

Preparation and photoluminescence of water-dispersible ZnSe nanocrystals

Norio Murase^{a,*}, Mingyuan Gao^{b,1}

^aNational Institute of Advanced Industrial Science and Technology (AIST), Ikeda-City, Osaka 563-8577, Japan

^bInstitute of Chemistry, the Chinese Academy of Sciences, Bei Yi Jie 2, Zhong Guan Cun, 100080 Beijing, PR China

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Abstract

Water-dispersible ZnSe nanocrystals (2–3 nm in diameter) producing photoluminescence (PL) in a blue region were prepared using several thiol-stabilizers. Thioglycerol (TG) gives the most intense PL having a shoulder at 387 nm and a maximum at 475 nm. The former was assigned to the excitonic emission, whereas the latter was assigned to a defect emission. Reflux increases the PL intensity, but did not change its peak wavelength significantly. TG plays an essential role in stabilizing the ZnSe colloidal solution, but it also creates defect emission. Therefore, the less the amount of surfactant, the more the PL intensity becomes in a range where the solution is not precipitated. The attachment and removal of TG on the surface of nanocrystals only occur at refluxing temperature (100 °C). On the other hand, removal of hydroxyl ions from the surface occurs at room temperature when pH is reduced. The ζ -potential and PL intensity are correlated strongly with the pH of the colloidal solution. This indicates hydroxyl ions passivate the surface significantly. Under optimized conditions of TG ratio and reflux time, the ZnSe nanocrystals in water produced whitish-blue emissions with an efficiency of 10% relative to rhodamine 6G. The nanocrystals in water are stable for months in a refrigerator.

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1. Introduction

Currently, we can prepare nanocrystals in vapor [1–3], solid [4–6] and liquid phases [7–9]. The advantage of the liquid-phase preparation is the easiness of size and shape control because mass transfer between nanocrystal and surrounding solvent continues intensively and homogeneously during preparation. This mass transfer plays a crucial role for a creation of highly photoluminescent nanocrystals. [10,11] The nanocrystals prepared in liquid phase should be fixed in some matrix for applications. Recently, emitting CdTe nanocrystals have successfully been incorporated into glass matrices by a sol–gel reaction. [12,13] Water-

dispersibility of nanocrystals was one of the most important features for the incorporation.

Luminescent ZnSe nanocrystals have been produced using various methods. By a sol–gel method, ZnSe ranging in diameter of 3–10 nm is prepared in glass [14]. The photoluminescence (PL) was heavily red-shifted to 600 nm, which is attributed to the presence of Se vacancies. A melt-quenched method prepares ZnSe particles of 4–6 nm in diameter dispersed in a glass matrix [15]. A simple aqueous colloidal method produces ZnSe nanocrystals 3 nm in diameter with a broad emission peaking at 455 nm [16]. A reverse micelle method is also used to prepare 3–4 nm particles showing an emission peak at 355 nm [17]. However, in all these cases, the efficiency of the PL was not clarified. In contrast, a recent preparation by an extension of the organometallic method has been proven to be more effective for controlling particle quality [18]. The resultant nanocrystals show size-dependent PL in the UV–blue region, with a quantum efficiency of 20–50%.

* Corresponding author. Tel.: +81 727 51 8483; fax: +81 727 51 9637.

E-mail addresses: n-murase@aist.go.jp (N. Murase), gaomy@iccas.ac.cn (M. Gao).

¹ Fax: +86 10 8261 3214.

However, the nanocrystals are in organic solvent and cannot be dispersed in water as they are.

In this article, the syntheses and PL properties of blue-emitting ZnSe nanocrystals in aqueous solution is reported. The effect of stabilizer and hydroxyl ions were investigated to clarify the PL mechanism.

2. Experimental

2.1. Sample preparations

The preparative method for the ZnSe nanocrystals is similar to that for CdTe. [9] Ultrapure water (Millipore, Milli-Q synthesis grade) was used in every case after degassing. Thioglycerol (TG) and other stabilizers (thioglycolic acid (TGA) and 2-mercapto-ethylamine (MEA, hydrochloride form)) were investigated. The molar ratio among Zn, Se and the stabilizer was initially set to 1:0.47:2.4 according to the ingredients adopted in the preparations of CdTe. However, other stabilizer ratios between the stabilizer and Zn^{2+} , such as 1.62, 1.70, 2.00, 3.50 and 5.00, were also tried as well for TG. Hereafter, the resultant TG-stabilized ZnSe solutions are abbreviated to TG1.62, TG1.70, TG2.00, TG3.50 and TG5.00, respectively.

