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RESEARCH ARTICLE

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Synthesis and characterization of monodisperse CdSe quantum dots in different organic solvents

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Abstract Nearly monodisperse CdSe quantum dots (QDs) have been prepared by a soft solution approach using air-stable reagents in different organic solvents. This scheme is a supplement to the conventional thermal decomposition of organometallic compounds at higher temperatures. CdSe nanocrystals of different sizes could be obtained by simply changing the solvent. This method is reproducible and simple and thus can be readily scaled up for industrial production. The reaction process was monitored by the temporal evolution of the UV-Vis absorption and room temperature photoluminensce spectra. The structures of the CdSe quantum dots were determined by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The phase-transfer of oleic acid–stabilized CdSe nanocrystals into PBS buffer solutions was also studied for their potentials in biological applications.

Keywords quantum dots, semiconductor, organic solvents

In the past decade, colloidal II-VI semiconductor nanocrystals, often referred to as quantum dots or QDs, have attracted scientists' intensive attention in the preparation methods, fundamental studies, and biomedical applications [1–4]. QDs, whose size falls in the range of 1~10 nm, have been made to be the ideal fluorescent labels for the wavelength-luminance multichannel transmission system, because of their unique optical properties. Because of the strong band gap luminescence tunable by size as a result of the quantum confinement effect, nanosized semiconductor clusters have marked advantages over traditional fluorescent dyes. For example, they are more stable in photooxidation than organic dyes, have almost continuous excitation spectra above the threshold of absorption together with a strong, narrow, and symmetric emission band peak whose position depends on the particle size, and allow simultaneous excitation of many colors by a single narrow-band excitation resource [5–10]. The monodisperse QDs with a certain emission wavelength can be obtained through strict growth control; hence, QDs' applications in fluorescent labels for biology, light-emitting diodes, photovoltaics, and biomolecular imaging are currently being pursued [11–14].

Research on the preparation of the QDs concentrates on the syntheses and characterizations of the monodisperse QDs, especially the studies of nucleation and growth mechanisms as well as the improvement of the luminescence quantum yields (QY). The most popular route to synthesize CdSe quantum dots is the method using organometallic compounds [11,15]: dimethylcadmium ($(CH_3)_2Cd$) reacts with a selenium reagent in the presence of trioctylphosphine oxide (TOPO) surfactant at a high temperature (300°C). Careful control of reaction conditions produces CdSe quantum dots that are quite homogeneous in size (<5% standard deviation in diameter for a given batch) and tunable in size from 2.0 to 8.0 nm. However, $(CH_3)_2Cd$ is extremely toxic, pyrophoric, unstable at room temperature, and explosive at elevated temperatures by releasing large amounts of gas. Because of these reasons, the $(CH_3)_2Cd$-related schemes require very restricted equipments and conditions and are not suitable for large-scale synthesis. In a recent development, Peng and coworkers [16, 17] reported the use of less toxic and reactive cadmium oxide (CdO) complexed to hexylphosphonic acid (HPA) or tetradecylphosphonic acid (TDPA), as an alternative to $(CH_3)_2Cd$, in TOPO syntheses of CdE (E = S, Se, Te).

Here we chose different organic reagents as reaction

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media and low-toxic, air-stable inorganic reagents as precursors to synthesize QDs at low temperatures. Meanwhile, research on the phase-transfer to the aqueous solution of the as-prepared QDs was done to explore the possible applications as biolabels.

1 Experimental

1.1 Materials

Cadmium acetate, cadmium chloride, selenium (99.5%), N,N-dimethylformamide (DMF), diphenyl ether (PE), N-methylpyrrolidone (NMP), methanol, and oleic acid (OA, 90%) were purchased from China National Pharmaceutical Group Corporation. Trioctylphosphine was purchased from Aldrich and thioglycollic acid (TGA) was obtained from ACROS. All chemicals were analytical grade and used directly without further purification.

1.2 Synthesis of CdSe QDs

In a typical synthesis, cadmium acetate and oleic acid (with certain molar ratio) were dissolved in a selected organic solvent under vigorous stirring, and the solution was refrigerated after stirring for 30 min to obtain precursor A. Some selenium powders (Cd^{2+}/Se^{2-}=1:2, molar ratio) were dissolved in TOP under sonication to gain precursor B. Precursor A and precursor B were fully mixed to produce stock C. Then 10 mL of an organic reagent was added into a 150 mL three-necked flask as the reaction solvent and heated to 140°C; stock C was quickly added to the mixture under vigorous stirring. According to the desired size of the QDs, the reaction time was adjusted from 5 min to 60 min, and then the reaction was terminated by rapid cooling while stirring. The resulting solution was precipitated by adding double volume of methanol and centrifugated to obtain a solid product.

