Formation of Luminescent CdTe–Silica Nanoparticles through an Inverse Microemulsion Technique

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CdTe quantum dots (QDs, 3–6 nmϕ) were incorporated into silica nanoparticles (20–30 nmϕ) by an inverse microemulsion technique. The transmission electron microscope image shows that the QDs are situated on the surface of silica particles. These QD-silica particles in solution exhibited a stable luminescence with at least the similar quantum efficiency (ca. 5%) as that of the initial colloidal solution over several weeks of storage. The particles taken out from the solution as a powder form showed the same quantum efficiency for a long time as well. This is because silica acts as an effective protective environment for the QDs.

Semiconductor nanoparticles, commonly called as quantum dots (QDs), exhibit unique optical properties that could be tailored for various applications ranging from QD lasers to biological tagging.[1–4] Until now two solution-based syntheses of emitting QDs have attracted a wide spread interest. The first one employs trioctylphosphine oxide and deposits a higher band gap material such as ZnS on the surface for a preparation of hydrophobic CdSe.[5] Another method is based on the synthesis of hydrophilic CdTe QD in water by using organic capping agents such as thioglycolic acid (TGA).[6,7] While these materials are rather stable in the parent solution of their preparation, exchanges to other solvents would affect their photophysical behavior.

In order to improve the photostability of QDs they need to be encapsulated within a rigid matrix. Silica matrix is an ideal choice because this further allows the introduction of a specific surface functionality such as hydroxy and carboxyl. Methods for silica coating of gold, silver, CdS and CdTe nanoparticles have been reported.[8–13] However, emitting one has not yet been reported except for a recent result in a bulk glass.[13] Herein we report a facile method in order to prepare highly stable luminescent CdTe QD–silica nanoparticles by using an inverse microemulsion technique. The approach applied involves using water dispersible QDs for a purpose to utilize a well-established sol–gel method.

The CdTe colloidal solutions were prepared using cadmium perchlorate and hydrogen telluride.[7] Thioglycolic acid (TGA) was used as the stabilizing agent. Two different particle sizes as shown by the color of the luminescence (green, ca. 3 nmϕ and red, ca. 6 nmϕ) were obtained.

An inverse microemulsion employing Aerosol OT (AOT: bis-2-ethylhexyl sulfosuccinate) was prepared with a different w_2 ratio where $w_2 = [H_2O]/[TEOS]$. Typically, 1.1 g (0.1 M) AOT was dissolved in 25 mL isooctane and stirred until the solution remained clear. Then, water (2–2.5 M) was added to form the microemulsion.[14] We used ammonia solution instead of pure water, and the aqueous CdTe QDs (0.3 mL) were injected. The water droplet size was estimated to be around 20–30 nm for $w_1 > 10$ where $w_1 = [H_2O]/[AOT]$. (Note that $[H_2O]$ is total volume of H_2O, NH_3, and colloidal CdTe) Since the QDs are highly hydrophilic, they should quickly move to the water phase. It was stirred until the solution remained optically transparent. A typical sol–gel precursor, tetraethoxysilane (TEOS), was finally added to perform the reaction in water phase.[15] The sign of silica formation was noted by the cloudy solution, especially with a higher concentration of TEOS after a few hours of stirring. The solution was allowed to stir for ca. 48 h. The luminescent QD–silica nanoparticles were characterized by UV–vis absorption, and photoluminescence (PL). Table 1 presents the reactant concentrations of green QD–silica nanoparticles in the microemulsion. The emission peak wavelength and PL efficiencies relative to quinine[16] (54.6%) are also tabulated. The PL peaks for QD–silica composites remain almost unaltered.

Figure 1a shows the absorption spectra of CdTe QDs in water (control) and of QD–silica particles in the microemulsion. Note that the concentration of QDs is equal in all the traces. Upon increasing TEOS concentration, the absorption also increases because of the scattering by silica particles. In Figure 1b the corresponding PL spectra are shown for QD–silica composites together with the control sample.

The TEM images [Figures 2a and b] show that the QDs are on the silica surface. The diameter of silica spheres is 29 ± 4 nm. The photographs of luminescent QD–silica composites in colloi-

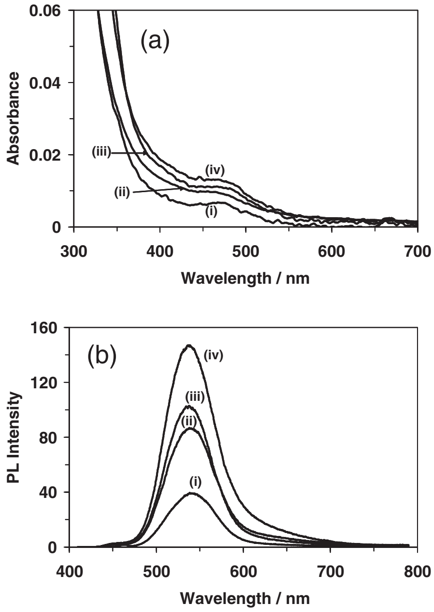

Figure 1. (a) The absorption spectra of CdTe QDs in solution and in silica-microemulsion. Traces: (i) Control (QD in water); (ii)–(iv): QD–silica nanoparticles. (ii) QD-S1; (iii) QD-S2; (iv) QD-S3. (b) PL spectra of the corresponding samples. For sample description see Table 1.

