Luminescent Properties of Water-Soluble Denatured Bovine Serum Albumin-Coated CdTe Quantum Dots

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Received: April 12, 2006; In Final Form: July 8, 2006

Chemically reduced bovine serum albumin (BSA) has been used to modify the surface of water-soluble CdTe quantum dots (QDs). It is demonstrated that the denatured BSA (dBSA) can be conjugated to the surface of CdTe QDs and thereby efficiently improve the chemical stability and the photoluminescence quantum yield (PL QY) of the QDs. It is inferred that a shell-like complex structure $CdTe_x(dBSA)_{1-x}$ will form on the surface of the CdTe "core", resulting in the enhancement of PL intensity and the blue shift of the PL peak. This study of the effects of pH and dBSA concentration on optical properties of dBSA-coated QDs suggests that, at pH 6−9, the solution of dBSA-coated CdTe QDs can keep substantial stability and fluorescent brightness, whereas further increase of pH value leads to a dramatic decrease in PL QY and chemical stability. On the other hand, too high or too low initial dBSA concentration in the QD solution results in a decrease of PL QY for dBSA-coated CdTe QDs. This study provides a new approach of preparing stable water-soluble QDs with high PL QY and controllable luminescent colors for biological labeling applications.

Introduction

One of the most highlighted applications of nanobiotechnology is the use of semiconductor quantum dots (QDs) for biological labeling applications.[1] Compared with organic dyes, II−VI semiconductor QDs have size-dependent tunable photoluminescence (PL) with broad excitation spectra and narrow emission bandwidths, which allow simultaneous excitation of particles of different sizes at a single wavelength. In addition, their high photobleaching threshold renders continuous or long-term monitoring of slow biological processes possible. Owing to the same surface properties of QDs, it is possible to use a similar approach to conjugate QDs of any color to the biomolecules of interest. These unique properties of QDs make them appealing as in vivo and in vitro fluorophores in a variety of biological investigations.[2−9] At present, the best available semiconductor QDs for biological applications are CdSe/ZnS core/shell ones due to their high chemical stability and photoluminescence quantum yield (PL QY).[1−9] However, these QDs are usually synthesized under high-cost and rigorous experimental conditions through a traditional organometallic approach, and QDs are non-water-soluble.[10−12] Therefore, a few complex and time-consuming phase-transfer steps are required to render them water-soluble and biocompatible, resulting in a decrease of PL QY.[2,3] In fact, water-soluble CdTe quantum dots can be directly synthesized in a water-phase system, and the synthesis is more reproducible, less expensive, and less toxic.[13−15] They have the potential of becoming one of the most important semiconductor labeling materials for biological and medical applications. Previously, Kotov et al. separately used thioglycolic acid (TGA)[16] or L-cysteine-coated CdTe QDs[17] to conjugate proteins such as bovine serum albumin (BSA). Similar to thiol-alkyl-COOH-coated CdSe/ZnS core/shell QDs, the chemically stable protein-conjugated CdTe QDs are difficult to obtain, and agglomeration of QDs is often observed, resulting in a loss of brightness.[1] The occurrence of agglomeration during the condensation reaction makes direct bioconjugation of CdTe QDs with biomolecules difficult, consequently affecting their potential for use as biological labeling agents. Therefore, any improvement in their chemical stability and PL QY is critical and of practical interest. Previously, Gao et al.[18] used denatured bovine serum albumin (dBSA) as a capping agent to modify the surface of CdSe/ZnS QDs. Denatured BSA is a biomacromolecule containing 37 thiol groups per monomer and can be prepared from the chemically reduced bovine serum albumin. In their work, the CdSe/ZnS QDs were initially synthesized in an organic phase via the traditional organometallic pyrolysis approach, followed by a ligand exchange to render the QDs water-soluble. The resulting water-soluble QDs were incubated in a dBSA solution to obtain dBSA-coated QDs. They found that the PL intensity of the dBSA-coated CdSe/ZnS QDs decreased slightly compared with the original QDs in an organic solvent, which could serve as an indicator of successful coating.[18]

In this paper, we use denatured BSA to chemically modify the surface of CdTe QDs and systematically study the effects of surface modification and storage time on the optical properties of the resulting QDs. Effects of QD size, initial dBSA concentration in the QD solution, and the pH value of the final QD solution on the optical properties of dBSA-coated CdTe QDs are also investigated. Furthermore, the stability and brightness of dBSA-coated CdTe QDs are compared with their original TGA-coated ones. Finally, the mechanism of blue shift in the PL peak of dBSA-coated QD solutions, which may provide a new approach for the control of the emission peak wavelength of the water-soluble QDs, is explored.

