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New Organometallic Approach to Synthesize High-quality CdSe Quantum Dots

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High-quality CdSe quantum dots have been synthesized through an organometallic method with cadmium methoxide as a cadmium precursor. Without any size sorting, the FWHM (full width at half-maximum) in PL spectra almost for all CdSe samples is less than 30 nm and only 22 nm from the best sample. The emission peaks with different particle size in toluene can be tuned from 478 to 654 nm corresponding to a color change from blue-green to red.

The size-dependent emission for II-VI semiconductor nanocrystals is an attractive property because it can be applied in many areas, such as light-emitting diode (LED),[1] Zener diodes,[2] thin-film transistors,[3] solar cells,[4] biological labeling,[5] and lasers.[6] Synthesis of high-quality semiconductor quantum dots with nearly monodisperse size has become an important topic in the field of materials chemistry in recent years[7,8] because of both fundamental and technical importance of these novel materials. Since Murray et al.[7] reported the synthesis of high-quality cadmium chalcogenides quantum dots using dimethyl cadmium ($Cd(CH_3)_2$) as a cadmium precursor, this approach for preparation of CdE (E = S, Se, and Te) has been well developed.[7–11] However, dimethyl cadmium was extremely toxic, pyrophoric, and unstable at room temperature. Furthermore, the reaction is difficult to control owing to an active $Cd(CH_3)_2$. For these reasons, Peng developed an alternative using CdO as a precursor to synthesize CdSe nanocrystals, then other cadmium sources such as $CdCO_3$, $Cd(Ac)_2$ were exploited too.[10,11] Definitely, these new routes provide green chemical approaches. However, this approach needs some assistant solvents, such as hexylphosphonic acid (HPA) or tetradecylphosphonic acid (TDPA) which is very strongly bound to the surface of CdSe nanocrystals and they are difficult to be replaced by other commonly used ligands such as tri-*n*-octylphosphine (TOP) or tri-*n*-octylphosphine oxide (TOPO). However, a good crystallinity and a narrow size distribution as well as well-confined surface passivation with organic ligands are very important for improving luminescence of semiconductor quantum dots.

In this communication, high-quality CdSe quantum dots have been synthesized through an organometallic method with cadmium alkoxide such as ($Cd(OCH_3)_2$) served as a precursor. Compared with traditional $Cd(CH_3)_2$, $Cd(OCH_3)_2$ is low toxic, non-pyrophoric, inexplosive, and more stable to oxygen in the air. Moreover, it can be usually carried out and even weighted accurately in the air. It should be mentioned that many kinds of ligands can be chelated directly, such as TOPO and hexadecylamine (HDA) without other assistant solvent.[10] We noticed that Boyle et al. synthesized CdSe nanorods with other complicated alternative $Cd(OR)(NR_2)$ and $Cd(OR)_2$ as cadmium precursors.[12]

A typical experiment is as follows. A mixture of $Cd(OCH_3)_2$ (0.052 g, 0.3 mmol), HDA (0.5 g), and TOPO (5.0 g) was heated to 250 °C. A solution of selenium (0.023 g, 0.3 mmol) in TOP (1.5 mL) was quickly injected into the above-mentioned hot solution, and then the mixture was allowed to cool to 230 °C for the growth of CdSe quantum dots. The reaction was carried out under nitrogen atmosphere. A little sample was taken at different time interval, and then UV–vis and PL spectra were recorded. Finally, the reaction was terminated by adding cold toluene or removing the vessel from the oven quickly.

The left of Figure 1 is a temporal evolution of UV–visible spectra and photoluminescence spectra of CdSe samples with the reaction time. Here, Cd/Se = 1:1 in molar ratio, both TOPO (4.5 g) and HDA (0.5 g) as ligands, reaction temperature at 280 °C. An obvious red-shift can be observed from 533 to 611 nm when the time varied from 2 to 120 min. This phenomenon is similar to other literatures reported before.[7] All the FWHMs are less than 30 nm, which indicates a narrow size distribution during a long time. It provides a broad reaction window of time to prepare CdSe quantum dots. The growth kinetics of quantum dots exhibits the longer "focusing" time about "focusing of size distribution" regime than $Cd(CH_3)_2$ as a precursor, which is useful to get reproducible and stable monodisperse nanocrystals especially in the ratio of cadmium precursors less than 1.1:1 (Cd/Se).[13] However, we still get high-quality CdSe quantum dots at different molar ratio of Cd/Se. A series of samples with different size were prepared and their PL spectra are displayed on the right of Figure 1. By adjusting the reaction temperature from 180 to 360 °C, the emission peak is tunable from 478 to 654 nm (478, 509, 538, 577, 613, and 654 nm from a to f, respectively) corresponding to a color change from blue-green to red with increasing the diameter of the CdSe quantum dots. The

