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Highly Fluorescent CdTe@SiO_2 Particles Prepared via Reverse Microemulsion Method

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Following on from our previous investigations, fluorescent core/shell CdTe@SiO_2 particles were prepared via the water-in-oil (W/O) reverse microemulsion method. It was found out that incubating the as-prepared aqueous CdTe quantum dots stabilized by thioglycolic acid in ammoniacal solution not only increased the fluorescence quantum yield of CdTe quantum dots but also gave rise to high retention of fluorescence throughout the silica coating. Under optimized conditions, the fluorescence quantum yield of CdTe quantum dots encapsulated in silica particles reached 47%. Both absorption and fluorescence spectroscopy were used in combination with X-ray photoelectron spectroscopy and electrophoresis to investigate the fluorescence enhancement effect occurring during incubation, the high retention of fluorescence quantum yield, as well as the formation of multicore/shell CdTe@SiO_2 particles as a result of the incubation process imposed on the as-prepared CdTe quantum dots.

Introduction

Semiconductor quantum dots (QDs) have been intriguing more and more considerable interests because of their fascinating optical and electronic properties governed by the quantum confinement effect.[1−3] Over the past 2 decades, tremendous efforts have been put into the synthesis of QDs by liquid phase-based chemical approaches, and significant progress has been achieved in synthesizing fluorescent QDs with emission covering a wide range of UV-blue to the infrared upon the size and composition manipulations.[4−14] Moreover, in comparison with organic fluorophores and fluorescent proteins, QDs also exhibit remarkable spectral features such as broad excitation range, narrow and symmetric emission, high photostability, large molar extinction coefficients, high quantum yields, and etc.[1−3,15,16] These superior properties are of great interest and make QDs as a new class of biological probes in high-throughput biodetections and multicolor bioimaging.[3,17] Nevertheless, the following problems remain when using QDs as bioprobes, i.e., strong dependence of the fluorescence on the surface states,[18] cytotoxicity as a result of the release of heavy metal ions upon photo-oxidation,[19] as well as chemical and colloidal instabilities of the QDs in harsh environments.

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An effective solution that can be relied on for overcoming these drawbacks is to encapsulate QDs by inert materials.[20−25] The inert encapsulation is expected to impede the leakage of heavy metal ions into environments and to suppress the surface defects generated by oxygen from the surrounding media, apart from enhancing the chemical stability of the QDs.[20−24] Silica is one of the proper inert materials for coating QDs. Silica coating on the one hand can render different types of hydrophobic QDs good water dispersibility,[24−26] and on the other hand offer versatile choices for further covalently functionalizing the silica-coated particles.[27−29] In this context, the silica coating is becoming an ideal platform for constructing versatile fluorescent bioprobes based on QDs.[3a,24,30−33]

In general, the encapsulation of QDs by silica can be realized by the following approaches, i.e., the Stöber process and reverse (water-in-oil) microemulsion method. By the Stöber process, a precoating upon the use of silane primers such as 3-mercaptopropyltrimethoxysilane (MPS)[22,34,35] or 3-aminoproprltrimethoxysilane (APS)[23,36] is typically required in order to make the QD surface vitreophilic, which is a prerequisite for the QDs to act as nucleation sites for the following silica encapsulation. The Stöber process applies for both hydrophobic[35,36] and hydrophilic QDs.[22,29,34] A ligand exchange is believed to be involved in the precoating procedure.[34,35] As an alternative approach, the reverse (water-in-oil) microemulsion method has also been demonstrated to be effective for coating both hydrophilic[21,37] and hydrophobic QDs.[38−41] With respect to hydrophobic QDs, e.g., CdSe core/shell/shell (CSS) QDs stabilized by hydrophobic amines, it is claimed that the original hydrophobic ligands are first replaced by hydrolyzed tetraethyl orthosilicate (TEOS), then the hydrophobic QDs enter the hydrophilic interior of the micelles where silica growth takes place.[40] With respect to hydrophilic QDs, e.g., CdTe stabilized by mercapto acids, it is demonstrated that electrostatic repulsion is responsible for holding CdTe QDs inside the resultant silica particles, especially for the formation of fluorescent CdTe@SiO_2 particles with single CdTe nanocrystal cores.[21]

Although the above-mentioned approaches present a different ability in controlling the morphology of the resultant composite silica particles, they all face the same problem, i.e., a dramatic decrease in the fluorescence quantum yield (QY) inevitably occurs during the encapsulation of QDs,[34−41] which is often interpreted by ligand exchanges of silane primer[34] or hydrolyzed TEOS.[40] Although more direct proof is required to support the molecular mechanism for the formation of surface traps, it remains conclusive that nonirradiative channels are generated during the encapsulation. Therefore, more careful surface engineering are necessary to increase the fluorescence robustness of the QDs prior to silica coating as higher fluorescence QY is definitely in favor of the sensitivity of biodetections by using QD-based fluorescent probes.

