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Water-soluble CdSe/ZnS quantum dots passivated by poly(glycino amino acid) phosphazenes

ZHANG Teng(张 腾), YUAN Hui-ping(袁慧萍), SUO Hong-li(索红莉)

Key Laboratory of Advanced Functional Materials, College of Material Science and Engineering,
Beijing University of Technology, Beijing 100124, China

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Abstract: Poly(organophosphazenes) have potential applications in making water-soluble and biocompatible quantum dots (QDs) due to their wide variety of properties. The CdSe QDs of green emission and the core-shell CdSe/ZnS QDs of red emission were prepared. Subsequently the trioctylphosphine oxide-stabilized CdSe/ZnS QDs were transferred from chloroform into water through a ligand exchange process with poly(glycino amino acid)phosphazenes, which can be obtained from the saponification of poly (glycino amino ester)phosphazenes at room temperature. The resulting QDs-polymer nanocomposite particles can form colloidally stable suspensions in water and exhibit good photostability.

Key words: polyphosphazenes; CdSe/ZnS quantum dots; water-solublity; nanocomposite particles

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1 Introduction

Colloidal quantum dots (QDs) are attracting considerable attention owing to their unique optical properties as a result of quantum confinement[1]. The unique properties, including photostability, bright photoluminescence (PL), size-dependent absorption and PL, narrow emission and broad absorption bands, make QDs promising candidates for biological labels in comparison with dyes[2−6]. One of the major challenges is to obtain water-soluble QDs with high PL quantum yield (PL QY). Three different approaches can be used to prepare water soluble semiconductor QDs: ligand-exchange[7], encapsulation into a water-soluble shell (i.e., the silica or phospholipids)[8] and surface coating with polymers[9]. In comparison, silica encapsulation produces good stability but with larger sizes which are about tens of nanometers to several micrometers. In ligand-exchange, the stability of the nanocrystals is limited by the stability of ligands at the QD surface. The proper choice of ligand is therefore crucial in order to achieve functionality and retain the optical properties of the QDs, and usually limits the final application range of the QDs. In this context, polymers may be used as suitable substitutes for the small organic ligands molecules due to their good stability on the surface of QDs.

A number of strategies were developed to obtain polymer-coated QDs: 1) the surface coating of amphiphilic polymers on the QDs surface by hydrophobic interactions between the surface ligands of nanocrystals and polymers[10]; 2) the attachment of multidentate polymeric ligands directly onto the QD surface via multiple or single bonds[11]; 3) the polymerization of polymeric chains directly from the QD surface[12]. However, most synthesized polymers in literatures are difficult to biodegrade and be further functionalized, which can't meet the requirements of making low-cost, low-toxicity and multi-functional water-soluble quantum dots. Poly(organophosphazenes) have potential applications as polymeric carriers for biologically active agents and as biomaterials for tissue engineering[13]. The advantages of these polymers come mainly from their wide variety of properties, which can be designed and attained through the nucleophilic substitution of poly(dichlorophosphazene) (PDCP) with various organic groups. Polyphosphazenes with amino acid ester substituents were reported by ALLCOCK and his coworkers[14], who found that these polymers were

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Corresponding author: SUO Hong-li; Tel: +86-10-67392947; E-mail: honglisuo@bjut.edu.cn

potentially biocompatible, biodegradable, and harmless products. So poly(glycino amino ester)phosphazenes and their derivatives are possibly good candidate for the stability and functionality of QDs.

In this work, a process was reported to produce water-soluble QDs by modifying the surface of CdSe/ZnS QDs with biodegradable poly(glycino amino acid)phosphazenes (PGAAP), which are obtained from the saponification of poly[bis(ethylglycino)phosphazene] (PBEP) at room temperature. During QDs transferring from chloroform into water, no decrease of photoluminescence intensity is observed. The obtained QDs-polymer nanocomposite particles exhibit good dispersibility and photostability in water.

