Synthesis and photoluminescence of bright water-soluble CdSe/ZnS quantum dots overcoated by hybrid organic shell

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ABSTRACT

Photoluminescence properties from water soluble CdSe/ZnS QDs encapsulated with hybrid trioctylphosphine-poly(acrylamide-co-acrylic acid)-ethanolamine (TOPO-PSMA-EA) shell have been investigated. It was found that PL efficiency of CdSe/ZnS QDs in water was increased 5–30% after introducing PSMA-EA polymers to encapsulate CdSe/ZnS-TOPO QDs. Higher PSMA concentrations were found to enhance the PL efficiency of QDs up to 1.8 folds, which is ascribed to a better packing and passivation of the TOPO-PSMA-EA shell over the QDs. Time-resolved photoluminescence suggested that the mean lifetime of photoexcited carriers in the water-soluble CdSe/ZnS-TOPO-PSMA-EA QDs elongated 2–17 ns compared with that of uncoated samples, indicating that PL quenching defects were effectively removed for CdSe/ZnS QDs with hybrid TOPO-PSMA-EA shell.

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1. Introduction

Colloidal semiconductor quantum dots (QDs) exhibiting excellent optical properties are promising for light-emitting, biological sensing and imaging, and photovoltaic applications [1–4]. For biological sensing and imaging, QDs must be water soluble. Unfortunately, high efficiency colloidal QDs prepared by the hot injection possess some hydrophobic ligands (e.g. trioctylphosphine oxide, TOPO) [5,6]. In order to disperse the QDs in water, a ligand exchange process is often used to replace the hydrophobic ligands with hydrophilic ones for the QDs. This process, however, may cause a certain degree of reduction in PL efficiency of QDs due to generation of nonradiative carrier traps [7]. Although post activation processes, for example, irradiating QDs with high energy light to eliminate the surface defects via the photooxidization mechanism (i.e. photo-activation) [8], or introducing amines to passivate the surface of QDs (i.e. chemical activation) [9] have been used to improve the PL efficiency, the manufacturing process is time- and energy-consuming.

On the other hand, direct encapsulation of TOPO-coated QDs with amphiphilic polymers via intercalating the TOPO molecules, followed by cross-linking requiring no any ligand exchange process has been reported [10]. More recently, Lees et al. used an amphiphilic polymer for directly entrapping the surface hydrophobic ligands of QDs (e.g. TOPO) to make the QDs water-dispersible[11]. The QDs possessed a hybrid TOPO-polymer-amine shell and their PL efficiencies were found to generally increase except blue emitting QDs. In this report, PL and photoexcited carrier lifetime of QDs capped with hybrid TOPO-polymer-amine shell are investigated.

2. Materials and methods

Cadmium oxide, selenium, stearic acid (SA), TOPO, trioctylphosphine (TOP), 1-hexadecylamine (HDA), poly(styrene-co-maleic anhydride) (PSMA, average Mn ~1600) and ethanolamine (EA) were purchased from Aldrich. CdSe/ZnS-TOPO QDs were synthesized by the standard hot injection approach [12]. Four CdSe/ZnS-TOPO QDs samples in different sizes; emission wavelengths 485 nm (dia. = 1.8 nm, photoluminescence (PL) efficiency = 43.5%), 539 nm (dia. = 2.6 nm, PL efficiency = 49.6%), 586 nm (dia. = 3.6 nm, PL efficiency = 51.1%), and 610 nm (dia. = 4.3 nm, PL efficiency = 32.3%) were used for the surface modification below.

The surface modification involves two steps; encapsulating CdSe/ZnS-TOPO with PSMA and modifying the PSMA from hydrophobic to hydrophilic [11]. PSMA stock solution (0.005 M) was prepared by dissolving PSMA powder into chloroform in ultrasonic bath for 1 h followed by stirring for another 1 h to assure that the polymer chains completely stretch in the solvent. EA stock solution (0.2 M) was prepared by directly mixing EA with deionized water. Prepared CdSe/ZnS QDs were re-dispersed in the PSMA stock solution and stirred for 1 h. A typical PSMA/QDs ratio used in this study was 1000, which had better improvement on PL efficiency and acceptable processing. EA stock solution was then added into the above solution. After stirring for 3 h, water-soluble PSMA-capped CdSe/ZnS-TOPO QDs could be transferred to the upper EA solution.