It was previously demonstrated that by the reverse microemulsion method, aqueous colloidal CdTe QDs can be incorporated in silica forming fluorescent silica particles with single CdTe QDs cores.[21] Moreover, the number of CdTe QDs can be tuned by manipulating the electrostatic interactions among the negatively charged CdTe QDs and the negatively charged silica intermediates within the micro water droplets.[21] Nevertheless, a large loss in fluorescence was observed, routinely by a factor of >3 in terms of the fluorescence QY for the CdTe QDs encapsulated. To solve this problem, we recently optimized the preparation by incubating the CdTe QDs in an alkaline solution for a certain time prior to the reverse microemulsion process. It was found out that the fluorescence QY of CdTe QDs incorporated reached 47% at room-temperature, with a very little loss presented in comparison with that of the initial CdTe QDs stabilized by TGA. Herein, we report the preparation of such highly fluorescent CdTe@SiO_2 particles and discuss the mechanism leading to high fluorescence QY of CdTe QDs encapsulated in the silica particles.

Experimental Section

Chemicals. All chemicals mentioned in the current investigations were used as received. They are cadmium perchlorate hydrate ($Cd(ClO_4)_2 \cdot 6H_2O$) (Aldrich, 99.9% product 40137-4),

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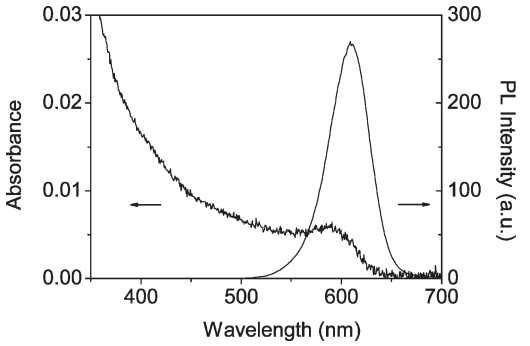

Figure 1. Absorption and fluorescence spectra of the as-prepared CdTe QDs obtained by 9 h reflux (the excitation wavelength for the fluorescence measurement was 360 nm).

thioglycolic acid (TGA) (Fluka, 97%+, product 475343), polyethylene glycol *tert*-octylphenyl ether (TritonX-100) (Acros, product 32737), tetraethyl orthosilicate (TEOS) (Fluka, 98+%, product 86580), agarose (Biowest Agarose; distributed by Gene Tech Company, Ltd., Shanghai, China, product no. 101710), and Tris (Amresco, 99.9%, code no. 0497, distributed by Biodee Biotechnology Co., Ltd.). Sodium hydroxide, ammonia aqueous solution (25 wt %), cyclohexane, *n*-hexanol, ethanol, and borate were purchased from Beijing Chemical Factory.

Synthesis of CdTe QDs Stabilized by Thioglycolic Acid. CdTe QDs were synthesized according to the method reported previously.[7,8,42] Briefly, 1.262 g of $Cd(ClO_4)_2 \cdot 6H_2O$ (3.01 mmol) was dissolved in 160 mL of water, and then 0.371 g of TGA (3.91 mmol) was then introduced while stirring. The pH value of the reaction mixture was adjusted to 12.00 by dropwise addition of 1 M NaOH aqueous solution before deaeration by bubbling N_2 through it for 1 h. After that, with stirring, H_2Te (note: H_2Te gas is highly flammable and toxic by inhalation), generated by dropwise addition of 13 mL of 0.5 M H_2SO_4 into an oxygen-free flask containing 0.257 g (0.589 mmol) of Al_2Te_3 lumps, was introduced into solution driven by a slow stream of N_2. After approximately 20 min, the resultant solution was heated to reflux under open-air conditions. The progress of the reaction was followed by absorption and fluorescent spectroscopy. The typical absorption and fluorescence spectra of the as-prepared CdTe QDs obtained after 9 h reflux are presented in Figure 1.

Incubation of As-Prepared CdTe QDs in Alkaline Solution. Typically, an alkaline condition was required for hydrolyzing TEOS to produce silica-coated CdTe composite particles. Different from our previous synthesis, an incubation process was imposed prior to the reverse microemulsion process with respect to the current investigations. Typically, the as-prepared CdTe QDs were incubated in an alkaline solution containing both ammonia and NaOH. In brief, 50 μL of crude CdTe colloidal solution was introduced into 450 μL of the alkaline solution containing 0.45 wt % ammonia and 15.9×10^{-3} M NaOH. The final concentration of CdTe QDs in the incubation system was of 1.53×10^{-6} M, and the pH of the resultant mixture was of 12.28. Then, the CdTe alkaline solution was sealed and kept in the dark at room temperature. The absorption and fluorescence spectra were measured during the incubation for investigating the evolutions of the optical properties of CdTe QDs against the incubation time. Meanwhile, CdTe QDs extracted at different incubation time points were used in the following preparation of silica-coated CdTe composite particles to show the effects of incubation time on the morphology and fluorescence QY of the CdTe QDs encapsulated.