2 Experimental

2.1 Reagents and materials

Trioctylphosphine oxide (TOPO), tributylphosphine (TBP), hexadecylamine, dioctylamine, stearic acid, CdO, Se powder, hexamethyldisllathiane ($(TMS)_2S$) and diethylzinc ($Zn(Et)_2$) were purchased from Sigma-Aldrich. Hexachlorocyclotriphosphazene with melting point of 112.5−113.0 ℃ was synthesized according to Ref.[15], and recrystallized from heptane and sublimed (60 ℃ and 6.65 Pa) before use. Other reagents were analytical-grade and purchased from Beijing Chemical Reagent Co. China. Glycine ethyl ester hydrochloride was dried in vacuum at 50 ^{o}C for 24 h before use. Triethylamine was refluxed over sodium hydroxide and distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenoneketal under a dry nitrogen atmosphere. Petroleum ether (boiling point=60−90 ℃) and *n*-heptane were dried for 48 h over calcium hydride.

2.2 Preparation of CdSe/ZnS QDs

Most details of the synthetic and characterizing methods were similar to the ones reported previously[16]. A typical synthesis is as follows. 0.012 7 g (0.1 mmol) CdO, and 0.114 0 g (0.4 mmol) stearic acid were added into a 25 mL three-neck flask and heated to 150 °C under Ar flow. After CdO was completely dissolved, the mixture was cooled to room temperature. TOPO and hexadecylamine, 1.94 g of each, were added to the flask, and the mixture was heated to 320 ℃ under Ar flow to form an optically clear solution. At this temperature, the Se solution containing 0.079 g (1 mmol) Se dissolved in a mixture solution of 0.238 g (1.18 mmol) TBP and 1.681 g of dioctylamine was swiftly injected into the reaction flask. After the injection, the nanocrystals grew at 290 ℃ for 2.5 min and the mixture was cooled to about 200 ℃. The mixture containing 150 μL $(TMS)_2S$ and 0.6 mL $Zn(Et)_2$ premixed in 1.2 mL TOP was gradually injected into the solution in 1 min. The reaction mixture was kept at 180 ℃ and stirred for 1 h. The solution was cooled to room temperature and the resulting sample of CdSe/ZnS QDs was washed three times with methanol and chloroform.

2.3 Preparation of Poly(glycino amino acid) phosphazenes

Poly(dichlorophosphazene) (PDCP) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene, as described in Ref.[17]. After the reaction stopped by cooling, anhydrous petroleum ether (with boiling point of 60−90 ℃) was applied to wash away the unreacted monomer and some oligomers. The remainder was dissolved in anhydrous benzene with vigorous stirring and then filtered to remove any possible cross-linked product. Soluble polymer PDCP was obtained by the precipitation of the polymeric solution into excess dry *n*-heptane.

Poly[bis(ethylglycino)phosphazene] (PBEP) was prepared in a similar method as described in Refs.[17−18]. Briefly, a benzene solution of glycine ethyl ester, which was obtained by the refluxing of mixtures of glycine ethyl ester hydrochloride and triethylamine in benzene for 6 h and filtration was added slowly to a PDCP solution in benzene. The system was stirred at 0 ℃ for 6 h, and this was continued at room temperature for another 10 h. A viscous solution resulted after triethylamine hydrochloride was filtered. The solution was concentrated by the vacuum evaporation of the solvent on a rotary evaporator and precipitated into petroleum ether with boiling point of 60−90 ℃ to produce a kind of yellow, solid polymer with yield of 75%.

Poly(glycino amino acid)phosphazenes (PGAAP) was synthesized by the saponification in NaOH solution of PBEP. Briefly, PBEP was added into the 2.5 mol/L NaOH aqueous solution and stirred for 5 h at room temperature. Then the superfluous methanol was injected into the above reaction system and the precipitate was washed by acetone and ether in turn. The product was dried in vacuum at 40 ℃.

