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# Aqueous Preparation of Highly Luminescent CdSe/ZnS Nanocrystals through Photochemical Processing

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Highly luminescent CdSe/ZnS nanocrystals were prepared in an aqueous solution. CdSe cores capped with thiolglycolic acid (TGA) were coated with a ZnS shell through photochemical decomposition of TGA in a Zn-dispersed solution. The molar ratios of $Cd^{2+}$:TGA:$Se^{2-}$ upon core synthesis were crucial to obtain CdSe/ZnS showing high photoluminescence (PL) efficiency. High PL efficiency (50%) with narrow spectral width (50 nm) was obtained after photochemically coating the core with a thick ZnS shell after optimizing the solution composition during ultraviolet irradiation.

Semiconductor nanocrystals (NCs) have been of great research interest for their application to light-emitting diodes, lasers, and biological labels due to their unique optical properties originating from the quantum confinement effect.[1,2] For biomedical applications, water-soluble CdSe NCs have been used most commonly.[2] The established method for preparing water-soluble CdSe/ZnS NCs is first preparing CdSe cores from an organometallic precursor through a hot injection route,[3] then depositing an inorganic shell with a high band gap such as ZnS around the cores,[4–7] and finally transferring the hydrophobic NCs into an aqueous solution through surface modification such as ligand exchange and polymer or silica coating.[2,8] This process requires multiple steps and may cause the photoluminescence (PL) to decrease.[8] Recently, progress has been made in preparing water-soluble NCs by depositing, in an aqueous solution, a ZnS or ZnCdS shell around CdSe cores prepared by an organometallic method.[9,10] The PL efficiency of CdSe/ZnS NCs thus prepared was increased to 40%.[10]

Compared with the organometallic routes, aqueous preparation has advantages such as simplicity, safety, and reproducibility.[11] Though the successful preparation of NCs such as CdTe and HgTe in aqueous solution has been well reported,[11–14] the aqueous synthesis of CdSe NCs with intense PL is still difficult. Aqueously prepared CdSe NCs have shown broad and weak PL spectra.[15,16] Progress has been made in using aqueous routes in order to prepare highly luminescent CdSe NCs by changing capping ligands or shell material.[16,17] However, the PL efficiency was still 20–30% at most, which is much lower than that of CdSe/ZnS NCs prepared by organometallic routes.

Ultraviolet (UV) irradiation after preparation was proven to be an effective method to substantially improve the PL efficiency of the NCs, since it enabled the creation of a thick ZnS shell around the cores in an aqueous solution.[18] Here, we report the preparation of highly luminescent CdSe/ZnS NCs, all of which were prepared in an aqueous solution. The ZnS shell was deposited around the thiol-capped CdSe cores by UV irradiation. When the synthesis conditions of both the CdSe cores and the ZnS shell were optimized, the PL efficiency of the irradiated NCs was substantially improved.

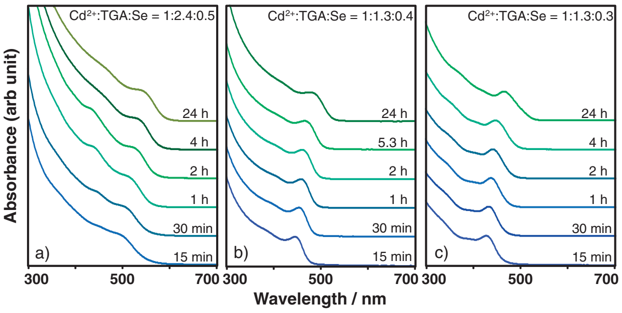

**Figure 1.** Temporal evolution of absorption spectra of CdSe cores prepared with different molar ratios of Cd:TGA:$Se^{2-}$. The core (c) was used for further processing of shell formation.

