Highly Photoluminescent and Stable Aqueous ZnS Quantum Dots

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We report an all-aqueous synthesis of highly photoluminescent and stable ZnS quantum dots (QDs) with water as the medium. The method involves first synthesizing ZnS QDs with 3-mercaptopropionic acid (MPA) as the capping molecule and then replacing some of the MPA with (3-mercaptopropyl)trimethoxysilane (MPS). The resultant MPS-replaced ZnS QDs were about 5 nm in size with a cubic zinc blende crystalline structure, and they had both MPA and MPS on the surface as confirmed by Fourier transform infrared (FTIR) spectroscopy. They exhibited blue trap-state emissions around 415 nm and a quantum yield (QY) of 75% with rhodamine 101 as the reference, and they remained stable for more than 60 days under ambient conditions. Through the capping-molecule replacement procedure, the MPS-replaced ZnS QDs avoided the shortcomings of both MPA/ZnS QDs and MPS/ZnS QDs and acquired the advantages of strong photoluminescence and good stability, which are important to QD applications, especially for bioimaging.

I. Introduction

Quantum dots (QDs) are semiconductor nanocrystals that have distinctive photoluminescence (PL) properties. Despite the enormous interest in using QDs as fluorescent markers,[1−5] the application of QDs in vivo, especially for the human body, remains elusive, primarily because of the toxic elements, such as Cd, Pb, and Hg, contained in QDs. Even though various coating strategies have been proposed, the cytotoxicity of QDs can only be reduced to some extent but not eliminated completely.[6,7] For QDs to become a viable in vivo imaging tool in clinical applications, it is necessary to have QDs without toxic elements. In addition, conventional QD synthesis routes call for tedious processes with organometallic precursors and organic solvents that are health-hazardous and incompatible with the physiological environment. It is therefore of great interest and importance to synthesize water-soluble QDs that are free of toxic elements in an environmentally friendly manner.

Because adult humans ingest 10−15 mg of zinc and absorb about 5 mg daily as a nutrient,[8] trace amounts of zinc are not considered hazardous to the human body. Therefore, ZnS QDs provide a good candidate system for avoiding toxic elements in traditional QDs. In an earlier study, an aqueous synthesis method was developed to produce ZnS QDs with 3-mercaptopropionic acid (MPA) as the capping molecule.[9] Although the MPA-capped ZnS (MPA/ZnS) QDs exhibited strong blue emission with a 31% quantum yield (QY), their PL intensity diminished after a few days when left at room temperature and under normal laboratory lighting conditions (ambient conditions). By a similar aqueous process but with (3-mercaptopropyl)trimethoxysilane (MPS) as the capping molecule, the resultant MPS-capped ZnS (MPS/ZnS) QDs exhibited blue emission with a QY of 42% and remained stable for more than 50 days when left under ambient conditions.[10] Although the MPS/ZnS QDs showed a higher QY and were more stable than the MPA/ZnS QDs, the MPS/ZnS QDs still exhibited a lower photoluminescence emission intensity than the MPA/ZnS QDs given the same excitation intensity and the same QD concentration because of their lower light absorbing capability. It is confirmed later in Figure 3a that the absorbance of MPS/ZnS QDs is much lower than that of MPA/ZnS QDs.

It would be desirable to have a ZnS QD system that combines the brightness of the MPA/ZnS QDs and the stability of the MPS/ZnS QDs while maintaining the health-friendliness of the aqueous process. Toward this goal, we developed a two-step aqueous method to produce brighter and more stable ZnS QDs. In the first step, the aqueous ZnS QDs are synthesized with MPA as the capping molecule. The second step involves replacing some of the MPA capping molecules with MPS. This two-step process results in MPS-replaced ZnS QDs that have a higher emission intensity and quantum yield than both MPA/ZnS QDs and MPS/ZnS QDs. The MPS-replaced ZnS QDs also exhibit good chemical stability equivalent to that of MPS/ZnS QDs under ambient conditions.