2.4 Preparation of water-woluble CdSe/ZnS QDs (CdSe/ZnS/PGAAP)

CdSe/ZnS in chloroform (5 mL, 100 μmol/L) was added to a three-necked. 5 mL DMSO and 2 mL mercaptoethanol were added successively, and chloroform was removed under vacuum at room temperature. After stirring for an additional 2 h under argon, the QDs were precipitated with the addition of excess ice-cold mixture of acetone and chloroform (volume ratio of 1:1). After centrifugation, the precipitate was washed with acetone and dried under vacuum.

QDs coated with mercaptoethanol were suspended in DMSO and centrifuged to remove possible nanocrystal aggregates. The nanocrystals were diluted to about 5 μmol/L. The QDs were then degassed extensively at room temperature and charged with argon. An anhydrous DMSO solution of about 5 mg/mL polymer was added under vigorous stirring. The solution was then heated to 60 ℃ and kept for 2 h. After cooling the QDs to room temperature, ice-cold aqueous sodium hydroxide (50 mmol/L, twice the volume of DMSO) was slowly added, and the solution was stirred for 2 h. The QDs were then extensively dialyzed against basic water for 2−3 d using 25 kDa molecular mass cut off dialysis tubing.

2.5 Photostability of synthesized QDs

CdSe (in chloroform), CdSe/ZnS (in chloroform) and CdSe/ZnS/PGAAP (in water) were irradiated with UV light using a 4 W UV lamp (115V, 60HZ, Model 22-UV, Optical Engineering, Inc.) with 254 nm radiation. The samples were also fixed 5 cm away from UV lamp.

2.6 Instrument

Absorption spectra were acquired with a Cary 5000 ultraviolet (UV)-visible (vis)-NIR spectrophotometer (Varian) with a scan speed of 600 nm/min. PL spectra were taken with a Fluorolog-3 system (Horiba Jobin Yvon) using an excitation wavelength of 350 nm. The PL QY of the nanocrystal sample was finally obtained by comparing the integrated PL intensities of the nanocrystals and the Rhodamine 6G (R6G, 528 nm, 95%). All the obtained polymers were characterized with ^{1}H NMR. The measurement was carried out with a Switzerland Bruker AV 600-MHz NMR instrument, with deuterated chloroform as the solvent and internal Me_4Si as the shift reference.

3 Results and discussion

3.1 Synthesis of semiconductor nanoparticles

The UV-vis absorption and PL spectra of the obtained CdSe and CdSe/ZnS are shown in Fig.1. The characteristic and narrow excitionic absorption peaks at 543 and 571 nm respectively are obtained(see Fig.1(a)). Narrow PL spectra (22 nm and 26 nm for full width at half-maximum of the spectrum, FWHM) are recorded for CdSe and CdSe/ZnS, and their PL peak positions are 550 and 587 nm, respectively (Fig.1(b)). In addition, the absorption spectra for the CdSe/ZnS dots are broader and slightly red-shifted from their bare CdSe dot spectra (from 543 nm to 571 nm). The red shift can be explained by a secondary CdSe core growth due to remaining precursors from the CdSe synthesis and by a tunneling of the charge carriers into the ZnS shell. The quantum yields for emission were found by direct comparison with Rhodamine R6G (QY=95%, ethanol) as 35% and 45% for CdSe and CdSe/ZnS QDs. The PL QY increase after coating ZnS of purified CdSe TOPO particles indicates that the presence of the ZnS shell on the particles improves the surface passivation of the CdSe NCs. Fig.2 shows the TEM images of the CdSe core and CdSe/ZnS core/shell nanocrystals. It can be seen that the synthesized QDs are nearly spherical.