Samples were measured by UV–vis optical absorption and photoluminescence spectrometers. Particle size was analyzed by transmission electron microscopy (TEM). Room temperature time-

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resolved PL (TRPL) of QDs was measured by NanoLED-375L with a Jobin Yvon detector.

3. Results and discussion

The PSMA is a hydrophobic polymer with maleic anhydrides, which can be transformed to carboxyl and hydroxyl functional groups by introducing an amino alcohol to open the anhydride rings, generating hydrophilic functional groups, as shown in Fig. 1. The CdSe/ZnS-TOPO QDs disperse well in the PSMA-chloroform solution. The density of the EA water solution is smaller so that the water phase is the upper layer. When the EA water solution is mixed with the QDs-PSMA-chloroform phase by stirring, the maleic anhydride-amine reaction takes place at the chloroform-water interface where the EA attacks the cyclic anhydride, turning PSMA into amphiphilic molecules with both hydrophobic and hydrophilic functional groups (Fig. 1). The attachment of the hydrophobic side of PSMA to TOPO should be based on the van der Waals force, while the hydrophilic functional groups form the hydrogen bonds with water molecules. The transfer of the QDs to water phase is determined by the net force among the hydrogen bonding, van der Waals force, particle weight, buoyancy, and mechanical stirring force. To transfer QDs from oil phase to water phase, the interaction between COOH and H_2O should be larger than that between hydrophobic groups and chloroform. The entrapping process depends on polymers-QDs collisions. It was found that transfer time of QDs from the oil phase to the water phase correlates to QDs size; smaller QDs were faster than bigger QDs because smaller particles are relatively easy to be entrapped by PSMA chains and have lighter weight to move to water phase.

