Articles

Coating Aqueous Quantum Dots with Silica via Reverse Microemulsion Method: Toward Size-Controllable and Robust Fluorescent Nanoparticles

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Fluorescent core−shell CdTe@SiO$_2$ particles with controllable particle sizes were prepared via a reverse microemulsion method by hydrolyzing tetraethyl orthosilicate within microwater droplets. Aqueous CdTe nanocrystals and CdS nanocrystals stabilized by different types of thiol molecules were prepared for elucidating the mechanism leading to the core−shell structures. Photo-oxidation experiments were performed to show the enhancement effect of the silica shell on the photostability of the CdTe nanocrystals encapsulated. Further surface modifications were also performed for grafting amino groups on the surface of the resultant fluorescent CdTe@SiO$_2$ particles.

Introduction

Over the past two decades, II−VI semiconductor quantum dots (Q-dots) have been attracting more and more interests because of their unique optical properties such as size-tunable fluorescence and narrow and symmetric emission profile with a broad excitation range, which make the Q-dots a new type of labeling materials useful for versatile biological and biomedical applications.[1] Nonetheless, Q-dot materials have to face the following problems in practical applications: ultra-sensitivity of their fluorescence to the surface states,[2] cytotoxicity due to the release of heavy metal ions upon photo-oxidation,[3] and chemical and colloidal stabilities in harsh chemical environments. Coating fluorescent Q-dots with inert materials such as silica could be one of the possible solutions for solving these problems.[4] A silica coating can not only suppress the photodegradation of Q-dots but also impede the release of heavy metal ions in harsh chemical environments,[3] and furthermore can provide the resultant core−shell composite nanoparticles with good water dispersibility, biocompatibility, and surface functionality,[5] as the silanol group on the silica shell offers versatile possibilities for covalently functionalizing the silica-coated particles.

Until now, coating inorganic nanocrystals with silica has received intensive investigations.[6−12] The preparative routes can generally be classified into two groups, i.e., the Stöber-process-based approaches and the reverse (water-in-oil) microemulsion method. For aqueous Q-dots, the Stöber

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process can be used straightforwardly and offers the possibility of forming either Q-dot@silica core−shell structures[4a] or "raisin bun"-type composite particles in which a number of Q-dots are simultaneously encapsulated in each silica particles.[7] For organic soluble Q-dots prepared by the TOP/TOPO method, prior to the Stöber process, ligand exchange is usually required for transferring the Q-dots from less polar solvents to polar media. Systematic investigations revealed that the Stöber process allows control of the thickness of the silica shell over a range from a few to hundreds of nanometers, even though laborious multistep procedures were required to achieve such a thickness control.[8,9]

As an alternative approach, the reverse microemulsion method can also be used for coating inorganic nanocrystals with silica.[4b,10−12] In comparison with the Stöber method, it can better control the particle size distribution, especially in a range of 30−150 nm.[11] In principle, the water-in-oil microemulsion method is more suitable for coating the aqueous Q-dots. However, very recent investigations have demonstrated that it can also be used in coating hydrophobic Q-dots capped by trioctylphosphine oxide (TOPO).[4b,12] Even though the mechanism for coating the hydrophobic Q-dots remains unclear, a ligand-exchange process involving TEOS (tetraethyl orthosilicate) has been proposed to interpret the resultant composite structure, i.e., one Q-dot locating at the center of each resultant silica particle.[12]

In comparison with the CdSe-based hydrophobic Q-dots prepared by the TOP/TOPO method, recent developments on the highly fluorescent CdTe Q-dots directly synthesized in aqueous system encourage us to further investigate the silica coating for the aqueous CdTe Q-dots with high fluorescence efficiency.[13] In our previous investigations, we have demonstrated that by the microemulsion method, CdTe@SiO$_2$ core−shell particles can be obtained in a straightforward manner.[14] The experimental results revealed that by choosing proper silica precursors, CdTe/SiO$_2$ composite particles with well-defined structures can be obtained, especially the core−shell-structured CdTe@SiO$_2$ particles. Following from our previous investigations, we report herein more details on the particle size control and the fluorescent properties of the resultant core−shell particles and provide more experimental results to support the structural formation mechanism for the single core composite particles.