CdSe cores were prepared by a process similar to that used for preparing CdTe NCs.[11] Specifically, $Cd(ClO_4)_2 \cdot H_2O$ and TGA and $H_2Se$ were used as starting materials. The molar ratio of $Cd^{2+}$:TGA:$Se^{2-}$ upon synthesis was varied systematically. The CdSe cores were obtained through prolonged refluxing at ca. 100 °C for several hours. The cores were then precipitated and irradiated by UV light after redispersion in an aqueous solution containing $Zn^{2+}$ and TGA to create a ZnS shell (see Supporting Information for details).[23] The PL efficiencies of NCs were estimated using a method previously reported.[19]

In order to obtain CdSe cores showing high PL efficiency after shell formation, the molar ratios between the starting precursors were investigated. Figure 1 illustrates the temporal evolution of the absorption spectra of CdSe NCs prepared using different molar ratios of $Cd^{2+}$:TGA:$Se^{2-}$. For the NCs synthesized with the molar ratios of $Cd^{2+}$:TGA:$Se^{2-}$ (1:2.4:0.5) in Figure 1a, the first excitonic peak was blunt for all samples, and the second was observed when the solution was refluxed for 30 min or longer. When the TGA ratio was reduced to 1.3, sharp excitonic peaks appeared probably due to a narrow size distribution of NCs (Figure 1b). The growth speed of CdSe NCs was also restrained (Figure S1).[23] When the molar ratio of Se was further reduced, the first excitonic peak of the absorption spectra blue-shifted about 20 nm (Figure 1c). This indicates the amount of the monomer decreased at the nucleation and growth stage, resulting in the generation of small particles.

When CdSe cores prepared with the molar ratio of $Cd^{2+}$:TGA:$Se^{2-}$ at 1:2.4:0.5 were irradiated with UV light for 15 min, two PL peaks were observed (Figure 2). The PL efficiency was as low as 2%. When the ratio of TGA upon core synthesis was reduced, the PL efficiency of the irradiated CdSe NCs was increased to 17% with an asymmetric PL spectrum.

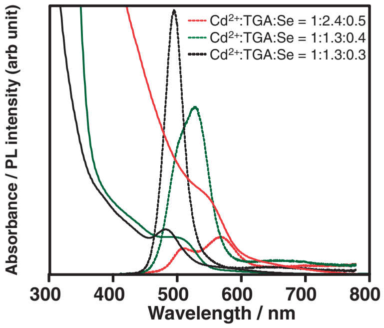

**Figure 2.** Absorption (solid line) and PL (dotted line) spectra of CdSe NCs being irradiated for 15 min. The CdSe cores used were synthesized with different molar ratios of $Cd^{2+}$:TGA:$Se^{2-}$.

This is similar to the case of CdTe NCs, where the PL efficiency substantially improved when the $Cd^{2+}$:TGA ratio was reduced to ca. 1.2.[14,20] For the CdTe NCs, the elemental analysis revealed that the molar ratio of (Te + S) to Cd approached unity when a low $Cd^{2+}$:TGA ratio was used during synthesis.[21] This indicates a high-quality CdTe core with a stoichiometric ratio was created at the beginning of synthesis. Furthermore, a large amount of CdTe NC was generated at the nucleation stage when the low $Cd^{2+}$:TGA ratio was used. This reduced the growth speed of CdTe NCs and resulted in the optimization of the surface structure of NCs during the NC growth.[20] Since the preparation procedure of CdSe cores here is the same as that used to prepare CdTe NCs except for the use of $H_2Te$ gas instead of $H_2Se$, we assert that the same phenomenon occurred during the synthesis when the low molar ratio of $Cd^{2+}$:TGA was used.

When the concentration of TGA and $Se^{2-}$ was further reduced ($Cd^{2+}$:TGA:$Se^{2-}$ = 1:1.3:0.3), the highest PL efficiency and symmetric PL spectra with narrow width were obtained after UV irradiation. The low concentration of TGA and $Se^{2-}$ also reduces the reaction speed (Figure S1),[23] providing further possibilities for smoothing the NC surface.[20] Our results show that a suitable selection of the molar ratio of $Cd^{2+}$:TGA:$Se^{2-}$ upon core synthesis results in the formation of CdSe cores with high PL efficiency after shell coating. Hereafter, CdSe cores prepared with a 1:1.3:0.3 molar ratio of $Cd^{2+}$:TGA:$Se^{2-}$ will be used because they showed the highest efficiency.