PL spectra show no obvious change in the peak position for CdSe/ZnS QDs overcoated by hybrid TOPO-PSMA-EA shell ($\lambda_{em} = 485$, 539, 586, and 610 nm), but PL efficiencies are significantly improved
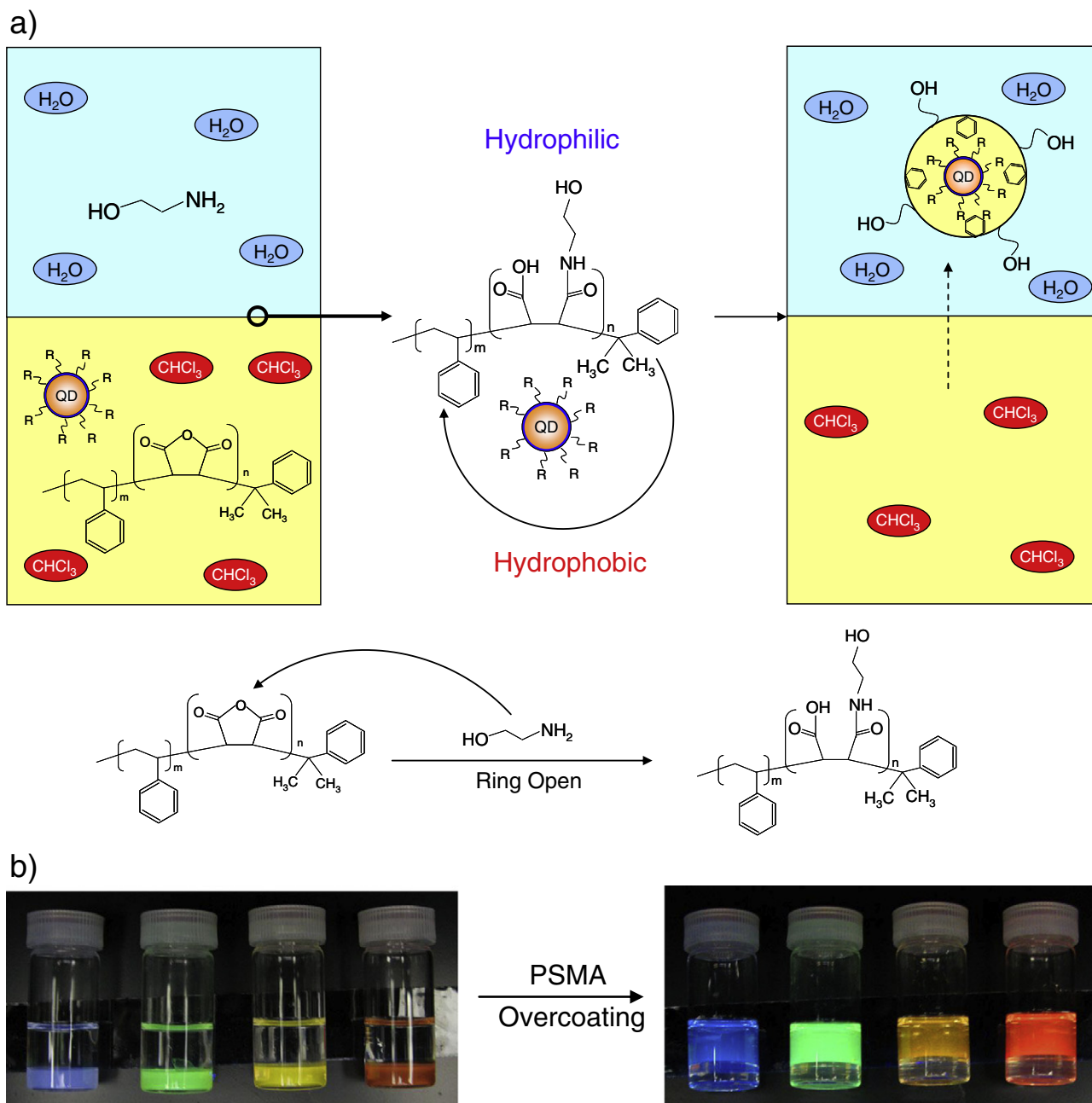

Fig. 1. A schematic presentation of the modification of CdSe/ZnS-TOPO QDs. (a) Transfer of the QDs from the lower PSMA-chloroform phase to the upper ethanolamine-water phase via a ring opening process. (b) Photos of CdSe/ZnS-TOPO QDs and PSMA overcoated CdSe/ZnS-TOPO QDs under UV 365 nm.
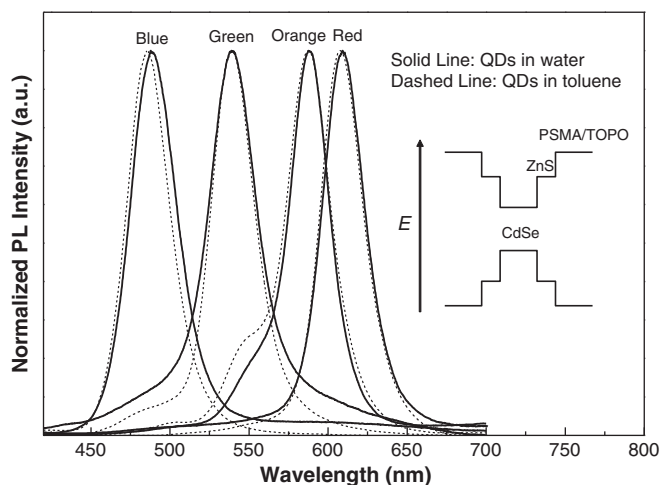
Fig. 2. PL spectra from CdSe/ZnS-TOPO QDs in toluene (dashed line) and PSMA-coated CdSe/ZnS-TOPO QDs in water (solid line). Inset: energy band gap diagram of PSMA-overcoated CdSe/ZnS-TOPO QDs.