Experimental Section

Chemicals. All chemicals mentioned in the current investigations were used as received; they are cadmium perchlorate hydrate (Cd-(ClO$_4$)$_2$·6H$_2$O; Aldrich, 99.9% product 40137-4), 1-thioglycerol (TGOL; Fluka, 99%+, product 88640), thiolglycolic acid (TGA; Aldrich, 97%+, product 475343), 3-mercaptopropionic acid (MPA; Aldrich, 99%+, product M5801), polyethylene glycol tert-octylphenyl ether (TritonX-100; Sigma, product X100), tetraethyl orthosilicate (TEOS; Fluka, 98+%, product 86580), aminopropyltris-(methyloxy)silane (APS; Aldrich, 97%, product 281778), and
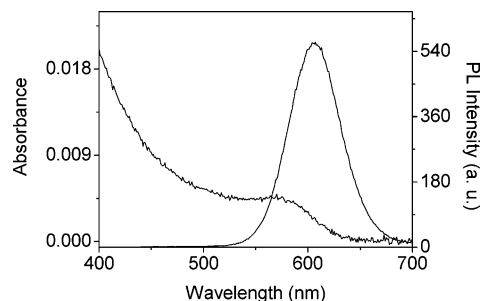

Figure 1. Absorption and fluorescence spectra of the as-prepared CdTe Q-dots costabilized by TGA and TGOL. The excitation wavelength was 400 nm for the fluorescence measurements.
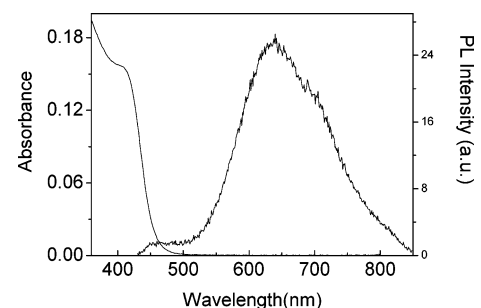

Figure 2. Absorption and fluorescence spectra of the as-prepared CdS nanocrystals stabilized by TGA. The excitation wavelength was 400 nm for the fluorescence measurements.

salicylaldehyde (Beijing Xudong Chemical Factory, 96%+). Sodium sulfide, ammonia aqueous solution (25 wt %), cyclohexane, *n*-hexanol, acetone, butanol, iso-propyl alcohol, and ethanol were purchased from Beijing Chemical Company.

Synthesis of Fluorescent Nanocrystals. CdTe nanocrystals were synthesized according to a previous report by employing both 1-thioglycerol (TGOL) and thioglycolic acid (TGA) as stabilizing agents.[15] Briefly, 1.401 g (3.35 mmol) of Cd(ClO$_4$)$_2$·6H$_2$O was dissolved in 180 mL of water followed by the addition of 0.56 mL (6.64 mmol) of TGOL and 0.11 mL (1.53 mmol) of TGA. The pH of the reaction mixture was then raised to 11.2 using 5 M NaOH. After that, H$_2$Te gas (***Caution: H$_2$Te gas is highly flammable and toxic by inhalation***) carried by a N$_2$ flow was introduced into the reaction mixture under stirring. Immediately, the color of the reaction mixture changed from colorless to orange. After approximately 20 min, the resultant orange solution was subjected to reflux. The particle size was controlled by refluxing time. Typical absorption and fluorescence spectra of the as-prepared CdTe Q-dots are presented in Figure 1. In a similar way, CdTe Q-Dots solely stabilized by either 3-mercaptopropionic acid (MPA) or thiolglycolic acid (TGA) were synthesized.

In addition, for comparing with CdTe nanocrystals, CdS nanocrystals were also prepared using TGA as stabilizing agent. The general preparative procedures were the same except that an aqueous solution of Na$_2$S was introduced into the solution of cadmium ions instead of H$_2$Te to generate CdS. The reflux time for CdS nanocrystals was fixed at 12 h. The absorption and fluorescence spectra of the aqueous CdS nanocrystals obtained are shown in Figure 2. Different from CdTe, CdS Q-dots presents a red-shift photoluminescence (PL) with respect to the absorption onset, indicating that the PL emission of CdS nanocrystals is dominated by trap emissions.

