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Highly Photoluminescent and Stable Aqueous ZnS Quantum Dots

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Abstract

We report an all-aqueous synthesis of highly photoluminescent and stable ZnS quantum dots (QDs) with water as the medium, i.e. first synthesizing ZnS QDs with 3-mercaptopropionic acid (MPA) as the capping molecule, followed by replacing some of 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 had both MPA and MPS on the surface as confirmed by the 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 remained stable for more than 60 days under the ambient conditions. Through the capping molecule replacement procedure, the MPS-replaced ZnS QDs avoided the shortcomings of both the MPA-ZnS QDs and the MPS-ZnS QDs, and acquired the advantages of strong photoluminescence and good stability, which are important to the QDs' applications especially for bioimaging.

I. Introduction

Quantum dots (QDs) are semiconductor nanocrystals which 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 human body remains elusive, primarily due to the toxic elements, e.g. 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 In order for QDs to be a viable *in vivo* imaging tool in clinical applications, it is necessary to have QDs without toxic elements. In addition, conventional QDs synthesis routes call for tedious processes with orgnaometallic precursors and organic solvents that are health-hazardous and incompatible with physiological environment. It is therefore of great interest and importance to synthesize water-soluble QDs free of toxic elements in an environmentally friendly manner.

Since an adult ingests 10–15 mg of zinc and absorbs about 5 mg daily as a nutrient,8 trace amount of zinc is not hazardous to human body. Therefore, the ZnS QDs is a good candidate system to avoid the toxic elements in traditional QDs. In earlier study, an aqueous synthesis method has been developed to produce ZnS QDs with 3-mercaptopropionic acid (MPA) as the capping molecule.9 While 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 if left at room temperature and under the normal laboratory lighting condition (ambient

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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 the 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 due to their lower light absorbing capability. This is confirmed later in Fig. 3(a) that the absorbance of the MPS-ZnS QDs was much lower than that of the MPA-ZnS QDs.

It would be desirable to have a ZnS QDs 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. Towards 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 were synthesized with MPA as the capping molecule. The second step involved replacing part of the MPA capping molecules with MPS. This two-step process resulted in the MPS-replaced ZnS QDs, which had higher emission intensity and quantum yield than both the MPA-ZnS QDs and the MPS-ZnS QDs. The MPS-replaced ZnS QDs also exhibited good chemical stability as the MPS-ZnS QDs under the 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 the synthesis and characterization of QD suspensions. All the QDs syntheses were carried out at room temperature.

Following the aqueous procedure described earlier,9 the MPA-ZnS QDs were first synthesized as below. Zinc nitrate ($Zn(NO_3)_2$) solution (0.04 M) and sodium sulfide (Na_2S) solution (0.02 M) were prepared in DI water, respectively. For a ratio of MPA:Zn:S = 8:4:1, 0.64 mmol MPA was added in 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. After that, the mixture was titrated with tetrapropylammonium hydroxide ($(CH_3CH_2CH_2)_4NOH$) to pH 12 and stirred for 10 min, followed by rapid addition of 4 ml of Na_2S solution. We waited for 5 min for the ZnS nanoparticles to form and grow before adding another 6 ml of the $Zn(NO_3)_2$ solution. When needed, more $(CH_3CH_2CH_2)_4NOH$ was added to adjust the pH of the suspension to 12 with constant stirring for 5 more minutes. The obtained MPA-ZnS QDs 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.

Having the MPA-ZnS QDs with the ratio of MPA:Zn:S = 8:4:1, we proceeded to replace some of the MPA capping molecules with MPS. The MPA-ZnS QDs suspension was first micro-centrifuged (MiniSpin plus, Eppendorf North America Co., Westbury, NY) with a 10 kD filter (Millipore Co., Billerica, MA) at 10000 rpm for 90 sec. After the micro-centrifugation, 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 appropriate concentration and with the pH adjusted to 12 by adding $(CH_3CH_2CH_2)_4NOH$. The MPS solution was then added to the retentate of the MPA-ZnS QDs suspension, resulting in a nominal ratio of MPS:Zn:S = 1/2:4:1. 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

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pre-centrifugation values. The final MPS-replaced ZnS QDs suspension remained clear and the approximate ZnS concentration was 1.6 mM based on the concentration of S.