An aqueous solution of zinc perchlorate (0.013 mol/L, 60 mL) was firstly mixed with one of the three stabilizers. The pH value of the resultant mixture was set to 11.3 by using NaOH solution. This is because hydroxyl ions also offer stabilizing effects on II–VI nanocrystals [19]. Another aqueous solution of NaHSe was prepared by introducing H_2Se gas into a NaOH solution. Using standard airless techniques, the NaHSe solution was injected into the pH-controlled mixture of Zn^{2+} and stabilizer under rigorous stirring. The resultant solution was subsequently refluxed in an atmospheric condition. The absorption and PL of the ZnSe solution were monitored in the course of reflux. A PL appeared and kept increasing until saturation was reached within a couple of tens of hours. After the PL saturation, the ZnSe solution was cooled down and readied for further investigations. In some cases, the ZnSe solutions were subject to centrifugation to remove small precipitates.

2.2. Measurements and observations

The stock solution was diluted by a factor of 13.2 before the absorption and PL measurements. The PL spectra were recorded by an excitation at 310 or 320 nm. The quantum efficiency of ZnSe was estimated by a conventional method [20]. Rhodamine 6G (R6G) in ethylene glycol from Radiant Dyes Chemie was used as a standard. The cross-section and PL efficiency of this dye were taken from a database [21].

The pH-dependent behavior of the PL was investigated for the prepared TG-stabilized ZnSe solution. A 6-wt.%

perchloric acid solution was used to tune the pH value of the 13.2-times diluted ZnSe solution. The influence of TG ratio (TG: Zn^{2+}) on the optical properties of the resultant ZnSe was also investigated by adding TG at room temperature into the TG1.62 solution at pH 10.3.

The ζ -potential was measured to investigate the effect of hydroxyl ions on PL by a help of a normal ζ -potential meter. The time-resolved PL measurements were performed using a frequency-doubled, pulsed Ti:Sa-laser system (100 fs pulse width, repetition rate of 78 MHz). To select a certain detection wavelength (400 or 477 nm), the PL was detected after passing through a monochromator.

A transmission electron microscope (TEM) was used to observe the ZnSe nanocrystals at magnifications between 50 and 200 K. X-ray diffraction (XRD) measurements of ZnSe solid samples were performed using a white powder precipitated from the colloidal solution by adding isopropanol.

3. Results and discussion

3.1. Size and structure of ZnSe particles

ZnSe nanocrystals prepared by six different TG ratios between 1.62 and 5.00 were inspected by TEM. In addition, the influence of refluxing time (0.5, 1 and 18 hrs for TG1.62 solution) was also examined. The results show that the mean particle diameters of all ZnSe specimens were roughly in a range of 2–3 nm.

XRD was used to characterize ZnSe nanocrystals. The size of the nanocrystals was estimated to be 2.0 nm using the line widths of diffraction peaks by the Scherrer's equation. The standard JCPDS database (ZnSe, cubic 37-1463, hexagonal 15-105) tells that the obtained ZnSe has a cubic structure. However, the lattice constants are contracted by ca. 2.8% comparing with that in the bulk counterpart [22]. Such lattice constant differences from a bulk counterpart have already been reported in CdS and ascribed to a surface effect [23].

3.2. Absorption and photoluminescence of ZnSe stabilized by several thiols

Fig. 1 shows an evolution of absorption spectra of TG1.70 recorded at different times throughout the reflux process. The red shift of the absorption edge induced by the reflux implies that ZnSe nanocrystals grow in size during the reflux. Accompanied by the changes in absorption, the PL intensity increases dramatically and reaches saturation during the reflux as shown in Fig. 2. Similar PL behaviors were also observed from TGA- and MEA-stabilized ZnSe nanoparticles. However, their PL emissions differ in spectral shape, position, as well as in intensity from the TG-stabilized ZnSe. Typical PL spectra of TG-, TGA- and MEA-stabilized ZnSe are shown in Fig.