Experimental Section

Preparation of NaHTe. NaHTe was prepared according to the previously published procedure with several changes.[13,15]

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10.1021/jp062279x CCC: $33.50
Published on Web 08/11/2006

Briefly, a mixture of 0.0319 g of tellurium (Te) powder (Aldrich, 99.8%, 200 mesh) and 0.0284 g of sodium borohydride (Aldrich, 98%) (molar ratio of Te to $NaBH_4$ is 1:3) was first loaded into a 50-mL single-necked flask fitted with a septum connected to the vacuum line and then deaerated by alternating between a vacuum pump and nitrogen flow. Then 0.2 mL of N_2-saturated pure water was added into the flask under magnetic stirring and nitrogen flow at room temperature. After the black Te powder fully disappeared and white sodium tetraborate precipitation appeared at the bottom of the flask (about 25 min), 24.8 mL of N_2-saturated pure water was injected into the flask to produce a 0.01 M of NaHTe solution for use as Te precursor in the following reaction.

Preparation of CdTe Quantum Dots (QDs). The colloidal CdTe QD solution was prepared by using $CdCl_2$ (Aldrich) and NaHTe as precursors, based on the method described elsewhere.[15] Briefly, in a three-necked flask with a condenser attached, the freshly prepared NaHTe solution was added to N_2-saturated $CdCl_2$ aqueous solution at pH 9.0 in the presence of thioglycolic acid (TGA, Fluka) as ligand or stabilizing agent under vigorous stirring to form a yellow CdTe colloidal solution. Herein the molar ratio of Cd^{2+}/TGA/Hte^- was fixed at 1:2.4:0.2. The resulting colloidal solution was refluxed under nitrogen flow at 100 °C for different times to obtain CdTe QDs of different sizes.

Preparation of Denatured Bovine Serum Albumin (dBSA). Denatured BSA was prepared by chemically treating bovine serum albumin (BSA) (Sigma) with $NaBH_4$, based on a previous literature report.[18] First, 0.165 g of BSA was dissolved in 50 mL of deionized water, and second 0.0042 g of $NaBH_4$ was added as a reductant into the solution under stirring. The reaction proceeded at room temperature for 1 h and then between 60 and 80 °C until no more gas (H_2) was generated. Under these conditions, BSA was denatured and most of its disulfide bonds were converted to sulfhydryl groups. The final concentration of dBSA aqueous solution was 5×10^{-5} mol/L.

Preparation of Denatured BSA-Coated QDs. The TGA-coated CdTe QDs were precipitated with acetone and then isolated by centrifugation and decantation to remove free TGA molecules. The purified QDs were redissolved into a measured amount of dBSA solution. The resulting solution was incubated at 60−80 °C for 15 min before PBS buffer (pH = 7.4) solution was added to reach the desired concentration, and then stored under air at room temperature.

To explore the effect of pH values on the optical properties of QD solutions, 0.5 N NaOH and HCl standard aqueous solutions were used to adjust the pH values and minimize the volume variation of CdTe QD solutions.

Gel Electrophoresis. SDS-PAGE was carried out using the method of Laemmli on an acrylamide gel with 7.5% resolving gel and 4% stacking gel in a Bio-Rad Mini-PROTEAN 3 cell. Fifteen microliters of sample was loaded into each gel well. The voltage was set at 120 V.