For comparison, an MPA-ZnS QDs suspension with MPA:Zn:S = 8:4:19 and an MPS-ZnS QDs suspension with MPS:Zn:S = 1/2:2:110 were also prepared by direct one-step synthesis as reported before. The precursor ratios were chosen to achieve the maximum emission intensity for each sample respectively. 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 the wavelength of 1.54 Å. The powder sample was prepared by adding acetone to precipitate the QDs from the suspension, followed by centrifugation and air-drying at 50°C overnight.

For transmission electron microscopy (TEM) study, the excess capping molecules and ions in the MPS-replaced ZnS QDs suspension were removed by micro-centrifugation, filtering and rinsing with DI water. The obtained QDs 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).

The 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 QDs and the 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.

The photoluminescence spectra of the QDs suspensions were collected using a QM-4/2005 spectrofluorometer (Photon Technology International, Birmingham, NJ). The 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 hr, and the PL spectrum was measured afterwards.

For the chemical stability study, the MPS-replaced ZnS QDs and the MPAZnS QDs were stored under the 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).

III. Results and discussion

The XRD pattern of the MPS-replaced ZnS QDs is shown in Fig. 1(a), which indicated a cubic zinc blend crystalline structure, same as that of the MPA-ZnS9 and MPS-ZnS QDs.10 The broadness of the peaks in the pattern indicated the nano-size of the particles. The TEM micrograph shown in Fig. 1(b) exhibited 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 that of the MPA-ZnS9 and MPS-ZnS QDs.10 The white dashed lines indicated the outline of individual nanoparticles, in which the fringes of the crystal structure were clearly shown. It suffices to say that the capping molecule replacement did not change the crystal structure

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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 has been replaced by MPS, the powders of three samples, i.e. the MPS-replaced ZnS QDs, the MPA-ZnS QDs and the MPS-ZnS QDs, were collected and investigated with FTIR spectroscopy. As the QDs were precipitated and the free capping molecules and ions were removed with the solvent, the observed signature of MPA and MPS in the spectra can only be attributed to the QD-bound MPA and MPS, respectively. The obtained FTIR spectrum of the MPS-replaced ZnS QDs (solid line) is shown in Fig. 2, along with that of the MPA-ZnS QDs (dash-dot-dotted line) and that of the MPS-ZnS QDs (dashed line). As can be seen, the MPS-replaced ZnS QDs exhibited two signature peaks of MPS at 980 cm^{-1} and 500 cm^{-1} which are associated with the 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} which are associated with the vibration of the C=O and C-OH bonds, respectively.13 Although exactly how many MPA molecules were replaced by MPS is unknown, the FTIR result confirmed that MPS indeed replaced some of MPA on the QD surface. This replacement implied that the thiol-binding of MPS to the zinc on QD surface was stronger than that of MPA. The result also indicated that the MPS on the QD surface was 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 had both MPS and MPA on the surface as capping molecules. We can use the intensity height of the MPA- and MPS- peaks in the FTIR spectra to estimate the ratio of MPA to MPS on the MPS-replaced ZnS QD surface. As shown in Fig. 2, the MPS peaks of MPS-replaced ZnS QDs exhibited the intensity height about 1/2 to 2/3 that of the MPS-ZnS QDs. This implied that 1/2 to 2/3 of the MPS-replaced QD surface was covered by MPS. On the other hand, the MPA peaks of the MPS-replaced ZnS QDs exhibited the intensity height about 1/3 to 1/2 that of the MPA-ZnS QDs, implying 1/3 to 1/2 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 estimated that the ratio of MPS:MPA on the MPS-replaced QDs surface was in the range of 2:1 to 1:1. In other words, 50–67% of MPA was replaced by MPS during the capping molecule replacement process.