II. Experiments

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and Fisher Scientific (Fairlawn, NJ) and used as received without further purification. Deionized (DI) water was used as the medium for all syntheses and characterizations of QD suspensions. All QD syntheses were carried out at room temperature.

Following the aqueous procedure described earlier,[9] MPA/ZnS QDs were first synthesized as follows. Zinc nitrate [$Zn(NO_3)_2$] solution (0.04 M) and sodium sulfide (Na_2S) solution (0.02 M) were prepared in DI water. For an MPA/Zn/S ratio of 8:4:1, 0.64 mmol of MPA was added to 36 mL of DI water and stirred for 5 min. Then, 2 mL of $Zn(NO_3)_2$ solution was dropped slowly into the MPA solution with constant stirring for 10 min. Next, the mixture was titrated with tetrapropylammonium hydroxide [$(CH_3CH_2CH_2)_4NOH$] to pH 12 and stirred for 10 min, after which 4 mL of Na_2S solution was added rapidly. A period of 5 min was allowed for the ZnS nanoparticles to form and grow before another 6 mL of the $Zn(NO_3)_2$ solution was added. When needed, more $(CH_3CH_2CH_2)_4NOH$ was added to adjust the pH of the suspension to 12 with constant stirring for an additional 5 min. The obtained MPA/ZnS QD suspension was clear and colorless. The final volume was about 50 mL, and the nominal ZnS concentration was 1.6 mM based on the concentration of S.

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Having MPA/ZnS QDs with an MPA/Zn/S ratio of 8:4:1, we proceeded to replace some of the MPA capping molecules with MPS. The MPA/ZnS QD suspension was first microcentrifuged (MiniSpin Plus, Eppendorf North America Co., Westbury, NY) with a 10-kD filter (Millipore Co., Billerica, MA) at 10000 rpm for 90 s. After the microcentrifugation, the excess MPA molecules in the suspension passed through the filter into the filtrate, which was discarded, and the QDs remained in the retentate without precipitation or aggregation. Meanwhile, an MPS solution was prepared in DI water with the appropriate concentration and with the pH adjusted to 12 by addition of $(CH_3CH_2CH_2)_4NOH$. The MPS solution was then added to the retentate of the MPA/ZnS QD suspension, resulting in a nominal MPS/Zn/S ratio of 0.5:4:1. Appropriate amounts of DI water and $(CH_3CH_2CH_2)_4NOH$ were added to restore the volume and pH of the QD suspension to the values before microcentrifugation. The final MPS-replaced ZnS QD suspension remained clear, and the approximate ZnS concentration was 1.6 mM based on the concentration of S.

For comparison, an MPA/ZnS QD suspension with MPA/Zn/S = 8:4:1[9] and an MPS/ZnS QD suspension with MPS/Zn/S = 0.5:2:1[10] were also prepared by direct one-step syntheses as reported before. The precursor ratios were chosen to achieve the maximum emission intensity for each sample. The three QD samples had the same nominal ZnS concentration of 1.6 mM based on the concentration of S, and the pH was 12 in all three samples.

The X-ray diffraction (XRD) pattern of the MPS-replaced ZnS QDs was obtained with a Siemens D 500 X-ray diffractometer using Cu Kα radiation with a wavelength of 1.54 Å. The powder sample was prepared by adding acetone to precipitate the QDs from the suspension and then centrifuging the mixture and air-drying the QDs at 50 °C overnight.

For transmission electron microscopy (TEM), the excess capping molecules and ions in the MPS-replaced ZnS QD suspension were removed by microcentrifugation, filtering, and rinsing with DI water. The obtained QD suspension was then dropped onto a carbon-coated copper grid, dried in air, and examined with a JEM-2010F FasTEM high-resolution analytical transmission electron microscope (Japan Electron Optics Ltd., Tokyo).

Fourier transform infrared (FTIR) spectroscopy was carried out using an Excalibur Series FTS 3000MX spectrometer (Digilab Inc., Canton, MA) on the MPS-replaced ZnS QDs, as well as on the MPA/ZnS and MPS/ZnS QDs for comparison. The QDs were precipitated from the suspension to remove the unbound capping molecules, dried in air, and then mixed with KBr powder at a fixed mass ratio and pressed into pellets for the FTIR spectroscopy experiments.

