Phosphine-free Fabrication of CdSe Quantum Dots with Good Thermal Stability and Promising Application in Multiplexed Bioassay

Bin Xing, Wan-wan Li, Hong-jing Dou, Peng-fei Zhang, and Kang Sun
State Key Lab of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 1954 Huashan Road, Shanghai 200030, P. R. China

(Received May 29, 2007; CL-070578; E-mail: ksun@sjtu.edu.cn)

High-quality cadmium selenide (CdSe) quantum dots (QDs) with good thermal stability were prepared by using liquid paraffin as a solvent and oleic acid as a ligand under relative low temperatures. Moreover, the as-prepared CdSe quantum dots were embedded into the porous polystyrene (PS) beads to fabricate optically encoded beads, which suggests their promising application in multiplexed bioassays.

Owing to the increasing applications of the QDs, the demand for high-quality (in terms of monodispersity, size tunability, and high luminescence quantum yield) QDs is growing enormously. CdSe nanocrystal is one of the most attractive QDs because of its size-dependent emission in the visible region and high photoluminescence (PL) quantum yield. This size-dependent optical property can be applied to fluorescent labelling,[1] photovoltaic cell,[2] light-emitting devices,[3] and lasers.[4] The use of solvents with high boiling temperatures[5] has made the fabrication of high-quality II–VI QDs possible for more than a decade. But the typical methods used must proceed under very strict conditions without oxide and water because of the as-used unstable organometallic precursors. In the past few years, QDs fabrication in organics without using the organometallic precursors has been studied,[6,7] but expensive, toxic phosphines were still used as coordinating solvents for this procedure, which often limits the production of QDs in organics to milligram quantities. Therefore, investigations on fabrication of CdSe quantum dots in phosphine-free organics have become more and more important and attractive. Recently, it has been shown that it is indeed possible to dissolve Se at high temperatures in octadecene[8,9] and other long-chain alkanes,[10,11] which makes the phosphine-free fabrication of CdSe quantum dots possible.

In this letter, we prepared high-quality CdSe QDs by using liquid paraffin as a solvent and oleic acid as a ligand at relatively mild temperatures (200–240 °C), without the need for the air-sensitive, toxic and expensive chemical trioctylphosphine (TOP). The as-prepared CdSe QDs are highly monodisperse, and have good optical properties. Moreover, temperature-dependent optical stability of CdSe quantum dots, which is an important property for their bio-applications, was investigated, and the as-prepared CdSe quantum dots were embedded into the hydrophilic porous PS beads for their potential application in multiplexed bioassays.

A typical experiment is as follows: 2 mmol of CdO was dissolved in mixed solvent of 4 mmol of oleic acid (OA) and 8.7 mL of liquid paraffin in a three-neck flask at 150 °C for the preparation of Cd precursor solution, meanwhile 0.4 mmol of Se was dissolved in 20 mL of liquid paraffin at 220 °C (above 217 °C, which is the melting temperature of Se) under vigorous stirring. Then 4 mL of solution containing 0.8 mmol Cd precursor was quickly injected into the Se precursor solution under vigorous stirring, and the reaction temperature was kept at 200 °C. Aliquots were taken at different time intervals and immediately put into *n*-hexane to avoid further growth, and then the UV–vis and PL spectra were recorded.

Figure 1a is the temporal evolution of UV–vis and PL spectra of the as-prepared CdSe QDs with the reaction time. Here, OA:Cd:Se equals to 2:1:0.5 in molar ratio. It can be observed that the small CdSe QDs with an absorption peak at 450 nm would be formed in 0.3 min and then developed to bigger QDs with an absorption peak at 542 nm in 5 min, finally the absorbance peak of the QDs reached 546 nm in 90 min. Thus, as the aging process proceeded from 5 to 90 min, the size of the QDs remained almost unchanged with the absorption peak at about 542 nm, and similar results were also obtained when the reaction temperature were changed from 200 to 240 °C and the Cd precursor concentration was 18.2 to 57.2 mM. It is believed that the capping ligand oleic acid not only determined the rate of growth but also played a major role in determining the number and size of the nuclei formed during injection.[12] By investigating in detail the effect of changing the concentration of the precursors, reaction temperature, and the quantity of the ligand, CdSe QDs with high PL quantum yield (up to 50%), broad emission spectral ranging from 470 to 610 nm (showed in Figure 1b) and narrow FWHM (full width at half-maximum) between 30–45 nm can be obtained. When 257 mg of CdO powder and 32 mg of Se powder were used in the preparation, we can obtain 77 mg CdSe QDs.

TEM image of Figure 2a indicates that the as-prepared CdSe

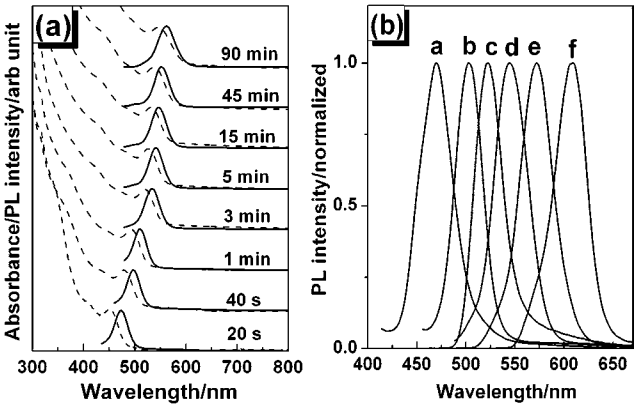

Figure 1. (a) Temporal evolution of UV–vis absorbance (dash) and PL (solid) spectra of OA-capped CdSe QDs prepared at 200 °C. (b) PL spectra of CdSe QDs with increasing size prepared in liquid paraffin under different conditions. The FWHM of the PL spectra from *a* to *f* are 41, 33, 33.5, 40, 39, and 39 nm, respectively.

