Blue-emitting Type-II Semiconductor Nanocrystals with High Efficiency Prepared by Aqueous Method

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Forming a type-II structure on alloyed ZnSe core through a facile aqueous method using Cd and S ions resulted in nanocrystals with a photoluminescence wavelength adjusted to the blue region. Their surface was additionally coated by wider band-gap ZnS shell through photodecomposition of the surfactant molecules. Optimizing the conditions for creating the core and shells increased their emission efficiency more than 40%.

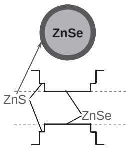
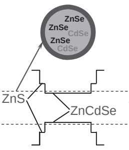
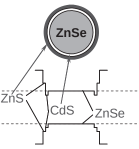
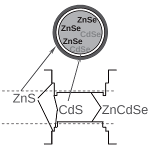
Research on the preparation of semiconductor nanocrystals (NCs) has been actively carried out because of their potential applicability to optoelectronic devices[1] and biological labels.[2] Initially, the particle size, i.e., the quantum size effect, was the only factor used to control the emission wavelength of NCs having a core–shell structure.[3,4] Subsequently, the composition of the core was modified to change the wavelength.[5,6] The resulting alloyed structure can improve NC quality by the narrowing of the photoluminescence (PL) spectral width and the improved chemical stability.[5] More recently, the creation of an additional band structure on the surface was found to shift the wavelengths of the PL to longer region.[7] NCs with this structure are called "type-II," whereas the former two kinds of NCs are called "type-I." The band gap of type-II NCs is such that only electrons or holes of the exciton are confined at the core. These NCs usually showed red-shifted PL peak wavelengths due to the narrower band offset between core and shell.

Type-II NCs are generally prepared using organic solution method. However, there have few reports of NCs with type-II being prepared using aqueous methods. Aqueous methods have several important advantages (good reproducibility, further processing to a sol–gel method, etc) when compared with the organic methods. Among the aqueous preparations, CdTe and ZnSe NCs have received the most attention.[4,8–12] Even though their PL efficiencies are significantly increased in the recent studies,[9–11] emission in the pure blue region has not yet been realized.

In this letter, we describe type-II NCs prepared by modifying the ZnSe NCs in an aqueous solution. We used Cd and S to obtain emission in the blue spectral region (450–490 nm) with sufficiently high efficiency. The preparation was facilitated owing to the advantages of aqueous preparation.

Four types of NCs were prepared, as listed in Table 1. The procedure was based on a method previously reported.[8–10] Briefly, thioglycolic acid (TGA) was used for the surfactant. The molar ratio of Zn^{2+}:Cd^{2+}:Se^{2-}:TGA was typically $1 - x$:x:0.47:2.43, while x was 0–0.1. The NCs were obtained through prolonged refluxing at ca. 100 °C for dozens of hours. The PL efficiencies of the solution were estimated by comparing them with those of quinine sulfate ($\eta = 54.6\%$).[13]

Table 1. Four kinds of NCs together with the spectral properties after post-preparative UV irradiation

No.	(i)	(ii)	(iii)	(iv)
Structure	Type I	Type I	Type II	Type II
Core	Single component	Alloyed	Single component	Alloyed
Band structure				
λ_{PL}/nm	408.4	450.2	449.4	483.4
FWHM[a]/nm	32.0	40.2	33.6	41.0
η/%	45	47	39	44

[a]Full-width at half maximum.

The NCs were then irradiated by UV light (365 nm, 500 mW/cm^2) in an aqueous solution containing Zn^{2+} and TGA to create a ZnS shell, as described elsewhere.[10] Table 1, (i) and (ii) show the properties of these NCs which had single and alloyed component cores, respectively.

We determined that the prepared ZnSe NCs were coated by CdS layer simply dispersing them in Cd^{2+}-containing solution. After the solution was kept for 48 h in the dark, the absorption peak wavelength had shifted to red by ca. 50 nm, and a very weak excitonic PL peak appeared at around the absorption peak wavelength. The same UV-irradiation procedure was taken to create the outer ZnS shell. Since the band gap of CdS is situated a little bit lower than that of ZnSe, the resultant NCs constitute the type-II structure, as shown in Table 1(iii). These NCs showed a similar PL peak wavelength as (ii) ones, but with a significantly narrower spectral width. To confirm the creation of the CdS layer, we irradiated the as-prepared ZnSe NCs in pH-controlled aqueous Zn^{2+} and TGA solution for 5 s. This created a thin ZnS layer on the surface. When the NCs thus prepared were dispersed in Cd^{2+}-containing solution, substantially the same spectrum was obtained (See the Supporting Information for details).[14] It was known that a significant amount of Se on the surface of as-prepared ZnSe NCs was replaced by S which was generated through hydrolysis of TGA during preparation.[4] Therefore, dispersing ZnSe NCs in Cd^{2+}-containing solution here is sufficient to create a type-II structure by the substitution between Zn^{2+} and Cd^{2+} on the surface. Energy dispersive X-ray fluorescence analysis showed that their Cd/Zn molar ratio was 6.5 ± 1.7%.