Photoluminescence spectra of the QD suspensions were collected using a QM-4/2005 spectrofluorometer (Photon Technology International, Birmingham, NJ). UV−vis absorption spectra were collected with a Lambda-40 UV−vis spectrometer (Perkin-Elmer Life and Analytical Sciences Inc., Boston, MA). To measure the quantum yield of the MPS-replaced ZnS QDs, rhodamine 101 (Acros Organics, Geel, Belgium) dissolved in ethanol was used as the reference. The dialysis of MPA/ZnS QDs was performed with DI water in a refrigerator at 4 °C for up to 28 h, and the PL spectrum was measured afterward.

For the chemical stability study, MPS-replaced ZnS QDs and MPA/ZnS QDs were stored under ambient conditions, and their PL intensities were measured once every several days. Both samples were stored in clear and sealed cuvettes to keep the concentration constant over time. The particle size distribution of the QDs was measured by dynamic light scattering (DLS) with a ZetaSizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK).

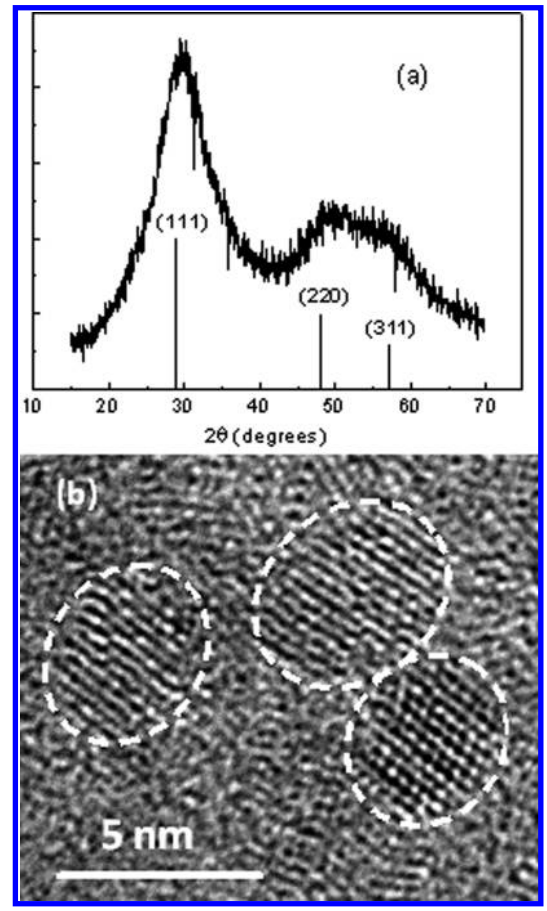

Figure 1. (a) XRD pattern and (b) TEM micrograph of MPS-replaced ZnS QDs. The vertical lines in a indicate the pattern and relative intensities of bulk ZnS with a cubic zinc blende structure. The white dashed lines in b indicate the outlines of MPS-replaced ZnS QDs.

III. Results and Discussion

The XRD pattern of MPS-replaced ZnS QDs is shown in Figure 1a, which indicates a cubic zinc blende crystalline structure, the same as was found for MPA/ZnS[9] and MPS/ZnS[10] QDs. The breadth of the peaks in the pattern indicates the nanosize of the particles. The TEM micrograph in Figure 1b shows that the size of the MPS-replaced ZnS QDs was about 5 nm, consistent with the result from DLS measurements (not shown) and also similar to the sizes of MPA/ZnS[9] and MPS/ZnS[10] QDs. The white dashed lines indicate the outlines of individual nanoparticles, in which the fringes of the crystal structure are clearly shown. Thus, the capping-molecule replacement did not change the crystal structure of the ZnS QDs and maintained their ultrafine size, which is much smaller than the 30-nm size of silica-coated QDs.[11]