(~13%, ~30%, ~5%, and ~8%). The results are similar to the previous study except that our blue-emitting QDs efficiency is also improved (~13%). The enhanced PL efficiency may be due to an additional passivation of ethanolamine for the QDs since amines can increase the PL efficiency via extra passivation to the QDs surface [13]. Another reason is that the hybrid polymer shell is served as a barrier layer to environment. With the hybrid shell, oxidization of the QDs surface can be effectively reduced. Besides, the hybrid shell also acts as an isolating shell, providing an additional carrier confinement layer to the CdSe/ZnS QDs, as shown in inset in Fig. 2. TEM images of the blue-emitting and red-emitting TOPO-PSMA-EA-overcoated CdSe/ZnS QDs are given in Fig. 3, showing that the hydrodynamic diameters are between 7 and 10 nm.

Using a centrifuge with various speeds, i.e. 6000 rpm (precipitate was collected) and 15000 rpm (precipitate and upper liquid were collected separately), TOPO-PSMA-EA-overcoated CdSe/ZnS QDs with different weights could be obtained. Fig. 4a shows that the PL peak position and shape of samples are similar, indicating the QDs have similar size and a size distribution. In other words, the process mainly produces samples with different weights of the PSMA-EA shell due to similar weight of CdSe/ZnS QDs in a narrow size distribution. As the PSMA-EA weight can be correlated to their thickness, it suggests that the shell thickness has no significant effect on the PL of QDs.

Fig. 4b shows PL spectra from samples prepared with various concentrations of PSMA. The PL intensity increases for QDs modified

with a higher PSMA concentration (~1.2 times and 1.8 times for 1000 and 3500 of PSMA/QDs ratio, respectively). Since the thickness of TOPO-PSMA-EA shell shows no obvious effect on the PL efficiency, increasing PL efficiency is thought to be caused by a higher packing density of PSMA-EA chains. In a higher concentration, PSMA chains would have more interactions with TOPO alkyl chains, leading to more complete coverage and density of the PSMA shell, so that PL quenching defects are diminished. The same phenomenon has recently been reported for CdSe/ZnS QDs passivated by sol–gel derived silica molecules [14]. Although higher PSMA concentration produced samples with a higher PL efficiency, samples become viscous because of strong interactions between polymer chains in the water phase and subsequent processing becomes difficult. A solution derived from QDs/PSMA = 1/1000 is acceptable for processing. In addition, no obvious change in the first excitonic absorption is observed (inset), indicating no aggregation or degradation occurs upon the transfer from the oil phase to the water phase [11].

TRPL provides information of the recombination dynamics of the photoexcited carriers in QDs. Room temperature TRPL spectra of CdSe/ZnS QDs before and after overcoated by PSMA-EA are shown in Fig. 5. The lifetime decay data of the carriers are fitted with bi-exponential function $I(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$, where B_1 and B_2 are the amplitude, τ_1 and τ_2 are the time constant, and the average lifetime τ_{ave} can be estimated by $\tau_{ave} = \left(B_1\tau_1^2 + B_2\tau_2^2 \right) / (B_1\tau_1 + B_2\tau_2)$. For uncoated samples, the τ_1 obtained are between 7 and 12 ns (11.3, 11.0, 10.1, and 7.5 ns for blue, green, orange, and red QDs), and τ_2 obtained are 33–48 ns (34.0, 47.1, 35.3, and 33.3 ns for blue, green, orange, and red QDs), respectively. For polymer-overcoated samples, the τ_1 has similar values 6–13 ns (12.1, 8.5, 9.2, and 6.8 ns for blue, green, orange, and red QDs), while τ_2 slightly increases to 36–60 ns (38.7, 59.2, 41.9, and 36.1 ns for blue, green, orange, and red QDs), respectively. The average lifetimes increases from 29.3 to 33.9, 37.5 to 54.0, 29.0 to 35.6, and 28.8 to 32.0 ns for blue, green, orange, and red CdSe/ZnS-TOPO-PSMA-EA QDs, respectively.