Table 1. Reactant concentrations in AOT microemulsion and PL efficiencies of green-emitting CdTe QD–silica composite particles together with the initial crude CdTe solution (Control)

Conditions	Molar Concentration			w_1 (=[H_2O]/	w_2 (=[H_2O]/	Emission Peak	PL Efficiency
Samples	[AOT]	[H_2O]	[TEOS]	[AOT])	[TEOS])	/nm	/%^{a}
Green-emitting QDs in water (Control)						541	4.5
QD-S1	0.1	2.3	0.1	23.0	23.0	537	6.1
QD-S2	0.1	2.3	0.2	23.0	11.5	538	9.6
QD-S3	0.1	2.3	0.3	23.0	8.5	539	5.5

^{a}: The PL efficiencies of the silica containing samples (QD-series) listed here are apparent ones due to a scattering shown in Figure 3.

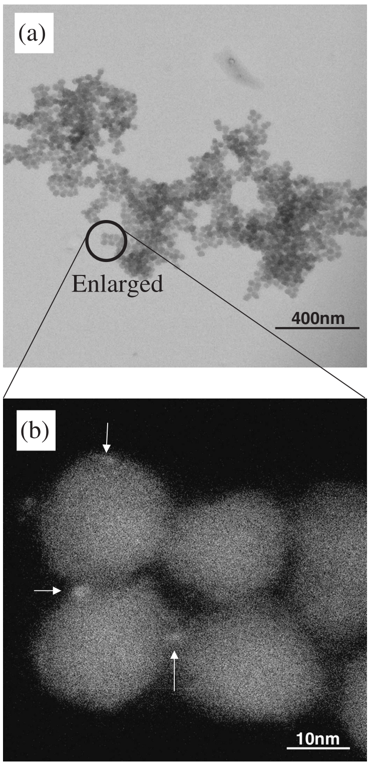

Figure 2. (a) TEM image of silica spheres taken from the sample of QD-S3 in Table 1. (Bright field) (b) High angle annular dark field image of the place shown by a circle in (a). Cd is detected at the places shown by arrows. The size of the QD is estimated to be 3 nmϕ.

dal suspension, which shows some scattering, are shown in Figure 3 together with a red-emitting sample prepared by the same procedure.

Silica powders could be extracted from the suspensions in Figure 3 by centrifuge. After several times of washing by isooctane, the dried powders show substantially the same PL efficiency when measured by a reported method.[17] This indicates that the QDs are fixed to the silica particles without a deterioration of the surface condition. This is a contrast to the CdTe–silica raisin bun composite structures (many QDs dispersed in a silica sphere) prepared by Rogach et al.,[6] where the PL from the QDs is significantly quenched.

Although we expected QD–silica as core-shell structures we ended up with the QDs on the surface of silica spheres. When injected, QDs are distributed quickly to the water droplet phase. After this distribution, sol–gel reaction proceeds at the surface of the water phase. However, silica tries to form networks by themselves. This might be the reason why the QDs sent away to the boundary of the silica spheres.

Figure 3. Photoluminescence from CdTe QD–silica nanoparticles in water under 365 nm UV excitation. The right sample is QD-S2, whereas the middle sample (lower TEOS concentration) is QD-S1 in Table 1. A sample prepared by using red-emitting CdTe QD (6 nmϕ) is also shown in the left side.

TGA-capped CdTe QDs exhibit a higher PL efficiency compared to bare QDs because of the formation of a shell of cadmium thiol. However, organic capping has its own demerits such as low durability and photostability. Silica provides an inert barrier for the QD, which could be used for several applications.

In conclusion, we have demonstrated a novel method to maintain the PL efficiency of QDs (ca. 5%, albeit an apparent increase owing to silica scattering) through a silica-coating procedure using an inverse AOT microemulsion. For a purpose to use versatile sol–gel techniques, water dispersible QD, namely TGA-capped CdTe (3–6 nmϕ), was used. The prepared QD–silica particles in solution could be extracted as a powder form without deterioration of emission efficiency.

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