Synthesis of Silica-Coated CdTe Composite Particles. Fluorescent CdTe@SiO_2 core/shell nanoparticles were prepared by the reverse microemulsion method according to previous reports.[21] The preparation was carried out typically as follows. Under vigorous stirring, 480 μL aqueous solution of CdTe QDs obtained after incubation was introduced into a liquid system containing 7.5 mL of cyclohexane, 1.8 mL of *n*-hexanol, and 1.77 mL of Triton X-100. After 30 min, 100 μL TEOS was introduced. Then, the reaction system was sealed and kept under stirring in the dark at room temperature for 3 days. Isopropanol was used to terminate the reaction, and the resultant precipitate of CdTe@SiO_2 composite particles was subsequently washed in sequence with ethanol and water, respectively. The particles suspended in liquid media were typically collected by centrifugation and then dispersed in pure water for further characterizations.

Determination of the Fluorescence QY of CdTe QDs Encapsulated in the Silica Particles. The fluorescence QY of CdTe QDs was measured using Rhodamine 6G as a fluorescence standard.[43] Typically, Rhodamine 6G was dissolved in anhydrous ethanol with its absorbance around 0.018 at the excitation wavelength, normally 475 nm, where the diluted CdTe QDs solutions showed the same absorbance. By comparison of the integrated areas of emissions from Rhodamine 6G and CdTe QDs, respectively, the fluorescence QY of the CdTe QDs was calculated by taking a QY of 95% for Rhodamine 6G in diluted solution.[44] The fluorescence QY of the as-prepared CdTe QDs shown in Figure 1 was determined to be ~61%.

The fluorescence QY of the CdTe QDs encapsulated in the CdTe@SiO_2 composite particles was determined according to literature method.[21] In general, by comparing with the parent CdTe QDs whose fluorescence QY was determined by the method mentioned above, the fluorescence QY of the CdTe QDs in SiO_2 particles was obtained. In detail, the cadmium content of a given aqueous solution containing CdTe@SiO_2 particles was first determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) after the CdTe@SiO_2 particles were digested by a mixture of HCl, HNO_3, and HF. Then, a colloidal dispersion of the CdTe@SiO_2 particles and a diluted aqueous solution of the parent CdTe QDs were prepared at the same cadmium concentration. The integrated areas of emissions from CdTe@SiO_2 and CdTe QDs solutions were then measured and compared to get the fluorescence QY of CdTe QDs encapsulated in the silica particles.

Characterizations. Fluorescence and UV−vis absorption spectra were recorded at room temperature with a Cary Eclipse fluorescence spectrophotometer and a Cary 50 UV−vis spectrophotometer, respectively. The transmission electron microscopy (TEM) images of the resultant CdTe@SiO_2 particles were recorded with a JEM-100CXII microscope operating at an accelerating voltage of 100 kV. The cadmium concentration was determined by the ICP-OES method using a Thermo Fisher IRIS Intrepid II XSP. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 220i-XL photoelectron spectrometer from VG Scientific using 300 W Mg Kα radiation ($h\nu = 1253.6$ eV). The binding energies for different elements were calibrated with respect to the C1s line at 284.8 eV from the contaminant carbon. A combination of

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a Shirley type background and a linear type background was used during curve-fitting. All fittings were carried out using Voigt shaped peaks with an equal fwhm (full width at half-maximum) for each data set. Agarose gel electrophoresis was employed to reveal the variation of surface charge density of the CdTe QDs obtained at different incubation time points. In detail, 1% agarose gel was cast in Tris-borate buffer (0.5× TB, pH = 8.59). Then, a 10 μL aliquot of CdTe QDs solution was mixed with 4 μL of 30 wt % glycerol in TB buffer. The mixture was run in 0.5× TB buffer at a constant voltage of 60 V for about 1 h. Following the electrophoresis, the gel was photographed under UV irradiation by Tanon GIS-1010 gel image analysis system (Tanon Science & Technology Co, Ltd., Shanghai, China).

Results

I. Optical Development of CdTe QDs during Incubation. To investigate the effects of incubation on the optical properties of the CdTe QDs, both absorption and fluorescence of the CdTe QDs were monitored during the incubation. The results are presented in Figure 2. In general, the incubation process leads to a gradual increase in absorbance within the whole absorption range of CdTe QDs and progressive red shifts at the absorbance onset. Accompanying with these variations in absorption, fluorescence intensity is greatly enhanced as a function of the incubation time. Meanwhile the emission peak progressively shifts to red, in accordance with the red shifts in the absorption onset. As the fluorescence QY stops increasing after 8 days of incubation, as shown in Figure 2b, the CdTe QDs obtained on the eighth day of incubation were chosen for the following preparation of the CdTe@SiO_2 composite particles. The fluorescence QY of the CdTe QDs incubated for 8 days was determined to be ~82%.

