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RESEARCH ARTICLE

Single-source precursor route for overcoating CdS and ZnS shells around CdSe core nanocrystals

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We reported a facile route for overcoating CdS and ZnS shells around colloidal CdSe core nanocrystals. To synthesize such double shelled core/shell nanocrystals, first, CdSe core nanocrystals were prepared in a much "greener" and cheap route, which did not involve the use of hazardous and expensive trioctylphosphine. Then, a low-cost and labor-saving route was adopted for the CdS and ZnS shell growth with the use of thermal decomposition of commercial available air stable single-source precursors cadmium diethyldithiocarbamate and zinc diethyldithiocarbamate in a non-coordinating solvent at intermediate temperatures. Powder X-ray diffraction patterns and transmission electron microscopy images confirm the epitaxial growth of the shell in the core/shell nanocrystals. The photoluminescence quantum yield of the resulting CdSe/CdS/ZnS core/shell nanocrystals can be as high as 90% in organic media and up to 60% after phase transfer into aqueous media. By varying the size of CdSe cores, the emission wavelength of the obtained core/shell nanostructures can span from 554 to 636 nm.

Keywords Luminescent quantum dots, core/shell nanostructure, CdSe/CdS/ZnS nanocrystals, single-source precursor

1 Instruction

Colloidal semiconductor nanocrystals (NCs), also referred as quantum dots (QDs), are of great interest for both fundamental studies and technical applications, such as light-emitting devices (LED), lasers, and fluorescent labels [1–5]. Among the various semiconductor materials, the CdSe-based NCs have been the most studied ones, and are considered as the most promising emitting material because their emission colors can be conveniently tuned across the visible spectrum from blue to red [6–11]. However, plain CdSe QDs often lose their luminescence after grafting with chemical or biological molecules due to the exposure of excitons to the surrounding [12,13]. How to gain stronger photoluminescence (PL) emission and better stability of QDs is one of the main aims in the domain of QDs research. It has been proven that surface passivation of NCs with suitable inorganic materials of higher bandgap is key to improve PL efficiency and stability of NCs due to the isolation of excitons with surrounding [12–20]. Depending on the specific application requirements of CdSe NCs, different semiconductor materials have been exploited for the shell growth around the CdSe core NCs. Several wide band gap semiconductors (including ZnS [12,13], CdS [14–16], ZnSe [17,18], and/or their alloys [19,20]) have been employed as the shell material to overcoat around the CdSe core NCs. ZnS is a non-toxic chemically stable wide band gap (3.2 eV) semiconductor material. Potentially, the ZnS shell should provide the best passivation of CdSe core NCs. However, the large mismatch (ca. 12%) between CdSe and ZnS lattice parameters is a problem. Recently, CdSe/CdS/ZnS or CdSe/ZnSe/ZnS "double shell" QDs have been reported [21–24]. In these QDs, the large lattice mismatch is buffered by the CdS or ZnSe layer, and accordingly, higher PL quantum yield (QY) and stability are obtained in these resulting nanostructures.

The initial inorganic shell growth method was invented by Hines and Guyot-Sionnest in 1996, and the route is still commonly adopted in some laboratories [12]. In this procedure, the high dangerous pyrophoric organometallic reagent zinc diethyl ($ZnEt_2$) and highly toxic bis(trimethylsilyl)sulfide, which serve as the Zn and S precursors, were added dropwise into the core NCs dispersed in a coordinating solvent (such as trioctylphosphine oxide, trioctylphosphine, amines, or their mixture) at intermediate temperatures (150°C–250°C). With the goal of avoiding the usage of these dangerous compounds, a much safer reagent zinc stearate was adopted by Reiss et al. to replace the original zinc diethyl [16]. In the subsequent modified procedure, zinc carboxylates and elementary sulfur were demonstrated to be the excellent Zn/S sources for the overcoating of the ZnS shell in a non-coordinating solvent octadecene [18]. In catering for the recent developments in the field of the synthesis of semiconductor NCs, the use of easy-to-manipulate, inexpensive, and environmentally benign precursors and solvents (necessary for an industrial up-scaling of the process) is preferred. Compared to the binary precursor system, the mono-molecule precursor in overcoating QDs would brings forward many conveniences. Single-source precursors, such as metal thiocarbamate and xanthate salts, can also be