The product was dispersed and stored in organic solvents such as *n*-hexane, chloroform, and toluene, and solutions with different colors from yellow to deep brown were gained due to different sizes of the QDs. Different reaction solvents with different molecular structures including DMF, NMP, and PE were chosen to observe the influence on the properties of the QDs.

The different CdSe QDs stock solutions previously prepared were added to the aqueous TGA solution, and the mixture was allowed to react for 8 h under room temperature, transferring the QDs fully into the water phase to form the final hydrosol product.

1.3 Optical characterizations

The ultraviolet-visible (UV-Vis) spectra were measured in a 1 cm quartz cuvette with a Unicam-UV 300 spectrophotometer in air at room temperature. The photoluminescence (PL) spectra were measured in 1cm quartz in air at room temperature using a PerkinElmer LS 55 spectrofluorimeter.

1.4 X-ray powder diffraction

XRD were recorded on a Philips X-ray diffractometer using Cu Kα radiation (λ = 0.1542 nm) operated at 50 kV and 100 mA. The experiments were performed in the range of the diffraction angle of 2θ =10°–80°. Specimens were prepared by spreading a thin layer of precipitated nanocrystals onto a (1 0 0) silicon wafer.

1.5 Transmission electron microscopic

Transmission electron microscopic analysis was performed with a Hitachi 600 microscope operating at 120 kV. Samples were prepared by drying a drop of the dilute solutions of nanocrystals on 300-mesh carbon-coated copper grids and allowed to dry completely at room temperature. Approximately 200 nanoparticles from each sample were measured manually for size distribution.

2 Results and discussion

2.1 Optical properties of CdSe QDs

UV-Vis spectrum is a basic and widely used approach to detect the energy gap structures and other related properties of semiconductors. In the ultraviolet-visible wave range, the transition of free electrons from valence band to conduction band causes a strong, wide absorption band range. For the semiconductors, CdSe QDs have an obvious absorption in the ultraviolet-visible wave range, and the formation process of the CdSe can be identified from both the color change as well as the UV-Vis and PL spectra of the solution.

As the reaction progressed, the solution was observed to be from colorless to transparent yellow to light brown and then red brown, which directly indicated the formation of different-sized CdSe nanocrystals. Meanwhile, the velocities of the color change were different in different organic solvents, which showed that the sizes and the formation rates of the as-prepared nanocrystals were different.

Figure 1 shows the absorption and photoluminescence spectra of CdSe nanocrystals grown in different solvents with the same reaction conditions (reaction molar ratio, temperature, etc.). In different reaction solvents, both absorption and emission spectra of as-prepared CdSe QDs were observed to have obviously different displacements at the same reaction time. With PE as the solvent, while the reaction time was 10 min, the absorption maximum was 478 nm and the emission maximum was 502 nm and while the reaction time was 60 min, the absorption maximum was 506 nm and the emission maximum was 520 nm. On the other hand, with NMP as the solvent, while the reaction time was