II. General Morphology of CdTe@SiO_2 Composite Particles. A representative TEM image of the CdTe@SiO_2 particles obtained by reverse microemulsion method is shown in Figure 3a. Quite similar to the literature results,[21] by the current synthetic protocol, nearly monodispersed CdTe@SiO_2 particles of 79.4 ± 6.7 nm were obtained. The fluorescence of the CdTe QDs encapsulated presents very small variation with respect to peak position in comparison to those of the as-prepared and the parent CdTe QDs as shown in Figure 3b. The fluorescence QY of the CdTe QDs in the resultant silica particles was determined to be 47%. Becasue of the high fluorescence efficiency, the aqueous dispersion of the resultant CdTe@SiO_2 particles exhibit reddish fluorescence even under ambient conditions, see Figure 3c. Close observation further reveals that, apart from particles containing single CdTe nanocrystal cores, the composite particle sample also contains 52% CdTe@SiO_2 particles with multiple cores, which was not observed in our previous investigations.

III. Effects of Incubation Time on Composite Structure of CdTe@SiO_2 Particles. As multicore CdTe@SiO_2 particles were obtained upon the use of incubated CdTe QDs, to further discover the effects of incubation time on the

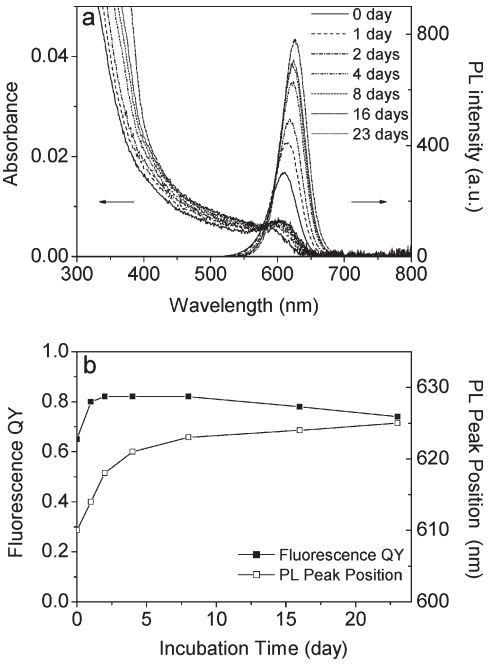

Figure 2. (a) Absorption and fluorescence spectra of the CdTe QDs recorded during the incubation; (b) temporal evolutions of the fluorescence QY (■) and peak position (□) during the incubation. The excitation wavelength for the fluorescence measurements was 360 nm.

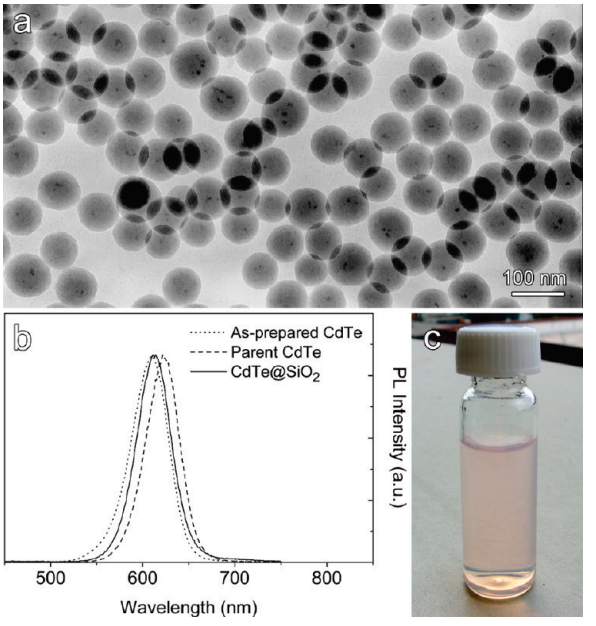

Figure 3. (a) Representative TEM image of CdTe@SiO_2 particles prepared using CdTe QDs incubated for 8 days; (b) normalized fluorescence spectra of the as-prepared CdTe QDs, incubated CdTe QDs (parent CdTe QDs), and the CdTe@SiO_2 particles; (c) photograph of an aqueous dispersion of CdTe@SiO_2 particles taken under ambient conditions.

composite structure, CdTe QDs were extracted at different incubation time points, i.e., 0, 4, 8, 23 days, and were used to prepare the fluorescent silica particles under the same preparative conditions. The TEM images of the resultant fluorescent particles are shown in parts a−d of Figure 4. It can be found out that as the incubation process is being prolonged, the percentage of multicore