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Synthesis of Fluorescent Silica-Coated Particles. Fluorescent core−shell CdTe@SiO$_2$ nanoparticles were prepared according to the literature by reverse microemulsion method.[14,16] In detail, 48 μL of aqueous solution of the as-prepared CdTe Q-dots and 240 μL of ammonia aqueous solution (25 wt %) were introduced into a liquid system containing 7.5 mL of cyclohexane, 1.8 mL of *n*-hexanol, and 1.77 mL of TritonX-100. Subsequently, 100 μL of TEOS was introduced under vigorous magnetic stirring. The reaction system was then sealed and kept under stirring in the dark at room temperature for 3 days. Acetone was used to terminate the reaction and the resultant precipitate of CdTe@SiO$_2$ composite particles were washed in sequence with butanol, iso-propyl alcohol, ethanol, and water. During each washing procedure, the particle dispersion was first subjected to centrifugation, followed by decantation of the supernatant and redispersion of the precipitate in the next solvent with the aid of supersonication. At the end, aqueous dispersions of the composite nanoparticles were obtained for further characterization. The fluorescence efficiency of the CdTe@SiO$_2$ composite particles obtained was determined according to the literature.[14] Usually, it was in a range of 1−10%. More efforts are currently underway to further increase the PL efficiency. By the same procedures, CdS/SiO$_2$ composite particles were synthesized.

Surface Modification of CdTe@SiO$_2$ Particles. Properly modifying the surface of the fluorescent composite particles is important for further using them as fluorescent biomarkers. To graft amine groups on the surface of CdTe@SiO$_2$ particles, we injected 2 μL of aminopropyltris(methyloxy)silane (APS) into the reaction system 3 days after the hydrolysis and condensation of TEOS. The reaction system was then kept under stirring for one more day. The resultant amine-funcationalized CdTe@SiO$_2$ particles were obtained by the same purification procedures as those for CdTe@SiO$_2$ particles.

Photostability of the CdTe@SiO$_2$ Core−Shell Particles. To exam the photostabilities of the CdTe nanocrystals encapsulated in silica particles with different shell thicknesses, we subjected aqueous dispersions of the composite particle samples to a continuum ultraviolet (UV) irradiation (292 nm) with a power density of 1.2 W/cm^2 at a focus where the light beam was 1 cm in diameter. Typically, the aqueous dispersions of various particle samples were aerated with oxygen before they were transferred into a 1 cm quartz corvette for the photo-oxidation experiments.

Characterizations. The size and morphologies of the resultant silica particles were characterized with the aid of JEM-100CXII transmission electron microscope (TEM) operating at 100 kV. Fluorescence spectra were recorded at room temperature using a fluorescence spectrophotometer (Cary Eclipse).

Results and Discussions

Figure 3 presents the general morphology of the fluorescent CdTe@SiO$_2$ composite particles based on the CdTe Q-dots co-stabilized by TGA and TGOL. The composite particles remained fluorescent after encapsulation with the emission peak position nearly unchanged even though the fluorescence quantum yield of the CdTe Q-dots decreased.[14] Apart from that, all composite particles present a universal structure, core−shell structure with single CdTe Q-dots locating at the center of each silica particles. Furthermore, the core−shell structure was also demonstrated to be independent of the initially feeding amount of the CdTe nanocrystals. Our previous investigations suggests that the
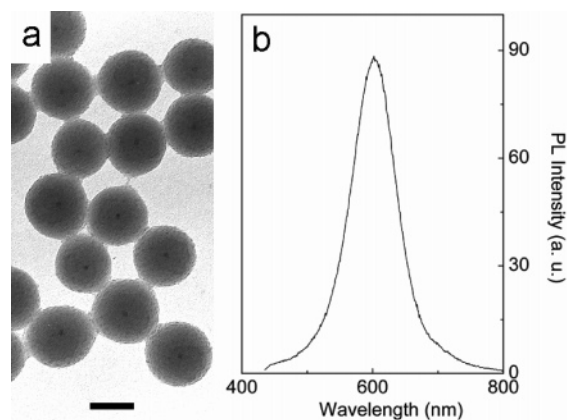

