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Non-heavy-metal ZnS quantum dots with bright blue photoluminescence by a one-step aqueous synthesis

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Abstract

We have examined the aqueous synthesis of non-heavy-metal ZnS quantum dots (QDs) using 3-mercaptopropionic acid (MPA) as the capping molecule at various pH and MPA:Zn:S ratios. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) indicated that the aqueous ZnS QDs were 3–5 nm in size with a zinc blende structure. We showed that, at pH 12 with a MPA:Zn:S = 8:4:1 ratio, the ZnS QDs with optimal blue emission could be obtained in a one-step, room-temperature aqueous process that exhibited a quantum yield of 31%, higher than that of the commercial CdSe/ZnS core–shell QDs. The present ZnS QDs could pass through a 50 kD filter. This indicated that they were smaller than 5 nm in size, consistent with those estimated from the UV–vis absorption edge and the TEM image. At a lower pH (e.g. pH = 8), the room-temperature synthesized ZnS QDs exhibited no photoluminescence. Although further hydrothermal annealing at 100 °C could improve the photoluminescence of the ZnS QDs, the resultant emission was not as bright as that obtained at pH 12 at room temperature. The blue emission of aqueous ZnS QDs was likely the result of trap-state emissions involving the defect states of the QDs. The present ZnS QDs were bright, small and contained non-heavy-metal elements, thus offering the potential for *in vivo* bioimaging.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recent advances in producing highly luminescent quantum dots (QDs) have led to the applications of QDs in imaging biological systems. For example, imaging tumors in animals using QDs have been demonstrated [1]. However, no QDs have been used in human bodies yet. It is known that QDs could interfere with the functions of biological systems and lead to impairment in several ways [2]. First and most critical is the toxicity that arises from the composition of the QDs. Derfus *et al* [3] reported that CdSe-core QDs were cytotoxic, when surface oxidation occurred through exposure to air or UV irradiation that led to the formation of reduced Cd on the particle surface and eventually the release of free, toxic Cd^{2+} ions. The size of the QDs has an effect, too. Lovric *et al* [4] showed that smaller CdTe QDs with green emission exerted more harmful effects than larger red-emitting CdTe QDs in molecular processes. Nanosize QDs are prone to dissolution due to their high surface-to-volume ratio and the increase of solubility with smaller size. Various coating strategies have been proposed and attempted to alleviate this problem. Coating with a ZnS shell or with bovine serum albumin (BSA) [4] was shown to reduce but not eliminate the cytotoxicity. CdSe and CdSe/ZnS QDs encapsulated with 3-mercaptopropionic acid, silanization, or polymer coatings still had concentration thresholds above which the onset of cytotoxicity occurred [5].

Clearly, the composition toxicity is the most urgent problem that must be addressed before QDs can be applied for *in vivo* applications.

Most QDs contain toxic heavy-metal elements such as Cd, Hg, Pb, etc. Recently, Evident Technologies developed a type of non-heavy-metal QDs, the T2-MP EviTags [6], which consist of an InGaP core with ZnS shell, and have a size of about 25 nm with red emission at 650–680 nm. Besides the commercial InGaP QDs, ZnS is another non-heavy-metal system with reported photoluminescence in the blue range [7–11]. However, many of the ZnS systems were made using an environmentally hazardous organic-solvent route [9, 11], or deposited in a silica matrix [10], which were not suitable for bioimaging applications. Denzler *et al* [8] precipitated ZnS colloidal particles in aqueous solution without using capping molecules. As a result, the ZnS particles had a large size and settled quickly. Becker *et al* [7] showed that, with the use of capping molecules, colloidally stable ZnS nanocrystals could be produced in an aqueous process at pH 8, but no bright emission was obtained from the as-synthesized sample.

The purpose of this study is to investigate aqueous synthesis of non-heavy-metal QDs with strong visible emission other than red. Here we report the synthesis of ultrafine ZnS QDs with bright blue emission using an environmentally friendly, one-step aqueous procedure [12]. Although the blue luminescence of the present ZnS QDs are due to trap-state emission, they are bright, exhibiting a quantum yield of 31%, higher than that of the commercial CdSe/ZnS QDs. Furthermore, the carboxyl groups on the surface of ZnS QDs are ready for bio-conjugation as-synthesized, and the small size of the present ZnS QDs is desirable as markers in biological systems.

