

Time-resolved photoluminescent spectra of CdSe quantum dots with surface treatment

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The surface morphology is one of the important factors to determine the optical properties of colloidal quantum dots. Colloidal CdSe dots were synthesized by the injection of precursor molecules in a hot surfactant, and a series of samples were obtained by partially replacing the ligands on the surface of these dots with 2-mercaptoethanol. 2-mercaptoethanol results in the decrease of the photoluminescent quantum yield, and the time-resolved photoluminescent (PL) spectra are significantly modified. The effect of the surface morphology is discussed.

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Colloidal inorganic nanocrystals have attracted great interest for fundamental research and industrial development in recent years due to their flexible processibility and unique properties^[1–3]. To keep colloidal nanocrystals stable, the most common method is that a monolayer of organic molecules called ligands is chemically attached to the atoms on the surface of nanocrystals. In addition to the protection function, this monolayer of ligands provides the necessary chemical accessibility for the nanocrystals. For both of the functions, the stability of the ligands is the key concern. However, not much is known regarding the nature and chemical properties of the binding between CdSe nanocrystals and their ligands. Cadmium ions on the surface of CdSe nanocrystals have been proposed to play a very active role in the strong absorption of nanocrystals, and the formation of the cadmium-ligand bonds on the surface of the CdSe nanocrystals can result in strong photoluminescence (PL) activities. It has been revealed that the photophysical properties of CdSe nanocrystals are strongly dependent on the surface environment^[4–7]. In this paper, we examine the PL and time-resolved PL spectra of CdSe nanocrystals samples injected with 2-mercaptoethanol solution. The optical properties of colloidal nanocrystals decorated with 2-mercaptoethanol has not been reported yet. 2-mercaptoethanol results in the decrease of the PL quantum yield, and the time-resolved PL spectra are significantly modified. The effect of the surface morphology is discussed.

Colloidal CdSe dots were synthesized by the injection of precursor molecules in a hot surfactant, and the synthetic process was similar to the ones reported previously^[8–10]. A typical synthesis is as follows. CdO, 0.0127 g (0.1 mmol), and 0.6838 g (2.4 mmol) of stearic acid were loaded into a 50-mL three-neck flask and heated to 180 °C under Ar flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. Hexadecylamine and 1-octadecene, 2.2283 g of each, were added to the flask, and the mixture was heated to 280 °C under Ar flow to form an optically clear solution. At this temperature, the Se solution containing 0.079 g (1 mmol) of Se dissolved in 0.238 g (1.18 mmol) of tributylphosphine (TBP) and 0.684 g of 1-octadecene was swiftly injected into the reaction flask. After the injection, the temperature was set at 250 °C for the growth of nanocrystals. At various time intervals, with a needle-

tip amount of the reaction mixture were removed and diluted by chloroform. Insoluble white solid, if it existed, dissolved by heating up to 30 °C. The aliquot with the maximum PL quantum yield ($\sim 20\%$) was chosen, then 8 mL was removed from it and divided averagely into four samples. The injection of 2-mercaptoethanol into these quantum dots (QDs) samples resulted in the decrease of the PL quantum yield. The more 2-mercaptoethanol was injected, the more the luminescence of the QDs was decreased. 2-mercaptoethanol was diluted into chloroform, and three solutions with the concentration of 0.5×10^{-4} , 1×10^{-4} , and 2×10^{-4} (volume ratio) were obtained. 40 μL of each three 2-mercaptoethanol solutions were respectively injected into three of the four QD samples. Hereafter, these three samples were labelled as sample S0.5, S1, and S2, respectively, and the one without injection is as Sample S0. All of these four samples were called S-series.

Figure 1 shows PL spectra of the S-series CdSe nanocrystals. All the four PL spectra, which have the same full-width at half-maximum (FWHM) of 30 nm and the same peak location at 616 nm, but their intensities exhibit an obvious step decline, in other words, the PL quantum yield comes down. The PL quantum yields are estimated to be 16%, 10%, and 4% for sample S0.5, S1, and S2, respectively. Figure 1 reveals that 2-mercaptoethanol has significant effect on the luminescence of CdSe QDs. It is very interesting that a very rare amount of 2-mercaptoethanol can obviously modify the luminescence of CdSe QDs, which indicates that colloidal QDs is very sensitive to their surrounding environment, and this can be utilized for making chemical sensors. PL decay measurements were taken at room temperature by use of a time-correlated photon-counting system. The excitation light was at $\lambda = 350$ nm with the resolution of the monochromator at 12 nm and a 40.18-kHz repetition rate. Figure 2 shows PL decays of the S-series CdSe nanocrystals. All the PL decays were obtained by monitoring at the wavelength of 616 nm, with the resolution of the monochromator at 10 nm. These PL decay curves can be fitted well by a bi-exponential function $[A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)]$, where the values of τ_1 and τ_2 are on the nanosecond time scale. Table 1 shows the fitted values of the parameters in the bi-exponential function. Figure 2 indicates clearly that there are two radiative recombination processes for these CdSe QDs.