Figure 3. Representative TEM image of the core−shell CdTe@SiO$_2$ particles prepared using CdTe Q-dots costabilized by TGA and TGOL (a), and the corresponding fluorescence spectrum of the composite particles suspended in neutral water (b). The scale bar corresponds to 50 nm. The excitation wavelength was 400 nm for the fluorescence measurements.

electrostatic repulsion between the negatively charged silica intermediates formed during the hydrolysis of TEOS and the negatively charged CdTe Q-dots is responsible for the core−shell structure of the resultant particles.[14]

In the reverse microemulsion system, cyclohexane served as a continue phase, and TritonX-100 and *n*-hexanol were used as surfactant and co-surfactant, respectively. The aqueous solution of CdTe nanocrystals and ammonia was emulsified under magnetic stirring forming micro water droplets. During this stage, the electrostatic repulsion between the negatively charged CdTe Q-dots was effectively screened by the positive background arising from cations, i.e., NH$_4^+$ and Na$^+$; therefore, the system is under an electrostatic equilibrium, which is supported by the fact that the aqueous solution of CdTe Q-dots have shown long term (over years) colloidal stability at pH 11. This electrostatic equilibrium can quantitatively be described by the Debye−Hückel theory, in which the screening potential around a CdTe Q-dot at distance r is given by $V(r) = (Q/\epsilon r)\,e^{-r/D}$. Here, Q is the charges on a CdTe Q-dot; ϵ is the dielectric constant; D is the Debye screening length given by $D = (\epsilon k_B T/n_0)^{1/2}$, where k_B is the Boltzmann constant; T is the temperature; and n_0 is the density of the cations. The average distance between CdTe Q-dots initially should be larger than D so that the electrostatic equilibrium can be preserved. After the introduction of TEOS, which can well-dissolved in cyclohexane, TEOS will pass the oil/water interface by diffusion and start to hydrolyze upon the catalysis of ammonia. It is well-known that the partly hydrolyzed TEOS molecules have strong hydrophilicity due to the deprotonation of the silanol groups.[17] When these hydrolyzed species gain enough hydrophilicity, they will completely enter the aqueous phase. The subsequent condensation between hydrolyzed species in reverse micelles results in silica oligomers or silica intermediates which can be taken as a negatively charged polyelectrolyte as the pKa of the silanol groups was reported to be around 7. Thereafter, the previous electrostatic equi-

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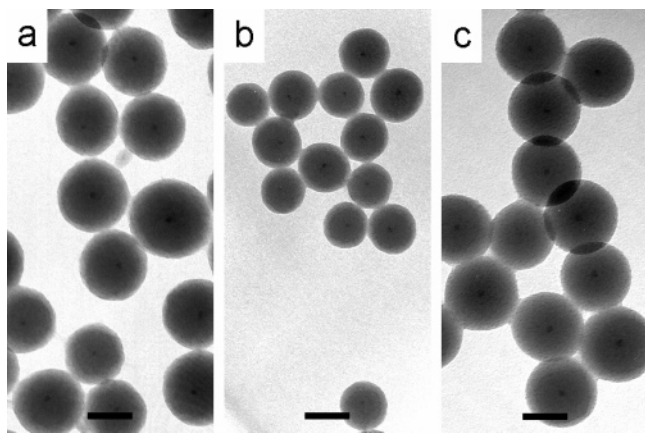
Figure 4. TEM images of the core−shell Q-dot@SiO₂ based on (a) CdTe nanocrystals stabilized by TGA, (b) CdTe nanocrystals stabilized by MPA, and (c) CdS nanocrystals stabilized by TGA, respectively. The scale bar corresponds to 50 nm.
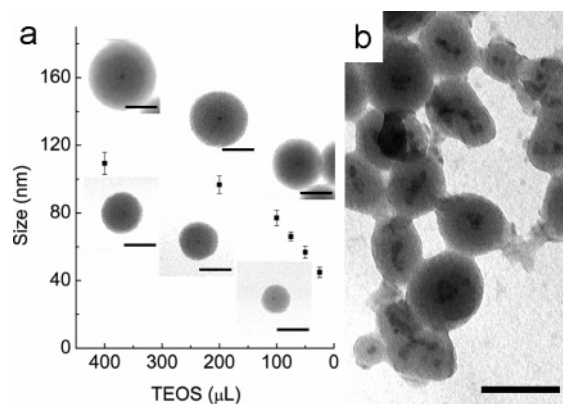