It has been reported that the slow-lifetime component of QDs PL decay arises from the core-related carrier recombination, while the long-lifetime component is determined by the surface-related one [15]. The coupling of photogenerated carriers with the surface states may elongate the radiative lifetime (e.g. 10 ns) due to less overlapping of the carrier wavefunctions [16]. The core-related lifetimes of the CdSe/ZnS-TOPO and the CdSe/ZnS/TOPO-PSMA-EA QDs have similar values (7–12 and 6–13 ns), showing that the PSMA-EA does not affect the carrier dynamics of the core state. On the other hand, the surface-related component τ_2 increases, inferring that the PSMA-EA chains alter the surface-related states of the QDs. This is because the hybrid TOPO-PSMA-EA polymer shell provides a better passivation than does sole TOPO molecules for CdSe/ZnS QDs. The hybrid polymer shell
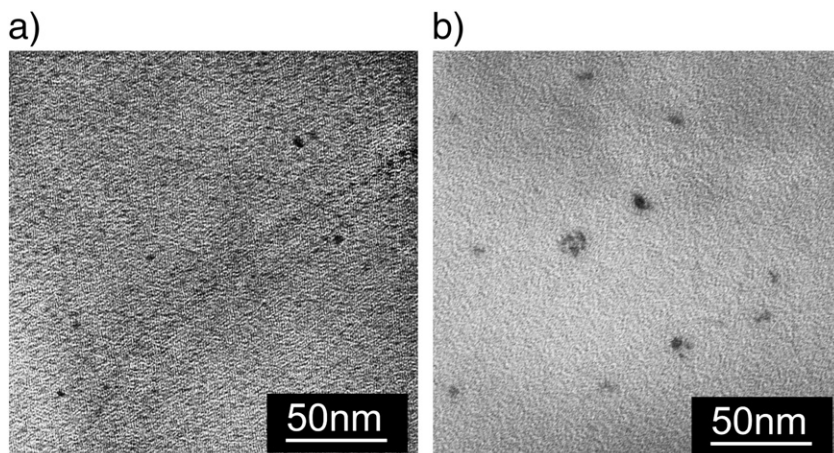

Fig. 3. TEM image of PSMA overcoated blue-emitting (a) and red-emitting (b) CdSe/ZnS QDs.
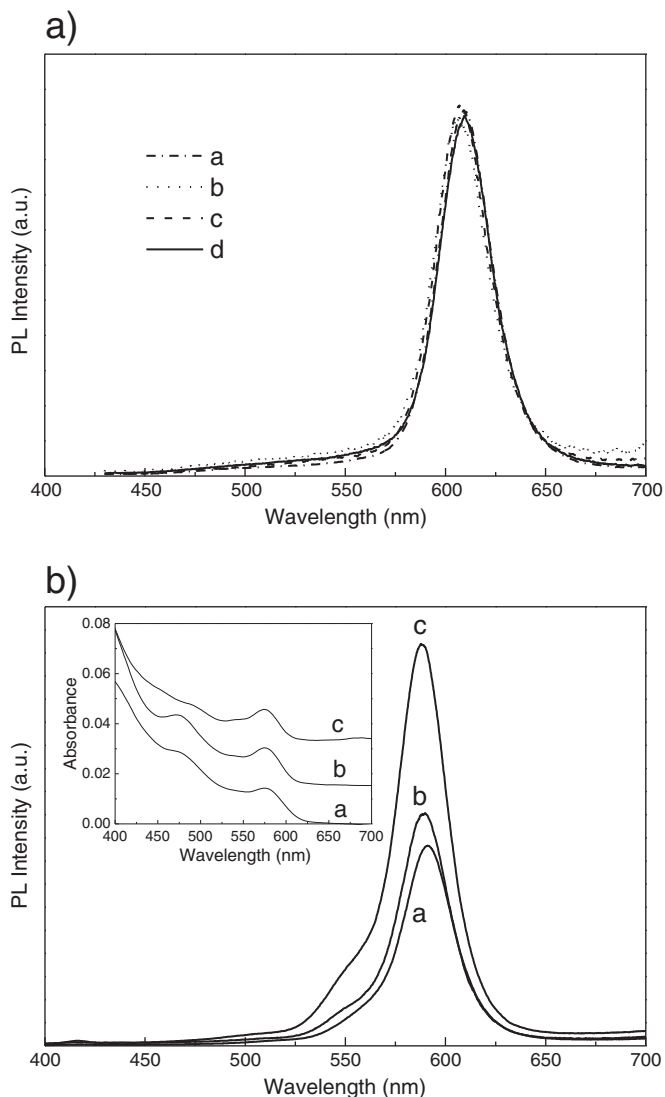
a)