3.2 Poly(glycino amino acid)phosphazenes

A new class of multidentate polymer ligands was reported to not only minimize the hydrodynamic size of QDs but also overcome the colloidal stability and photobleaching/signal brightness problems encountered in ligand exchange or amphiphilic polymers method[19−20]. Poly(organophosphazenes) can easily be designed and turned into multidentate polymer ligands through the nucleophilic substitution of poly (dichlorophosphazene) with various organic groups. Especially poly(amino acid ester)phosphazenes and their derivatives were proved to be biodegradable and biocompatible. So the poly(glycino amino acid) phosphazenes with acid groups was prepared by the saponification of poly[bis(ethylglycino)phosphazene] in NaOH solution, and their structures were confirmed by ^{1}H NMR (see Fig.3). Polymer PBEP exhibited peaks at

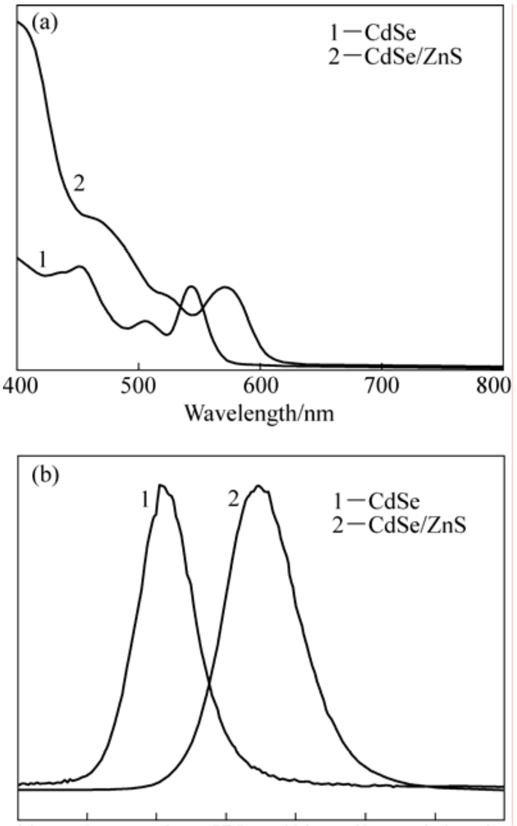

Fig.1 Absorption (a) and fluorescence emission (b) spectra of CdSe and CdSe/ZnS in chloroform

4.2×10^{-6}, 3.7×10^{-6}, and 1.3×10^{-6}, and these were attributed to methylene or methyl protons in $-OCH_2-$, $-NHCH_2-$ and $-CH_3$, respectively. After saponification, the peaks at 4.2×10^{-6} and 1.3×10^{-6} disappeared and the new peaks around 3.3×10^{-6} ($-NHCH_2COO-$) were detected. This implied that the saponification is realized and the polymer PGAAP is formed.

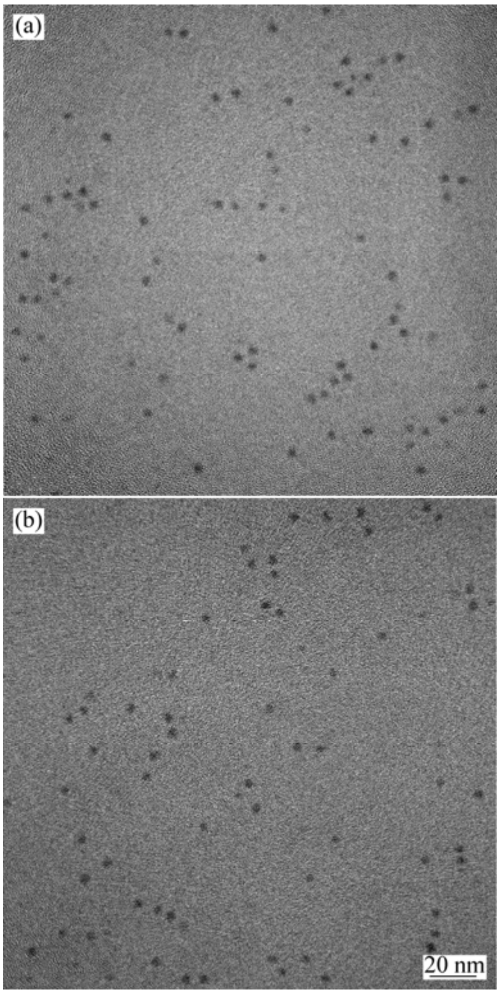

Fig.2 TEM images of CdSe core (a) and corresponding CdSe/ZnS core/shell (b) nanocrystals

