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Low Temperature Synthesis of MPA Capped ZnS Quantum Dots and its Characterization Studies

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ABSTRACT

ZnS QDs with bright blue photoluminescence have been synthesized via an aqueous one-step process at room temperature with MPA as the capping molecule. The TEM and XRD results indicated that the MPA-capped ZnS QDs were 4-5 nm in size with a cubic zinc blend structure. Various processing parameters were adjusted and studied to optimize the properties of the obtained ZnS QDs.

Keywords*: ZnS Quantum Dots, Blue shift, Semiconductors, MPA Capped*

1. INTRODUCTION

Since the first demonstration of quantum dots for biological imaging applications in 1998 [1,2], numerous breakthroughs in QDs technology have led to the recent success of targeted imaging using QDs both *in vitro* and *in vivo*. For example, various cellular components and proteins (in live or fixed cells) have been labeled and visualized with functionalized QDs [3,4], such as the nuclei, mitochondria, microtubules, actin filaments, cytokeratin, endocytic compartments, mortalin, and chaperonin proteins. The biocompatible QDs [7,8] have also been used in living mouse, chick and pig models for the mapping of tumors, lymph nodes, vasculature, and neural system [9-10], etc. However, no QDs have been used in human bodies yet. There have been many serious questions and concerns raised regarding the cytotoxicity of the QDs containing Cd, Se, Te, Hg, and Pb. These chemicals, especially the heavy-metal elements, can be potent toxins, neurotoxins, and/or teratogens depending on the dosage, complexation, and accumulation in the liver and the nervous system.

Zinc has been considered as a good candidate to replace the heavy metals contained in QDs. Since an average adult ingests 10-15 mg of zinc daily as a nutrient and absorbs about 5 mg, trace amount of zinc is not hazardous to human body. Mn or Cu doped ZnSe QDs have been reported and can cover a similar emission range as that of CdSe QDs [11]. Such QDs are less sensitive to environmental changes such as thermal, chemical, and photochemical disturbances. The Cd-free $ZnSe_{1-x}Te_x$ QDs were also reported with necessary post-preparative UV irradiation at high temperature to show luminescence in the blue region [12]. Evident Technology Inc. developed a type of non-heavy-metal QDs, the T2-MP EviTags, which consist of an InGaP core with ZnS shell, and have a size of about 25 nm with red emissions at 650-680 nm. Similar InGaP/ZnS core/shell QDs bound to chitosan were demonstrated for deep tissue imaging with the diameter of about 29 nm. Furthermore, pure ZnS can be another good candidate as non-heavy-metal QDs. Many of the ZnS systems were made using the complicated method with organic solvents [13,14], or deposited in a silica matrix, which were not suitable for bioimaging applications. Denzler *et al.*[15] precipitated ZnS colloidal particles in aqueous solution without using capping molecules. As a result, the ZnS particles had large size and settled quickly. Becker *et al.*[16] showed that with the use of a capping molecule, 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.

For human health and environmental considerations, it is important to have bright stable QDs that are free of heavy metals and are produced through a simple aqueous synthesis route. The purpose of this study is to investigate the aqueous synthesis of non-heavy-metal ZnS QDs with strong visible emissions and excellent stability. In this work we developed new aqueous syntheses of MPA-capped ZnS QDs which can be used to produce high quality QDs with various compositions.

2. EXPERIMENTAL

2.1. Materials

The zincnitrate [$Zn(NO_3)_2$], sodiumsulfide[Na_2S], MPA,(3-mercapto propionic acid) and tetrapropyl ammonium hydroxide [$(CH_3CH_2CH_2)_4NOH$] were

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purchased from Sigma-Aldrich, St Louis, MO. All the chemicals were of analytical grade and used as purchased without further purification.