Figure 5. Left: Diameter control, achieved by varying the feeding amount of TEOS, for the resultant CdTe@SiO₂ core−shell particles based on CdTe nanocrystals costabilized by TGA and TGOL. The average particle size together with the error bars are shown in the underlying graph. The insets are selective images from differently sized composite particles for showing the core−shell structures. Right: Composite particles obtained by feeding 5 μL of TEOS into the reaction system with the other synthetic parameters remaining the same as those for the particles shown in the left panel. The scale bars in all TEM images correspond to 50 nm.

librium was destroyed. As the molecular weights of the oligomeric silica intermediates increase, the cations induced by the oligomertic silica intermediates evenly distributed throughout the microscale water pool, and the region around the oligomertic intermediates is locally negatively charged. This local negatively charged background will reduce the screen between two CdTe Q-dots; consequently, the Debye screening length for CdTe Q-dots will increase, which induces a net repulsive interaction between two neighboring CdTe Q-dots. As the sol−gel process goes on, especially when the Debye screening length becomes larger than the radius of the microwater pool, most of the Q-dots will be driven to boundary of the aqueous microdroplet, except for the last CdTe Q-dot, which will locate at the center of the water pool because of the symmetry of the repulsive interaction between this specific CdTe Q-dot and the others locating at the surface of the microwater pool. Previous investigations have demonstrated that those CdTe Q-dots on the surface of the silica particles finally formed can be removed during the following washing procedures.[14]

As the real system is too complicated to quantitatively describe, more experiments were designed to support the mechanism proposed. First, the surface capping agent for CdTe was switched to either TGA or MPA. The resultant silica particles are shown in panels a and b of Figure 4, respectively. Independent of the surface capping agents, these two samples also present the same core−shell structure. To test the validity of the mechanism, CdS nanocrystals stabilized by TGA were also adopted as model particles. The TEM result shown in panel c of Figure 4 demonstrates that core−shell CdS@SiO₂ composite particles can also be formed. Furthermore, the core−shell structure for the CdS@SiO₂ composite particles was also found out to be independent of the initial concentration of CdS nanoparticles.

Typically, the concentration of TEOS is an important parameter for tuning the thickness of the silica shell for the Q-dot@SiO₂ particles prepared by the Stöber method.[9] The same effect was also expected for the CdTe@SiO₂ particles prepared by the current approach. Therefore, the feeding amount of TEOS was varied in a range of 25−400 μL, whereas all the other parameters were kept constant. Detailed results are provided in the Supporting Information. The TEM

results shown in Figure 5a demonstrate that the average size of the resultant particles can successively be tuned from 45 to 109 nm, suggesting that the concentration of TEOS also plays a determined role in the particle size control with respect to the current systems. Moreover, in this size regime, independent of the particle size, all composite particles exhibit the same core−shell structure, even though the smaller particles exhibit a relatively narrower particle size distribution. Nevertheless, further decreasing the feeding amount of TEOS to 5 μL leads to a worse defined composite structure for the resultant particles. Apart from their irregular shapes, most composite particles have a couple of CdTe particles as core, as shown in Figure 5b. This morphological change also manifests the mechanism proposed above. Because the amount of TEOS was tremendously reduced, the concentration of negatively silica intermediates in the microwater pool was consequently much lower than that producing the well-defined core−shell particles. The Debye screening length in this case could never reach the radius of the water droplets. As a result, a certain percentage of the CdTe Q-dots remained in the silica particles after the condensation of TEOS.