b)

Fig. 4. PL spectra from CdSe/ZnS-TOPO-PSMA-EA QDs. (a) Samples were weight-selected by centrifugation with 6000 (curve b), 15000 rpm (curve c), and 15000 rpm (curve d, upper liquid). Curve a is a sample without centrifugation. (b) Samples synthesized with various PSMA concentrations; PSMA/ QDs = 100 (curve a), 1000 (curve b), and 3500 (curve c). Inset shows the corresponding optical absorption spectra.

would protect CdSe/ZnS QDs from oxidization when exposing to water and air. Consequently, the average exciton lifetime increases, which may explain the enhanced PL of CdSe/ZnS/TOPO-PSMA-EA QDs.

4. Conclusions

Water-soluble CdSe/ZnS QDs with four different sizes (dia. = 1.8 nm, 2.6 nm, 3.6 nm, and 4.3 nm) have been prepared by overcoating oil-
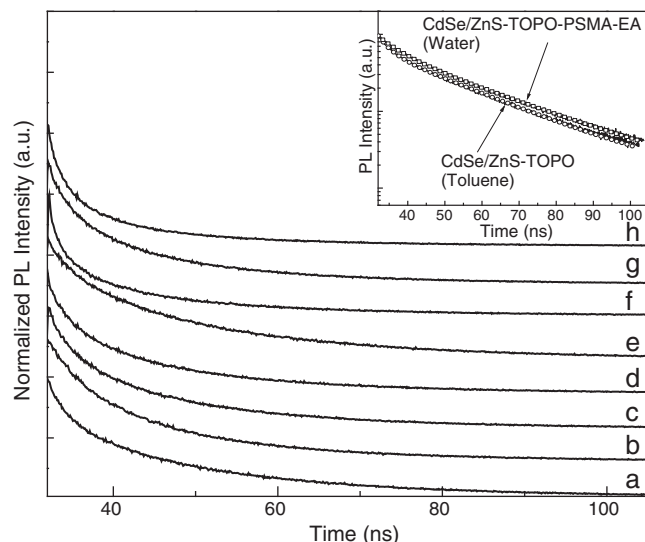

Fig. 5. Room temperature PL decay curves from CdSe/ZnS-TOPO QDs (curves a–d, for blue, green, orange, and red QDs) and CdSe/ZnS-TOPO-PSMA-EA QDs (curves e–h for blue, green, orange, and red QDs). Inset shows PL decay curves of blue QDs plotted on the logarithmic scale.

soluble CdSe/ZnS-TOPO QDs with PSMA-EA polymers. The hybrid TOPO-PSMA-EA shell enhanced the PL efficiency from 5 to 30% for CdSe/ZnS QDs. Time-resolved PL data demonstrated that the mean lifetime of photoexcited carriers in the QDs with hybrid shell in water increased 2–17 ns compared with that of the oil-soluble CdSe/ZnS QDs in toluene. The result suggested that improvement of PL of the QDs was due to removal of the PL quenching defects by the hybrid TOPO-PSMA-EA shell.

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