2.2. Instruments

A Perkin Elmer Lamda 20 UV–vis Spectrophotometer was used to carry-out absorption spectra in the 200–1100 nm wavelength range, while room temperature photoluminescence (PL) spectra were recorded on a Perkin Elmer LS 55 luminescence spectrometer.Samples were placed in quartz cuvettes (1 cm path length). The powder XRD pattern was measured by a Siemens D 500 X-Ray Diffractometer operated in the Bragg configuration using Cu Kα radiation with the wavelength of 1.54 A^o. operated at 40 kV and 30 mA. transmission electron microscopy (TEM) was carried out with a 2000 FX electron microscope (Japan Electron Optics Ltd., Tokyo, Japan) operated at 200 kV and a Perkin Elmer spectrum one FT-IR Spectrometer with universal ATR sampling accessory was used for the FT-IR spectra.

2.3. Synthesis method of MPA capped ZnS Quantum Dots

The zinc nitrate [$Zn(NO_3)_2$] solution (0.04 M) and the sodium sulfide [Na_2S] solution (0.02 M) were prepared in DI water, respectively. For a sample with a MPA:Zn:S composition ratio of 8:4:1, 0.64 mmol (56 μl) MPA was added in 36 ml of DI water and stirred for 5 min. 2 ml of the 0.04 M $Zn(NO_3)_2$ solution was dropped slowly into the MPA solution with constant stirring for 10 min. Subsequently, the mixture was titrated with tetrapropyl ammonium hydroxide [$(CH_3CH_2CH_2)_4NOH$] to pH 12 and stirred for 10 min, followed by rapid addition of 4 ml of the 0.02 M Na_2S solution. We then waited for 5 min before adding another 6 ml of the 0.04 M $Zn(NO_3)_2$ solution. The pH of the suspension was maintained at 12 by adding $(CH_3CH_2CH_2)_4NOH$ with constant stirring for 5 more minutes. The obtained ZnS QDs suspension was clear and colorless. The final volume of the sample was about 50 ml and the nominal ZnS concentration was 1.6 mM based on the concentration of S. The aqueous ZnS QDs suspension was quenched to 0 °C in a freezer and stored in a refrigerator at 5 °C.

3. RESULTS AND DISCUSSION

3.1. TEM and XRD Analysis

A typical TEM micrograph of the MPA-capped ZnS QDs with a MPA:Zn:S ratio of 8:4:1 is shown in Figure 1. As can be seen, the nanoparticles were 4-5 nm in size, well-separated, more or less spherical in shape, and with clear lattice fringes. The contrast of the image was not very high due to the inevitable background of the carbon film which is in an amorphous phase.

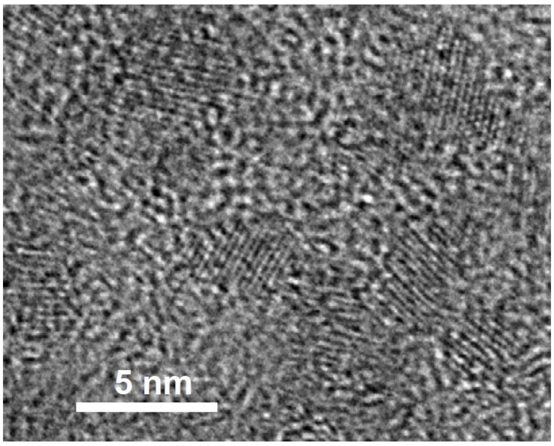

Figure 1: TEM micrograph of the MPA-capped ZnS QDs with a MPA:Zn:S ratio of 8:4:1.

Because of the ultra-small particle size, it is very difficult to differentiate the crystal structure of QDs between the hexagonal wurtzite and the cubic zinc blende using electron diffraction with TEM. Therefore, the XRD pattern of the ZnS QDs powder was collected using 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^{o}C overnight.

Figure 2 shows the XRD pattern of the MPA-capped ZnS QDs with a MPA:Zn:S ratio of 8:4:1 as an example. By comparing with the pattern of the bulk ZnS material, it was indicated that the MPA-capped QDs had a cubic zinc blende crystal structure. Due to the small crystalline size, the peaks in the pattern of QDs were broad and overlapped at the higher diffraction angle.