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thermolysed to yield nanoparticles [25,26]. Mono-molecule precursors have also been used in the shell growth process [27–29]. Herein, we adopt the monomolecule precursor route for the construction of the most developed and also one of the best optical performance systems CdSe/CdS/ZnS. We demonstrate a facile procedure for the preparation of nearly monodisperse CdSe/CdS/ZnS core-shell nanoparticles with the use of mono-molecule precursor metal thiocarbamate. Furthermore, an efficient "green" protocol without the use of expensive and hazardous alkylphosphine was adopted for the synthesis of CdSe core NCs.

2 Experimental section

2.1 Chemicals

Cadmium oxide (CdO, 99.99 + %), selenium powder (– 100 mesh, 99.999%), 1-octadecene (ODE, 90%), cadmium chloride hydrate ($CdCl_2 \cdot xH_2O$, 99.99%), stearic acid (90%), 3-mercaptopropionic acid (MPA, 99%), tetramethylammonium hydroxide pentahydrate (TMAH, 98%), sodium diethyldithiocarbamate (SDC, 99%), and zinc diethyldithiocarbamate (ZDC, 98%) were purchased from Aldrich. All chemicals were used as received without any further purification. All solvents were obtained from commercial sources and used as received.

2.2 Synthesis of zinc blend CdSe core NCs

CdSe core NCs were prepared via a modified literature method [30]. Typically, selenium powder (15.8 mg, 0.2 mmol) and 4.0 mL of ODE were added into a three-neck flask clamped in a heating mantle. The mixture was heated to 210°C under argon flow and a clear solution was observed. The solution was then kept at this temperature. Then, 0.4 mmol of cadmium stearate solution in 1.5 mL of ODE, obtained by dissolving CdO in stearic acid at 200°C, was injected into the reaction flask. After the injection, a certain reaction temperature (200°C ~ 240°C) was set for the NCs growth to desired sizes with different periods of time (30 s ~ 6 min). The reaction mixture was then allowed to cool to ~ 60°C. 10 mL of hexane/CH_3OH (*v*/*v*, 1∶1) was used as the extraction solvent to separate the NCs from byproducts and unreacted precursors if they existed. The as-prepared CdSe NCs solution was further purified by centrifugation and decantation with the addition of acetone. By this approach, one can obtain CdSe NCs with an average size of 2.0 – 3.3 nm and corresponding emission wavelength at λ = 518 – 610 nm.

2.3 Stock solutions for CdSe and ZnS shell growth

The CdS precursor cadmium diethyldithiocarbamate (CDC) was prepared by the reaction of $CdCl_2$ solution with SDC. CDC was precipitated from aqueous solution as white powders. The precipitates were washed with distilled water for 3–4 times and dried for later use. The CdS and ZnS precursor solutions (0.05 mol·L^{-1} for each solution) were prepared by dissolving CDC or ZDC, respectively, in OAm and ODE (*v*/*v*, 1∶1) at room temperature by sonication. Each stock solution was stored at room temperature.

