Size-tuning and Optical Properties of High-quality CdSe Nanoparticles Synthesized from Cadmium Stearate

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High-quality CdSe nanoparticles were synthesized with a hot-injection method from cadmium stearate and selenium powder in the size range of 2.0 ± 0.2 to 8.6 ± 2.3 nm, corresponding to blue to red emission. The pod-shaped nanoparticles were formed at low reaction temperature, and exhibited sharp emission peak.

Semiconductor nanoparticles have generated great fundamental and technological interests in recent years. The size-dependent emission is the most attractive property of semiconductor nanoparticles. Cadmium selenide (CdSe) nanoparticles are one of the most attractive materials because of their size-dependent emission in a visible region as well as high photoluminescence quantum efficiency. This size-dependent optical property can be applied to LEDs (light-emitting diodes),[1,2] lasers,[3] nonlinear optics,[4] and biolabeling/biotagging agents.[5] For this purpose, the size control of CdSe semiconductor nanoparticles is quite important. To date, the CdSe nanoparticles have been mainly synthesized by using dimethylcadmium as a cadmium precursor,[6–8] although this material is extremely toxic, pyrophoric, unstable at room temperature, and explosive at high temperature by releasing large amount of gas. Recently, other synthetic routes for CdSe nanoparticles using alternative cadmium precursors[9–11] or single-source precursors[12] have been developed, but an addition of some organic acids or a preliminary preparation of precursors is requisite to form high-quality nanoparticles.

Here, we report a modified synthetic route toward high-quality CdSe nanoparticles using cadmium stearate, as a lower toxic, nonexplosive, and stable precursor, in place of dimethylcadmium, where the size of CdSe nanoparticles was tuned mainly by changing the reaction temperature and time. Interestingly, the pod-shaped nanoparticles were formed at low reaction temperature. The size- and shape-dependent optical properties of the CdSe nanoparticles are also presented.

A typical synthesis of CdSe nanoparticles is as follows. Cadmium stearate (0.204 g, 0.3 mmol), oleylamine (5.0 g), and trioctylphosphine oxide (TOPO, 5.0 g) were loaded into a 100 mL three-neck flask and heated at 250 °C under N_2 flow. Cadmium stearate was completely dissolved and formed an optically clear solution. At this temperature, a selenium solution comprising selenium powder (0.036 g, 0.45 mmol) dissolved in 4.0 g of tributylphosphine (TBP) or trioctylphosphine (TOP) was swiftly injected into the reaction flask with a syringe. The resulting products were purified with acetone/methanol mixed solvent. During the reaction, aliquots of the reaction mixture were taken out to investigate the process of the nucleation and growth of CdSe nanoparticles. The reaction temperatures of 300, 250, and 200 °C were chosen to examine the temperature dependence of the size and size distribution of CdSe nanoparticles when synthesized using TOP.

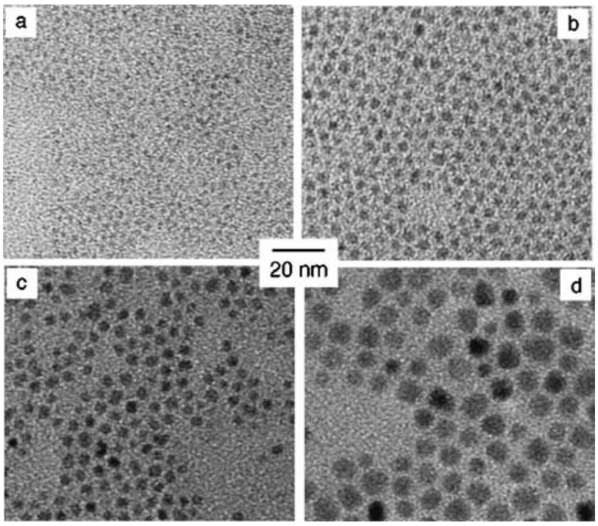

Figure 1. TEM images of (a) 2.0 ± 0.2 nm, (b) 3.8 ± 0.4 nm, (c) 4.5 ± 0.7 nm, and (d) 8.6 ± 2.3 nm CdSe nanoparticles.

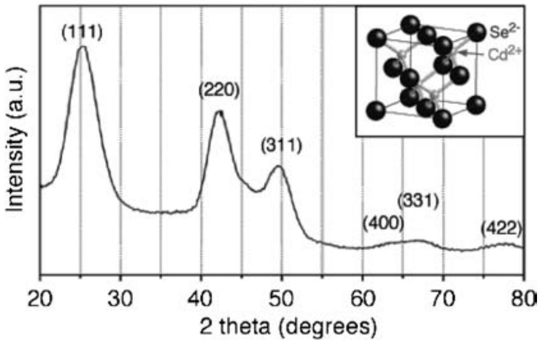

Figure 2. X-ray diffraction pattern of 3.3 ± 0.4 nm CdSe nanoparticles. The inset shows the unit cell of zincblende phase.