To examine how much of the MPA on the QD surface was replaced by MPS, powders of the three types of QDs were collected and investigated by FTIR spectroscopy. As the QDs were precipitated and the free capping molecules and ions were removed with the solvent, the observed signatures of MPA and MPS in the spectra can be attributed only to QD-bound MPA and MPS, respectively. The obtained FTIR spectrum of MPS-replaced ZnS QDs (solid line) is shown in Figure 2, along with those of MPA/ZnS QDs (dash-dot-dotted line) and MPS/ZnS QDs (dashed line). As can be seen, the MPS-replaced ZnS QDs

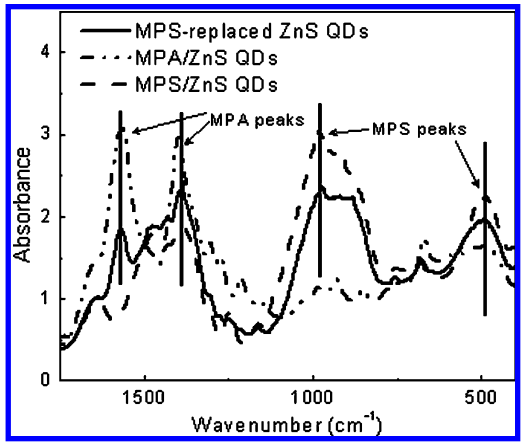

Figure 2. FTIR spectrum of MPS-replaced ZnS QDs (solid line), along with those of MPA/ZnS QDs (dash-dot-dotted line) and MPS/ZnS QDs (dashed line) for comparison. The vertical lines indicate the signature peak positions of MPA and MPS.

exhibited two signature peaks of MPS at 980 cm^{-1} and 500 cm^{-1} that are associated with Si—OH and Si—O—Si bonds, respectively.[12] Meanwhile, they also exhibited two signature peaks of MPA with reduced intensities at around 1570 cm^{-1} and 1400 cm^{-1} that are associated with vibrations of C═O and C—OH bonds, respectively.[13] Although the exact fraction of MPA molecules replaced by MPS molecules is unknown, the FTIR results confirm that MPS indeed replaced some of the MPA on the QD surface. This replacement implies that the thiol binding of MPS to the zinc on the QD surface is stronger than that of MPA. These results also indicate that the MPS on the QD surface is more stable, which can be attributed to the cross-linking of the hydrolyzed silane groups of MPS. It is interesting to note that the resultant MPS-replaced ZnS QDs have both MPS and MPA on the surface as capping molecules. The intensity heights of the MPA and MPS peaks in the FTIR spectra can be used to estimate the ratio of MPA to MPS on the MPS-replaced ZnS QD surface. As shown in Figure 2, the intensity heights of the MPS peaks of the MPS-replaced ZnS QDs are about one-half to two-thirds those of the MPS/ZnS QDs. This implies that one-half to two-thirds of the MPS-replaced QD surface was covered by MPS. On the other hand, the intensity heights of the MPA peaks of the MPS-replaced ZnS QDs are about one-third to one-half those of MPA/ZnS QDs, implying that one-third to one-half of the surface was covered by MPA. This is consistent with the comparison of the MPS peaks of the MPS-replaced QDs with those of the MPS/ZnS QDs. Thus, we estimate that the MPS/MPA ratio on the MPS-replaced QD surface was in the range of 2:1—1:1. In other words, 50—67% of the MPA was replaced by MPS during the capping-molecule replacement process.

The PL and UV—vis absorption spectra of MPS-replaced ZnS QDs (solid lines) are plotted in Figure 3a, along with those of MPA/ZnS and MPS/ZnS QDs for comparison. Apparently, the MPS-replaced ZnS QDs exhibit stronger emission than both MPA/ZnS and MPS/ZnS QDs. Although we do not have a full explanation for this, a possible reason is that the excess MPA molecules in the suspension absorb light, so that their presence reduces the PL of MPA/ZnS QDs. This argument is supported by the data in Figure 3a, where the MPA/ZnS QDs show a higher absorbance, and by the dialysis data in Figure 3b, where a higher PL intensity was obtained when the excess MPA molecules in the suspension were removed. It was found that the PL intensity of MPA/ZnS QDs increased by about 30% after they had been dialyzed for 28 h. Similarly, the microcentrifugation and filtering process during the capping-molecule replacement also removed the excess MPA and therefore resulted in a brighter PL of the MPS-replaced ZnS QDs. On the other hand, for MPS/ZnS QDs, the MPS was used as the capping molecule at the beginning of synthesis. The strong bonding between MPS and the QD surface tends to limit the growth of nanoparticles, which might impair the PL of the obtained MPS/ZnS QDs. This argument is supported by the data in Figure 3a, where the emission peak wavelength and absorption edge of