2.4 Synthesis of CdSe/CdS and CdSe/CdS/ZnS core/shell QDs

In a typical procedure, a chloroform solution of the purified CdSe QDs (containing 0.06 mmol of CdSe) with emission wavelength of 554 nm, 1.0 mL of OAm, and 2.0 mL of ODE were loaded in a 50-mL flask. The flask was then pumped down at room temperature for 20 min to remove the chloroform and at 100°C for another 20 min while flushing the reaction system twice with a flow of argon. Subsequently, the reaction mixture was further heated to 150°C for the overgrowth of CdS shell. A CdS precursor stock solution (containing 72.8 mg of CDC) was added via a syringe and kept at 150°C for 30 min. The temperature was then raised to 200°C and maintained for another 20 min. The amount of used CDC depends on the thickness of shell required. When thick shell was required, the CDC can be added in several batches. When the optical spectra showed no further changes, another cycle of CdS precursor solution was added repeatedly. With the addition of the CdS precursors, the original slightly red solution gradually turned to deep red. To monitor the reaction, aliquots were taken before a new cycle of injection, and their corresponding UV-Vis and PL spectra were recorded.

In the process of overcoating CdS shell around CdSe core template, when the desired thickness of obtained CdS shell and the emission wavelength of the resulting CdSe/CdS approached the desired value, the addition of CdS precursors was stopped, and the reaction temperature was lowered down to 140°C for further overgrowth of ZnS shell. A ZDC stock solution stock solution (containing 110.2 mg of ZDC) was added into the CdSe/CdS crude reaction solution, and kept at this temperature for 20 min. The temperature was then raised to 190°C and maintained for another 20 min. The reaction was terminated by allowing the reaction mixture to cool down to room temperature. The purification procedure was similar to that for CdSe core NCs as mentioned above.

2.5 Water solubilization of the oil-soluble NCs into water-soluble ones

The water solubilization of the initially oil-soluble CdSe/CdS and CdSe/CdS/ZnS NCs was achieved by replacing the initial

hydrophobic capping ligands (OAm) with hydrophilic thiol ligand (MPA) according to literature method [31]. Typically, MPA (0.5 mL) was dissolved in 5.0 mL of methanol, and the solution was then adjusted to pH 12 with the addition of a certain amount of organic base TMAH. MPA-methanol solution, about 0.5 mL, was then added into 5.0-mL QDs chloroform solution and stirred for 30 min to get the precipitation of the QDs. Then, 5.0 mL of distilled water was added into the mixture and kept stirring for another 20 min. Finally, The solution was separated into two phases, and the QDs were transferred into the superincumbent aqueous phase from the underlying chloroform. The underlying organic phase was discarded, and the aqueous phase containing the QDs was collected. The free MPA ligand in the QDs aqueous solution was isolated by precipitating the QDs with addition of acetone. The supernatant was discarded, and the pellet was then redissolved in water for use in next step.

2.6 Characterization

UV-Vis and PL spectra were obtained on a Shimadzu UV-2450 spectrophotometer and a Cary Eclipse (Varian) fluorescence spectrophotometer, respectively. The room-temperature PL QYs of the QDs were determined by comparing the integrated emission of the QDs samples in solution with that of a fluorescent dye (such as rhodamine 6G with a QY of 95% in ethanol) with an identical optical density [32,33]. Also, the known QYs of the QDs in solution can be used to measure the PL efficiencies of other QDs by comparing their integrated emission. To conduct investigations in the transmission electron microscopy (TEM), the NCs were deposited from dilute toluene solutions onto copper grids with carbon support by slowly evaporating the solvent in air at room temperature. TEM images were acquired using a JEOL JEM-1400 transmission electron microscope operating at an acceleration voltage of 120 kV. Powder X-ray diffraction (XRD) was obtained by wide angle X-ray scattering using a Siemens D5005 X-ray powder diffractometer equipped with graphite monochromatized Cu K_α radiation (λ = 1.5406 Å). XRD samples were prepared by depositing nanocrystal powder on a piece of Si (100) wafer.

