration. Another batch of CdTe nanoparticles was similarly prepared by refluxing the precursor solution for different duration at 100°C. TEM was conducted on a JEM200 CX transmission electron microscope to observe the microstructure of the samples. For TEM observations, a drop of as synthesized colloidal solution was placed on carbon coated copper grid.
grids and allowed to dry. UV-vis optical absorption was measured by means of a Shimadzu UV-vis spectrophotometer. Photoluminescence (PL) measurements have been performed at room temperature using an argon ion laser system and a Bentham monochromater system.

Results and Discussion

Refluxing at 100°C

Figure 1 (a,b) shows the absorption and luminescence spectra of the as prepared colloidal CdTe NCs grown for different reflux (100°C) period. On prolonging the refluxing time, the growth of the CdTe NCs was clearly evident by the shift of both absorption and emission spectra to longer wavelength. The emission peak shifted to 610 nm on refluxing for 20 h.

The luminescence intensity of as prepared sample was low but on increase in reflux time the luminescence intensity increases. High PL intensity and narrow emission width indicates growth of NCs with few electronic defect sites. FWHM of about 35-45 nm obtained for these samples shows a rather narrow particle size distribution (~10%).

Hydrothermal synthesis at different temperatures

Figure 2 (a,b) shows the absorption and emission spectra for CdTe NCs synthesized at different conditions.
temperatures for 30 min. As shown, CdTe NCs grew quickly at 170ºC with a PL peak near to 710 nm, however the emission intensity is quite low. It appears that higher temperature (170ºC) induce faster surface degradation, which reduces the luminescence intensity shortly after the maximum emission intensity has been reached. At somewhat lower temperatures 120ºC and 140ºC, the growth of the particles is better than at 100ºC and larger sized CdTe NCs with high emission intensity could be synthesized. The formation of larger particles at higher temperature may be correlated to increased kinetics of particle formation. The temperature influences the rate at which the ligands attach or detach from the particle surface. At higher temperatures the growth rate is highly accelerated. For example, CdTe NCs with a peak at 650 nm was synthesized within 30 min at 140ºC, while it took about 20 h by reflux to obtain a powder showing PL peak at 610 nm. Emission intensity enhanced by a magnitude more than five times when CdTe NCs were synthesized at 140ºC as compared to 120ºC. However, TGA synthesized powder at 170ºC showed lower emission intensity. This may be due to some decomposition of TGA at high temperatures.

**Hydrothermal synthesis at 140ºC**

Figure 3 (a,b) shows the absorption and photoluminescence spectra of CdTe NPs synthesized on hydrothermal heating at 140ºC. The absorption spectra showed well developed maximum near the absorption onset (exciton peak). On increasing the reflux time, the exciton peak shifts towards higher wavelength side due to increase in particle size. With increasing reaction time, the emission intensity increases initially and started decreasing after reaching a peak value. Maximum intensity at 140ºC was observed at 650 nm synthesized for 1 h.

**Microstructure**

Figure 4 shows the TEM microstructure of as synthesized CdTe NCs prepared by hydrothermal treatment at 140ºC for 4 h. Size of few particles was shown in the figure. The as synthesized powder shows NCs of average size about 5 nm.
Growth kinetics

The growth process of these CdTe NPs can be understood by examining the Fig. 5a, which shows changes in particle size with time at different temperatures. The particle size of the thiol-capped CdTe QDs was calculated from optical absorption spectra using the following empirical expression:

\[
D = (9.8127 \times 10^{-7}) \lambda^3 - (1.7147 \times 10^{-3}) \lambda^2 + (1.0064)\lambda - 194.84 \ldots (1)
\]

In the above equations, \(\lambda\) (nm) is the wavelength of the first excitonic absorption peak of the UV-vis absorption spectrum. The growth of CdTe NCs in aqueous media may be divided into two stages: the early fast growth stage and the later slow growth stage. The growth in the later stage is dominated by Ostwald ripening (OR), due to the depletion of monomers resulting in an increased particle size distribution. As shown in Fig. 5 (a,b) due to the accelerated diffusion at higher temperatures in hydrothermal conditions, the rate of particle growth is enhanced during both stages. For example, it takes about 30 min to grow CdTe particles with an average size of 3.4 nm at 140°C, but takes about 20 h at 100°C. These results clearly show that the growth rate of CdTe NCs is much higher at higher temperature. A plot of the growth rate \(dD/dt\) against \((1/r)\) is shown in Fig. 5b. A linear plot at both temperatures shows that the growth is dominated by diffusion control.