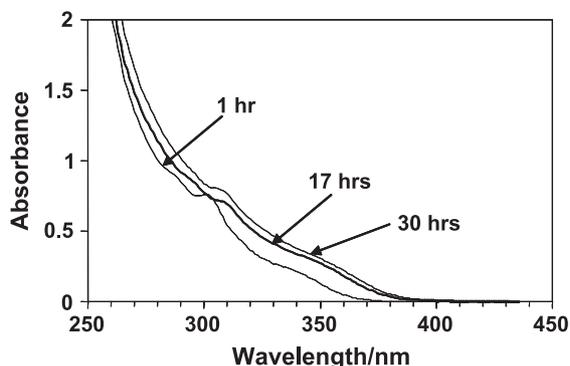


Fig. 1. Absorption spectra of TG1.70 ($\text{TG}:\text{Zn}^{2+}=1.70$) recorded at different times during reflux. The refluxing time for each spectrum is indicated in the figure.

3. The MEA-stabilized ZnSe exhibits a narrow emission with one maximum. This is similar to the ZnSe synthesized by TOPO method [24], except for the low PL intensity of the current system. The TGA system shows a narrow emission peak and a long emission tail toward the lower-energy side. Its PL intensity is the lowest in comparison with two other systems in spite of its success for CdTe [9]. The TG system presents a PL with one broad emission peak and one shoulder located at the high-energy side. Because the TG-stabilized ZnSe showed the most intense PL, additional TG ratios from 1.5 to 5.0 were adopted in the preparation as described in the following section.

3.3. PL properties and ζ -potential of TG-stabilized ZnSe nanocrystals

The PL spectra of ZnSe prepared by different TG ratios were measured after reflux as shown in Fig. 4. In this series of samples, the TG1.62 solution presents the most intense PL which looks whitish-blue under UV irradiation. Its quantum efficiency is estimated to be 10% relative to

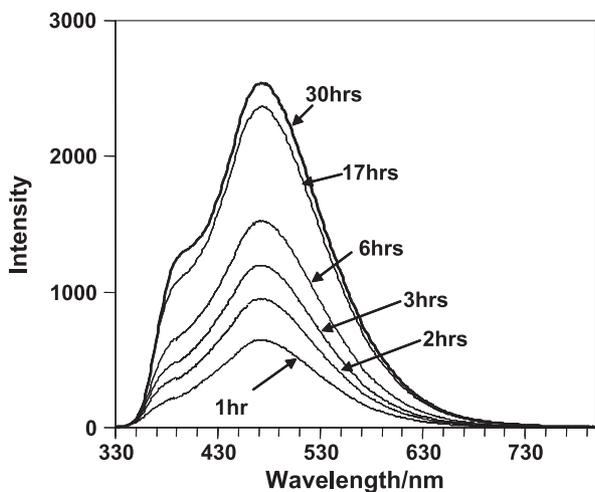


Fig. 2. Evolution of PL spectra recorded from TG 1.70 during reflux. The refluxing time for each spectrum is indicated in the figure.

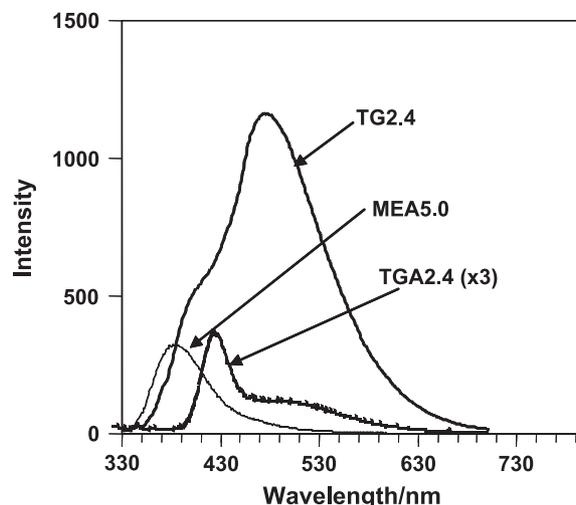


Fig. 3. PL spectra of TG-, TGA- and ME-stabilized ZnSe recorded after the PL reaches its maximum by reflux. The molar ratio between stabilizer and Zn^{2+} ion is shown as a number after the name of each stabilizer in the figure.