3 Result and discussion

3.1 Epitaxial growth of CdSe/CdS and CdSe/CdS/ZnS core/shell NCs

A two-step procedure was adopted for the preparation of CdSe/CdS/ZnS core/shell NCs. In the first step, CdSe NCs with zinc-blende (ZB) structure were prepared via a non-TOP-based route following a modified literature method [30]. The CdSe NCs were obtained via the reaction of elemental selenium with cadmium stearate in a non-coordinating solvent ODE at high temperature. This method did not involve the use of the expensive and hazardous reagent alkylphosphine (such as trioctylphosphine (TOP)) to prepare Se precursor between the reaction of Se and TOP as for the synthesis of CdSe QDs in most methods [6–11]. When the purified CdSe NCs were obtained, a CdS shell was then overcoated around the CdSe cores. In previous reports, in order to grow the CdS shell around CdSe cores, expensive high-boiling-point solvents, such as TOP, TOPO, and/or amines with long alkyl chain, were adopted as solvents and surfactants. Our experiment adopted a labor-saving and cost-saving method that employed a single molecule precursor CDC as CdS precursor. The expensive solvent trioctylphosphine oxide (TOPO) and TOP as normally used in the shell overgrowth procedure were excluded [12–17]. The CdS shell was overcoated through the thermal decomposition of the precursor CDC in a dispersion of the purified CdSe NCs in a mixture solvent containing ODE and OAm at 150°C. The synergic effect of the selected surfactants (OAm), the appropriate reactivity of the precursors, and the low deposition temperature (150°C) ensured that heterogeneous growth of CdS at the surface of the CdSe NCs prevails and also prevented the further growth of the CdSe cores by Ostwald ripening or alloying due to interdiffusion. High-quality CdSe/CdS core/shell QDs with desired shell thickness and corresponding emission wavelength can thus be obtained. Due to the similar lattice parameter (compared with the CdSe core), CdS capped CdSe NCs can result in high PL QYs. While in the CdSe/CdS system, the band offsets in the conduction band is as small as 0.26 eV, which cannot confine the charge carriers completely in the core region [34]. This results in the low stability of PL, especially in aqueous media. Such phenomenon was reported in previous literature and is also demonstrated in our experiment, as will be discussed below. It is necessary to further overcoat an inorganic shell material with higher bandgap for the improvement of PL stability. ZnS is undoubtedly the preferable choice. When the CdSe shell grew to a desired thickness and the corresponding PL emission wavelength of the resulting CdSe/CdS core/shell QDs approached the desired value, a ZnS shell was consecutively epitaxially overcoated around the outer layer of the CdSe/CdS template to form the CdSe/CdS/ZnS core/shell nanostructures. When zinc carboxylate salts (such as zinc acetate) and elemental sulfur were adopted as the Zn and S precursors for the formation of ZnS shell, as used in most reported literatures [18], our experimental results showed that it did not work well in overcoating ZnS shell around the CdSe/CdS QDs. Following the experience of overcoating CdTe NCs developed by our own group recently [28], we also used the mono-molecule precursor ZDC as ZnS precursor for

overcoating ZnS shell. Our experimental results demonstrated that it is an efficient route to obtain highly luminescent and highly stable CdSe/CdS/ZnS NCs with desired thickness of ZnS layer via the thermal decomposition of ZDC at an intermediate temperature in the crude CdSe/CdS reaction solution.