2. Experiment

All chemicals were used as purchased without further purification. The aqueous ZnS QDs were synthesized at room temperature as follows. First, appropriate amounts of zinc nitrate ($Zn(NO_3)_2$), sodium sulfide (Na_2S) and 3-mercaptopropionic acid (MPA) (Alfa Aesar, Ward Hill, MA) were dissolved separately in deionized (DI) water. For a MPA:Zn:S composition of 1:1:1, 0.08 mmol $Zn(NO_3)_2$ was first dropped slowly into the solution containing 0.08 mmol MPA with continuous stirring. The pH of the mixture was adjusted by adding the tetrapropylammonium hydroxide (($CH_3CH_2CH_2$)$_4$NOH) (Alfa Aesar, Ward Hill, MA). After the desired pH was obtained, 0.08 mmol Na_2S was added quickly with vigorous stirring to precipitate ZnS nanoparticles. We generally allowed 5 min for the precipitation to complete. If a higher Zn content was desired, the excess Zn was added after the initial precipitation, and the suspension was allowed to cure at room temperature for five more minutes. The final QDs suspension had a volume of 50 ml and a nominal ZnS concentration of 1.6 mM based on the concentration of S, as the concentration of Zn varied depending on whether the sample had excess Zn. The obtained QDs suspension was then stored in a refrigerator at 4 °C and remained clear for months. Unless mentioned otherwise, all ZnS QD suspensions described below had a 1.6 mM nominal concentration.
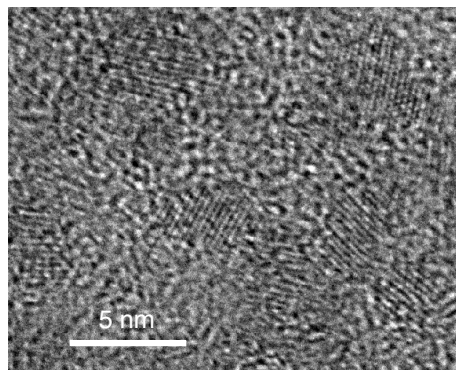

Figure 1. TEM image of the MPA-capped ZnS QDs with a MPA:Zn:S ratio of 8:4:1.

For transmission electron microscopy (TEM), the excess capping molecules and ions were removed by filtering, microcentrifugation and rinsing with DI water. The obtained QD suspension was then dropped on the surface of a TEM grid with an ultra-thin carbon film, dried in air, and was examined with a JEM-2010F FasTEM high resolution analytical transmission electron microscope. The powder x-ray diffraction pattern of the ZnS QDs was collected on a Siemens D 500 x-ray diffractometer. The powder sample was prepared by adding ethanol to precipitate the QDs from the suspension, followed by centrifugation and air-drying at 50 °C overnight.

All photoluminescence (PL) spectra of the ZnS QDs suspension were measured using a QM-4/2005 spectrofluorometer (Photon Technology International, Birmingham, NJ) with both the excitation and the emission slit width set at 2 nm. From the excitation spectra, the wavelength for the optimal emission intensity was identified first, and the PL emission spectra were then obtained using the optimal excitation wavelength. UV–vis absorption spectra were collected using a Lambda-40 UV–vis spectrometer (Perkin Elmer Life And Analytical Sciences Inc., Boston, MA) with the slit width of 2 nm. All spectra including the PL spectra and the absorption spectra were obtained by scanning the samples loaded in a 4.5 ml plastic cuvette at the speed of 4 nm s^{-1} and with the data interval of 1 nm.

3. Results

3.1. Morphology and structure of aqueous ZnS QDs

A typical TEM micrograph of the QDs with a MPA:Zn:S ratio of 8:4:1 is shown in figure 1. As can be seen, the nanoparticles were 3–5 nm in size, well separated and more or less spherical with clear lattice fringes. Because of the small particle size, it was difficult to differentiate between the wurtzite and the zinc blende structures using electron diffraction. Therefore, the XRD pattern of the ZnS QDs powder was collected. As an example, the XRD result of ZnS QDs with a MPA:Zn:S ratio of 4:2:1 is shown in figure 2. One can see that the QDs exhibited a zinc blende structure. The broad peaks indicated the small particle size.