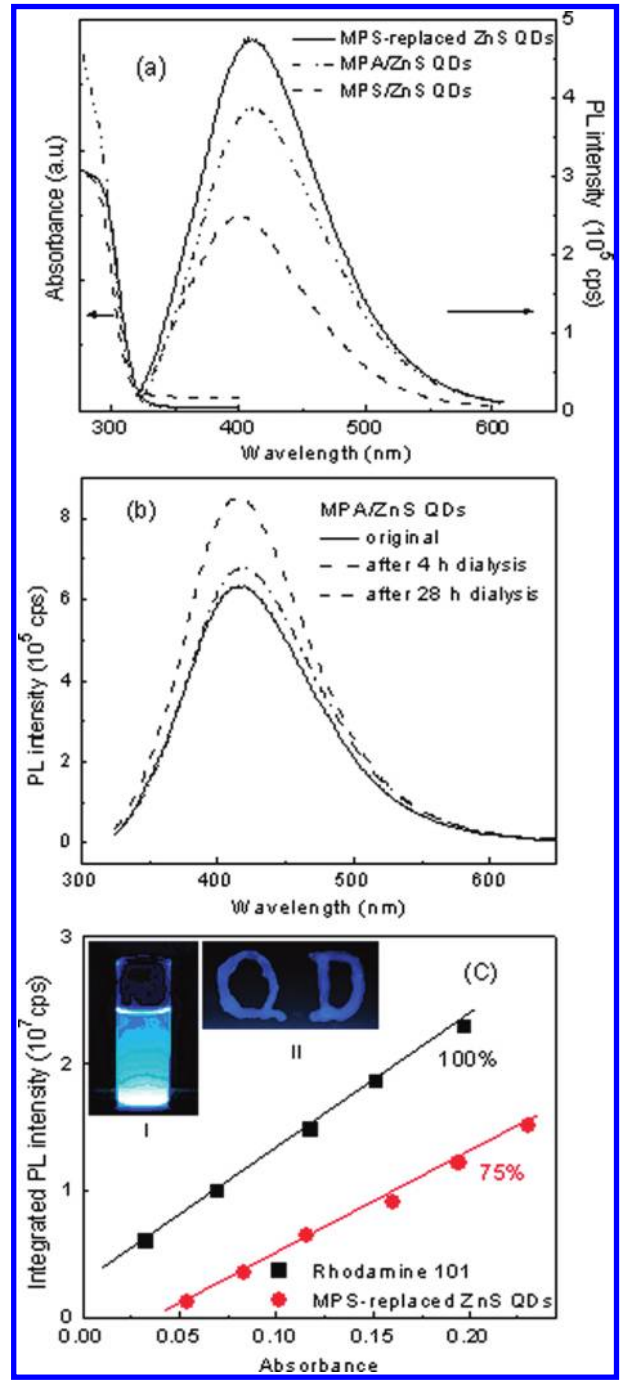

Figure 3. (a) PL and UV—vis absorption spectra of the MPS-replaced ZnS QDs (solid lines), along with those of the MPA/ZnS QDs (dash-dot-dotted lines) and MPS/ZnS QDs (dashed lines) for comparison. (b) PL spectra of MPA/ZnS QDs after dialysis for 0 h (solid line), 4 h (dash-dotted line), and 28 h (dashed line). (c) Integrated PL intensity versus absorbance of the MPS-replaced ZnS QDs (circles), along with that of rhodamine 101 (squares), with linear fitting lines. Insets I and II, respectively, show a vial of a suspension of MPS-replaced ZnS QDs and a pattern written with the QD suspension on a glass slide, excited by a UV lamp with a wavelength of 302 nm.