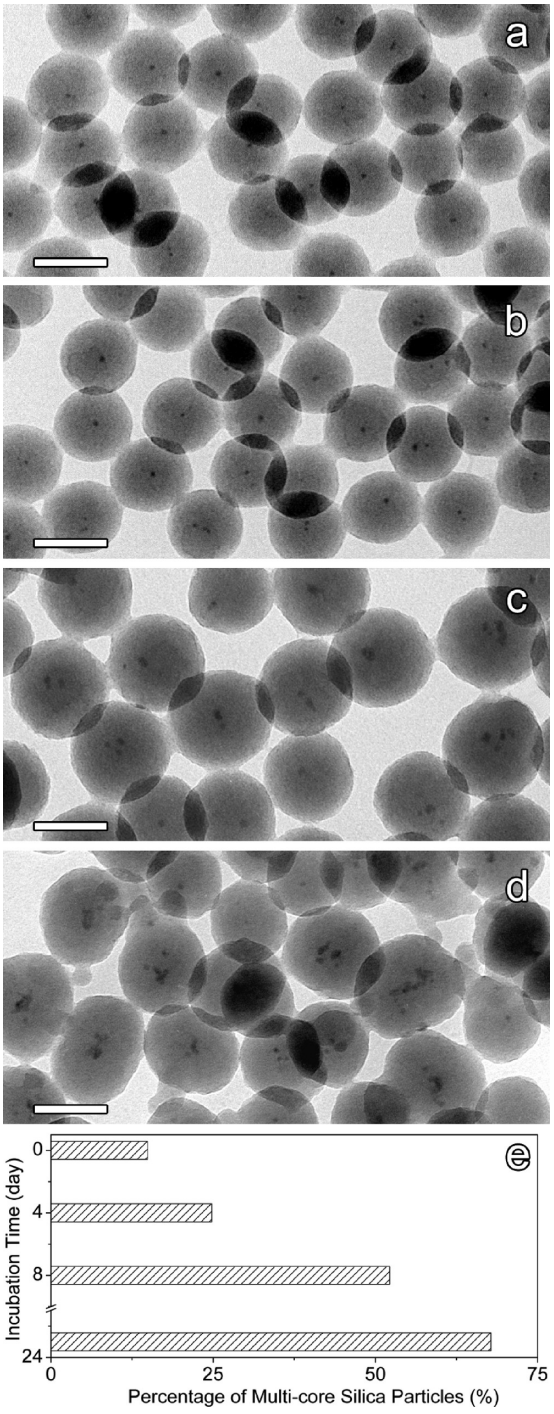

Figure 4. TEM images of CdTe@SiO_2 particles using CdTe QDs incubated for 0 day (a), 4 days (b), 8 days (c) and 23 days (d), respectively. The scale bar corresponds to 50 nm. The percentage of multicore/shell CdTe@SiO_2 against the incubation time is shown in panel e.

CdTe@SiO_2 increases, eventually leading to the formation of irregularly shaped particles after the incubation process proceeded for 23 days. The variation on the percentage of multicore silica particles is more clearly seen in Figure 4e.

Discussion

As mentioned in the Introduction, the silica coating for fluorescent QDs displays a number of significant advantages over the naked QDs with respect to bioapplications.[3a,24,30−32] However, huge drops of fluorescence QY always occur inevitably during the silica coating independent of the coating methodology,[21,34−41] suggesting that generation of nonirradiative pathways cannot simply be avoided. The decrease of fluorescence QY was explained by various mechanisms mainly involving ligand exchanges.[34,40] In addition, the impurity was also taken as a key factor responsible for the loss of fluorescence QY.[40] Even in the most successful case, only 58% of the initial fluorescence QY was preserved for similarly structured core/shell type of CdSe@SiO_2 silica particles that were prepared by reverse microemulsion method upon the use of hydrophobic CSS type CdSe QDs.[40] As the CSS type of structure was constructed for increasing the fluorescence QY of the parent QDs, the fluorescence QY of the resultant CdSe@SiO_2 core/shell particles also reached 35% which is to our best knowledge the highest fluorescence QY value ever achieved for QDs incorporated in silica particles.[40] In our previous investigation, although the fluorescent CdTe@SiO_2 core/shell particles with single CdTe nanocrystal cores were also achieved by reverse microemulsion method, only 35% of the initial fluorescence QY was preserved.[21] Partly because of the relatively low fluorescence QY of the parent CdTe QDs costabilized by 1-thioglyerol and thioglycolic acid, the fluorescence QY of the resultant CdTe@SiO_2 core/shell composite particles was only of 7%. Different from our previous investigations, the CdTe QDs used herein were stabilized solely by thioglycolic acid. The fluorescence QY of as-prepared CdTe QDs already reached 61%. In addition, the incubation process further increased the fluorescence QY up to 82% under optimized conditions. Consequently the fluorescence QY of the resultant CdTe@SiO_2 reached 47%. In comparison with that of the incubated CdTe QDs, 57% of the initial fluorescence QY is retained, which is quite comparable to the ratio achieved by using CSS type of hydrophobic CdSe QDs.