Spectroscopy. Ultraviolet−visible (UV−Vis) absorption spectra were recorded on a CARY Eclipse UV spectrometer. Photoluminescence (PL) spectra were recorded on a CARY Eclipse Fluorescence Spectrophotometer with an excitation wavelength of 400 nm. Room-temperature photoluminescence quantum yields (PL QY) were estimated by using Rhodamine 6G in ethanol as reference sample (QY = 95%) as described elsewhere.[19] The absorbances of the samples and the reference at the excitation wavelength (400 nm) are similar and smaller than 0.1; thus, self-absorbance can be avoided. Attenuated Total Reflectance Fourier Transform Infrared (ATR−FT-IR) measurements were performed using a Nicolet Nexus 670 FT-IR spectrometer with 4 cm^{-1} spectral resolution. One hundred scans were averaged. All the solid QD samples for IR measurements were prepared by three-day dialysis (Spectra/Por dialysis membrane with molecular weight cutoff [MWCO] equal to 1000) to remove small molecules, followed by freeze-drying. All measurements were performed at room temperature.

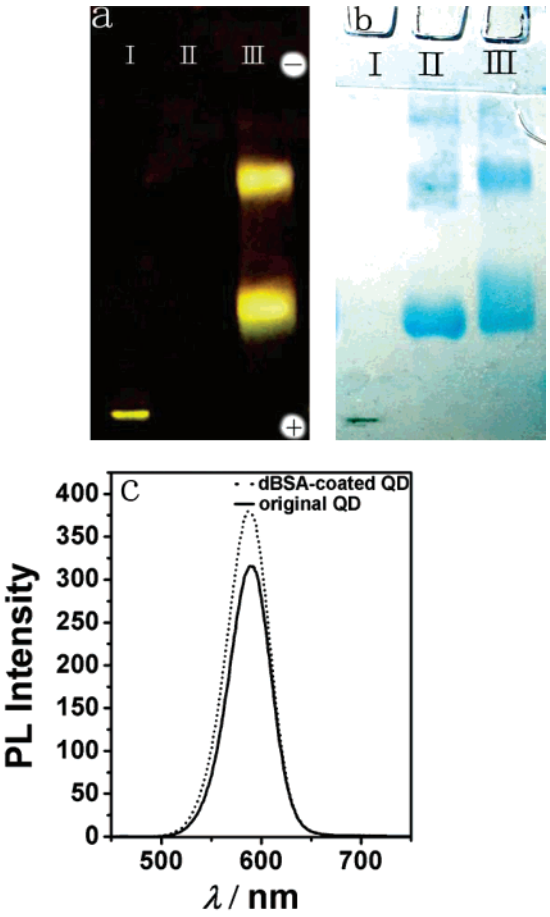

Figure 1. (a) SDS-PAGE luminescence image. (b) SDS-PAGE image of gel plate stained by Coomassie Blue. Wells: thioglycolic acid (TGA)-coated CdTe QDs (I), pure denatured bovine serum albumin (dBSA) (II), and dBSA-coated CdTe QDs (III); (c) photoluminescence (PL) spectra of original TGA-coated QDs (solid line) and dBSA-coated QDs (dot line) incubated for 2 days.

Results

To enhance the stability and PL QY of the CdTe QDs, denatured bovine serum albumin (dBSA) was used to modify the surface of CdTe QDs. To prove the conjugate formation, we carried out SDS-PAGE on dBSA-coated CdTe QDs. Figure 1a shows the luminescent image of native electrophoresis results of the original TGA-coated CdTe QD (well I), pure dBSA (well II), and dBSA-coated CdTe QD (well III). The evidence supporting conjugation of CdTe to dBSA can be found from the luminescent image of the gel plate in Figure 1a, where the bands of dBSA-coated CdTe shows strong luminescence (well III), while the free dBSA does not have any detectable signal in the luminescence image (well II). Figure 1b shows the image of the stained gel plate corresponding to Figure 1a. In well II, there are three bands originating from dBSA monomer, dBSA−dBSA dimer, and globulins, respectively, as indicated in the specifications of Sigma.[16] After conjugation of protein with QDs, there are still three bands shown in well III of Figure 1b.