As mentioned in the introduction part, one of the aims for coating CdTe with silica was to suppress the photodegradation of CdTe nanocrystals as demonstrated by Liz-Marzán et al. with respect to CdS nanocrystals.[4a] Because the photodegradation will start from the particle surface in most cases involving oxygen and consequently lead to the fade of the fluorescence due to the formation of nonradiative pathways, the silica coating was expected to stabilize the fluorescence of the CdTe particles by isolating them from the environment. To demonstrate this effect, we dispersed the CdTe@SiO₂ particles with different shell thickness in O₂-aerated water for photo-oxidation experiments. The results shown in Figure 6 indicate that at earlier stage of the UV irradiation, the silica-coated CdTe nanocrystals presents an increased PL intensity followed by a slow decrease. The loss in PL intensity decreases generally with the increase in the thickness of the silica shell. The early increase in PL intensity
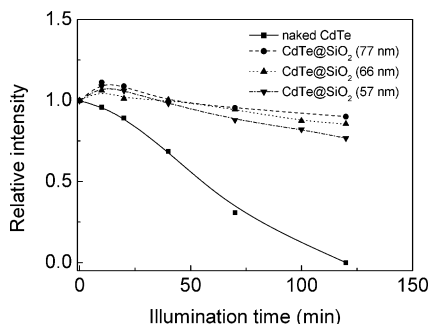
Figure 6. Photo-oxidation experiments on CdTe nanocrystals coated by silica shells with different shell thicknesses. The photostability of mother CdTe nanocrystals costabilized by TGA and TGOL is also given for comparison. The power density of the UV light (292 nm) at 1 cm focus was about 1.2 W/cm^2.

Figure 7. Absorption and fluorescence spectra of the mother CdTe nanocrystals costabilized by TGA and TGOL recorded before (black lines) and during (red lines) the photo-oxidation experiments. The excitation wavelength was 400 nm for the fluorescence measurements.

Figure 8. Fluorescence spectra of APS-coated CdTe@SiO$_2$ core−shell particles before (dot line) and after (solid line) reacting with salicylaldehyde. The dashed line spectrum was recorded from pure salicylaldehyde. The excitation wavelength was 400 nm for the fluorescence measurements.

is not well-understood at the current stage. However, it was previously demonstrated that the photodegradation of the thiol molecules capped on the surface of CdTe nanocrystals can also lead to such an effect even in the absence of oxygen.[13c] Moreover, such photo enhancement effects were also observed with respect to CdSe nanocrystals by different groups and interpreted by different mechanisms.[18] The following decrease was believed to be caused by photodegradation of CdTe nanocrystals. Water and trace oxygen are typically involved in such photo-oxidation processes. Because of the hydrophilic nature and porous structure of the silica shell, oxygen dissolved in the aqueous medium could slowly penetrate through the silica shell, leading to the photo-oxidation of the encapsulated CdTe Q-dots. Although the thickness of the silica shell does not show a clear relationship with the PL enhancement effect during the early stage of illumination, over long-term illumination, the thicker the silica shell, the more PL emission intensity is preserved, which strongly suggests that the fade of PL emission of CdTe encapsulated in silica involves oxygen diffusing from the surrounding medium. The photodegradation of CdTe dots encapsulated in a silica shell can more clearly be seen from the photodegradation of the mother CdTe nanocrystals. Accompanying the decrease in PL intensity achieved by illumination, as shown in Figure 7, the absorbance of the mother CdTe nanocrystals also decreases, demonstrating that in the presence of oxygen, CdTe nanocrystals can be photodegraded. Therefore, it can be concluded that the silica shell can effectively impede the diffusion of oxygen from the surrounding environment to contact the CdTe Q-dots in the center of silica nanoparticles as more than 75% of the PL emission was preserved after the PL emission of the uncoated CdTe nanocrystals completely died out.

