

Surface Treatment to Enhance the Quantum Efficiency of Semiconductor Nanocrystals

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The photoluminescence quantum efficiency of semiconductor nanocrystals at room temperature was markedly enhanced about 50 times by surface treatment of the nanocrystals after synthesis, and the original photoluminescence peak position and narrow line width were maintained. Simply, the nanocrystal surface was treated with a small amount of sodium borohydride (NaBH_4) in toluene at room temperature. The surface-treated nanocrystals showed very high quantum efficiency, up to 75%, even in the blue region of 490 nm. The TGA and XPS data revealed that some of the surfactants on the nanocrystal surface were removed by the reaction with NaBH_4 and that the exposed cadmium on the surface was converted to cadmium oxide. The cadmium oxide functioned as a robust passivation layer on the CdS surface and contributed more electron density toward the inside of the CdS core to enhance exciton recombination. The surface treatment was powerfully effective in improving the quantum efficiency of II–VI compound semiconductors such as CdS, CdSe, and CdTe, and generally their mixture-type nanosized materials synthesized under a variety of conditions.

Semiconductor nanocrystals have become an important class of materials because of the flexibility to control optical and electronic properties by changing only the size of the materials.^{1–5} In the past decade, preparation methods of colloidal nanocrystals have been refined to yield high-quality products, which have homogeneous size and regular shape.^{6–11} The luminescence range of the high-quality nanocrystals spans from the infrared to the UV, and the narrow bandwidth gives fine color purity. Therefore, it is advantageous to use these materials as phosphors in light-emitting devices because all the color can be obtained from same material by controlling the size only, which makes the device structure universal.¹² However, to make a high-quality phosphor we need to maximize the luminescence efficiency as well as the color purity. Although the mechanism of energy band gap tuning is relatively well understood, it is still not clear how to control the luminescence efficiency, and there are only a few reports explaining the luminescence enhancement phenomena.^{13–15} Since the nanocrystals have a large fraction of surface atoms because of their small volume, many inhomogeneous defect points exist on the large surface area. Therefore, proper passivation of the nanocrystal surfaces is necessary to achieve a high quantum yield. The inorganic passivation of nanocrystals with higher band gap materials, resulting in core/shell structure nanocrystals such as CdSe/ZnS and CdSe/CdS, showed high quantum efficiency up to 50% because of the robust passivation of the surface defects and also the quantum confinement effect which enhances exciton recombination in the core.^{16–18} However, the synthesis of core/shell nanocrystals should go through additional coating procedures using highly active precursors, which have to be chosen very selectively for appropriate passivation and quantum confinement effect. Also, the coating procedures could result in an energy shift and a broader size distribution. The ternary

structure nanocrystals such as CdSeS, prepared by simultaneous injection of selenium and sulfur precursors into cadmium, show better luminescence efficiency than CdSe nanocrystals because the resulting nanocrystals consist of a CdSe core with a CdS rich shell.¹⁹ To date, the light-emitting core part of most nanocrystals is CdSe, which can be prepared under mild conditions using well-known precursors. However, CdSe nanocrystals have a spectral limitation, and they should be smaller than 2 nm to emit light at wavelengths shorter than 490 nm.²⁰ To achieve high quantum efficiency in the blue region, CdS is a suitable candidate which can be prepared under mild conditions. Since the bulk CdS has an energy band gap of 2.5 eV, it is possibly easier to make CdS nanocrystals emit bluer light than the same size of CdSe. Not much research has been previously done to obtain a high luminescence efficiency of blue-emitting nanocrystals. Therefore, we were challenged to prepare highly luminescent blue-emitting CdS nanocrystals. We attempted to reduce the surface trap sites of the nanocrystals not by additional crystal growth with different inorganic precursors but by control of the electronic state of the surface. To change the electronic state of the nanocrystal surface, we added reducing agents. By a simple surface treatment with a reducing agent in the solution phase, we improved the quantum efficiency of CdS nanocrystals up to 75%, which is increased by 50 times from the initial efficiency over the whole spectral range with reproducibility and stability.