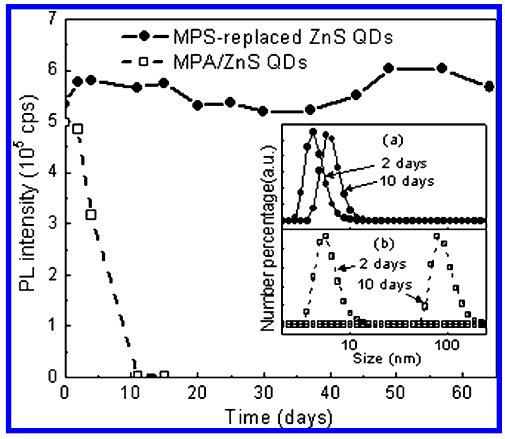

Figure 4. PL intensity versus time under ambient conditions for MPS-replaced ZnS QDs (full circles with solid line) under ambient conditions and for MPA/ZnS QDs (open squares with dashed line). Inset: Size distributions of (a) MPS-replaced ZnS QDs and (b) MPA/ZnS QDs, 2 and 10 days after synthesis.

the MPS-replaced ZnS QDs are about the same as those of the MPA/ZnS QDs and slightly red-shifted relative to those of the MPS/ZnS QDs, indicating that the sizes of the former two are the same but larger than that of the latter.[14] As the MPS-replaced ZnS QDs contained no excess MPA in the suspension and avoided the limitation of MPS during nanoparticle growth, it is reasonable that they exhibited higher PL intensity than both the MPA/ZnS and MPS/ZnS QDs. Note that, for all three samples, the emission peak wavelengths were about 100 nm larger than the absorption edges, indicating that they involved trap-state emissions.[9,10]

To quantify the quantum yield of the MPS-replaced ZnS QDs, rhodamine 101 dissolved in ethanol was used as a reference as before. The PL and absorbance spectra of MPS-replaced ZnS QDs and rhodamine 101 were measured at various concentrations, using 295 nm as the excitation wavelength because it is optimal for the ZnS QDs. The integrated PL intensities of the emission peak versus absorbances are plotted in Figure 3c and fitted with straight lines. Having rhodamine 101 as the reference with a known QY of 100%,[15] we compared the slopes of the fitting lines and deduced[16] that the QY of MPS-replaced ZnS QDs is 75%. More QY measurements were carried out for a 15-month old sample, which exhibited a QY of 51%. These results indicate that, even though the present MPS-replaced ZnS QDs exhibit trap-state emissions, the photoluminescence efficiency is higher than those of both MPA/ZnS QDs (31%)[9] and MPS/ZnS QDs (42%).[10] Note that all of these QY values are relative to the same reference of rhodamine 101 and were measured under the same experimental conditions. Although rhodamine 101 might not be the best reference for blue-emitting ZnS QDs, the three QD systems have the same absorption and emission ranges, so it is still meaningful to compare the obtained QY values among these three QD systems. The bright blue emission of the MPS-replaced ZnS QDs is illustrated in insets I and II of Figure 3c, which show the strong fluorescence of the QD suspension and a "QD" pattern written with it, excited by a UV lamp with a wavelength of 302 nm.