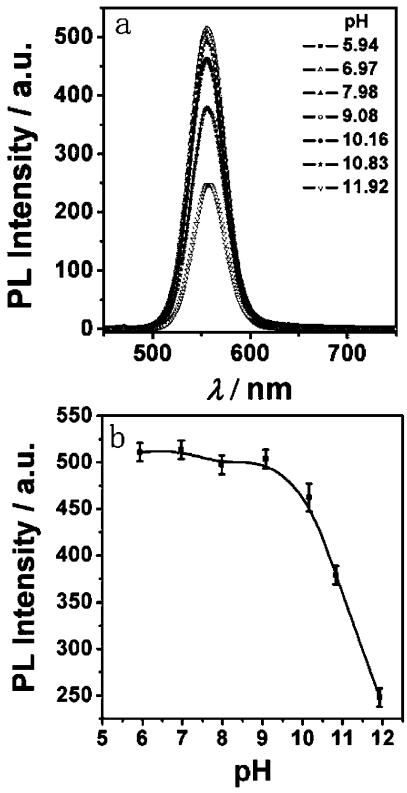

Figure 2. Photoluminescence (PL) spectra of denatured bovine serum albumin (dBSA)-coated QDs at different pH values (a) and the plot of corresponding PL intensities versus pH values (b).

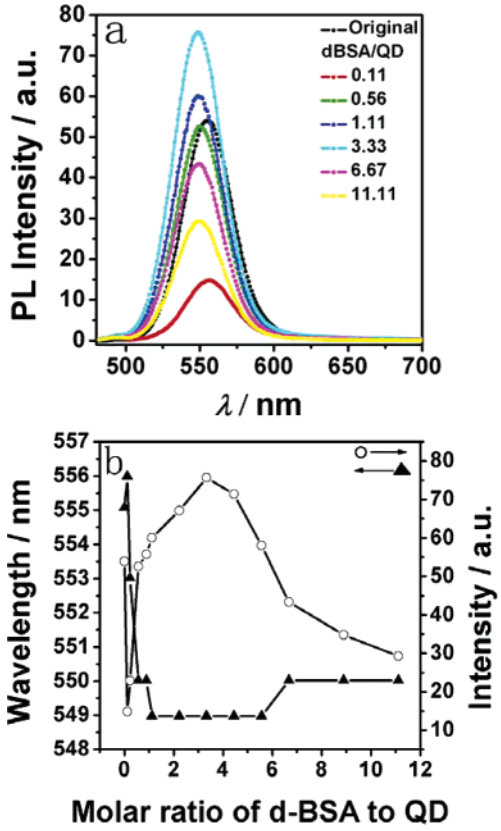

Figure 3. Photoluminescence (PL) spectra of a serial of aqueous solutions with the same CdTe QD concentration but different denatured bovine serum albumin (dBSA)-to-QD ratios (a) and the plots of PL wavelengths and intensities versus dBSA-to-QD molar ratios (b).

However, by comparison of the two bands in well III of Figure 1a and Figure 1b, it is found that only dBSA monomer and dBSA−dBSA dimer can be conjugated with QDs, as suggested by the two bright fluorescent bands. On the other hand, it is known that the mobility of a chemical in SDS-PAGE is determined by the mass/charge ratio of that chemical. Since the dBSA-coated QDs have a larger mass/charge ratio than TGA-coated QDs, they show less mobility on the gel plate, as shown in Figure 1a. In Figure 1b, however, it is noted that band positions of dBSA are slightly lower than those of dBSA-coated QDs. This is because the increase of mass due to conjugation of QD to dBSA is almost counteracted by the increase of the overall charge density of the conjugate.[16,17] Compared with the original TGA-coated CdTe QDs, the dBSA-coated CdTe QDs show a higher photoluminescence quantum yield, as illustrated in Figure 1c, which is opposite to Gao's results from CdSe/ZnS QDs.[18] This difference may be due to the fact that the thiol group has a larger affinity to Cd atoms than to Zn atoms. Therefore, many surface defects and dangling bonds can be removed efficiently. It should be pointed out that the brightness of TGA-coated QDs decreased after electrophoresis, as shown in Figure 1a. In contrast, the dBSA-coated QDs maintain similar brightness during electrophoresis.