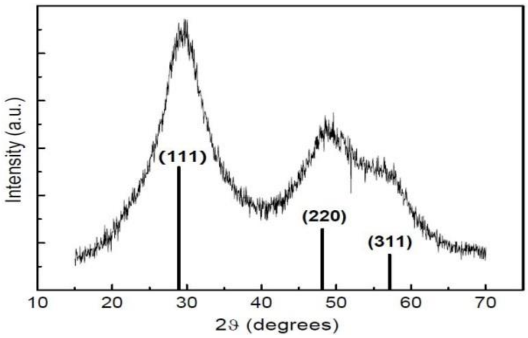

Figure 2: XRD pattern of the MPA-capped ZnS QDs with a ratio of MPA:Zn:S = 8:4:1. The vertical lines indicate the pattern and relative intensities of bulk ZnS with cubic zinc blende structure.

3.2. Bright Blue Emission

The photoluminescence spectra of the ZnS QDs suspension were measured using the QM-4/2005 spectro fluorometer. The UV-Vis absorption spectra were also collected using the Lambda-40 UV-Vis spectrometer. As can be seen, the QDs had an absorption edge near 315 nm and an emission peak at around 415 nm.

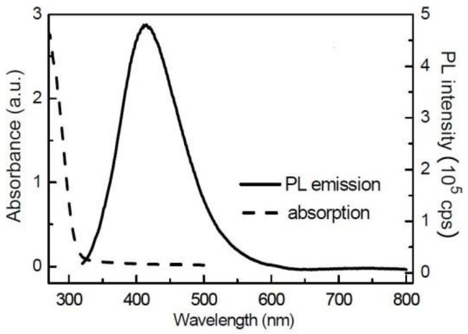

Figure 3: PL emission (solid line) and absorption (dashed line) spectra of the MPA-capped ZnS QDs with the ratio of MPA:Zn:S = 8:4:1.

Note that the bulk ZnS has a band gap of 3.6 eV.159. According to the quantum confinement effect and the relationship between band gap and particle size of semiconductor nanocrystals, the ZnS QDs were expected to have a band gap larger than 3.6 eV and emit light in the UV range. However, as shown in Figure 3, our aqueous ZnS QDs exhibited visible blue photoluminescence with the wavelength around 415 nm, which was about 100 nm larger than the absorption edge. This broad Stokes shift indicated that the present ZnS QDs had the trap-state emissions, rather than the band-edge emissions. As discussed by Denzler *et al*, [15] the bulk defects such as vacancies (Schottky defects) and interstitials (Frenkel defects) were the main source of trap states in the aqueous ZnS QDs. With cubic zinc blende structure, ZnS usually has Schottky defects predominant over Frenkel defects [17]. Therefore, the observed photoluminescence of the aqueous MPA-capped ZnS QDs could be ascribed to a recombination of electrons at the sulfur vacancy donor level or in the conduction band with holes trapped at the zinc vacancy acceptor level or in the valence band [18]. There are many possible recombination paths and thereby many trap-state emissions, each with different emission energy, causing the relatively wide emission peak. The PL spectrum of our aqueous ZnS QDs had the full width at half maximum of about 100 nm.

3.3. Effect of pH

It is worth noting that usually the aqueous ZnS QDs were synthesized at pH 12, while the CdS QDs can be produced at pH 9 with good photoluminescence properties. The emission intensity of the ZnS QDs could be strongly affected by the pH at which they were synthesized. To examine the pH effect, two samples were prepared with the same composition ratio of MPA:Zn:S = 8:4:1, but at two different pH values, 12 and 8. The PL emission spectra of these two ZnS QDs suspensions were shown in Figure 4. Clearly the QDs synthesized at pH 12 had a strong emission peak around 415 nm, while the QDs at pH 8 did not exhibit appreciable photoluminescence. As a result, compared with the aqueous CdS QDs, the bright blue emission of ZnS QDs can only be obtained from the sample synthesized at very high pH. This can be attributed to the higher solubility of ZnS than that of CdS at the same pH, 100 only at much higher pH, the solubility of ZnS decreases, which allows the ZnS QDs to precipitate and crystallize better and hence possess better PL properties.