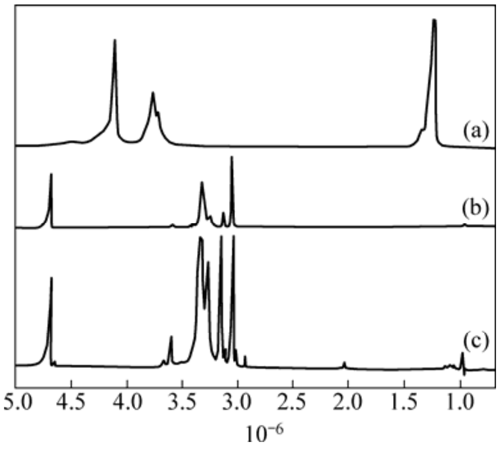

Fig.3 ^1H NMR spectra of poly[bis(ethylglycino) phosphazene] (PBEP) and its saponification products (PGAAP): (a) Before saponification; (b) Saponification in 1.25 mol/L NaOH solution; (c) Saponification in 2.5 mol/L NaOH solution

3.3 Passivation of CdSe/ZnS by PGAAP and stability

To examine the influence of polymer on the absorption and emission spectra of CdSe and CdSe/ZnS QDs, CdSe/ZnS and CdSe/ZnS/polymer PGAAP of closely matched optical density were prepared. Fig.4 shows the absorption (a) and fluorescence emission spectra of CdSe/ZnS in chloroform and CdSe/ZnS/Polymer PGAAP (red curves) in water. Closer inspection of the UV-vis absorption spectrum shows that the first exciton peak centered at 571 nm for CdSe/ZnS is blue shifted by a few nanometers for the nanocrystals bearing polymer PGAAP, indicating a very small decrease in nanocrystals size. In contrast to the almost imperceptible effect of surface-bound polymer on the UV-vis absorption spectra, the polymer has a striking effect on the photoluminescence (PL) intensity. Fig.4(b) shows that the presence of PGAAP leads to a 1.2-times increase in PL intensity. The CdSe/ZnS QDs passivated by PDMA have a quantum yield of 52%. The obtained CdSe/ZnS/polymer PGAAP is the water-soluble red QDs and has good colloidal stability for several months (see Fig.5).

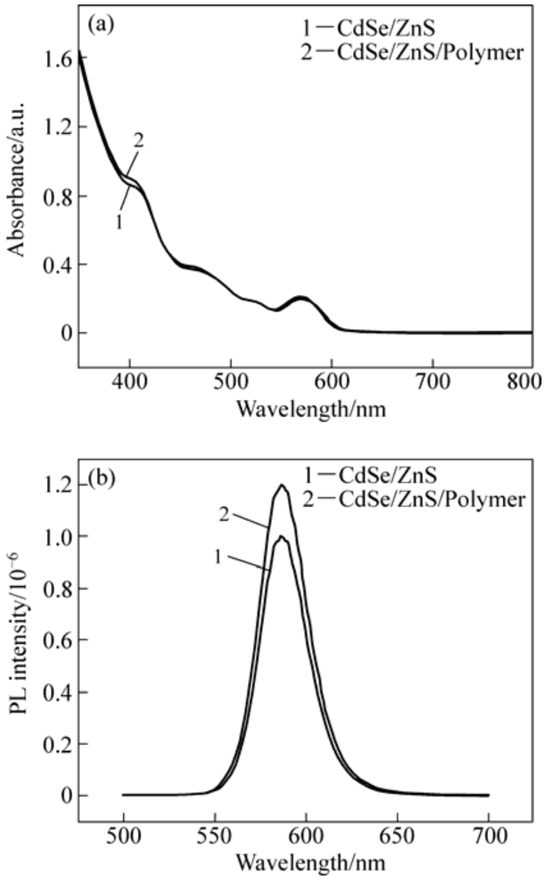

Fig.4 Absorption (a) and fluorescence emission (b) spectra of CdSe/ZnS in chloroform and CdSe/ZnS/polymer PGAAP in water