Thiol stabilized CdTe NCs were formed in aqueous solution as stabilizers by reaction of Cd\(^{2+}\) and Te\(^{2-}\) ions. The thioglycolic acid plays a role of the stabilizer, a source of sulfur and as a surfactant in the system. With the increase of reaction temperature the nucleation is followed by growth, this process depends on the diffusion of monomers. It has been shown that the thiol stabilizer can partially hydrolyze under prolonged reflux, which leads to a partial incorporation of sulfur into the CdTe lattice. In this context, it has been supposed that the S is mainly concentrated at the nanocrystal surface and there is a gradient of sulfur content into the core of the particles. Aqueous growth of CdTe NCs mainly occurred via diffusion controlled OR, but a fast crystal growth was encountered at the early stage. This fast growth was dominated by the addition of monomers, or primary clusters to NCs rather than by OR. NCs synthesized during this period correspond to particles synthesized in the focusing region. In this context, the effect of hydrothermal heating at high temperatures may be understood as an increased rate of TGA hydrolysis, i.e., an increased rate of addition of Cd monomers which may be responsible for fast growth at the early stage of particle growth. It is well known that a slow flux of the cadmium precursor provides the possibility to grow the particles under diffusion control, which is preferable for the narrowing of the size distribution. OR arises from the depletion of precursors or monomers during the growth, which took place in the later stage of particle growth. In the hot injection technique, the nucleation and further growth of the NCs occur in separate time frame. Hot injection leads to instantaneous nucleation, quenched by fast cooling.
of the reaction mixture. Further growth of the nuclei occurs at a low temperature, such that new nucleation events do not occur. After initial Ostwald ripening defocusing (broadening in the particle size distribution) takes place. A constant supply of \( S \) ions due to slow hydrolysis of thiol compounds increases the possibility to grow the particles under diffusion control, which has been preferable for the narrowing of the particle size distribution. As is well known, the nanocrystal size can be “focused” through the addition of monomer reagents (the initial reagent solution) during the course of the reaction. The strategy was designed to overcome Ostwald ripening, or “defocusing” of the size distribution. Ostwald ripening occurs when smaller nanocrystals in the distribution dissolve and become smaller and the monomers released allow the larger nanocrystals in the solution to grow further, subsequently broadening the size distribution. When the monomer reagent is used up the critical size becomes larger than the average size and Ostwald ripening occurs. The nanocrystal size distribution can be partially recovered by adding more monomer at this time. By varying the initial monomer concentration the focusing time as well as the focused size varies. Diffusion controlled acceleration at higher temperature results both in the increase of the reaction rate and the gradual growth of forming nanocrystals due to the Oswalds ripening (OR). In aqueous route, the hydrolysis of TGA controls the Cd and S ions supply, which is responsible for surface ordering and reconstructions of CdTe NCs, which probably induced the increase in QY of CdTe QDs. Similar to metallorganic pyrolysis route, this fast crystal growth in aqueous media is dominated by the addition of monomer, which gets accelerated during the hydrothermal heating. Our results indicate that even though the nanocrystal growth in aqueous media predominantly occurs via OR, it does encompass a fast growth at the early stage. Comparing the results of hydrothermal growth at 140°C with refluxing at 100°C, it was revealed that the hydrothermal conditions affected the growth in the initial stage of growth region drastically, that is the region where the focusing of the particle size distribution took place. Hence, larger sized particles were produced with narrow PL at longer wavelengths before the onset of OR ripening.

Conclusions

CdTe nanocrystals were prepared in aqueous solution using thioglycolic acid (TGA) as stabilizing agent. Hydrothermal synthesis conditions were optimized to obtain CdTe nanocrystals with high PL intensity and narrow PL spectra. The growth mechanism of CdTe NPs has been examined. The growth rate in the initial stage of synthesis was higher in hydrothermally synthesized NPs, resulting in an increased growth in focused region.

References