3.2 Structure characterization of CdSe/CdS/ZnS core/shell QDs

The shell thickness of the CdSe/CdS/ZnS core/shell structures was controlled by the amount of used precursor. We use several techniques, including direct and indirect methods, to monitor and characterize the shell's thickness, structure, and composition. Figure 1 shows wide-field TEM graphs of the initial 2.4 nm CdSe cores with corresponding PL emission wavelength λ = 548 nm, the representative CdSe/CdS core/shell NCs with size of 3.8 nm, and CdSe/CdS/ZnS core/shell/shell NCs with size of 5.0 nm. The sizes were derived from the initial CdSe cores via the consecutive overgrowth of the CdS and ZnS shells. Taking the thickness of CdS and ZnS monolayer (ML) as 0.35 and 0.30 nm, respectively, there are about 2 MLs of CdS and 2 MLs of ZnS around each CdSe core. The increased size of the nearly dot-shaped core/shell NCs in Figure 1 approximately matches the theoretical thickness calculated from the amount of injected precursor solution, which gives strong evidence for the epitaxial growth of CdS onto the CdSe cores and growth of ZnS around CdSe/CdS template. The match can also exclude the independent homogeneous nucleation of shell precursor. The nearly monodisperse core/shell NCs formed good well-ordered two-dimensional (2D) superlattices in part areas, as shown in the TEM images. This result demonstrates that the size and shape of the obtained core/shell particles are uniform. All the samples of the as-prepared CdSe/CdS and CdSe/CdS/ZnS core/shell QDs have a narrow size distribution with a relative standard deviation (σ) of 5%–7% without any post-preparation size sorting. The corresponding histograms of the size distribution are given in insets in Figure 1. It should be noted that the size distribution of the core/shell QDs is significantly improved in comparison to that of the corresponding CdSe core nanoparticles. This observation is contrary to the commonly reported shell growth procedures, in which by the increase of the shell thickness, the size distribution of the resulting core/shell particles usually deteriorates severely [12–17]. The nearly uniform size and shape distribution in the obtained CdSe/CdS and CdSe/CdS/ZnS core/shell NCs mainly originate from the suitable deposition temperature and shell precursors used (CDC and ZDC, respectively). The steady and gradual release of free precursor molecules through the thermal decomposition of CDC or ZDC at proportional temperature leads to the smaller particle bearing a larger shell growth rate, resulting in the size focusing similar to the previously studied "focusing" mechanism for the growth of binary nanocrystal systems [7,35,36]. The steady and slow supply of the precursor molecules can also promote the even deposition of shell molecules to all core NCs, resulting in shell layers with nearly the same thickness around each core nanoparticle. Our control experiments demonstrated that when the shell deposition was carried out at higher temperatures ($>$ 250°C) and accelerated the release rate of the free shell molecules, the size distribution of the resulting core/shell structure would deteriorate severely.

Powder X-ray diffraction (p-XRD) patterns for the CdSe cores and for the representative CdSe/CdS, CdSe/CdS/ZnS core/shell NCs are presented in Figure 2. As observed in previous literature [30], the CdSe XRD pattern consists of the characteristic peaks of zinc blende (cubic) CdSe, which are broadened due to the finite crystalline size. When the CdS and ZnS shells are overgrown consecutively onto the cubic CdSe

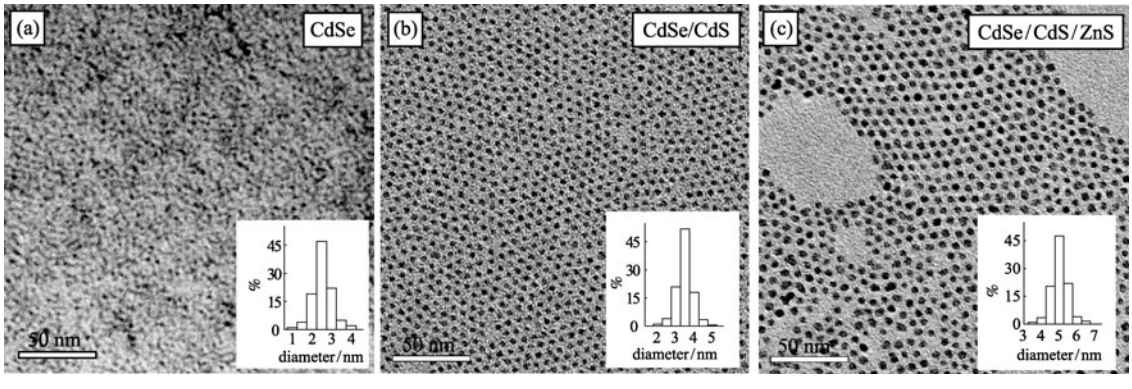

Figure 1 Wide-field TEM images of (a) 2.4 nm CdSe cores, (b) the resulting 3.8 nm CdSe/CdS, and (c) 5.0 nm CdSe/CdS/ZnS core/shell NCs obtained by consecutively growing CdS and ZnS shells on the initial CdSe cores. Insets are corresponding histograms of the size distribution.