3.2. Bright blue emission of aqueous ZnS QDs

Figure 3(a) depicts the photograph of a ZnS QDs suspension synthesized at room temperature at pH 12 and with the
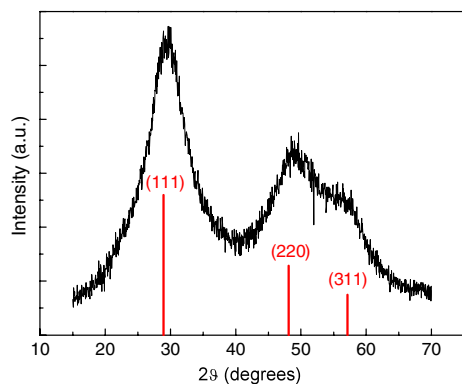
Figure 2. XRD pattern of ZnS QDs with a MPA:Zn:S ratio of 4:2:1. The lines indicate the pattern and relative intensities of bulk ZnS with cubic zinc blende structure.

composition of MPA:Zn:S $= 8:4:1$. The sample was placed on a 302 nm UV lamp (UVM-14, Ultra Violet Product Inc., Upland, CA), displaying the bright blue photoluminescence. As shown in figure 3(b), the QDs had the absorption edge near 312 nm and the emission peak at 415 nm.

Measurements have also been carried out to quantify the quantum yield (QY) of the present ZnS QDs. Quantum yield describes the efficiency of a material in converting the excitation into fluorescent emission. According to Williams' method, the quantum yield of a test sample can be obtained from the ratio of the slope of the integrated fluorescence intensity versus absorbance of the sample to that of a standard [13]. In our experiment, Rhodamine 101 was used as the standard. The commercial EviTags CdSe/ZnS QDs (Evident Technologies, Troy, NY) were also included for comparison. The absorption and emission spectra were measured using a fixed excitation wavelength of 312 nm for all three systems at several concentrations. The absorbance was kept below 0.15 to avoid the reabsorption effect. The integrated fluorescence intensity was obtained by integrating the emission intensity over the entire wavelength range under the emission peak. In figure 3(c), we plotted the integrated emission intensity versus absorbance for Rhodamine 101 (squares), EviTags CdSe/ZnS QDs (circles) and the present aqueous ZnS QDs (triangles). With the QY of Rhodamine 101 taken as 100% [14], we obtained the QY of the ZnS QDs as 31%, which was much higher than that of the commercial QDs, 11%.

3.3. Particle size of ZnS QDs

In the aqueous synthesis, MPA was used as the capping molecule to stabilize the ZnS QDs. In the basic solution, the thiol group of MPA bonded to the Zn ions on the QD surface, and the negative charge of the dehydrogenized carboxyl group of MPA stabilized the QDs by electrostatic repulsion.

Furthermore, we obtained the ZnS QDs with different particle sizes by adjusting the ratio of MPA to ZnS. The Zn:S ratio was kept at 1:1 while the MPA:ZnS ratio was varied as 2:1, 4:1 and 8:1. The absorption spectra were measured as shown in figure 4(a) and the particle sizes were calculated from the absorption edge according to the relationship between the bandgap energy shift and the crystalline size [15]. As listed
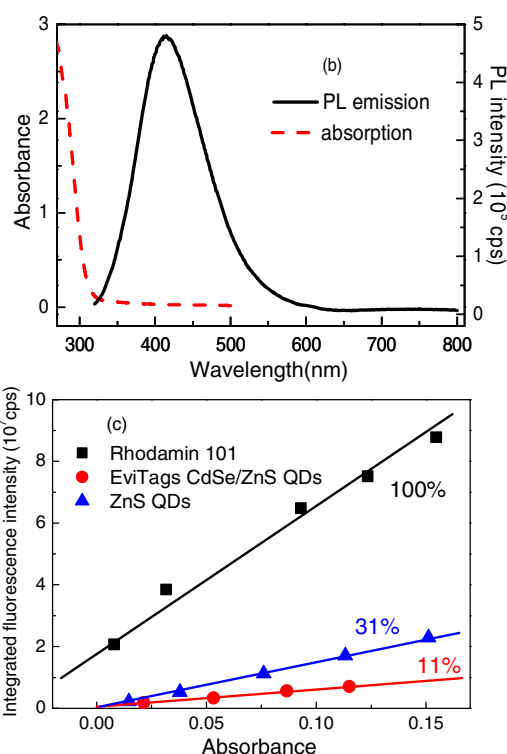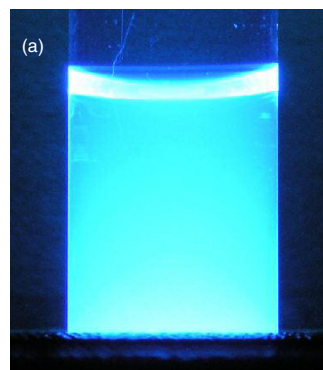