Figure 3a shows a temporal evolution of the absorption and PL spectra of CdSe NCs before and during UV irradiation. The formation of a ZnS layer caused the PL intensity along with the UV irradiation to increase substantially. An obvious red shift of the absorption spectra was observed after the irradiation because of the formation of thick shell. This is similar to the results reported for CdSe/ZnS NCs synthesized through an organometallic route.[6] The irradiation conditions such as UV intensity, molar ratio of $Zn^{2+}$/TGA, and solution temperature were further optimized in order to obtain high PL efficiency (Figures S2–S4).[23] The ratio between the CdSe cores and the TGA in the solution was an important factor in obtaining high PL efficiency. Figure 3b shows the PL efficiencies of irradiated CdSe NCs as a function of the molar ratio between TGA and CdSe NCs. High PL efficiency was obtained for the ratio of TGA/NCs higher than $9.5 \times 10^4$ when the NC concentration in the solution was fixed at $2.5 \times 10^{-6}$ M. This is because the concentrated TGA in the solution provides enough of the sulfide ions required to form the ZnS layer during the irradiation. When the TGA concentration was constant, the PL efficiency decreased at the molar ratios of TGA/CdSe more than $1.3 \times 10^5$. In this case, the NC concentration in the solution was quite low. The large amount of sulfide ion supplied by decomposition of TGA enabled the quick formation of a thick ZnS shell. Rapid formation of a thick shell produced defects due to the lattice mismatch between the core and shell. Therefore, the decreased PL efficiency might be due to these defects. PL decay curves revealed that highly luminescent sample had short lifetime as compared with that of low luminescent NCs prepared with a low ratio of TGA/NCs (Figure S5 and Table S2).[23] This means a low ratio of TGA/NCs results in the creation of defect centers upon UV irradiation.

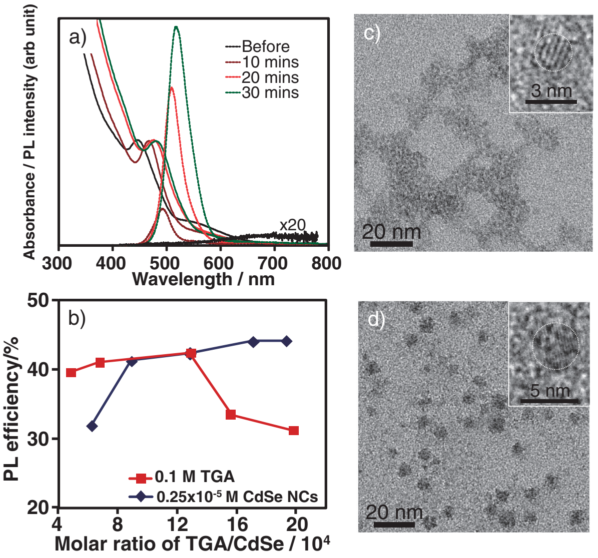

**Figure 3.** (a) Temporal evolution of absorption and PL spectra of CdSe NCs during UV irradiation. (b) PL efficiencies of irradiated CdSe NCs as a function of the molar ratio between TGA and CdSe NCs. TEM images of CdSe NCs before (c) and after (d) UV irradiation. The inserts show HRTEM images of a single NC.