The fast recombination process predominates over the slow one, and its predominance is enhanced with the injection of 2-mercaptoethanol. On the other hand, both the two radiative processes are sped up by the injection.

Figure 1 reveals that 2-mercaptoethanol can obviously darken colloidal QDs. The detail mechanism involved is not clear so far. It is proposed that the injection of 2-mercaptoethanol cause some degree of damage on the TBP ligands surrounding the dots, engendering some disfigurements to the surface of these QDs, and thus enhancing the nonradiative recombination. Excitons, which are yielded under the excitation of the incident light, oscillate inside the CdSe dots, and a portion of them recombine radiatively, while the other transfer to the surface of the dots, captured by surface disfigurements and non-radiatively recombine. The enhancement of nonradiative

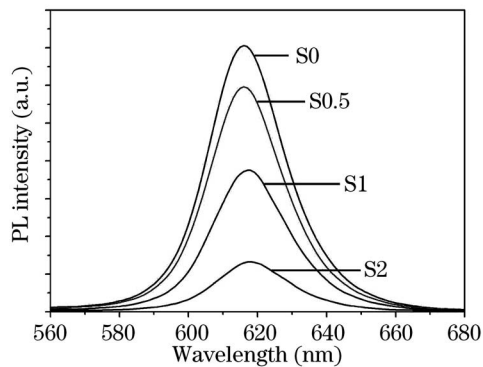


Fig. 1. The PL spectra of the S-series CdSe dots.

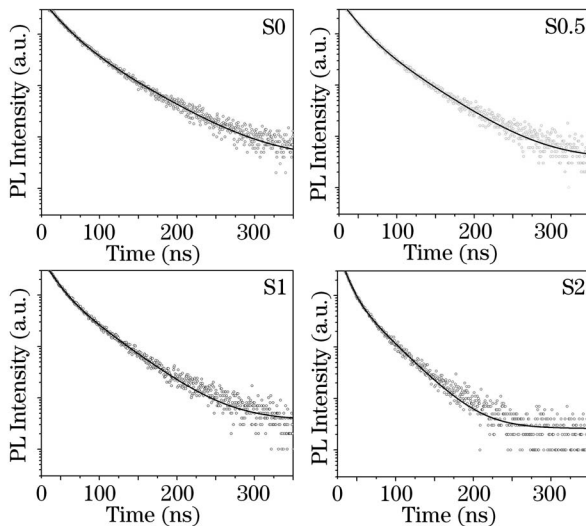


Fig. 2. The PL decay spectra of the S-series CdSe nanocrystals. Plots are in logarithm scales, and solid curves are bi-exponential fits to the data.

Table 1. The Fitted Parameters of the PL Decay Spectra with the Bi-Exponential Function

	τ_1 (ns)	τ_2 (ns)	A_2/A_1
S0	49.9	19.9	5.62
S0.5	44.2	17.4	5.85
S1	39.4	13.7	7.86
S2	29.3	8.8	30.92

recombination reduces the PL quantum yield of QDs, and results in the decline of τ_1 and τ_2 . The fast radiative recombination process and the slow one may correspond to the exciton recombinations inside the dots and at the surface respectively. The influence of surface modification to the excitons at the dots surface must be stronger than to those inside the dots, which means the intensity ratio between the QDs' internal and surface PL will become larger when the amount of 2-mercaptoethanol injected is increased. This trend is well incarnated by the fitted parameter A_2/A_1 of the S-series' PL decay measurement.

In conclusion, a series of colloidal CdSe dots are synthesized, and given surface modification with 2-mercaptoethanol, and the PL measurement reveals that the PL quantum yield decreases. The PL decay spectra are fitted well by a bi-exponential function, and their fitted parameters substantiate the model that the exciton recombination exists both inside and at the surface of the dots.

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