Figure 3. (a) The colour photograph of ZnS QDs suspension synthesized at pH 12 with the composition of MPA:Zn:S $= 8:4:1$, which was placed on a UV lamp with the excitation wavelength of 302 nm, displaying the bright blue photoluminescence. (b) The absorption (dashed line) and PL emission spectra (solid line) of the present ZnS QDs. (c) Integrated fluorescence intensity versus absorbance of the standard Rhodamine 101 (squares), the commercial EviTags CdSe/ZnS QDs (circles) and the present ZnS QDs (triangles).

in table 1, the sample with higher MPA to ZnS ratio had the smaller particle size with a blue-shifted absorption edge. Specifically, the QDs with MPA:ZnS $= 8:1$ were 4.7 nm in size.

We then filtered the samples by microcentrifugation (MiniSpin plus, Eppendorf North America Co., Westbury, NY) through a 50 kD filter (Millipore Co., Billerica, MA) which has the pore size of about 5 nm. After centrifugation at 12 000 rpm for 2 min, the smaller particles in the original suspension passed through the filter into the filtrate, while the larger particles remained in the retentate. In figure 4(b), we
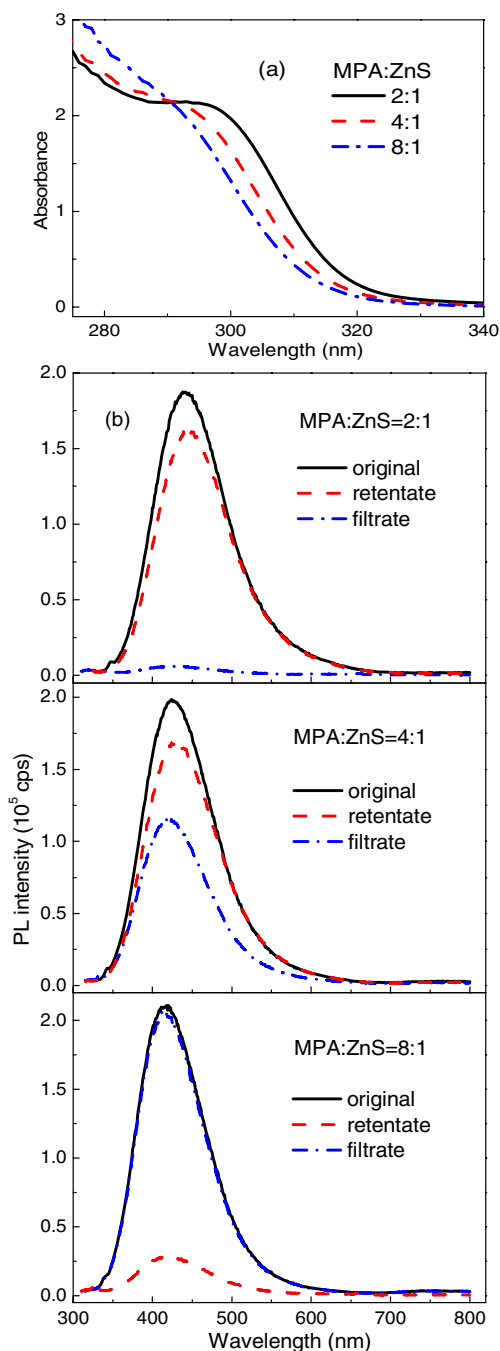
Figure 4. (a) The absorption spectra of ZnS QDs with different MPA:ZnS ratios, 2:1, 4:1 and 8:1. (b) The PL spectra of the original, retentate and filtrate of the three samples with different MPA:ZnS ratios.

showed the PL spectra of the initial suspension (solid line), retentate (dashed line) and filtrate (dotted–dashed line) for the three samples with different MPA:ZnS ratios. As we can see, with MPA:ZnS = 2:1, the retentate retained most of the PL intensity while the filtrate showed negligible luminescence; with MPA:ZnS = 4:1, decent emission was observed in both the retentate and filtrate; and with MPA:ZnS = 8:1, the filtrate displayed a PL intensity as strong as the original suspension, but the retentate had little intensity. These results suggested
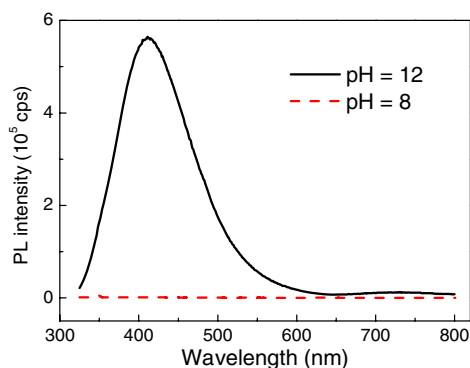

Figure 5. The PL spectra of two ZnS QDs samples with the same composition of MPA:Zn:S = 8:4:1, synthesized at different pH, 8 and 12.