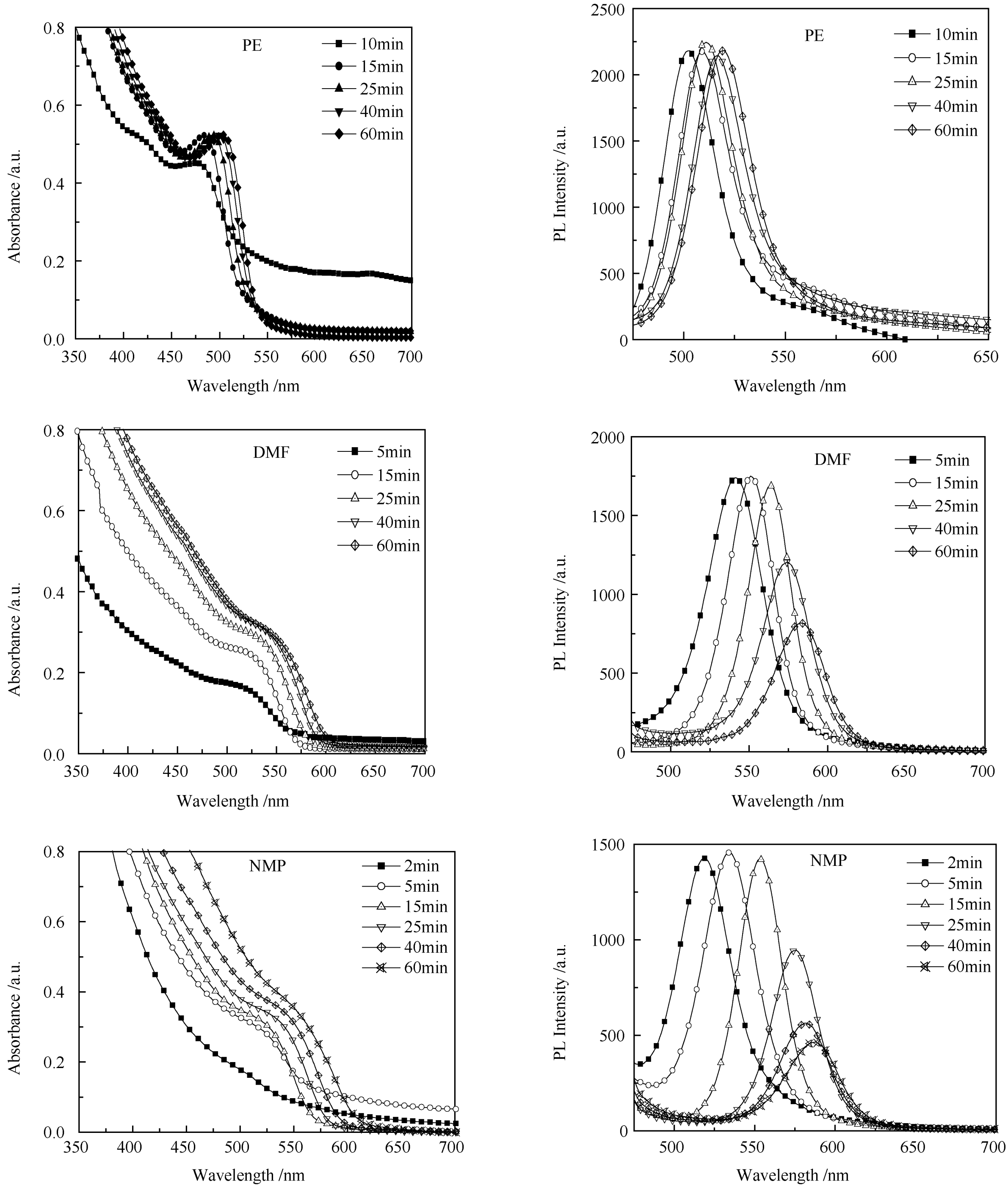

Fig. 1 Temporal evolution of UV-Vis and PL spectra of the CdSe quantum dots prepared in different organic solvents

5 min, the absorption maximum was 516 nm and the emission maximum was 533 nm and while the reaction time was 60 min, the absorption maximum was 556 nm and the emission maximum was 588 nm. During the whole reaction process, the growth of the particles was clearly evidenced by the shifts of both absorption and emission spectra to longer wavelengths because of the quantum confinement effect. The width of the absorption band reflected the size distributions of the nanocrystals in the crude solutions. The sharp absorption features suggested highly monodisperse samples. Rather narrow PL peaks of CdSe nanocrystals (FWHM 35–45 nm) corresponded to a particle size distribution of about 10%, and high quantum yields and narrow emission line widths indicated growth of crystallites with few electronic defect sites.

It can be deduced that both the polarity of the solvent and the interaction between the solvent and the nanocrystals have an influence on the size and the optical properties of