Colloidal CdS nanocrystals were made by a sulfur precursor injection into hot coordinating solvent containing a cadmium precursor and a surfactant: 2 mmol of CdO powder was dissolved in 16 g of trioctylamine (TOA) solvent with 8 mmol of oleic acid at 300 °C. After the red color of the CdO disappeared, the mixture was cooled to 280 °C. While the mixture was stirred vigorously, 2 mmol of elemental S in trioctylphosphine (TOP) was quickly injected. The color of the reaction mixture became light yellow after 2 min, which indicated the formation of nanocrystals. The product was cooled to room temperature by the addition of 25 mL of ethanol to

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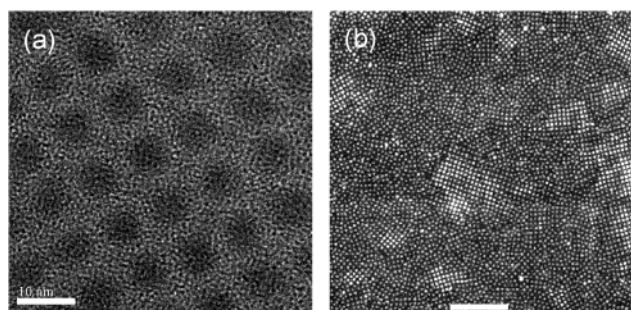


Figure 1. (a) Transmission electron microscopy image of CdS nanocrystals; the scale bar is 10 nm. (b) Scanning transmission electron microscopy image of CdS nanocrystals; the scale bar is 50 nm.

quench any further reaction. The resulting CdS nanocrystals were separated from the mixture by centrifugation and redispersed in anhydrous toluene. The CdSe and CdTe nanocrystals were synthesized in a similar way using elemental Se or Te instead of S. All the nanocrystals were dispersed in toluene as 1 wt % solutions, and they were treated with reducing agent. Sodium borohydride (NaBH_4) as a reducing agent was added to the CdS nanocrystal solutions, and the mixture was stirred for about 1–2 h at room temperature. The NaBH_4 concentration in the solution was about 1 wt % of the nanocrystal amount. After the treatment, the NaBH_4 powder was removed using 0.2 μm filters. The quantum efficiency of the nanocrystal solution was calculated by comparison with the value of reference organic dyes at similar optical density. It was reported that 9,10-diphenylanthracene in ethanol solution with an optical density of around 0.1 has a quantum efficiency of 91%.²¹ The photoluminescence (PL) intensities of the nanocrystal samples and the reference organic dye were measured with an ISS PC1 photon-counting spectrofluorometer, and the quantum efficiency of the nanocrystals was calculated.²¹

Figure 1 shows that the synthesized CdS nanocrystals have a very uniform size distribution and regular shape. Depending on the synthetic condition in general, the CdS nanocrystals could be zinc blende, wurzite, or their mixed structures. The photo shows that the 5 nm size CdS nanocrystals form cubical arrays when they are close-packed, and the distance between the nanocrystals is about 2 nm. From the cubical array of the nanocrystals in Figure 1a, we expect that zinc blende CdS has been prepared under our synthetic conditions since the wurzite nanocrystals tend to be hexagonally packed. We checked the diffraction pattern of the transmission electron microscopy (TEM) image, and the measured lattice constant of the zinc blende CdS nanocrystals was 5.7 Å in mean value among 10 collected data sets. The scanning transmission electron microscopy (STEM) image in Figure 1b also shows a very homogeneous size of CdS forming mostly checked patterns when they are close-packed. The luminescence spectrum from these very homogeneous CdS nanocrystals was symmetric and narrow; however, the PL efficiency was very low to 1% of quantum yield. We found that even the well-controlled reaction scheme could also produce surface defect sites acting as traps for holes and electrons.