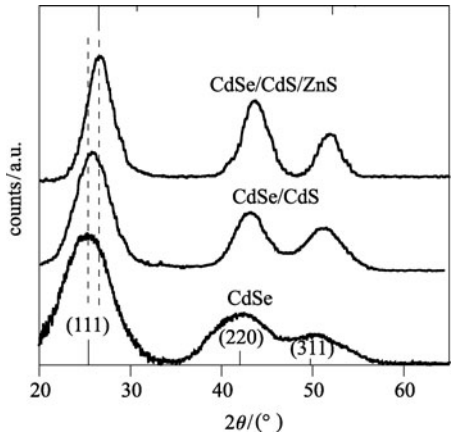

Figure 2 XRD patterns of the initial 2.4 nm CdSe core and the resulting CdSe/CdS and CdSe/CdS/ZnS core/shell QDs with 2 MLs of CdSe, 2 MLs of ZnS shell. The line XRD spectra correspond to bulk zinc blende CdSe (bottom) and zinc blende CdS (top).

template, the general pattern of the cubic lattice is maintained in the core/shell structures, but the diffraction peaks shift to larger angles consistent with the smaller lattice constant for CdS and ZnS (compared with CdSe). In addition, the diffraction peaks get narrower. This narrowing indicates that the crystalline domain of the core/shell structure is larger, which provides direct evidence for the epitaxial growth mode of the shell.

3.3 Optical properties of CdSe/CdS and CdSe/CdS/ZnS core/shell QDs

The most direct and immediate evidence for the shell growth comes from the optical spectra. Figure 3 shows the evolution of the absorption and PL spectra measured for typical samples of overgrowth of 2 MLs of CdS shell on the CdSe cores with an average diameter of 2.4 nm and emission wavelength of 548 nm and the further deposition of 2 MLs of ZnS shell around the CdS layer in the original CdSe/CdS reaction solution via the addition of the ZnS single molecular precursor ZDC. The spectra labeled with the letters (a)–(c) were taken from the same samples that led to the TEM graphs (a)–(c) in Figure 1. It can be found that with the overgrowth of CdS shell around the CdSe cores, both the absorption onsets in the absorption spectra and the band-edge PL emission peaks in the PL spectra shift to the red (or lower band gap energy). The corresponding PL emission wavelengths shift from 548 to 584 nm. The red-shift of the bandgap mainly comes from the partial leakage of the excitons into the shell matrix as observed in other core/shell structures [12–20]. Single PL emission peak in the PL spectra can rule out the separate homogeneous nucleation of CdS NCs. The small Stokes shift (~ 20 nm) between the emission peaks and the corresponding first excitonic absorption onsets indicates the dominant band-edge luminescence from the core/shell NCs. The absence of deep trap emission at the long-wavelength side indicates the decent emissive properties of the core/shell QDs. Upon the growth of the additional ZnS shell, no substantial change in the PL emission spectra was observed, although a slight red shift (~ 8 nm) of the emission wavelength was observed (Figure 3). By changing the shell thickness and the core size, the emission wavelength of the CdSe/CdS/ZnS structures can be readily tuned. Figure 3(d) gives an example of emission wavelength at 635 nm starting from the 3.1 nm CdSe cores with an emission wavelength of 590 nm.