Effect of pH. For biological applications, it is important to study the influence of pH on the PL intensity of biomolecule-coated QDs. 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) is a commonly used reagent in the formation of amide bonds during bioconjugation. In most cases, it will be better to perform the coupling reaction in the presence of EDC at pH between 6 and 8.[3−5] Figures 2a and 2b show the PL spectra of dBSA-coated QDs at different pH values and the corresponding PL intensities as a function of pH value. In the pH range between 6 and 9, the PL intensity has negligible change, and CdTe QDs can preserve substantial luminescent brightness and chemical stability. However, the PL intensity of dBSA-coated QDs decreases dramatically at pH higher than 9, and agglomeration emerges after the QD solution is stored at pH ∼ 12 for 3 days. In contrast, the conjugation of denatured BSA to CdTe QDs facilitates the improvement of chemical stability of QDs and the proper choice of covalent coupling reagents as well as coupling conditions for subsequent bioconjugation. Unlike TGA-coated QDs, where aggregate formation often occurs after the addition of EDC,[1] no aggregate formation is observed after EDC is added into the dBSA-coated QD solutions under vigorous stirring for bioconjugation of dBSA-coated QDs to other biomolecules.

Effect of dBSA/CdTe QD Ratio. Figure 3a shows the PL spectra of a serial of aqueous solutions with the same QD concentration but different dBSA-to-QD ratios. These samples were incubated at room temperature for 3 days after the addition of dBSA. Among them, the black solid-circled curve is the PL spectrum of the original TGA-coated CdTe QDs. Figure 3b depicts the changes of the PL peak positions and relative intensities as functions of dBSA/QD molar ratios (r). The points at ratio r equal to 0 represent the PL peak position and the relative intensity of the original TGA-coated QDs. Five regions are observed in the PL peak position versus r plot: (1) at $r \leq 0.11$, PL peak position exhibits a red shift with the increase of r; (2) at $0.11 < r < 1$, PL peak position shows a significant blue shift with the increase of r; (3) at $1 < r < 5.6$, PL peak position remains constant; (4) at $5.6 < r < 6.7$, PL peak position shows a slight red shift with r; and (5) at $r > 6.7$, PL peak position remains constant with r again. On the other hand, three regions are observed in the PL intensity versus r curve: (1) at $r < 0.11$, the PL intensity decreases significantly with an

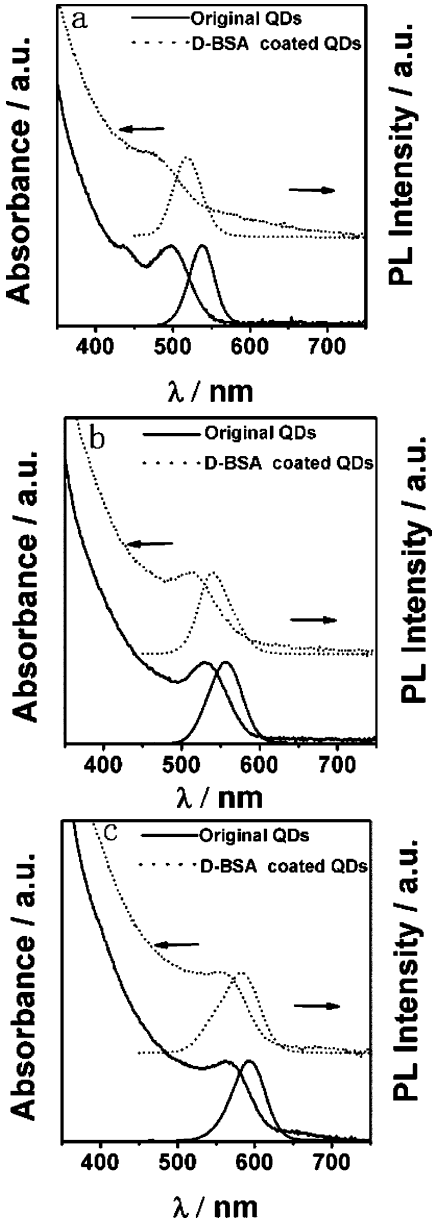

Figure 4. UV−Vis absorption and photoluminescence (PL) spectra of original thioglycolic acid (TGA)-coated CdTe QDs (solid lines) and denatured bovine serum albumin (dBSA)-coated CdTe QDs stored at room temperature for 68 days (dotted lines) with three different emitting colors: green (a), yellow (b), and orange (c).

increase of r; (2) at $0.11 < r < 3.33$, the PL intensity increases monotonically with r before it reaches a maximum at $r = 3.33$; and (3) at $r > 3.33$, the PL intensity monotonically decreases with r.