The PL spectra of the initial CdS nanocrystals and CdS surface-treated with NaBH_4 exhibited emission peaks at the same wavelength with an unchanged narrow distribution (18 nm) (Figure 2a). The UV absorption spectrum for the initial CdS and the NaBH_4 -treated CdS nanocrystals revealed almost the same shape, and both of the first absorption peaks appeared at 480 nm. Although the absorption intensities of both nanocrystals did not change much at the same concentration, the PL strength

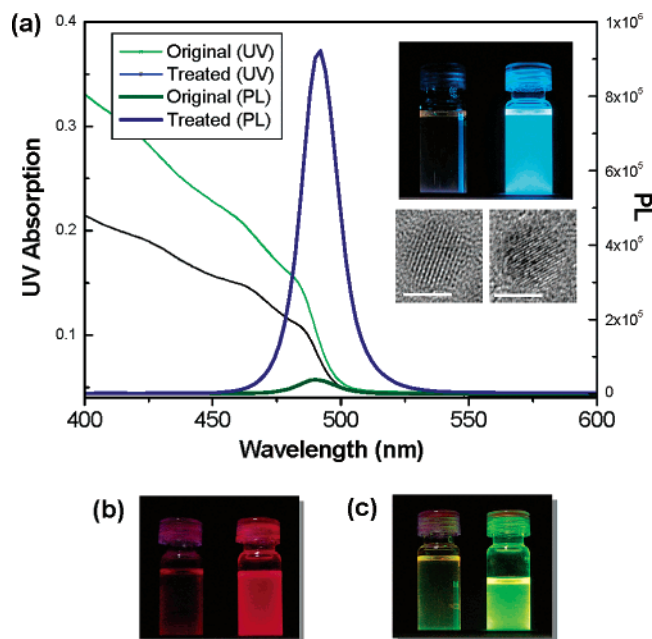


Figure 2. (a) UV absorbance spectra and photoluminescence spectra of the original CdS nanocrystal and the nanocrystal surface-treated with NaBH_4 excited at 365 nm. Inset: photos taken under a 365 nm UV lamp (left, original; right, treated with NaBH_4) and HR-TEM images (left, original; right, treated with NaBH_4) of the nanocrystals in toluene solvent. (b) Photos of original (left) and surface-treated (right) CdTe and (c) original (left) and surface-treated (right) CdSe taken under a 365 nm UV lamp.

of the NaBH_4 -treated CdS increased enormously. The quantum efficiency for the initial CdS nanocrystals and surface-treated CdS are 1.4% and 78%, respectively, which is a 54 times improvement after the treatment. The inset photo, taken under a 365 nm UV lamp, clearly shows the remarkable enhancement of the quantum efficiency after surface treatment. The shape and the size of the crystals before and after treatment did not change much according to the inset TEM images. Since this post-treatment was not dependent on the reaction conditions or reagents, the treatment with NaBH_4 could be generally used to improve the PL quantum efficiencies of other II–VI nanocrystals. The reaction between CdSe or CdTe and NaBH_4 progressed more vigorously than the treatment of the CdS so that better luminescence was observed within a few minutes. The quantum efficiencies of the original CdTe and CdSe were too low to be measured, and they increased to 24% and 26% for the respective samples after treatment (Figure 2b). The CdSe and CdTe have wurzite and zinc blende crystalline phases, respectively; therefore, we supposed that the phase structure did not affect the PL enhancement much.

We examined the change of the nature of the CdS nanocrystal surface before and after NaBH_4 treatment using X-ray photoelectron spectroscopy (XPS) (PHI Q2000 system equipped with a monochromatized Al K α (1486.6 eV) source). The analytical samples were prepared as two forms: spin-coated nanocrystal film on Si wafer and powder. The XPS analyses were all done for two kinds of samples, and they showed the same results. We used the result from the powder sample in this work. The main peak of the C 1s level at 284.8 eV did not shift after the treatment, so it was used as a reference. The binding energies of 284.8 eV and 288.4 eV are in good accordance with the values for aliphatic carbon and carboxyl carbon ($-\text{COO}$), respectively (Figure 3a). This indicates that the nanocrystal surfaces mainly coordinate with oleic acid surfactant. We have also used the Si peak position as the reference when we analyzed