At first, CdSe nanoparticles were synthesized by following the above method using TBP as a solvent for selenium at 250 °C. The obtained CdSe nanoparticles are spherical and have the diameters of 2.0 ± 0.2–3.8 ± 0.4 nm in the reaction time from 10 s to 180 min. Figures 1a and 1b show the TEM images of 2.0 ± 0.2 and 3.8 ± 0.4 nm CdSe nanoparticles, indicating that these CdSe nanoparticles are monodisperse, and their size increases with the reaction time. Figure 2 presents X-ray diffraction pattern of 3.3 ± 0.4 nm CdSe nanoparticles, which demonstrates that the obtained nanoparticles are good crystallites with typical zincblende phase. Figure 3 shows the UV–vis and PL spectra of a chloroform solution of the CdSe nanoparticles. The absorption and emission peaks are tunable in the 460–

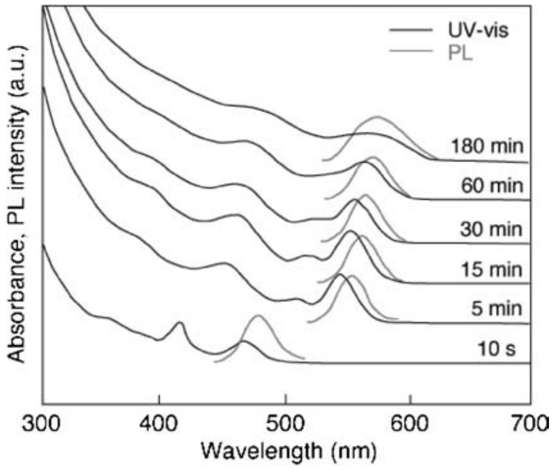

Figure 3. UV–vis and PL spectra of different sized CdSe nanoparticles synthesized in TBP/TOPO system (excitation wavelength: 350 nm).

570 nm range by the reaction time. In case that the CdSe nanoparticles were synthesized using TOP, the resulting CdSe nanoparticles have the sizes of 2.1 ± 0.2–4.5 ± 0.7 nm in the reaction time from 10 s to 180 min at 250 °C. TEM measurements indicate that these CdSe nanoparticles have narrow size distributions, and grow larger with increasing the reaction time as well (see Figure 1c). From the UV–vis and PL measurements, the absorption and emission peaks can be tuned in the 460–570 nm range by changing the reaction time. In comparison with the case of TBP, the TOP system gave the larger CdSe nanoparticles, probably because of the lower reactivity of TOPSe species due to larger steric hindrance. The reaction would follow the conventional TOP/TOPO mechanism[10] except for the preliminary formation of organic acid–Cd^{2+} complex. It might be noteworthy that the molecular size of the solvent for Se could control the nucleation rate.

Next, we have investigated an influence of the reaction temperature on the size and shape of the CdSe nanoparticles in TOP/TOPO system. At the reaction temperature of 300 °C, the CdSe nanoparticles of 2.4 ± 0.2 to 8.6 ± 2.3 nm were obtained in the reaction time from 10 s to 180 min. The UV–vis and PL measurements demonstrate that the absorption and emission peaks are tunable in the 530–660 nm range, these wavelengths corresponding to green to red emission. It seems that the particle growth follows the Ostwald ripening process rather than the precursor-consuming process because the size distribution drastically increases for larger particles showing red emission (see Figure 1d). Consequently, a series of photoluminescence from blue to red by the excitation with 365 nm UV light was obtained (see the Graphical Abstract).

Then, the CdSe nanoparticles were synthesized in TOP/TOPO system at low temperature of 200 °C. Figure 4 shows a TEM image and UV–vis and PL spectra of the resulting CdSe nanoparticles. Their shape is not sphere, but bipod, tripod, or tetrapod.[13] These pod-shaped nanoparticles display sharp emission peak (FWHM = 29 nm) with a clear Stokes shift compared with the spherical particles (FWHM = 56 nm) with the similar size (3.3 ± 0.4 nm). The PL quantum yields (QYs) of the as-synthesized spherical and pod-shaped nanoparticles are 6.3 and 9.3%, respectively.[14] These values are predictable for the nanoparticles synthesized in TOP/TOPO system without surface passivation with inorganic (e.g., ZnS) or organic (e.g., alkylamine) shell,[15] but the pod-shaped nanoparticles exhibit significantly higher PL QY than the spherical ones, the reason remaining to be determined.

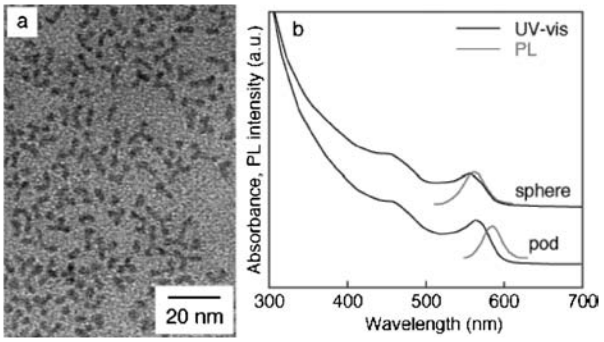

Figure 4. (a) TEM image and (b) UV–vis and PL spectra of pod-shaped CdSe nanoparticles together with 3.3 ± 0.4 nm CdSe nanoparticles.

In conclusion, we have succeeded in developing a modified synthetic method of CdSe semiconductor nanoparticles by using cadmium stearate in place of dimethylcadmium as a cadmium precursor. The size can be tuned from 2.0 ± 0.2 to 8.6 ± 2.3 nm, corresponding to blue to red emission. Now we have investigated the formation mechanism and optical properties of the pod-shaped CdSe nanoparticles as well as the solventless synthesis of CdSe nanoparticles for mass production.

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