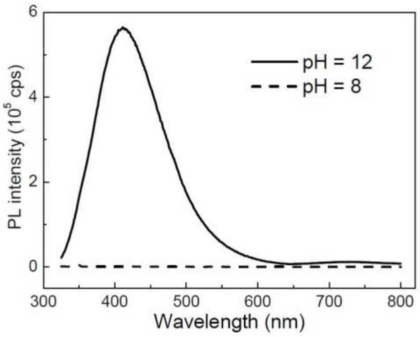

Figure 4: PL spectra of the MPA-capped ZnS QDs with the same ratio of MPA:Zn:S = 8:4:1, but synthesized at different pH, 12 (solid line) and 8 (dashed line).

3.4. Effect of Temperature

We heated the sample to 100 ^{o}C in a hydrothermal bomb for various period of time and monitored the emission spectrum at each step. Note that the sample was sealed in the bomb during the heat treatment. Therefore the concentration of the QDs didn’t change over time.

As shown in Figure 5, the PL intensity of the ZnS QDs initially increased with time and reached the maximum value after being heated for 18 hrs, beyond which the intensity started to decrease. The emission peak position shifted to larger wavelength slowly and continuously. After 40 hrs, not only the PL intensity reduced but the suspension was observed cloudy, indicating that aggregation occurred. It is speculated that the increase of emission intensity resulted from the rearrangement and crystallization of the ZnS QDs at the elevated temperature, which improved the quality of the nanocrystals and minimized the surface defects, like other post-treatments such as UV irradiation and reflux. Meanwhile, the QDs would grow to larger size during heating, causing the red-shift of the emission spectrum. Since we did not control the atmosphere during the heat treatment, at the presence of oxygen and thermal energy, it was likely that the disulfide bond formed between adjacent MPA, and the capping molecules detached from the QD surface, 97 leading to the aggregation and degradation of the QDs gradually. It should be noted that even though the ZnS QDs synthesized at pH 8 had the enhanced PL intensity after 18 hrs hydrothermal treatment, it was still not as bright as the sample synthesized at pH 12. In other words, as long as the aqueous ZnS QDs were synthesized at high enough pH, no post-treatment is necessary to obtain the strong photoluminescence.

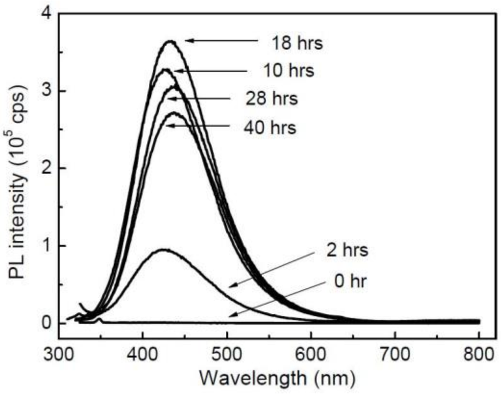

Figure 5: PL spectra of the MPA-capped ZnS QDs with MPA:Zn:S = 8:4:1 and synthesized at pH 8, after hydrothermal treatment at 100 ^{o}C for various period of time, i.e., 0 hr (no heat treatment), 2 hrs, 10 hrs, 18 hrs, 28 hrs, and 40 hrs.

4. CONCLUSIONS

Non-heavy-metal ZnS QDs with bright blue photoluminescence have been synthesized via an aqueous one-step process at room temperature with 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 usually contain toxic heavy metal elements and are synthesized through an organic route. The TEM and XRD results indicated that the MPA-capped ZnS QDs were 4-5 nm in size with a cubic zinc blend structure. The very high synthesis pH and optimal composition ratio are important to achieve the strong PL intensity. The present aqueous ZnS QDs synthesized at pH 12 with the ratio of MPA:Zn:S = 8:4:1 exhibited strong emission with the quantum yield of 31%, higher than that of the commercial CdSe/ZnS core-shell QDs. Although the present ZnS QDs had the trap-state emissions, they were bright, small, and contained no heavy metal elements, thus offering great potential for *in vivo* bio imaging of single targets.

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Biblographic Sketch

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