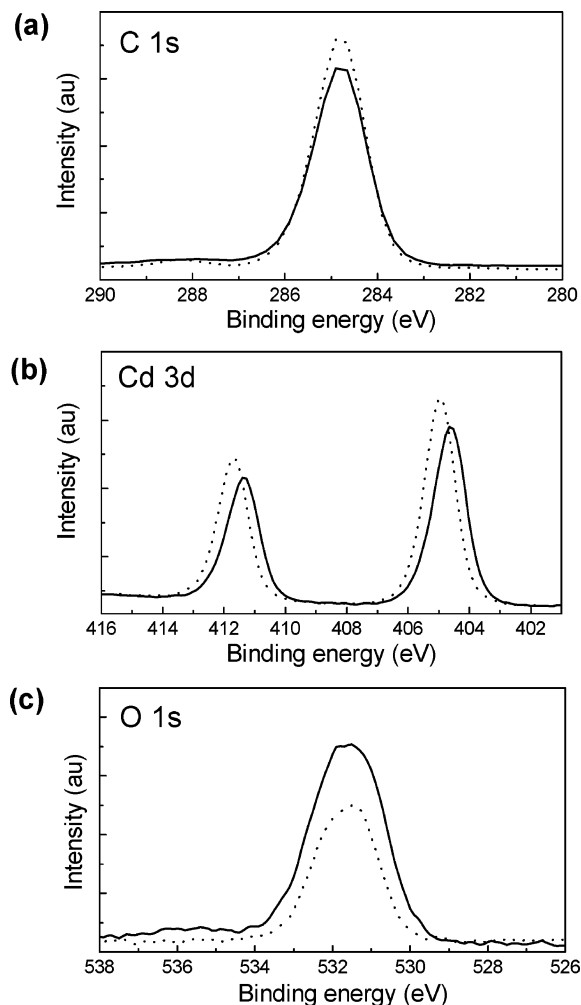


Figure 3. XPS spectra of the original (dot lines) and surface-treated CdS nanocrystals (solid lines); (a) C 1s, (b) Cd 3d, and (c) O 1s.

the nanocrystal film on Si wafer, and the movement of the peak position was not significant between samples. The spectra of the Cd 3d level were significantly broadened and shifted by 0.5 eV to lower binding energy after the surface treatment (Figure 3b). The original binding energies of Cd 3d_{5/2} at 405 eV and S 2p at 161.4 eV are in good accordance with the values for bulk CdS. The chemical shifts of 0.5 eV toward lower binding energies for both levels are probably assigned to the oxidized Cd state after the treatment. The spectra of the O 1s level were significantly broadened and intensified after the treatment (Figure 3c). The original binding energy of the O 1s level was 531.7 eV, and this came from the carboxyl oxygen of oleic acid. The feature of the O 1s level of CdO was reported to have two peaks at 530.5 eV and 532.5 eV.²² The peak at 532.5 eV was assigned to hydroxyl oxygen on the surface, and the peak at 530.5 eV could imply oxygen binding to metal cadmium. Therefore, the spectral broadening of the O 1s level and the peak shift of Cd 3d_{5/2} could be due to the formation of the CdO state. The intensity of the spectra of the O 1s level markedly increased after the treatment although the intensity of the spectra of C 1s and Cd 3d decreased. The ratio of the atomic concentration of oxygen to the atomic concentration of cadmium increased from 1.29 (before the treatment) to 2.39 (after the treatment). The layers on sphere model was employed to determine the thickness of the oxygen layer and carbon layer with a variation of the emission angle (see the Supporting Information). The nanocrystals before and after the treatments have a spherical shape, so the thickness of the oxygen and