The PL and UV-vis absorption spectra of the MPS-replaced ZnS QDs (solid lines) are plotted in Fig. 3(a), along with those of the MPA-ZnS QDs (dash-dot-dotted lines) and those of the MPS-ZnS QDs (dashed lines) for comparison. Apparently, the MPS-replaced ZnS QDs exhibited stronger emission than both the MPA-ZnS and MPS-ZnS QDs. Although we do not have a full explanation, a possible reason is that the excess MPA molecules in the suspension absorb light and thus their presence reduces the PL of MPA-ZnS QDs. This argument is supported by the data in Fig. 3(a) where the MPA-ZnS QDs showed a higher absorbance, and by the dialysis data shown in Fig. 3(b) 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 about 30% after being dialyzed for 28 hr. Similarly, the micro-centrifugation 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 the 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 tended to limit the growth of nanoparticles, which may impair the PL of the obtained MPS-ZnS QDs. This arguement is supported by the data in Fig. 3(a) where the emission peak wavelength and absorption edge of the MPS-replaced ZnS QDs were 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 were the same but larger than that of the latter.14 As the MPS-replaced ZnS QDs had no excess MPA in the suspension and

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they avoided the limitation of MPS during the nanoparticles growth, it is reasonable that they exhibited the higher PL intensity than both the MPA- and MPS-ZnS QDs. Note that for all the 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 referance as before. We measured the PL spectrum and absorbance of the MPS-replaced ZnS QDs and of Rhodamine 101 at various concentrations, using 295 nm as the excitation wavelength which was optimal for the ZnS QDs. The integrated PL intensities of the emission peak versus absorbances are plotted in Fig. 3(c) 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 deduced16 the QY of MPS-replaced ZnS QDs was 75%. More QY measurement was carried out for a 15-month old sample which showed the QY of 51%. These results indicated that even though the present MPS-replaced ZnS QDs exhibited trap-state emissions, the photoluminescence efficiency was higher than both that of the MPA-ZnS QDs (31%)9 and that of the MPS-ZnS QDs (42%).10. Note that all these QY values are relative to the same reference of Rhodamine 101, and were measured under the same experimental conditions. Although the Rhodamine 101 may not be the best reference for the blue-emitting ZnS QDs, the three QD systems have the same absorption and emission ranges, and thus 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 Fig. 3(c), which show the strong fluorescence of the QDs suspension and a “QD” pattern written with it, excited by a UV lamp of 302 nm.

The chemical stability of the MPS-replaced ZnS QDs under the ambient conditions was studied and compared with that of the MPA-ZnS QDs by monitoring their PL intensities over time. As shown in Fig. 4, the MPS-replaced ZnS QDs (full circles with solid line) maintained the high PL intensity of 500–600 kcps for more than 60 days without discernable degradation. The small fluctuation of intensity could be due to the day-to-day slightly different measurement conditions, i.e. the environment temperature and the excitation light intensity, etc. In contrast, the PL intensity of MPA-ZnS QDs (open squares with dashed line) decreased to zero at day 10, indicating their instability under the ambient conditions. The inset of Fig. 4 shows the size distribution of the MPS-replaced ZnS QDs (a) and of the MPA-ZnS QDs (b), measured by dynamic light scattering at day 2 and 10 after synthesis. As can be seen, the MPS-replaced ZnS QDs retained the average size of around 4–6 nm, consistent with their chemical stability result shown in Fig. 4 and the TEM result shown in Fig. 1(b). However, the size of MPA-ZnS QDs increased from about 5 nm to 80 nm after 10 days. Apparently, under the ambient conditions, the MPA-ZnS QDs aggregated and lost their emission over time, probably due to 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 aggregation even though not all MPA on the QD surface were replaced. With the ratio of MPS:Zn:S = 1/2:4:1, it was estimated that on average there are two layers of MPS on the surface of each QD, which would be enough to form the cross-linked network covering the QDs. As the MPS-replaced ZnS QDs showed little sign of aggregation even under the harsh ambient conditions for ten days, and they maintained the 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, the antibody can be conjugated without aggregation and the target antigen/cells can be imaged successfully.18

It is worth noting that the MPA and MPS were purposely chosen for the capping molecule replacement procedure. Particularly, the reagent with only thiol and amine functional groups cannot substitute either MPA or MPS during synthesis. Because the solubility of ZnS