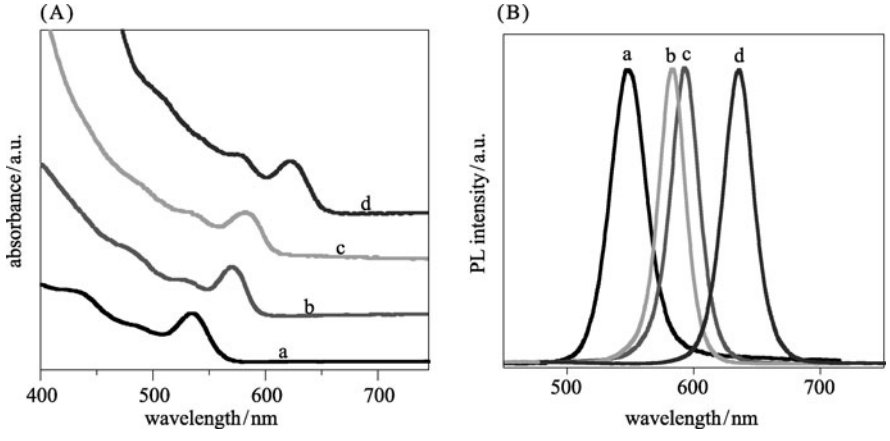

Figure 3 (A) Normalized UV-vis spectra and (B) PL spectra (λ_{ex} = 400 nm) of (a) 2.4 nm CdSe cores, (b) the resulting CdSe/CdS, and (c) CdSe/CdS/ZnS core/shell QDs obtained by consecutively growing 2 MLs of CdS and 2 MLs of ZnS shells on the initial CdSe cores. Spectrum (d) is corresponding to CdSe/CdS/ZnS QDs starting from the CdSe core diameter of 3.1 nm with an emission wavelength 590 nm.

The PL QYs and corresponding PL peak width (full-width-at-half-maximum, FWHM) of the same series of core/shell NCs are measured and shown in Figure 4. While the QY of the plain CdSe-core particles is of the order of 20%, it can increase to about 80% upon coverage of 2 MLs of CdS. Additional growth of ZnS shells leads to no significant improvement of PL QY (corresponding QY up to 90%). Upon overcoating of the CdS and ZnS shells on the CdSe cores, the spectra widths of the resulting CdSe/CdS and CdSe/CdS/ZnS core/shell NCs narrowed furthermore from the original ~33 nm to ~26 nm, which demonstrates the corresponding size distribution of the core/shell structure narrowed further.

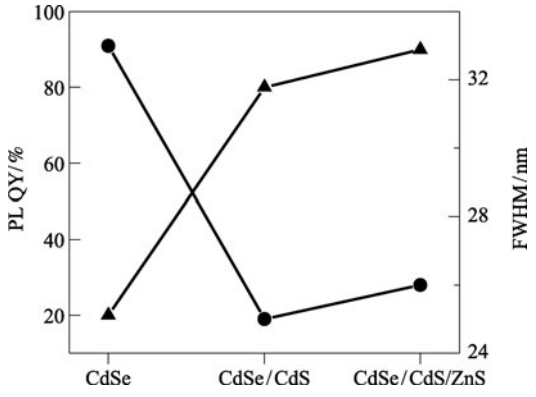

Figure 4 PL QYs and corresponding FWHMs of the CdSe cores, CdSe/CdS, and CdSe/CdS/ZnS core/shell QDs samples.