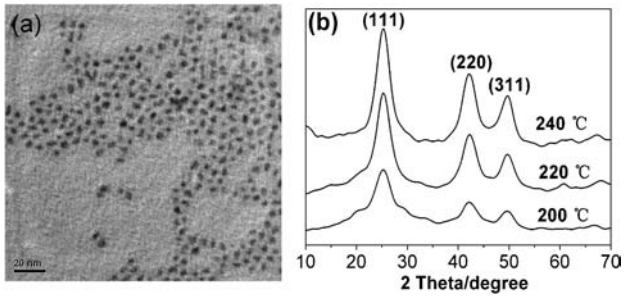

Figure 2. (a) Transmission electron micrograph of the as-prepared CdSe QDs. (b) X-ray powder diffraction patterns of CdSe QDs prepared at different temperatures.

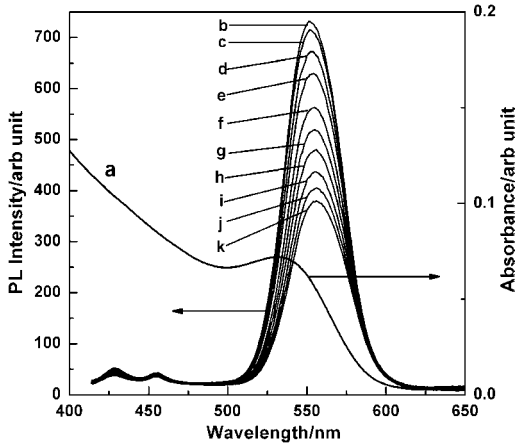

Figure 3. Spectra of temperature-dependent CdSe QDs. (a) absorption spectrum at 12 °C. (b)–(k) PL spectrum at: 12, 15, 20, 25, 30, 35, 40, 45, 50, and 55 °C.

QDs (the absorption peak is at 575 nm) have narrow size distribution with a deviation less than 15% but without any size sorting. The diameter of CdSe QDs is about 4.0 nm, which is in a good accordance with the result of 3.7 nm calculated from the first absorption peak in UV–vis spectra. The X-ray powder diffraction pattern (XRD) (Figure 2b) shows that the CdSe QDs obtained at different temperatures (200–240 °C) have a single crystal phase and a typical zinc-blende structure, which may result from their low growth temperature.

Figure 3 shows the absorption and fluorescence spectra of as-prepared CdSe QDs at different temperatures from 12 to 55 °C (below the boiling point of the solvent). As shown, with temperature increasing from 12 to 55 °C, the PL intensity declined by about 50% without any change of the absorption spectra, and this intensity change is not reversible. The decline of PL intensity may result from nonradiative emission of carriers that were in deep trap sites as temperature increased.[13] However, the declining PL intensity degree of as-prepared CdSe QDs is less than that of the water-soluble CdSe@ZnS core–shell QDs, whose PL intensity declined by nearly 90% when the temperature increases from 12 to 55 °C.[14] Therefore, CdSe QDs prepared here show better thermal stability than that of water-soluble CdSe@ZnS core–shell QDs.

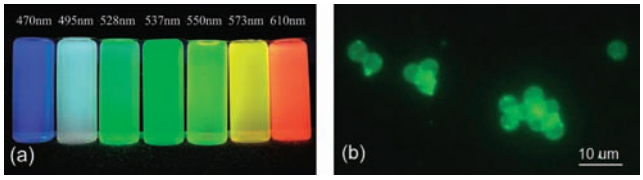

Figure 4. (a) Seven distinguish emission colors of differently sized CdSe QDs in *n*-hexane. (b) Fluorescence micrograph of PS beads embedded with CdSe QDs emitting at 537 nm.

Figure 4a shows the emission colors of differently sized CdSe QDs in *n*-hexane with the low concentration of 0.2 mM under the irradiation of a handheld UV lamp at the wavelength of 365 nm. Due to the high PL quantum yield of the as-prepared CdSe QDs, the obvious emission colors could be observed. In addition, optically encoded beads have been successfully prepared by using porous PS beads and the as-prepared CdSe QDs according to the literature procedures[15] (showed in Figure 4b), which suggests the promising application in multiplexed bioassays.

In summary, here, we have successfully fabricated high quality CdSe QDs by using liquid paraffin and oleic acid instead of TOPO and TOP as solvent and ligand at relative low temperatures. The route enables us to obtain CdSe QDs with high PL quantum yield (up to 50%), broad emission spectral range (470–610 nm), narrow FWHM (30–45 nm), and good thermal stability. Moreover, the as-prepared CdSe quantum dots were embedded into the porous PS beads to fabricate optically encoded beads, which suggests the promising application in multiplexed bioassays.

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Published on the web (Advance View) August 11, 2007; doi:10.1246/cl.2007.1144