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decreases with increasing pH,19 it is required to synthesize the QDs at high pH (at pH = 12 in our case). But the amine group can only be positively charged at low pH. Therefore the amine-containing molecule is not a good candidate like MPA to keep the QDs charged and dispersed in the basic solution during synthesis. On the other hand, the amine-containing molecule would not form an inorganic shell for the QDs like MPS, due to lack of the cross-linking effect of hydrolyzed silane group. Moreover, if the amine-containing molecule is used in the second step for replacement, they could react with the carboxyl group of MPA and form a peptide bond. As a result, the charge of the QDs surface may be reduced to result in aggregation. With both MPA and MPS on the surface, the present MPS-replaced ZnS QDs also have the advantages to be conjugated with a biomolecule either through the free thiol group (-SH) of the MPS or the carboxyl group (-COOH) of the 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 the MPA on the QD surface can be conjugated with any amine-containing biomolecules. Meanwhile, MPS may form more than one layer on the QD surface via cross-linking of silane groups. Thus, amine-containing biomolecules can be covalently conjugated to the free thiol group of the MPS on the QD surface by means of a bi-functional linker, sulfosuccinimidyl 4-[n-maleimidomethyl]cyclohexane-1-carboxylate (sulfo-SMCC).

IV. Conclusions

In conclusion, our work provided a novel procedure to synthesize aqueous ZnS QDs with high quality in a simple, environmental friendly way. The ZnS QDs were first synthesized at pH = 12 with MPA, then followed by replacing some of MPA with MPS, which was confirmed by FTIR. Through the capping molecule replacement, the obtained ZnS QDs maintained a desirable particle size of about 5 nm and the cubic zinc blende crystal structure. Compared with the MPA-ZnS QDs and the MPS-ZnS QDs, the MPS-replaced ZnS QDs exhibited the enhanced PL intensity and quantum yield, probably due to the removal of excess MPA by the replacement process and without the limitation effect of MPS to the nanoparticle growth during synthesis. The chemical stability of the MPS-replaced ZnS QDs was much better than that of the MPA-ZnS QDs. Therefore, via the capping molecule replacement, the MPS-replaced ZnS QDs reaped the benefits of both the MPA and MPS capping, while avoided their shortcomings. Improvements in both the PL intensity and the chemical stability are very important for the applications of QDs. These aqueous ZnS QDs with high quality and free of toxic elements will generate interests and benefit other research, especially critical to *in vivo* bioapplications.

Acknowledgments

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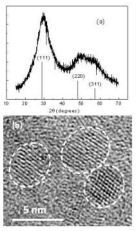

Fig. 1.
(a) XRD pattern and (b) TEM micrograph of the MPS-replaced ZnS QDs. The vertical lines in (a) indicate the pattern and relative intensities of bulk ZnS with a cubic zinc blende structure. The white dashed lines in (b) indicate the outline of the MPS-replaced ZnS QDs.

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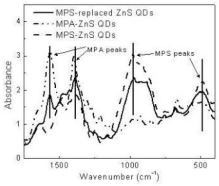

Fig. 2.

FTIR spectrum of the MPS-replaced ZnS QDs (solid line), along with that of the MPA-ZnS QDs (dash-dot-dotted line), and that of the MPS-ZnS QDs (dashed line) for comparison. The vertical lines indicate the signature peaks position of MPA and MPS.

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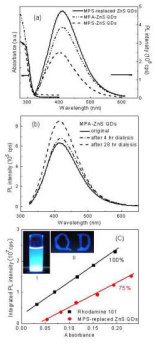

Fig. 3.

(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 those of the MPS-ZnS QDs (dashed lines) for comparison. (b) PL spectra of the MPA-ZnS QDs after dislysis for 0 hr (solid line), 4 hr (dash-dotted line) and 28 hr (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 the MPS-replaced ZnS QDs suspension and a pattern writtern with the QDs suspension on a glass slide, which were placed on a UV lamp of 302 nm.