Although the ZnS shell has no remarkable influence on the PL QY of the core/shell NCs in organic media, it has a critical effect on the maintenance of high luminescence of the NCs when transferred into aqueous media via ligand replacement. Our experimental results demonstrated that the high QYs of the obtained CdSe/CdS QDs can be retained for several weeks in an ambient atmosphere when dispersed in common nonpolar organic solvents. The luminescence was quenched almost completely if the original oil-dispersible QDs were transferred into aqueous media through ligand replacement with the use of hydrophilic thiol ligands, such as MPA (as shown in Figure 5). Even though high QYs were obtained for the CdSe/CdS QDs, the instability of the PL, especially in aqueous media, renders these QDs unsuitable for practical applications. In comparison with the original CdSe/CdS NCs, the PL QYs of the CdSe/CdS/ZnS NCs in the organic media improve a little bit (from 80% to 90%) but increase remarkably (up to 60%) when dispersed in an aqueous media via the replacement of the hydrophobic ligands by MPA (Figure 5). For visibility, Figure 5(b) shows the luminescence photographs of three representative CdSe/CdS/ZnS samples with corresponding emission colors of green, yellow, and red, respectively, to demonstrate the highly bright luminescence in both oil media and aqueous media under the illumination of a UV lamp. The high luminescence of the CdSe/CdS/ZnS in aqueous media can be retained for several weeks without observable quenching. This high PL stability of the water-soluble highly luminescent QDs renders them to be of special interest in the in vivo imaging application.

4 Conclusion

High-quality CdSe/CdS/ZnS double shelled core/shell nanostructures have been prepared via a facile and economy route. The CdSe core NCs were prepared through a non-TOP route, resulting in the zinc-blende structure, which is better for growing shell more uniformly. The CdS and ZnS shell grown via a single precursor route over the CdSe core leads to PL

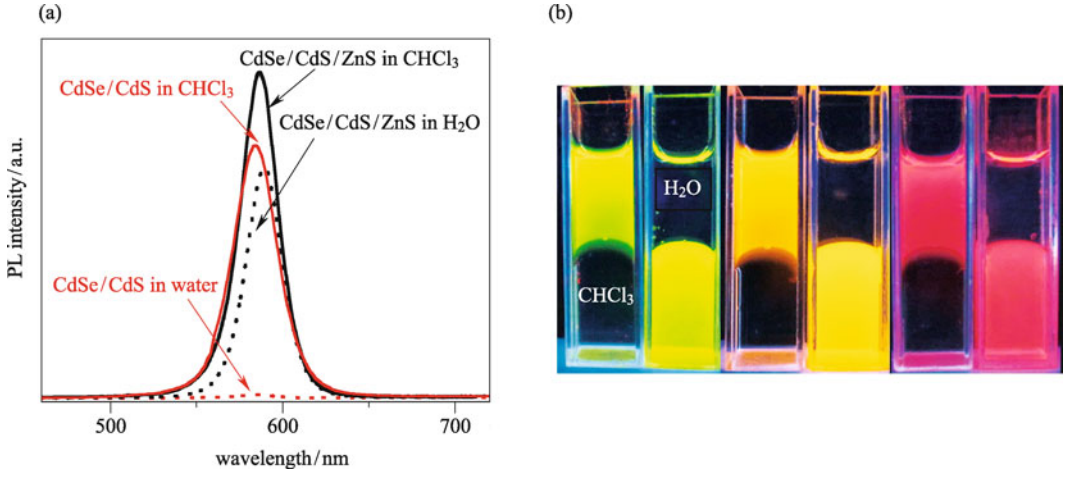

Figure 5 (a) PL spectra (λ_{ex} = 400 nm) of CdSe/CdS and CdSe/CdS/ZnS NCs before (chloroform solutions) and after (aqueous solutions) phase transfer with the use of MPA. All colloidal solutions exhibit identical absorbance at the excitation wavelength. (b) Photographs of typical CdSe/CdS/ZnS samples in H_2O and in $CHCl_3$ under the illumination of a UV lamp.

emission efficiencies up to 90% in organic solvents and up to 60% after ligand exchange with MPA in water. The commonly commercial available air stable molecules CDC and ZDC were used as the CdS and ZnS single-source precursors to replace hazardous organometallic reagents usually applied in this procedure, i.e., bis(trimethylsilyl)sulfide and diethylzinc. It is clear that this preparation route is much "greener" and economic than the previous reported methods. For the low-cost, green, and environmentally friendly precursors and reagents, as well as the facile procedure, it may be helpful for making NCs in large quantities.

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