Table 1. The absorption edge, particle size and emission peak wavelength of the original, filtrate and retentate for three ZnS QDs samples with different MPA:ZnS ratios: 2:1, 4:1 and 8:1.

		MPA:ZnS		
		2:1	4:1	8:1
Absorption edge (nm)		321	317	313
Particle size (nm)		5.4	5.0	4.7
Emission peak	Original	442	426	418
wavelength	Filtrate	426	420	418
(nm)	Retentate	446	429	420

that a higher MPA:ZnS ratio can produce smaller particle sizes, which was consistent with the calculation from the absorption edge. Meanwhile, the QDs with higher MPA:ZnS ratio also exhibited a smaller emission peak wavelength, as listed in table 1. For QDs with a particular MPA:ZnS ratio, the filtrate usually had a smaller emission peak wavelength and the retentate a larger emission peak wavelength than the original QD suspension.

During synthesis, the particle growth is controlled by the competition between the S^{2-} ions and the thiol groups of MPA for linking to the cations on the growing particle surface [16]. With a higher MPA concentration in the solution, more particle surface was covered by MPA, thus the particle growth was restrained. In the present study, we have achieved ZnS QDs smaller than 5 nm (or the pores of 50 kD filter) with MPA:ZnS = 8:1. In comparison, the commercial QDs typically have a size of 25–40 nm due to the core–shell structure. The ZnS particles studied earlier were also much larger, with a size about 100 nm [9, 17].

4. Discussion

4.1. pH effect

The emission intensity of the ZnS QDs could be strongly affected by the pH at which they were synthesized. To examine the pH effect, we prepared two samples at room temperature with the same composition of MPA:Zn:S = 8:4:1, at two different pH values, pH 8 and pH 12. The PL emission spectra of these two ZnS QD suspensions were shown in figure 5. Clearly the QDs synthesized at pH 12 had a strong emission
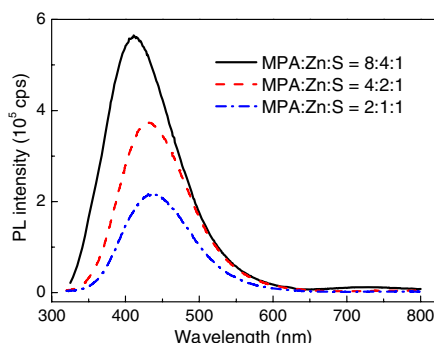
Figure 6. The PL spectra of three ZnS QDs samples synthesized at pH 12, with different MPA:Zn:S ratios, 8:4:1, 4:2:1 and 2:1:1.

Figure 7. The PL spectra of the ZnS QDs with MPA:Zn:S = 8:4:1 and synthesized at pH 8, after hydrothermal treatment at 100 °C for various periods of time.

peak around 412 nm, while the QDs at pH 8 did not exhibit appreciable photoluminescence. Therefore, the bright blue emission of ZnS QDs can only be obtained from the sample synthesized at very high pH. This was attributed to the lower solubility of ZnS at higher pH [18], which allowed the ZnS QDs to precipitate and crystallize better and hence possess better PL properties.

4.2. MPA:Zn:S ratio effect

The composition ratio of MPA:Zn:S played an important role for the photoluminescence of ZnS QDs. For comparison, several samples were produced at room temperature and pH 12, with the different ratios of MPA:Zn:S = 2:1:1, 4:2:1 and 8:4:1. As shown in figure 6, the sample with more excess Zn displayed higher emission intensity. Under the basic condition and with the excess Zn, a $Zn(OH)_2$ shell was expected to form and cover the surface of ZnS QDs [19]. The core–shell structure has been studied in many QD systems and found to be able to increase the photoluminescence greatly [20, 21]. The ratio of MPA:Zn:S = 8:4:1 was the optimal composition we have studied, showing the strong emission and high quantum yield. In addition, the sample with more MPA exhibited smaller emission peak wavelength, which was consistent with the results discussed in section 3.3.