Figures 3c and 3d show transmission electron microscopy (TEM) images of CdSe/ZnS NCs before and after UV irradiation. The particle size of the NCs before UV irradiation is estimated to be 2.1 nm from both absorption spectra[22] and TEM image. After irradiation, the average particle size of CdSe NCs increased to 4.1 ± 0.3 nm (Figure S6).[23] This means the CdSe NCs were covered by a 1-nm ZnS shell (3.2 monolayers). This value is similar to that previously reported for ZnSe and InP NCs prepared by UV irradiation.[18] The ZnS shell created by UV irradiation was thicker than that for NCs with the maximum PL efficiency prepared by an organometallic method (ca. 1.5 monolayers).[4,6] This was attributed to the difference in shell density. For the organometallic route with high reaction temperature, a densified ZnS shell was created. In this case, a thinner shell (1.5 monolayers) was enough to passivate the NCs.[4] However, dislocations were formed to relax the strain between the core and the shell due to the lattice mismatch of CdSe and ZnS when the shell exceeded ca. 2 monolayers. In our case, the ZnS shell was formed at room temperature and the shell density was low, possibly due to the incorporation of organic materials. There-

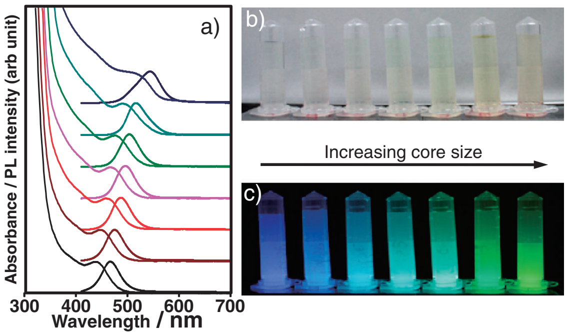

**Figure 4.** (a) Absorption and PL spectra of CdSe/ZnS NCs after irradiation using different core size. Also shown are PL images of the prepared NCs placed under the room light (b) and excited by a UV lamp at 365 nm (c).

**Table 1.** PL properties of NCs after depositing a ZnS shell around different sized CdSe cores

| Sample | $\phi^a$/nm | $\lambda_{PL}$/nm | $\eta$/% | FWHM/nm |
|---|---|---|---|---|
| 1 | 1.79 | 467 | 48.2 | 42 |
| 2 | 1.83 | 475 | 49.3 | 42 |
| 3 | 1.86 | 488 | 50.4 | 43 |
| 4 | 1.90 | 496 | 51.3 | 44 |
| 5 | 1.94 | 503 | 49.9 | 44 |
| 6 | 2.08 | 518 | 43.4 | 47 |
| 7 | 2.18 | 546 | 37.7 | 48 |

[a]Particle size of CdSe cores before irradiation calculated from the excitonic peak.[22]

fore, a thicker ZnS shell was required in order to confine the electrons inside the particles.

Figure 4a shows the absorption and PL spectra of CdSe NCs after irradiation using various sizes of cores. Photographs of the NCs under room light and under a UV lamp are shown in Figures 4b and 4c. After UV irradiation, the first excitonic peaks were slightly smoother and somewhat featureless in comparison with those in crude CdSe solution (Figure 1c). We were able to tune the PL peak wavelengths from blue to green with a spectral width of less than 50 nm (Table 1). Though the as-prepared CdSe cores showed poor PL efficiencies (<1%), PL efficiencies of CdSe/ZnS NCs were increased up to 50% after irradiation. This value is much higher than those reported for CdSe NCs (20–30%) prepared in an aqueous solution[16,17] and is comparable to those for commercial NCs prepared by the organometallic route.

In summary, highly luminescent CdSe/ZnS NCs were prepared in an aqueous solution through photochemical processing. A ZnS shell was deposited on the thiol-capped CdSe cores by UV irradiation. The key points to obtain high PL efficiency were preparation of high-quality CdSe cores with an optimum ratio of $Cd^{2+}$:TGA:$Se^{2-}$ and subsequent formation of a thick ZnS shell around the cores by optimizing of the UV irradiation conditions. The CdSe/ZnS NCs thus prepared show strong PL from blue to green with spectral width of less than 50 nm and the PL efficiency reached 50%. These water-dispersible CdSe/ZnS NCs with high PL efficiency can be expected to find potential application in biomedical labeling. We are currently synthesizing highly luminescent CdSe/ZnS NCs using large cores as a means of obtaining PL in the red region.

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