Surfactant-dependent Photoluminescence of CdTe Nanocrystals in Aqueous Solution

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(Received September 30, 2004; CL-041157)

Photoluminescence (PL) efficiency of CdTe nanocrystals was investigated as a function of the ratio of surfactant (thioglycolic acid, TGA) to Cd^{2+} used in aqueous preparation. When the ratio was 1.3, a maximum PL efficiency of 65% was obtained. Within our knowledge, this value is the highest ever reported for as-prepared aqueous solution. Surfactants added more than the optimal amount tend to gather densely on the nanocrystals, and distort the surface. This might be one explanation of the decrease of efficiency.

Preparing and processing emitting semiconductor nanocrystals are one of the most competitive areas in present-day research. Preparation is mainly done in two ways, i.e., aqueous[1,2] and organometallic routes.[3,4] The aqueous route has advantages of ease, cost, and safety when compared with the other.[5] However, this preparation needs an appropriate surfactant. When research began, the kinds of surfactants available were investigated intensively.[1] However, little research has been done on the amount of surfactant required for preparation. When ZnSe is prepared in aqueous solution, it has only recently been reported that less surfactant yields the most intense PL.[6] For CdTe, the ratio of thioglycolic acid to Cd^{2+} has been fixed at 2.4, which was selected for the earlier stages of preparation.[1] The PL efficiency obtained with this ratio has reportedly been ca. 4% in the green region before a post-preparative procedure is applied.[7]

In this letter, we have systematically investigated the dependence of the amount of the surfactant (TGA) on PL efficiency. For the purposes of obtaining further information, particle concentration, spectral width of emission, and ζ-potential of particles were analyzed.

CdTe colloidal solutions were prepared according to a previously reported method.[1] Typically, 1.095 g (2.61 mmol) of $Cd(ClO_4)_2 \cdot 6H_2O$ was dissolved in 200 mL of pure water, and TGA was added at molar ratios from 1.00 to 2.43 against Cd^{2+}. Then, the pH values of the solution were adjusted to 11.4 by adding dropwise 1 M NaOH solution. After the solution was saturated with Ar, H_2Te gas was passed through the solutions. The molar ratio of Te^{2-} to Cd^{2+} was fixed at 0.47. Clusters were formed quickly after the introduction of H_2Te. CdTe nanocrystals grew gradually by refluxing at ca. 100 °C. When the molar ratios of the TGA in the solution were less than 1.54, the solution remained slightly turbid even when the pH value was adjusted to 11.4. However, the solution became transparent after the H_2Te addition. When the solution became turbid again during refluxing, it was filtered with a 0.22-µm filter before measurements. The PL efficiencies of the solution were estimated by comparing them with those of quinine sulfate in 0.5 M H_2SO_4 (PL efficiency: 54.6%).[8] The ζ-potentials of as-prepared nanocrystals were measured with an electrophoretic light scattering spectrophotometer.

Figure 1 plots typical examples of the temporal evolution of particle concentration and PL efficiency. Particle concentration has been estimated from the first absorption peak value and the molar extinction coefficient as has been reported.[9] The rapid reduction in the number of particles at the beginning of reflux in Figure 1a is well explained by Ostwald ripening, where smaller particles are dissolved to provide monomers for the growth of larger particles. Accompanied by this reduction, PL efficiency is quickly increased at the beginning of reflux as shown in Figure 1b. However, the efficiency depends on the amount of surfactant.

Figure 2a shows the PL efficiency of green (ca. 3 nm Φ) and red (ca. 6 nm Φ) emitting particles as a function of the TGA ratio. In both cases, the PL efficiencies are the maximum at a TGA ratio of ca. 1.3. Figure 2b plots this situation differently. When the TGA ratio is 2.43, the efficiency begins from ca. 2% in the green region and rises up to ca. 10% in the red region. The PL efficiency of a TGA ratio of 1.25, on the other hand, becomes ca. 30% in the green range and reaches ca. 65% at the latest stage of reflux. When the molar ratio of TGA is 1.00, PL efficiency is a little less than 30% at the beginning. However, a drastic decrease is observed after 30 min of reflux. The precipitation coming out during reflux may be related to this decrease. The solution becomes turbid accompanied by this decrease and only much diluted nanocrystals are obtained after filtration.