4.3. Hydrothermal treatment effect

Although the ZnS QDs synthesized at pH 8 at room temperature with MPA:Zn:S = 8:4:1 did not show appreciable photoluminescence in figure 5, they can be improved by hydrothermal treatment after synthesis. We heated the sample to 100 °C in a hydrothermal bomb (Parr Instrument Co., Moline, IL) for various periods of time and monitored the emission spectrum at each step. As shown in figure 7, the PL intensity initially increased with increasing time and reached the maximum value at 18 h, beyond which the intensity started to decrease with time. The emission spectrum shifted to larger wavelength continuously. After 40 h, not only the PL intensity of the ZnS QDs reduced but the suspension became cloudy, indicating that aggregation occurred. Since we did not control the atmosphere during the heat treatment, with the presence of oxygen and thermal energy, it was likely that the aggregation occurred due to the formation of disulfur bonds [22], which eventually detached the capping molecules
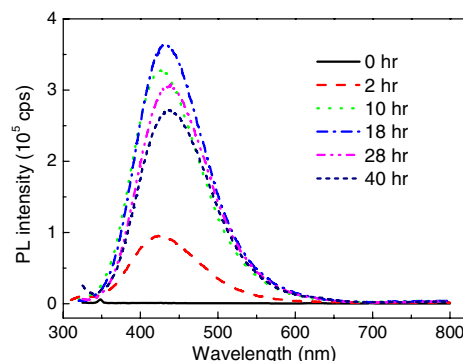
from the QD surface and led to the aggregation and degradation of photoluminescence. It should be noted that, even though the ZnS QDs synthesized at pH 8 had enhanced PL intensity after 18 h hydrothermal treatment, it was still not as bright as the sample synthesized at pH 12 at room temperature.

4.4. Trap-state emission

The bulk ZnS has a bandgap of 3.6 eV [23]. Due to the quantum confinement effect and their small size, the ZnS QDs were expected to have a bandgap larger than 3.6 eV and emit light in the UV range. However, our aqueous ZnS QDs exhibited blue photoluminescence within the wavelength range of 415–440 nm. This can be attributed to the trap-state emission, which has smaller energy (larger wavelength) than the band-edge emission of ZnS QDs. As discussed by Denzler *et al* [8], the bulk defects such as vacancies and interstitials were the main source of trap states in the aqueous ZnS QDs. The electron transitions could occur between the trap states and the conduction band (or the valence band), giving rise to the trap-state emission. There are many possible trap-state emissions each with different emission energy. All these emissions could contribute to the photoluminescence of the aqueous ZnS QDs, resulting in the relatively wide emission peaks. The PL spectrum of our aqueous ZnS QDs had the full width at half maximum (FWHM) about 100 nm. However, it seems that the trap-state emissions did not prohibit the present ZnS QDs from exhibiting a high quantum yield. Potentially the ZnS QDs can be used for imaging single targets.

The electron–hole recombination via surface localized states can lead to other possible trap-state emission as well. The interaction between zinc atoms and capping molecules may play a role in the surface state and the broad visible emission [24]. More studies on the effect of different capping molecules for the aqueous ZnS QDs are on the way.

5. Conclusions

Non-heavy-metal ZnS QDs with blue photoluminescence have been synthesized in an aqueous one-step process at room temperature using MPA as the capping molecule. They present a step forward in reducing the potential hazards to the environment and to human health, as the conventional QDs

contain toxic heavy-metal elements and are also synthesized with an organic route. The TEM and XRD results indicated that the ZnS QDs were well separated, nearly spherical and 3–5 nm in size with a zinc blende structure. The present aqueous ZnS QDs synthesized at pH 12 with the composition of MPA:Zn:S = 8:4:1 displayed strong emission with the quantum yield of 31%, higher than that of the commercial CdSe/ZnS core–shell QDs. With MPA:ZnS = 8:1, we have obtained ZnS QDs as small as 4.7 nm that passed through a 50 kD filter. The very high synthesis pH and optimal composition ratio are important to achieve the strong PL intensity. The ZnS QDs synthesized at pH 8 were not as bright as those synthesized at pH 12, even though they could be improved by the hydrothermal treatment at 100 °C for 18 h. Although the trap-state emission caused a relatively wide PL peak, the present non-heavy-metal ZnS QDs are bright with a high quantum yield, promising for potential single-target imaging applications.

Acknowledgments

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