Rhodamine 6G. Further lowering the TG ratio to 1.50 resulted in turbid solution even before the injection of NaHTE. This is probably due to the formation of $\text{Zn}(\text{OH})_2$ gel [19]. It is worth mentioning that a mixture of two stabilizers was also tested for improving the excitonic emission by using a MEA:TG: Zn^{2+} ratio of 2.0:2.0:1 at pH 11.4. However, a precipitation comes out of the solution at an early stage of reflux.

The emission lifetime measurements at 400 and 477 nm show that there are at least two decay components, ca. 1 ns and the other, several tens of nanoseconds. The decay curve detected at a shorter wavelength (400 nm) has a larger amount of faster components. PL from a free excitonic in epitaxially grown ZnSe (5 nm thickness)/ZnMgSSe (barrier layer, 30 nm thickness) quantum well of 10 layers also shows two lifetime components of ca. 0.4 ns and ca. 2 ns at 4.6 K [25]. The emission from defect states in ZnS quantum well is reported to be ca. 100 ns [26]. Therefore, it is reasonable to conclude from the lifetime results that the PL

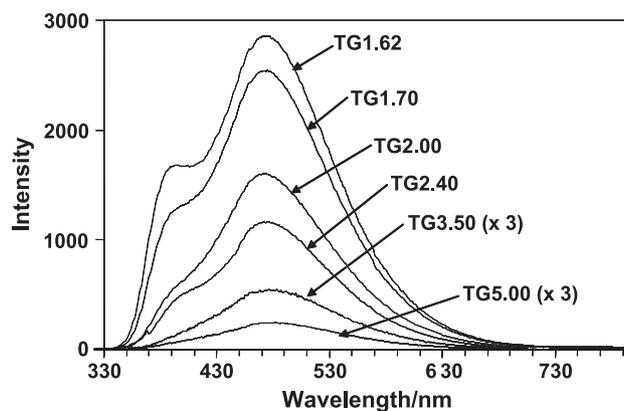


Fig. 4. Saturated PL spectra of ZnSe particles prepared by different TG ratios from 1.62–5.00.

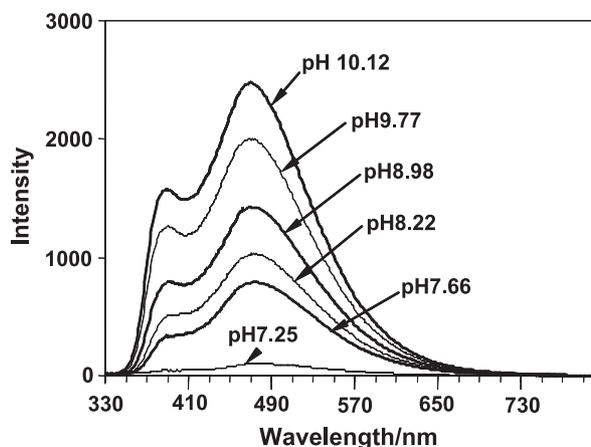


Fig. 5. PL spectra of TG1.70 recorded at different pH values as indicated in the figure. When the pH is decreased, the excitonic emission at 387 nm diminished quickly.

component at ca. 387 nm is the excitonic emission, whereas the PL peaking at ca. 475 nm is a defect emission.

Fig. 5 shows PL intensity is decreased when the pH value of the ZnSe solution is decreased from 10.12 to 7.66. In addition, the intensity at 387 nm (excitonic emission) decreases a bit faster than that at 475 nm and becomes a shoulder when the pH is lower than 8.22. The PL intensity at the peak position (475 nm, defect emission) is re-plotted against pH value in Fig. 6(a). When the pH becomes 7.25, the PL is suddenly quenched almost completely. Even after

