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Aqueous Synthesis of Highly Luminescent Amorphous CdSe Quantum Dots at Low Temperature

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Highly defect-related luminescent aqueous CdSe quantum dots (QDs) were successfully synthesized by using sulfanylsuccinic acid (SSA) as capping ligands at low temperature by water bath. The photoluminescence quantum yields (PL QYs) of as-prepared CdSe QDs could reach up to 30%. XRD and HRTEM characterization suggest an amorphous state.

Semiconductor quantum dots (QDs) have been of great interest for both fundamental research and technical applications due to the unique physical, chemical, and optical properties.[1] CdSe QDs are unanimously one of the most widely researched materials because of the tunable photoluminescence (PL) in the visible region and the progress in their preparation.[2,3] Aqueous QDs with high PL have drawn much attention in fundamental research and technical applications attributing to their properties.[4] Recently, the synthesis of CdSe QDs in water by using sulfanyl acids as capping ligands has been developed as an alternative choice for using trioctylphosphine oxide (TOPO)[5–7] in organic solvents. These sulfanyl acids have stronger affinity to the surface of QDs than TOPO, and the carboxyl groups can contribute to the electrostatic stabilization of the colloidal QDs as well as to the further surface modification for various applications. Besides simple preparation and excellent reproducibility, the aqueous synthesis of CdSe QDs thus has distinct advantages over the organic solvent approach. In this study, a facile strategy had been presented for the synthesis of highly luminescent and water-soluble CdSe QDs using sulfanylsuccinic acid (SSA) as stabilizer. Without any post-treatments, the sizes of the particles were tunable between 2 and 3 nm depending on the reaction time.

In a typical synthesis, 4 mL of cadmium chloride solution ($CdCl_2$, 40 mmol L^{-1}) was diluted to 46 mL with ultrapure water, and then 100 mg trisodium citrate dihydrate, 4 mL of sodium selenite solution (Na_2SeO_3, 10 mmol L^{-1}), sulfanylsuccinic acid (SSA), and sodium borohydride ($NaBH_4$) were added in sequence under continuous magnetic stirring. The optimal molar ratio was $Cd^{2+}/Se = 6/1$. The molar ratio of Cd^{2+}/SSA was 1/2.5. The crude solution was then heated by water bath to 40–50 °C under continuous magnetic stirring, aliquots were taken out at regular time intervals for UV–vis absorption and PL spectra measurement. UV–vis absorption spectra were collected using a TU1901 UV–vis spectrophotometer (Beijing, China). Photoluminescence (PL) spectra were recorded with a WGY-10 spectrofluorimeter (Tianjin, China). High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM 2100 (JEOL, Japan) electron microscope operating at 200 kV. X-ray powder diffraction (XRD) spectra were recorded on a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Rhodamine 6G (laser grade, Lambda Physik) in ethanol was used as a standard for determining the PL QYs of the CdSe QDs.

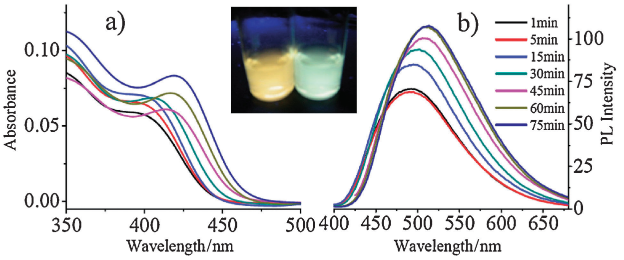

Figure 1. Time-dependent evolution of a) UV–vis absorption and b) PL spectra of CdSe QDs prepared at 40 °C by water bath. The insert a sample photo at reaction time of 10 min (right) and 60 min (left).

Figure 1a illustrated the temporal evolution of the absorption and corresponding PL spectra of CdSe QDs prepared at 40 °C for different heating time by water bath. PL irradiated under a handheld ultraviolet lamp is illustrated as an insert. The clearly resolved absorption maximum of the first exciton peak of CdSe QDs synthesized only for 1 min appeared at 393 nm, which continuously shifted to 412 nm with increased heating time. Then it remained unchanged despite prolonging heating time from 60 to 75 min at the set reaction temperature. The sharp absorption spectra suggested a narrow size distribution and the monodispersity of the CdSe QDs.[8] The size of CdSe QDs was estimated from the first exciton absorption maximum using an empirical formula according to Peng's group,[9] and the results showed that the diameters of the CdSe QDs were around 2.0 nm.

The PL emission showed the same tendency. PL spectra in Figure 1b were obviously broader than the corresponding UV–vis absorption spectra and had long tails at long wavelength. The optical data of the as-prepared CdSe QDs are listed in Table S1. The Stokes shifts between UV–vis and PL peaks were near 100 nm, which was bigger than those CdSe QDs prepared through an organometallic route.[10] The PL QYs could match a maximum (31%) after heating for 45 min and then declined as heating time prolonged. The full width at half maximum (FWHM) of PL spectra were between 117 and 123 nm during the whole growth process of the CdSe QDs. The small increment further confirmed the narrow size distribution and high monodispersity.