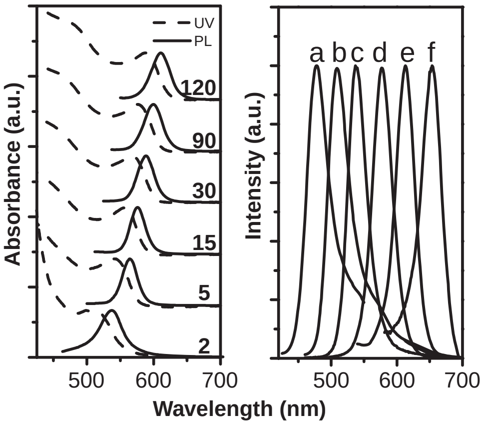

Figure 1. Temporal evolution of UV–vis absorption (dash) and PL (solid) spectra of TOPO–HDA capped CdSe nanocrystals (left) and PL spectra of different ligand-capped CdSe nanocrystals with different particle size (right).

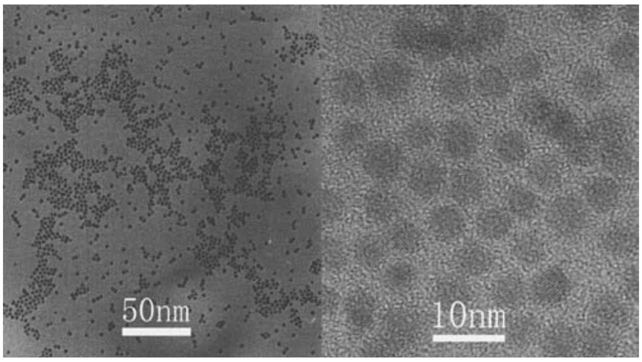

Figure 2. TEM and HRTEM images of TOPO–HDA-capped CdSe nanocrystals.

detailed conditions were described in the reference.[14] In order to get good samples, the initial molar ratio of Cd/Se was varied from 1:1 to 1:5, followed different kinds of ligands and different weight ratio of them in the experiments. Reaction time and temperature are two significant factors for as-synthesized quantum dots. It should be noticed that all shoulders in PL spectra are located at around 580 nm no matter where their main peaks are located. Moreover, no shoulder can be found when the main peak locates at around 580 nm. We considered that this reaction system facilitates to produce some nanoparticles whose emission is at around 580 nm and small amount of such nanoparitlces still exist in samples at different conditions. The small amount of those nanoparticles only results in a shoulder in PL spectra. Thus, it is reasonable that two major size distributions of the nanoparticles in the samples lead to a shoulder in PL spectra. On the other hand, those traps on the surface also gave rise to the emission shoulders as reported in literature.[15] But we noticed that the trap emission is usually located at the longer wavelength in respect to main PL peak. Most PL QY of these samples is in the range of 10–30% while some dyes as references.[16] Possibly, the relatively high QY comes from that of cadmium alkoxide more than dimethyl cadmium, since the former can be readily dispersed in the solution before injection of a stock of Se source. The nuclei are formed at primary stage in homogeneous cadmium system and the monomer of precursors keeps steady for a long time.

Transmission electron microscopy (TEM) image on the left of Figure 2 indicates that as-prepared CdSe quantum dots have very narrow size distribution in entire size range with a standard deviation of 5–15% without any size sorting. The diameter of CdSe quantum dots is about 4.5 nm and it is in a good accordance with the result of 4.1 nm calculated from the first absorption peak in UV–vis spectra.[17] High resolution transmission electron microscopy (HRTEM) image (right one in Figure 2) indicates a single crystal phase and a typical hexagonal structure, which is also confirmed by X-ray powder diffraction pattern (XRD). The lattice parameters were calculated from XRD data to be $a = 4.30$ Å, $c = 7.13$ Å which were in good agreement with the reported date (Joint Committee on Powder Diffraction Standards Card No. 080459). The surface composition of the CdSe quantum dots was analyzed by X-ray photoelectron spectra (XPS). The molar ratio calculated from peak areas (Cd_{3d} and Se_{3d}) as described by Katari[18] is 0.99/1 for Cd/Se. The XPS spectra further proved a good purity of the resulting samples.

In summary, the new organometallic approach provides a simple, low-toxic, inexplosive route to synthesize high-quality CdSe quantum dots with quantum yield of 10–30%. It also develops a feasible, reproducible approach to synthesize II-VI semiconductor nanocrystals at a large scale in the future.

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