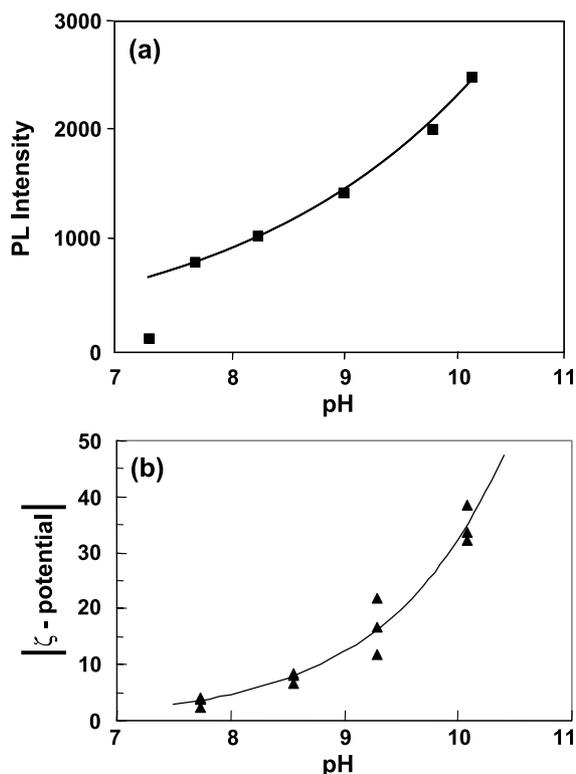


Fig. 6. (a) PL intensity against pH (■) shown in Fig. 4. (b) Absolute value of ζ -potential as a function of pH (▲).

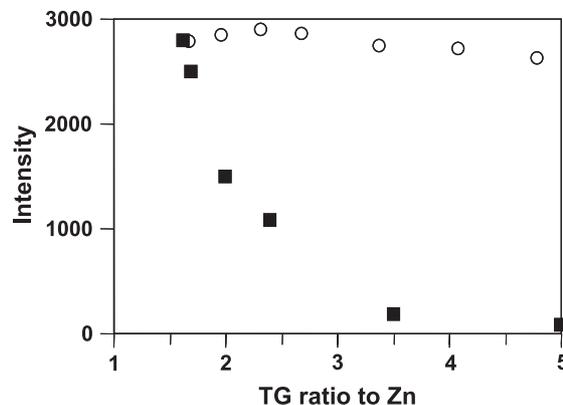


Fig. 7. PL intensities of ZnSe against TG ratios which is achieved either before reaction (■) or after reaction (○) by addition of TG into TG1.62 at room temperature.

the solution is brought back to higher pH range, the PL has never been recovered. The ζ -potential of the nanocrystals in the solution is negative in the alkaline range. When the pH is reduced, the potential decreased as shown in Fig. 6(b). The pH dependence of PL intensity correlates strongly with that of the ζ -potential. This shows that the hydroxyl ions passivate the nonradiative centers on the surface and create a negatively charged barrier around the nanocrystals. When the pH is reduced, the excitonic emission is diminished strongly than the defect emission. This indicates that the hydroxyl ions on the ZnSe nanocrystals surface favor the excitonic emission by reducing defect centers on the surface.

When TG is added at a fixed pH value of 11.34 at room temperature to the TG1.62 solution, the PL intensity decreases very slightly as shown by open circles in Fig. 7. For comparison, the PL intensities shown in Fig. 4 versus different initial TG:Zn²⁺ ratios are also given in Fig. 7 by solid squares. This indicates that the attachment and detachment of the TG from the surface of nanocrystals only occurs at refluxing temperature (ca. 100 °C). The less the amount of TG on the surface of the nanocrystals, the more the PL becomes probably because TG creates some defect centers on the surface.

4. Conclusion

ZnSe nanocrystals were produced in aqueous solutions using TG, TGA or MEA as a stabilizer. The nanocrystals were 2–3 nm in diameter. XRD results indicate that the TG-stabilized ZnSe nanocrystals had a cubic structure. Among all three stabilizer systems, the TG led to the most intense PL, which had two components peaking at 387 and 475 nm. Lifetime measurements showed that the two components in the PL were excitonic (387 nm) and defect emissions (475 nm). The refluxing was shown to be the most critical process for generating emitting ZnSe nanocrystals. The hydroxyl ions enhance the surface potential

and PL intensities. The final PL of TG-stabilized ZnSe was whitish-blue. The quantum efficiency was estimated to be ca. 10% relative to R6G in the best case by using a standard method [20].

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