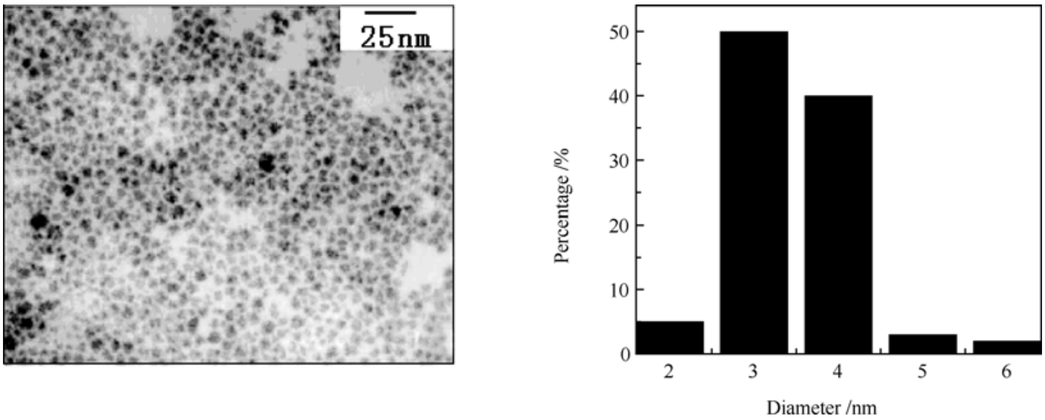

Fig. 2 TEM image of a sample of CdSe quantum dots, and the corresponding size distribution histogram

the nanoparticles. Different organic reagents can be selected as reaction solvents to obtain the desired nanocrystals of certain sizes according to the application conditions.

Both the colors and the purity of colors of the nanocrystals strongly depend on the sizes, shapes, and size distributions of the nanocrystals [18]. Figure 1 shows that in the reaction process, the size of the CdSe nanocrystals increases and the conduction band energy decreases; thus, the color of the emission light varies continuously (obvious red shift). No matter which solvent is chosen, the CdSe QDs synthesized have a narrow and strong band edge PL emission and a FWHM of about 35–40 nm, which indicate an excellent size distribution (~10%)[19] as well as a good PL color purity.

Different solvents have different properties including polarity, boiling point, and functional group; hence, under the same reaction condition, the differences of the surface interaction and the intensity of the interaction between the solvents and the nanocrystals are the main factors causing the formation of nanocrystals of different sizes. On the other hand, the surface state of the nanocrystals is a main factor affecting their optical properties. Furthermore, the interactions between the solvents and the OA, which functions as the stabilizer, have some differences for different solvents. OA, a long-chain fatty acid, exhibits the stabilization and modification functions through the chelation between the carboxyl and the surface of the nanocrystals as well as the steric effect of the long aliphatic chain. The differences of the extensibility and the conformation caused by the influence of solvents also lead to the differences in the adsorption and desorption rates on the surfaces of the nanocrystals in different solvents, causing the differences of the sizes and properties of the nanocrystals.

2.2 TEM analysis

The diameter and size distribution of the CdSe nanocrystals synthesized in this work were also determined by TEM. A representative example for a sample of CdSe quantum dots grown in NMP for 60 min is presented in Fig. 2. The nanocrystals were dispersed well and no aggregation was detected. The mean particle diameter is 3 nm and the size distribution is about 10%, which was consistent with the result estimated from the UV-Vis and PL spectra.

2.3 XRD analysis

The crystallinity of the derivatized particles was determined by X-ray diffraction. The sample was prepared in DMF with a reaction time of 60 min. Typical XRD pattern is shown in Fig. 3. Three distinct diffraction peaks were observed at 2θ values of 25.5°, 42.4°, and 50.0°, respectively, corresponding to the (1 1 1), (2 2 0), and (3 1 1) crystalline planes of cubic CdSe (JCPDS No. 19–191). The broad nature of the XRD peaks could be attributed to the nanocrystalline nature of CdSe particles. The average particle size of the CdSe calculated from Debye–Sherrer formula according to the FWHM of the XRD peaks was about 3 nm, which was consistent with the statistical result from the TEM results.

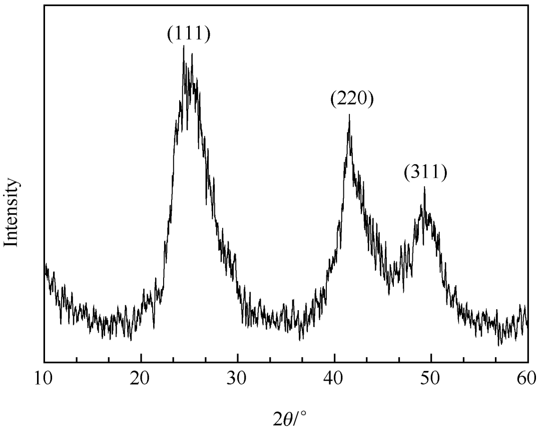

Fig. 3 XRD pattern of the CdSe quantum dots (the same sample as TEM image)