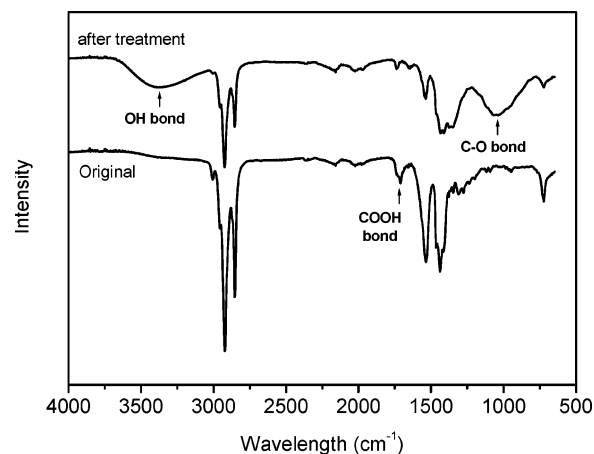


Figure 4. IR spectra of the original and surface-treated CdS nanocrystals.

carbon layers is assumed to be uniform when the nanocrystals are viewed from different angles. The average thickness of the oxygen layer on the CdS surface increased to 3 Å after the surface treatment. The bond length of cadmium and oxygen is about 2.3 Å,²⁰ so piled-up oxygen may form a monolayer of cadmium oxide on the surface of the CdS. However, the average thickness of the carbon layer decreased to around 3 Å. The carbon layer is derived from oleic acid surfactants on the surface, and the reduction of the effective thickness could result from the decrease of surfactant density on the surface. TGA analysis also showed that about 25% of the surfactants decreased after the treatment. The less dense surfactants around the nanocrystal surface could allow oxygen diffusion to the active cadmium surface. The valence band offset moved by 0.3 eV to lower binding energy after the treatment (see the Supporting Information). This is due to the newly formed CdO layer, which has a valence band binding energy of 5.4 eV,²³ effectively smaller than that of bulk CdS (6.9 eV).

The atomic concentrations measured by inductively coupled plasma spectroscopy (ICP) and XPS disclosed that CdS nanocrystals have an excess ratio of cadmium to sulfur of about 1 to 0.7. The excess cadmium is supposed to be more concentrated on the surface, and the noncoordinated surface cadmium should be passivated with an organic surfactant. After the NaBH₄ treatment, the IR spectrum of the nanocrystal solution showed that the COOH band from oleic acid was retrenched and a corresponding alcohol band was observed (Figure 4). Also, the filtrate removed from the nanocrystal solution after the treatment contained the sodium salt of oleic acid, which was identified in the IR spectrum of the solids.

On the basis of the above results, we concluded that the treatment with NaBH₄ caused the oxidation of the nanocrystal surfaces. First, NaBH₄ reduces some oleic acid surfactants to the corresponding alcohols or sodium salts which causes the surfactants to lose their coordinating properties and come off from the nanocrystal surface. Then oxygen diffuses to the exposed cadmium to form a cadmium oxide layer around the cadmium sulfide. The oxygen could be derived from atmospheric air since the treatments carried out in the glovebox were not effective at brightening the emitting light from the nanocrystals. The CdO layers passivate the surface defects very effectively, and the resulting nanocrystal shows an enhanced quantum yield. When we used an excess amount of NaBH₄ and stored the treated sample without filtering out the NaBH₄ powder, the nanocrystals in the solution started to precipitate. The continuous stripping out of the surfactants from the

nanocrystal surface by the reaction with NaBH₄ might cause the aggregation of the nanocrystals. Therefore, it is preferable to use the appropriate quantity of NaBH₄ for oxygen diffusion to form a passivation layer without nanocrystal aggregation. The properly treated nanocrystals are stable for almost a year when they are stored under atmospheric conditions.

In conclusion, we improved the quantum efficiency of II–VI group semiconductor nanocrystals remarkably by a simple surface modification using NaBH₄. This treatment procedure provided a clear and general scheme to improve only the quantum efficiency, without changing the PL wavelength and narrow bandwidth of the nanocrystals throughout the whole emission range.

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Supporting Information Available: Thickness of the layers of the nanocrystals; valence band offset of the nanocrystals before and after treatment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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