Figure 2 showed the typical HRTEM images of CdSe QDs prepared at 40 °C, which further displayed the monodispersity. The average size estimated from the HRTEM was 2.0–3.0 nm, which was consistent with the absorption spectra. However, the diffraction stripes were not found in the HRTEM image. The HRTEM images of CdSe QDs showed typical diffraction stripes prepared at 80 and 120 °C are demonstrated in Figure S1.[12] The precursor solution of the CdSe QDs was stored in a refrigerator (4–5 °C) for 90 days and then taken out for UV–vis and PL

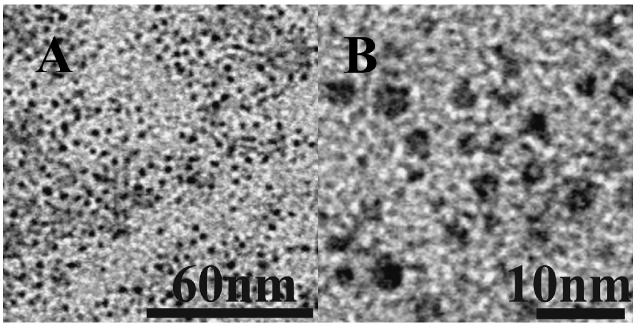

Figure 2. HRTEM images of CdSe QDs prepared at 40 °C by water bath.

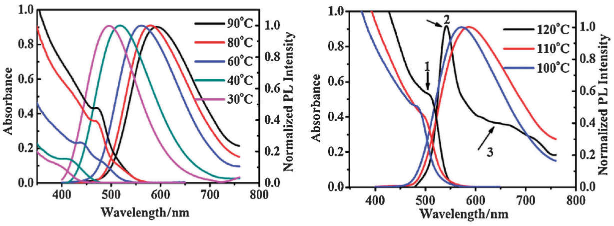

Figure 3. UV–vis and PL spectra of CdSe QDs obtained under microwave irradiation.

measurement as shown in Figure S2.[12] The absorption spectrum showed obvious exciton peaks, and the Stokes shift was almost the same as those prepared at 40 °C. As we all know, QDs had most of their constituent atoms exposed to surfaces resulting in high surface-to-volume ratio. Fast growth of particles stablized by short chain ligands would bring on vacancies and/or missed coordination of positive and negative ions. Herein, the PL of CdSe QDs should originate from defect-related emission[11] corresponding to deep trap states.

Further experiments were carried out under microwave irradiation at 30–120 °C to verify the defect-related emission of the CdSe QDs, as illustrated in Figure 3. The optical data are summarized in Table S2. Most of the corresponding PL emission possessed broad FWHMs, large Stokes shifts and long tails at long wavelength side when the irradiation temperature was lower than 110 °C. When the irradiation temperature increased to 120 °C, the PL emission showed both typical exciton and defect-related emission as indicated by arrow 2 and 3, respectively. The Stokes shift between absorption and emission was 33 nm, which was in sharp contrast to those CdSe QDs prepared at 30–110 °C, where the Stokes shifts were 88–120 nm. CdSe QDs almost completely lost their photoluminescence as the temperature increased up to 80 °C, as listed in Figure S3.[12] We can infer from the above discussion that the high fluorescent emission of the CdSe QDs were defect-related, which was similar to the tendency discussed in ref. 11e.

The XRD patterns of the CdSe QDs are illustrated in Figure 4. The CdSe QDs prepared at low temperature (30–60 °C, via a water-bath reaction or under microwave irradiation) had no obvious diffraction peaks. The distinct diffraction peaks of (111) and (220) appeared when the reaction temperature is above 80 °C (via a water-bath reaction or under microwave irradiation). The apparent diffraction peaks corresponding to (111), (220), and (311) appeared when the reaction temperature further increased to 120 °C (under microwave irradiation). At the same time the appearance of diffraction peaks went with the decrease of PL QYs, as shown in Figure S3.[12] All these results confirmed the defect-related emission of CdSe QDs.

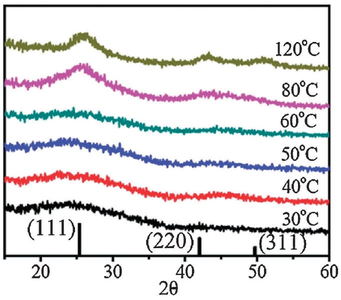

Figure 4. XRD patterns of CdSe QDs prepared under microwave irradiation.

In summary, highly luminescent CdSe QDs were synthesized using SSA as stabilizer in aqueous medium. The sizes of CdSe QDs were 2.0–3.0 nm. The as-prepared CdSe QDs with high PL QYs would find potential applications in biochemistry and chemical probes.

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