It was previously demonstrated that the fluorescence QY of CdTe QDs can strongly be enhanced by forming a CdTe@CdS core/shell structure through the photodegradation of thioglycolic acid upon illumination.[43] The construction of the CdTe@CdS core/shell structure leads to quite comparable red-shifts as shown in Figure 2 with respect to both absorption onset and fluorescence peak position. Therefore, it can be deduced that a CdS shell structure was also formed during the incubation, which can find supportive evidence from the following spectroscopy analysis.

To better present the variation in absorption caused by incubation, the difference absorption spectra between those recorded during incubation and that recorded before incubation are presented in Figure 5. It is quite obvious that the increases of absorbance are mainly located in the spectroscopic region lower than 400 nm. After approximately 8 days, an absorption shoulder at around 370 nm develops and transforms into a clear absorption peak later on. According to previous

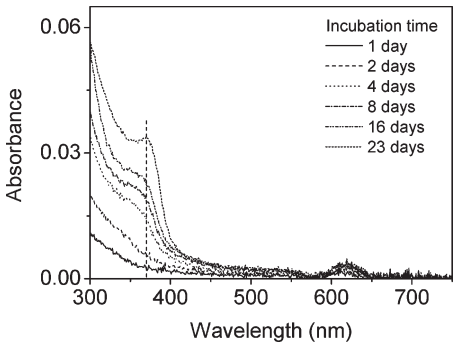

Figure 5. Difference absorption spectra obtained by subtracting the absorption spectrum of the as-prepared CdTe QDs from those recorded from the incubated CdTe QDs. The dashed line is an eye guide for the evolution of the peak located around 370 nm.

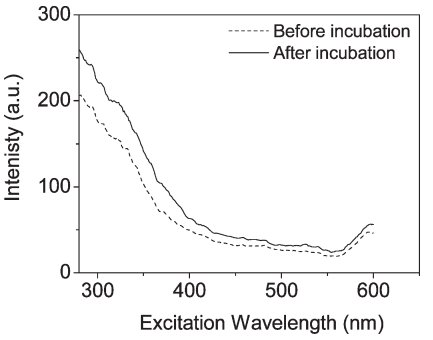

Figure 6. Fluorescence excitation spectra of the as-prepared CdTe QDs and the CdTe QDs obtained after 8 days of incubation for emission at 610 nm.

investigations,[45−49] this newly developed absorption peak is very likely the characteristic exciton absorption of CdS clusters. The slight increase in the absorbance around the exciton peak position of CdTe and the red-shift of absorption onset further suggest that CdS was formed on the surface of CdTe via epitaxial growth.[5,43,50−54] As CdS has a wider bandgap than CdTe, a few monolayers of CdS shell should be sufficient for effectively increasing the fluorescence QY of the CdTe particle core according to investigations on similarly structured nanocrystals.[5,43,50−54] Another important indication for the formation of CdTe@CdS core/shell structure is that nearly no difference between the fluorescence excitation spectra recorded before and after incubation is presented as shown in Figure 6, which suggests that incubation did not alter the fluorescent center.[43]

It should be pointed out that the CdTe@CdS core/shell structure observed in our previous investigations was achieved by illumination.[43] Although within a comparable time frame, the incubation process gave rise to a very similar fluorescence enhancement effect as shown in Figure 2, the CdTe QDs were incubated in the dark in the current investigations rather than under illumination. To discover the mechanism leading to the formation of CdS under the current experimental conditions, the following experiments were carried out. Three solutions containing cadmium ion and TGA were prepared according the ratio and concentrations used for the preparation of CdTe QDs but in three different alkaline media, i.e., aqueous solution containing NaOH (15.9×10^{-3} M), aqueous solution containing ammonia (0.45 wt % $NH_3 \cdot H_2O$), and aqueous solution containing both NaOH (15.9×10^{-3} M) and ammonia (0.45 wt % $NH_3 \cdot H_2O$). The absorption spectra of Cd-TGA in these three solutions were recorded before and after 8 days of incubation in the dark. The results shown in Figure 7 demonstrate that quantum-sized CdS is formed only in the presence of ammonia, suggesting that ammonia can catalyze the decomposition of TGA, leading to the formation of CdS. However, in the real incubation system, the amount of Cd^{2+} ions existing in various forms of Cd−TGA complexes is greatly reduced as most of them had been converted to CdTe QDs after reacting with H_2Te. Therefore, CdS slowly formed during incubation