The second aim of the silica coating was to reduce the cytotoxicity of CdTe nanocrystals by blocking cadmium ions, generated by photo-oxidation, from diffusing into surrounding media. The photo-oxidation results therefore suggest that
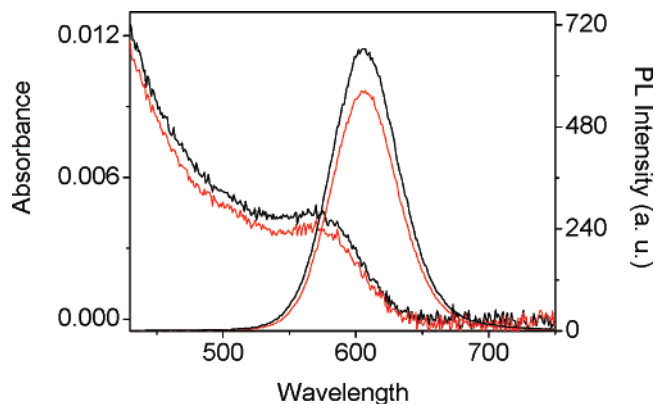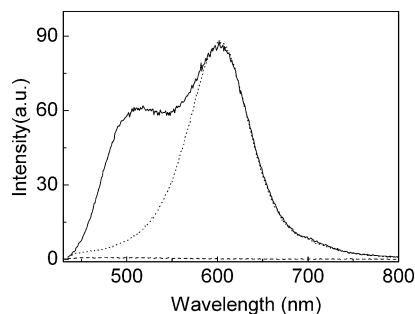
the diffusion of heavy metal ions could be impeded or at least slowed down by the silica shell,[21] which is very important for using Q-dot-based fluorescent markers in in vivo biomedical applications.

The third aim of the silica coating was to provide an easy surface modification route for further covalently binding biomolecules with CdTe dots. In fact, there have already been a plenty of investigations on functionalizing the surface of silica beads by different silicane coupling agents. Herein, amino groups were grafted on the surface of CdTe@SiO$_2$ particles by coating the particles with APS. Because excessive APS will cause aggregation of silica nanoparticles and consequently reduce their aqueous dispersibility,[19] the feeding ratio of APS:TEOS was carefully optimized as 1:50 (volume). Because salicylaldehyde can react with the primary amino group to form imines, which are strong chromophores,[20] salicylaldehyde was introduced into the aqueous dispersion of APS-grated CdTe@SiO$_2$ particles, after the resultant particles were thoroughly washed with alcohol, to detect the existence of surface amino groups. The fluorescence spectra of the APS-coated CdTe@SiO$_2$ particles before and after reaction with salicylaldehyde are shown in Figure 8. Because salicylaldehyde does not show fluorescence under ultraviolet radiation, the appearance of a new PL emission peaking at 500 nm suggests that amino groups were successfully grafted on the surface of the CdTe@SiO$_2$ particles.

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Conclusions

Fluorescent core−shell-structured CdTe@SiO$_2$ particles have successfully been prepared by a reverse microemulsion method. Systematic experimental results suggest that the electrostatic repulsion between the silica intermediates formed upon the hydrolysis of TEOS and CdTe Q-dots is responsible for the core−shell structure of the resultant composite particles, which was further supported by the experiments using CdS nanoparticles as a model. The feeding amount of TEOS has been demonstrated to be a critical parameter in tuning the particle size. Under optimized conditions, the size of the CdTe@SiO$_2$ particles can be varied from 109 to 45 nm. Further photo-oxidation experiments demonstrate that the silica coating can greatly increase the photostability of the CdTe Q-dots encapsulated. Under the same UV irradiation conditions, the thicker the silica shell, the more PL intensity is persevered. Consequently, reduced cytotoxicity could also be expected from the core−shell CdTe@SiO$_2$ particles, as a silica shell may effectively impede the diffusion of cadmium ions generated by the photodegradation of CdTe core, which is very important for using fluorescent Q-dots as biomarkers. Toward bioapplications, amino groups have also successfully been grafted on the surface of the fluorescent CdTe@SiO$_2$ particles. We believe our current investigations will be interesting for developing robust and low cytotoxicity biomarkers based on fluorescent Q-dots.

Supporting Information Available: Detailed results of the diameter control of CdTe@SiO$_2$ core−shell-structured particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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