2.4 Phase-transfer analysis

The biological applications such as biolabels and bioprobes require excellent water dispersibility and bioaffinity [20], but the QDs synthesized in organic solvents are always hydrophobic (lipophilic). Generally, water-dispersible nanocrystals can be directly synthesized in aqueous solution, or can be obtained by surface modification of the nanocrystals using different surfactants. TGA is selected as the surfactant for two main reasons: stable, water-dispersible TGA-modified QDs can be obtained; and the bare carboxyls of TGA on the surfaces of the nanocrystals offer special sites for further reactions and conjugations. Thus, this process makes the QDs novel materials and promising biolables of target biomolecules and cells.

Figure 4 shows the pictures of the state of CdSe QDs before and after the phase-transfer, respectively. The pictures clearly indicate that TGA can perform the phase-transfer of the oleic acid–stabilized CdSe QDs quite well. Phosphate-buffered saline (PBS, pH=7.4) widely used in bioanalyses was chosen as the redisperse medium, in which CdSe QDs can be stably dispersed for months without any obvious changes.

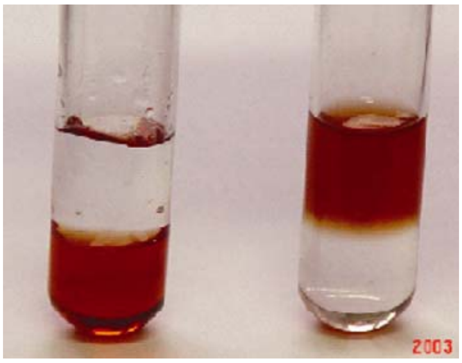

Fig. 4 Photographs of a two phase-mixture of CdSe quantum dots before and after phase-transfer

Figure 5 shows the UV-Vis and PL spectra of CdSe QDs before and after phase-transfer. No clear shifts are observed on the absorption spectra (just 1～2nm red shift), which demonstrates that no obvious change happens to the particle diameter. However, after phase-transfer, the PL spectra show a visible red shift (from 581 to 587nm) and a strong intensity decrease, which illuminates the surface states of the nanocrystals and have a crucial effect on the PL properties.

3 Conclusion

Nearly monodisperse CdSe quantum dots have been prepared using low-cost, low-toxic, air-stable inorganic reagents as precursors at low temperatures. This scheme is a supplement to the conventional organometallic approach, also regarded as an environment-preferred method. A series of CdSe nanocrystals of different sizes (502 nm~588 nm) can be obtained by simply changing the reaction solvent. The surface modification of the QDs via water-soluble TGA is a convenient approach to realize the phase-transfer of CdSe nanocrystals from organic solvent to aqueous solution. This simple method explores the possible application of the QDs in the fields of bioconjugations and biolables.

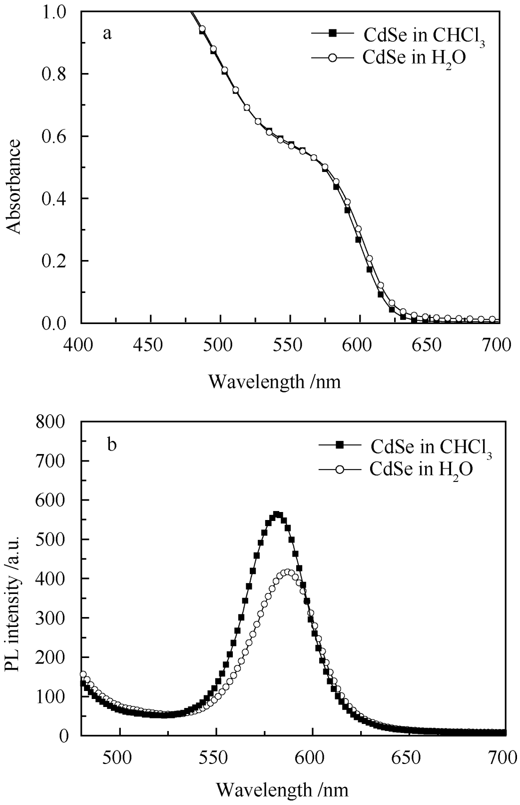

Fig. 5 UV-Vis (a) and PL (b) spectra of CdSe quantum dots capped with OA in $CHCl_3$ and that capped with TGA in PBS

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