Full widths at half maximum (FWHM) of PL emission during reflux are strongly dependent on the TGA ratio as shown in Figure 3. When the ratio becomes small, the FWHM becomes

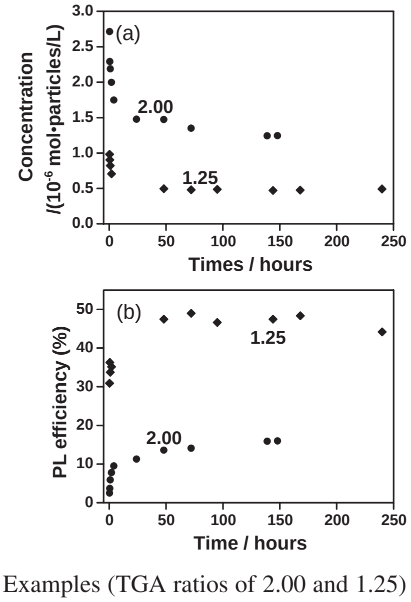

Figure 1. Examples (TGA ratios of 2.00 and 1.25) of temporal evolution of concentration of nanoparticles in solution (a) and their PL efficiency (b) during reflux.

narrow. The first absorption peak widths show the same tendency as well. Namely, it is 23 nm when the ratio is 1.25 whereas it increases to 63 nm when the ratio becomes 2.43 for example in the case of green emitting region. The ζ-potential (negatively charged) also shows a maximum (ca. 50 mV) at TGA ratio of 1.3 for both green- and red-emitting particles when the pH is ca. 9.5.

Recently, the mechanism responsible for particle growth in solutions has been investigated extensively.[10,11] The theory deals with Ostwald ripening of particles less than 10 nm in diameter. This successfully explains how ensemble particles grow and dissolve during reflux. When certain values for parameters were assumed, it was demonstrated that the low surface energy of nanocrystals result in larger particle-size distribution. (Figure 6 in Ref. 10). When the amount of surfactant is increased in the present solution, the surface energy should be reduced. This explains FWHM dependence we observed on the amount of surfactant.

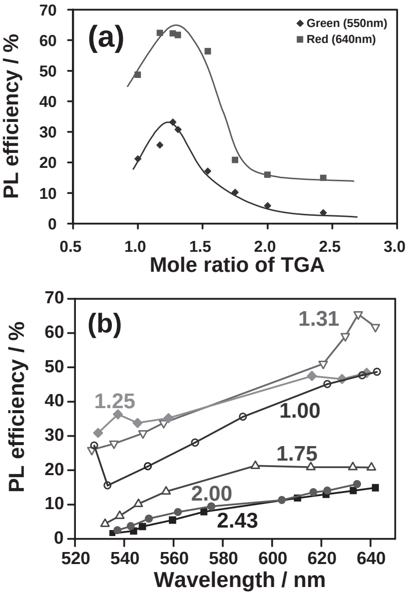

Figure 2. (a) PL efficiency of CdTe nanocrystals as a function of molar ratio of TGA for green- and red- emitting solutions. (b) PL efficiency of CdTe nanocrystals obtained at different stages of particles growth. Numbers in figure indicate molar ratios of stabilizer to Cd^{2+} in preparation.

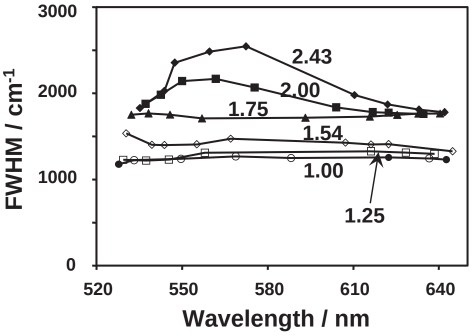

Figure 3. The FWHM of as-prepared CdTe nanocrystals obtained from different stages of particles growth for the various molar ratios of the surfactant against Cd^{2+}.

When the surfactants are more than the optimum value, their population on the surface of the nanocrystals is increased. This might distort the surface and create some nonradiative defect centers. This could be ascribed to the observed decrease in PL efficiency. Usually, hydroxy ions in the solution passivate the surface of the nanocrystals. When the surface is densely covered with an excess amount of surfactant molecules, hydroxy ions can not attach to the surface effectively. This might be the reason for the decrease in ζ-potential in the region with the larger amount of surfactant.

The tendency of PL efficiency and the amount of surfactant are the same as those for ZnSe.[6] Even though the particles were very bright, the solution form is not appropriate for most applications. Therefore, the brightest particles with the narrowest emission width obtained here were incorporated in a glass matrix to develop a new type of phosphor.[12,13]

In conclusion, highly photoluminescent CdTe nanocrystals (efficiency of 35% for green and 65% for red) were prepared in aqueous solution by adjusting the amount of surfactant (TGA). The optimal TGA required was a molar ratio of ca. 1.3 times the Cd^{2+}. Within this range, the PL emission width reaches a minimum and the ζ-potential reaches a maximum. These could be ascribed to the density of surfactant molecules on the surface of the nanocrystals. Further investigations are currently underway.

This study was supported in part by the Nano-Glass Project of the Nanotechnology Materials Program, sponsored by the New Energy and Industrial Technology Development Organization (NEDO).

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