Effect of Storage Time. Before QDs are used for biological and medical applications, it is necessary to understand the effect of QDs storage time on their PL QY and stability. We select three dBSA-coated CdTe QD samples with different colors of luminescence for tracking the variation of optical properties of QDs with their storage time. Figures 4a−4c show the UV−Vis absorption and PL spectra of three as-prepared original TGA-coated CdTe QDs with different emission colors (green, yellow, and orange), and the corresponding dBSA-coated CdTe QDs ($r = 4.0$) incubated at room temperature for 68 days. Obvious blue shifts are observed in both UV−Vis absorption and PL spectra for each of the three samples. One interesting observation is that the emission color of small-sized green-emitting QDs

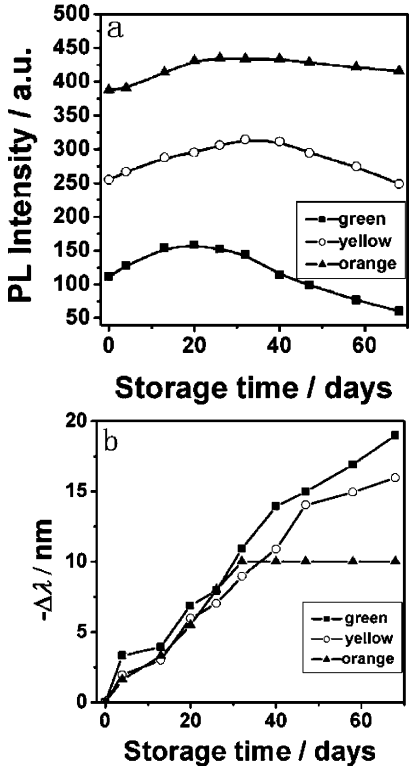

Figure 5. Plots of photoluminescence (PL) intensities (a) and peak shifts (b) of the three dBSA-coated samples with different emitting colors stored at room temperature versus storage time. The dBSA/QDs ratio is 4:1. The concentration of PBS buffer is 0.01 mol/L, and its pH is 7.4.

can shift close to dark cyan ($\lambda_{PL} = 516$ nm), which is usually difficult to achieve through direct synthesis of CdTe QDs. In fact, a similar blue-shift phenomenon has also been reported by Akamatsu et al.[20] They found that, after the addition of 1-decanethiol (DT) into the CdTe toluene solution, which was obtained from water-phase system through phase transfer, an obvious blue shift occurred. It is believed that the complex shell $CdTe_{1-x}(SC_{10})_x$ forms on the surface of the CdTe QDs.[20]

Figures 5a and 5b show the PL peak intensities and peak position shifts of the three dBSA-coated samples (green, yellow, and orange) stored at room temperature as a function of storage time. The PL intensities of all three samples increase initially, reach a maximum, and then gradually decrease with the increase of storage time (Figure 5a); at the same time, their PL peak positions shift to blue (Figure 5b). In addition, these changes are more obvious for the smaller sized green-emitting QDs. For example, their PL peak intensities increase faster during the first stage and then decrease more dramatically, and their peak positions have a greater degree of blue shift than those of the larger sized QDs. Finally, the PL QYs of these samples were also measured using Rhodamine 6G in ethanol as the reference sample. Compared with the original TGA-coated QDs (PL QYs are 12, 26, and 39 % respectively for green-, yellow-, and orange-emitting samples), the corresponding dBSA-coated QDs have a significant increase in PL QYs (maxima up to 22, 35, and 46%, respectively).