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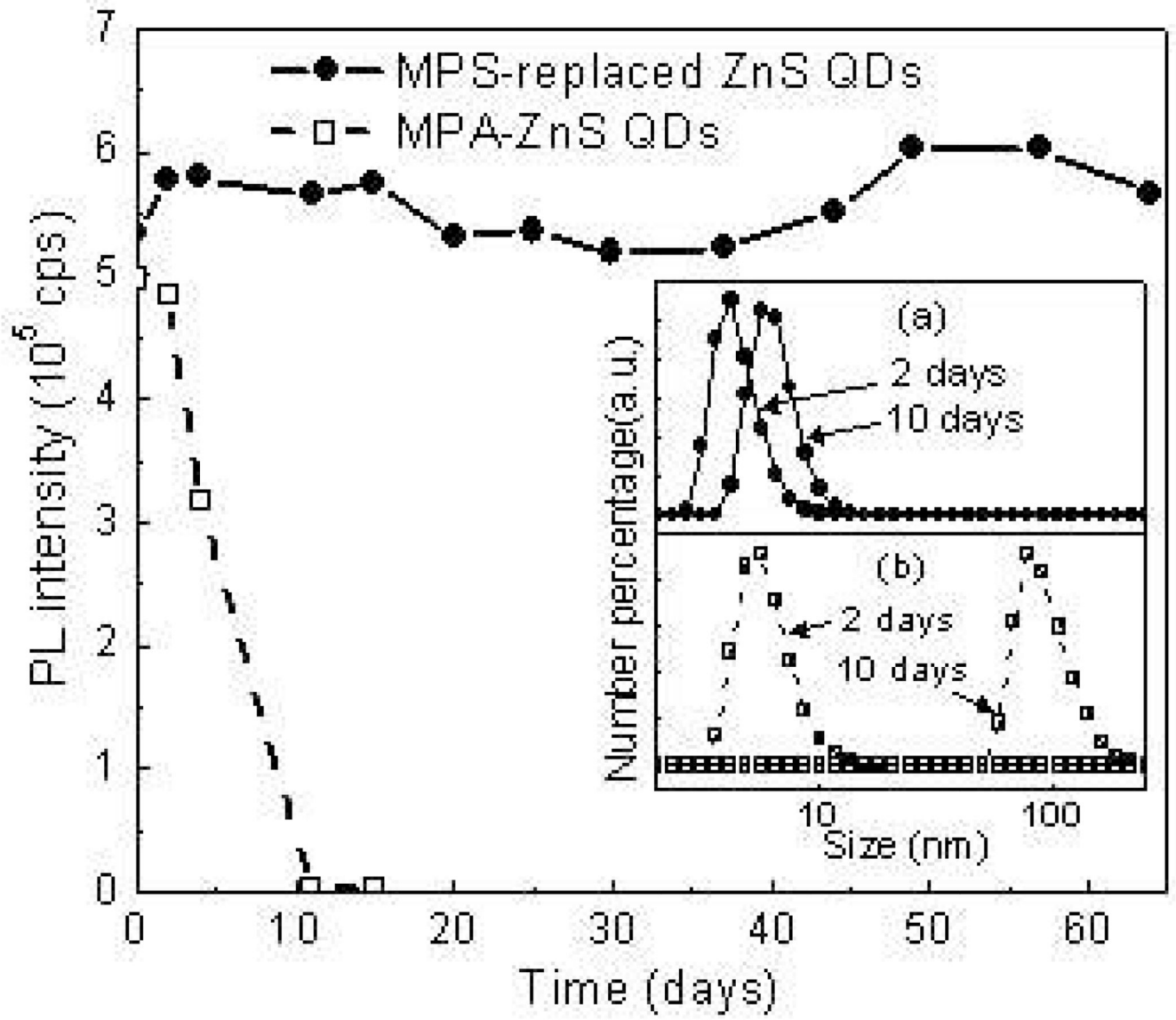

Fig. 4.

PL intensity versus time of the MPS-replaced ZnS QDs (full circles with solid line) under the ambient conditions, and that of the MPA-ZnS QDs (open squares with dashed line). Inset: size distribution of (a) the MPS-replaced ZnS QDs and (b) the MPA-ZnS QDs, 2 and 10 days after synthesis.