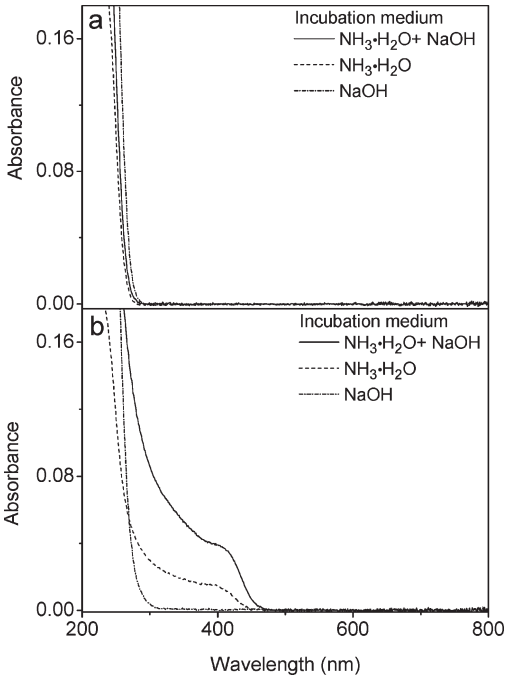

Figure 7. Absorption spectra of Cd−TGA complexes in different alkaline media. Spectra shown in panel a were recorded right after the solutions were prepared, while the spectra shown in panel b were recorded 8 days later after the solutions were kept in the dark.

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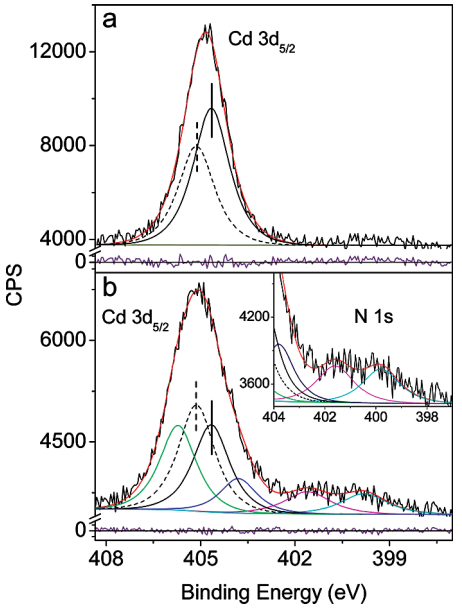

Figure 8. XPS spectra of the as-prepared CdTe QDs (a) and CdTe QDs incubated for 8 days (b), together with best fits for Cd $3d_{5/2}$ and N 1s. The N 1s signals were enlarged and shown in the inset.

can only choose to condense on the surface of CdTe particles forming the core/shell particles rather than forming nuclei by itself, which interprets the fluorescence enhancement effect shown in Figure 2.

Apart from catalysis of the formation of CdS, ammonia has great probability to form a coordination bond with the cadmium ion on the surface of CdTe QDs, because at the given pH of 12.28, 99.9% of ammonia molecules were unprotonated. To further investigate the chemisorbtion of NH_3 on CdTe QDs, XPS characterizations on both as-prepared and incubated CdTe QDs were carried out. Figure 8 presents XPS spectra of the as-prepared and incubated CdTe QDs. The Cd $3d_{5/2}$ and N 1s signals were carefully fitted using a Shirley-type background. The best fits are tabulated in Table 1. Before incubation, the Cd $3d_{5/2}$ peak was fitted by two peaks located at 404.7 and 405.1 eV, which can be attributed to cadmium binding with Te and S, respectively.[55,56] These binding situations remained after incubation. However, two additional signals appear at 403.8 and 405.7 eV, respectively. According to references, these two signals can be assigned to Cd−O[56] and Cd−N,[57] respectively. The Cd−O coordination is probably caused by surface binding OH groups at pH 12.28, partly due to the degradation of surface capping TGA. The appearance of Cd−N coordination is also supported by the fact that N signal appears in the incubated sample. The N 1s signal is primarily a convolution of two peaks at 399.8 and 401.6 eV, respectively. These two peaks can be assigned according to references to ammonia binding with Lewis acid (399.8 eV), and Brønsted-acid (401.6 eV), respectively,[58] i.e., cadmium on the nanocrystal surface and carboxylic acid from the surface binding TGA.

Table 1. Best Fitting Data for Cd ($3d_{5/2}$) and N (1s) Signals Recorded from the As-Prepared CdTe QDs and the CdTe QDs Incubated in Ammoniacal Solution for 8 Days

BE (eV)	fwhm	area (%)	assignment of chemical state
Cd ($3d_{5/2}$) (As-Prepared CdTe QDs)			
404.7	1.4	58.1	Cd−Te
405.1	1.4	41.9	Cd−S
Cd ($3d_{5/2}$) (CdTe QDs Incubated for 8 Days)			
403.8	1.4	11.1	Cd−O
404.7	1.4	27.9	Cd−Te
405.1	1.4	33.9	Cd−S
405.7	1.4	27.1	Cd−N
N (1s)			
399.8	1.7	48.3	N−O(CO)[a]
401.6	1.7	51.7	N−Cd

[a] Ammonia binding with carboxylic acid.