When we used the alloyed core instead of the single component core of Table 1(iii), the emission wavelength red-shifted further by 34 nm, as shown in Table 1(iv). The combined effect of the alloyed core and type-II structure resulted in NCs that emit

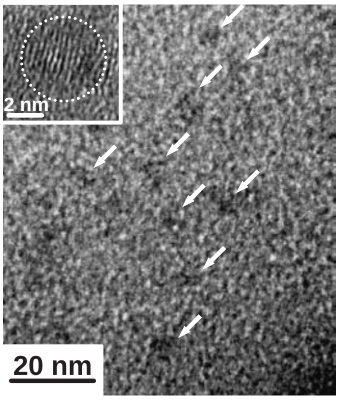


Figure 1. High-resolution transmission electron microscopy images of ZnSe–CdS NCs with type-II heterostructure. White arrows show locations of several NCs.

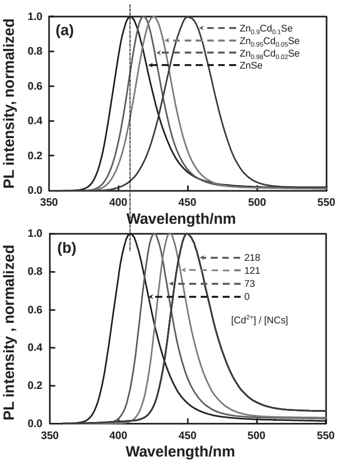


Figure 2. Evolution of PL spectra of alloyed $Zn_{1-x}Cd_xSe$ NCs (a) and ZnSe–CdS NCs with type-II heterostructure (b) after UV irradiation. Leftmost spectra in (a) and (b) are for same sample of pure ZnSe NCs.

pure blue (483 nm) with relatively high efficiency (44%). Transmission electron microscope observations showed that the NC diameter was roughly 4.9 nm (Figure 1).

Figure 2a plots the PL spectra of alloyed $Zn_{1-x}Cd_xSe$ NCs with a Type-I structure for several x values from 0–0.1. When the amount of Cd was increased, the spectrum shifted towards red accompanied by broadening. The spectral properties in Table 1(ii) correspond to the rightmost plot ($Zn_{0.9}Cd_{0.1}Se$).

Instead of the differentiating core structure, the PL peak wavelength can be controlled by creating a type-II structure. When ZnSe NCs were dispersed in the pH-controlled Cd^{2+} and TGA solution for 48 h, the spectrum shifted towards red, and the amount of the shift depends on the concentration of Cd^{2+} ions in the solution, as shown in Figure 2b. The numbers showed in the figure correspond to $[Cd^{2+}]/[NCs]$. The concentration of NCs, namely [NCs], was estimated using the first absorption peak intensity.[15] The number 218 corresponds to a $[Cd^{2+}]$ of 1.3×10^{-3} M in solution. The spectral properties of the rightmost plot in this figure are listed in Table 1(iii).

Figure 3 shows a different aspect of the properties listed in Table 1. As the concentration of Cd^{2+} in the NC solution was increased, the PL peak wavelength shifted towards red because of the creation of a type-II structure. If the core contained some amount of Cd, the wavelength further shifted toward red by band mixing (Figure 3a). When the preparation conditions were optimized, the PL efficiency remained almost the same, as shown in Figure 3b, without significant broadening of the PL spectral width, as shown in Table 1(iv). The prepared blue-emitting, water-soluble NCs are stable and can be easily incorporated into a glass matrix for the application of a new type of phosphor.[16,17]

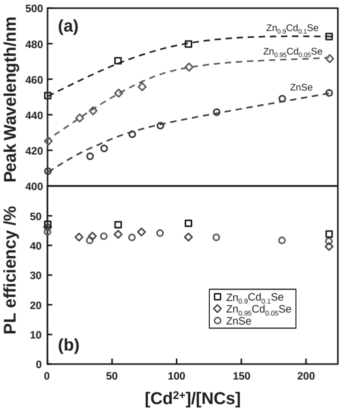


Figure 3. (a) Peak PL wavelength of ZnSe NCs with the alloyed core and type-II heterostructure after UV irradiation. (b) PL efficiencies of alloyed ZnSe NCs as a function of the Cd^{2+} concentrations in post-preparative UV irradiation.

In conclusion, we have developed a simple method for preparing blue-emitting ZnSe-based NCs in aqueous solution. Creating a type-II structure on an alloyed core, the PL peak wavelength of NCs shifted from 408 to 483 nm sequentially. The PL efficiency of these NCs was increased more than 40% after creating a ZnS shell on their surface. This method can be extended to other kinds of water-soluble NCs.

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