The stability of QDs obtained was investigated under the radiation of UV lamp (see Fig.6). The results show that the stability of quantum dots increases remarkably after ZnS shell coating the surface of CdSe core. After the CdSe/ZnS QDs transfer into water through multidentate ligands PGAAP, the polymer-coated QDs (CdSe/ZnS/PGAAP) still have good stability of PL intensity under UV illumination. This indicates that ZnS shell greatly enhances the long-term fluorescence stability of CdSe core even after CdSe/ZnS QDs are transferred into water.

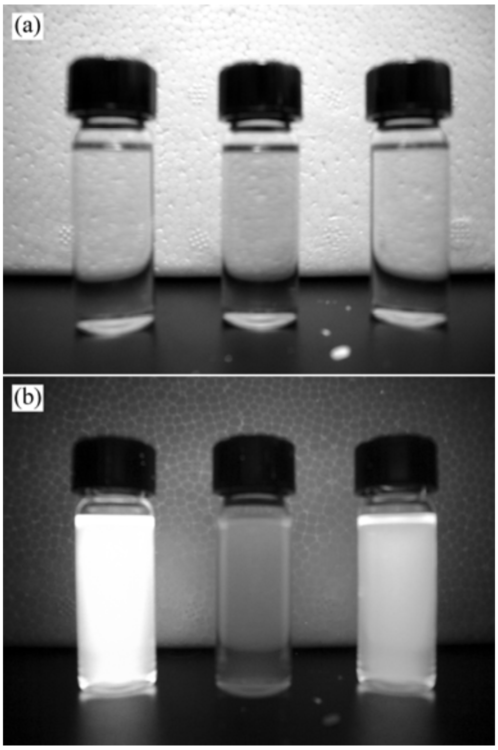

Fig.5 Photographs of CdSe (left, in chloroform), CdSe/ZnS (middle, in chloroform) and CdSe/ZnS/Polymer (right, in water) before (a) and after (b) UV illumination

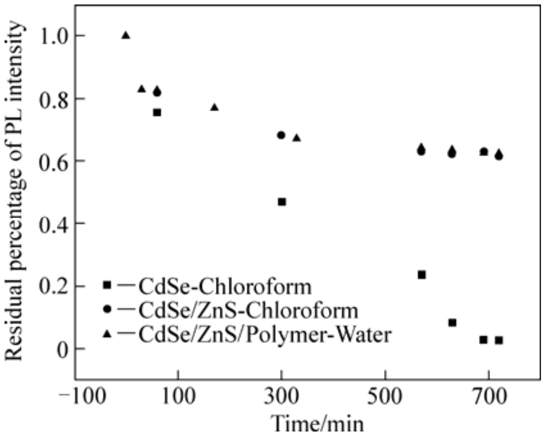

Fig.6 Photostability of synthesized CdSe (in chloroform), CdSe/ZnS (in chloroform) and CdSe/ZnS/polymer PGAAP (in water) under UV illumination

4 Conclusions

1) Fluorescent CdSe/ZnS quantum dots (QDs) were encapsulated into biocompatible poly(glycino amino acid)phosphazenes (PGAAP). PGAAP, acting as a multidentate ligand, is effective on surface passivation and colloidal stability in water for CdSe/ZnS QDs.

2) ZnS shell provides robust fluorescence stability in various environments. These fluorescent hybrid nanocomposite particles have potential application in genomics, drug discovery, and other applications that could exploit the high-throughput afforded by multicolor coding.

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