The chemical stability of the MPS-replaced ZnS QDs under ambient conditions was studied and compared to that of MPA/ZnS QDs by monitoring their PL intensities over time. As shown in Figure 4, the MPS-replaced ZnS QDs (full circles with solid line) maintained a high PL intensity of 500−600 kcps for more than 60 days without discernible degradation. The small fluctuations in intensity could be due to slight variations in the day-to-day measurement conditions, such as the environmental temperature and the excitation light intensity. In contrast, the PL intensity of MPA/ZnS QDs (open squares with dashed line) decreased to 0 at day 10, indicating their instability under ambient conditions. The inset of Figure 4 shows the size distributions of MPS-replaced ZnS QDs and MPA/ZnS QDs, measured by dynamic light scattering at days 2 and 10 after synthesis. As can be seen, the MPS-replaced ZnS QDs retained an average size of around 4−6 nm, consistent with the chemical stability result shown in Figure 4 and the TEM result shown in Figure 1b. However, the size of the MPA/ZnS QDs increased from about 5 nm to 80 nm after 10 days. Apparently, under ambient conditions, the MPA/ZnS QDs aggregated and lost their emission over time, probably as a result of the dissociation of MPA via the disulfide reaction and the subsequent exposure of the QD surface.[17] In contrast, for the MPS-replaced ZnS QDs, the replacing MPS molecules were effective in preventing the QDs from aggregating, even though not all of the MPA on the QD surface was replaced. For an MPS/Zn/S ratio of 0.5:4:1, it was estimated that, on average, there are two layers of MPS on the surface of each QD, which would be enough to form a cross-linked network covering the QDs. As the MPS-replaced ZnS QDs showed little sign of aggregation even under the harsh ambient conditions for 10 days and maintained a strong emission for months, it is evident that they have a long lifetime and will be suitable for various imaging applications. In our studies, we have found that only with the MPS-replaced QDs can antibodies be conjugated without aggregation and target antigen/cells imaged successfully.[18]

It is worth noting that MPA and MPS were purposely chosen for the capping-molecule replacement procedure. In particular, reagents with only thiol and amine functional groups cannot substitute either MPA or MPS during synthesis. Because the solubility of ZnS decreases with increasing pH,[19] it is required that the QDs be synthesized at high pH (pH 12 in our case). However, the amine group can be positively charged only at low pH. Therefore, amine-containing molecules are not good candidates like MPA for keeping the QDs charged and dispersed in basic solution during synthesis. On the other hand, amine-containing molecules would not form an inorganic shell for the QDs as MPS does, because of a lack of the cross-linking effect of hydrolyzed silane groups. Moreover, if an amine-containing molecule were used in the second step for replacement, it could react with the carboxyl group of MPA and form a peptide bond. As a result, the charge of the QD surface could be reduced, resulting in aggregation. With both MPA and MPS on the surface, the present MPS-replaced ZnS QDs also have the advantages of being conjugated with a biomolecule either through the free thiol group (−SH) of MPS or the carboxyl group (−COOH) of MPA. For example, using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and *n*-hydroxysulfosuccinimide (sulfo-NHS) as the cross-linkers, the carboxyl group of MPA on the QD surface can be conjugated with any amine-containing biomolecules. Meanwhile, MPS can form more than one layer on the QD surface through the cross-linking of its silane groups. Thus, amine-containing biomolecules can be covalently conjugated to the free thiol group of MPS on the QD surface by means of a bifunctional linker, sulfosuccinimidyl 4-(*n*-maleimidomethyl)cyclohexane-1-carboxylate (sulfo-SMCC).

IV. Conclusions

In conclusion, our work has provided a novel procedure for the synthesis of aqueous ZnS QDs with high quality in a simple,

environmentally friendly way. ZnS QDs were first synthesized at pH 12 with MPA and then some of the MPA was replaced with MPS, as confirmed by FTIR spectroscopy. Through a capping-molecule replacement procedure, the obtained ZnS QDs maintained a desirable particle size of about 5 nm and the cubic zinc blende crystal structure. Compared with MPA/ZnS and MPS/ZnS QDs, the MPS-replaced ZnS QDs exhibited an enhanced PL intensity and quantum yield, probably because of the removal of excess MPA by the replacement process and the elimination of the limiting effects of MPS on nanoparticle growth during synthesis. The chemical stability of the MPS-replaced ZnS QDs was much better than that of MPA/ZnS QDs. Therefore, through capping-molecule replacement, the MPS-replaced ZnS QDs reaped the benefits of both MPA and MPS capping, while avoiding their shortcomings. Improvements in both PL intensity and chemical stability are very important for the applications of QDs. These high-quality and toxic-element-free aqueous ZnS QDs will generate interest and benefit other research, especially critical to in vivo bioapplications.

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