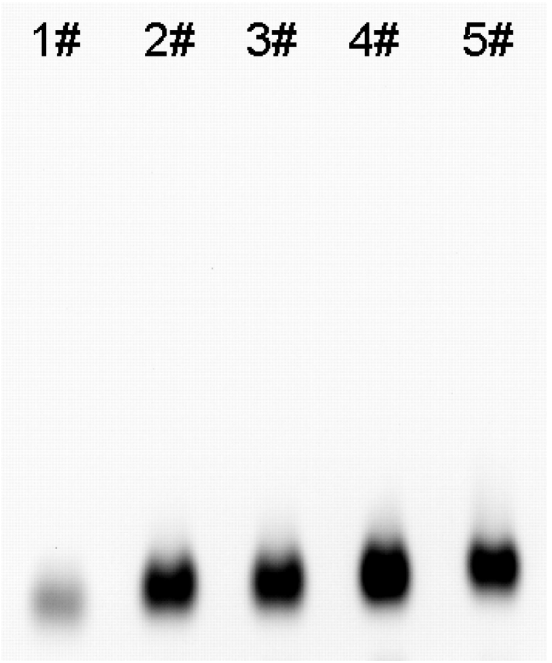

Figure 9. Agarose gel electrophoresis (1%) in 0.5 TB buffer (pH = 8.59) of CdTe QDs incubated for 0 (lane 1#), 4 (lane 2#), 8 (lane 3#), 16 (lane 4#), and 23 days (lane 5#), respectively.

As stated above, the incubation process not only increased the fluorescence QY of the CdTe QDs but also the number of CdTe nanocrystal cores in the resultant CdTe@SiO_2 particles as shown in Figure 4. That latter effect is greatly desirable for increasing the fluorescence brightness of the CdTe@SiO_2 particles. According to our previous investigations, the formation of well-defined single core/shell CdTe@SiO_2 is independent of the initially feeding amount of the parent CdTe QDs.[21a] Further investigations suggest that as the molecular weight of

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oligomeric silica intermediates increases, the cations induced by the oligomeric silica intermediates evenly distributed throughout the microscale water pool and the region around the oligomeric intermediates is locally negatively charged. This local negatively charged background will reduce the screen between two CdTe QDs; consequently, the Debye screening length for CdTe QDs will increase, which induces a net repulsive interaction between two neighboring CdTe QDs. 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 QDs will be driven to the boundary of the aqueous microdroplet, except for the last CdTe QD located at the center of the water pool due the symmetry of the repulsive interaction between this specific CdTe QD and the others located at the surface of the microwater pool.[21]

According to the XPS analysis mentioned above, the chemisorptions of ammonia on CdTe QDs will reduce the surface charge density of CdTe QDs, consequently weakening the electrostatic repulsion among CdTe QDs and leading to the formation of multicore/shell structures for CdTe@SiO_2 particles. To provide direct proof of this hypothesis, agarose gel electrophoresis was employed to probe the variation of surface charge density of CdTe QDs incubated for different periods of time. A typical migration pattern 1% agarose gel electrophoresis of QDs in 0.5 TB buffer, pH = 8.59, is shown in Figure 9. It is quite clear that incubated QDs migrate slower than the as-prepared CdTe QDs. Furthermore, the migration of the incubated QDs shows an incubation time-dependent behavior, indicating that the surface charge density of incubated CdTe QDs is gradually reduced against incubation time. Therefore, it can be concluded that the functions of ammonia used for incubating CdTe QDs are twofold: (1) it promotes the decomposition of TGA leading to the formation of CdTe@CdS core/shell QDs that present higher fluorescence QY in comparison with the as-prepared CdTe QDs, and (2) it reduces the surface charged density of CdTe QDs during the incubation, giving rise to the formation of a large percentage of multicore/shell CdTe@SiO_2 particles.

Conclusions

In summary, highly fluorescent core/shell CdTe@SiO_2 particles with fluorescence QY up to 47% were prepared by the reverse microemulsion method. The key procedure was to incubate the as-prepared CdTe QDs stabilized by TGA in ammoniacal solution prior to the reverse microemulsion process. As ammonia can catalyze the degradation of the surface capping TGA, the fluorescence QY of the CdTe QDs was consequently enhanced due to the formation of CdTe@CdS core/shell type structures, while the buildup of such a semiconductor−semiconductor core/shell structure was greatly in favor of the retention of fluorescence QY throughout the silica coating. Consequently, highly fluorescent core/shell CdTe@SiO_2 particles with uniform size were obtained. Further experimental results also suggested that the incubation process decreased the surface charge density of the incubated CdTe QDs, consequently giving rise to multicore/shell structured CdTe@SiO_2 particles that are greatly desirable as high brightness fluorescence probes. The current investigations thereby provide a simple and useful method for coating aqueous fluorescent QDs with silica to achieve high-quality fluorescent probes.

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Supporting Information Available: The contents of Supporting Information on the (1) temporal evolution of the pH value of incubation medium, (2) PL peak position and PL quantum yield as a function of the pH of the incubation medium, and (3) PL intensity of CdTe@SiO_2 versus time (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.