Discussion

Due to their high surface energy and reactivity, the surfaces of the small-sized QDs can be attached preferably and dynamically by dBSA. Therefore, they will be passivated more efficiently,[21,22] resulting in a more obvious enhancement in PL

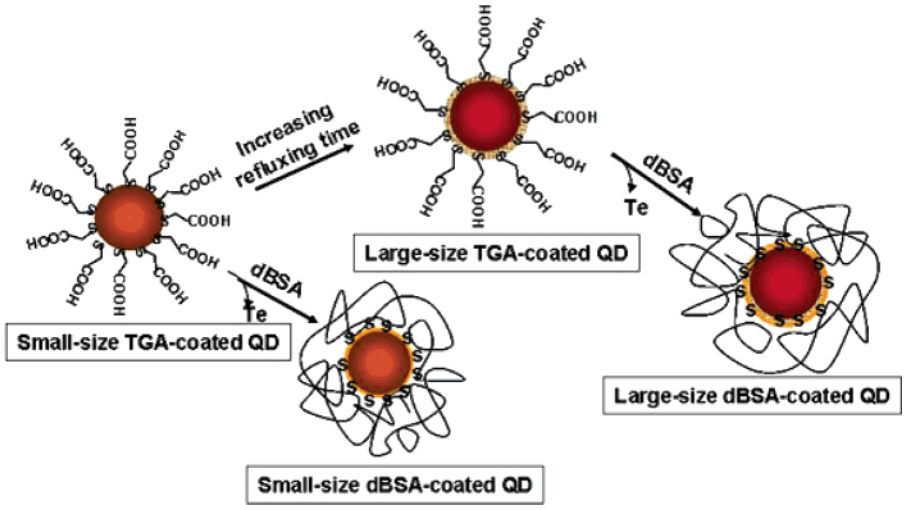

Figure 6. Schematic diagram of the formation of denatured bovine serum albumin (dBSA)-coated CdTe QDs.

intensity during the initial storage stage. With the increase of storage time, some of the thiol groups in dBSA may be oxidized by residual oxygen in the solution, leading to the falloff of some ligand groups from the QD surface. The exposed surface Te atoms can be easily oxidized due to their intrinsic instability, causing a decrease of PL intensity.[14,23−25] Previous publications[14,26,27] suggested that the prolonged refluxing of the aqueous solution of CdTe QDs in the presence of excessive TGA in basic media in general caused partial hydrolysis of TGA, and the mixed CdTe(S) QDs might form due to the partial incorporation of sulfur into the CdTe lattice. Moreover, sulfur had a gradient distribution in the whole QD and was mainly concentrated on the QD surface.[14,26] This is possible because Cd^{2+} can react with Te^{2-} faster than with S^{2-}, preferably forming CdTe with a smaller solubility product K_{sp} ($-\lg K_{sp(CdTe)}$: 34.06; $-\lg K_{sp(CdS)}$: 27.19−28.2).[28] In addition, if refluxing time is not too long, e.g., <20 h, it is possible that only a mixed CdTe(S) shell around the pure CdTe "core", rather than a mixed CdTe(S) entity, is formed. The formation of such surface shell structure will both reduce the amount of Te atoms with dangling bonds on the QD surface and build a potential barrier, partially preventing the leakage of excitons in CdTe "core". Therefore, the larger sized QDs, at least in this work, show a relatively higher stability and PL QY. Theoretically, if a pure CdS shell is formed, any external environmental changes should not have any influence on the optical properties of the QDs. After the surface modification with dBSA, the formation of the mixed CdTe(S) shells causes a smaller change in optical properties compared with the QDs without the inorganic CdS shell. Figure 5a indicates that the larger sized QDs can endure surface environmental changes by showing less change in PL intensity. Here, it should be pointed out that the dBSA-modified QDs with the orange fluorescence can maintain substantial PL QY which is not lower than that of the original QDs, even though the sample has been stored at room temperature for a long period of time (i.e., 68 days). Of course, all the dBSA-coated QDs stored in the refrigerator, regardless of their sizes, can achieve PL intensity higher than the original ones for at least 6 months.

On the other hand, although the PL peak position of the small-sized green-emitting QDs can shift monotonically to blue by up to 19 nm, the PL peak position of larger sized QDs remains constant with storage time after the initial blue shift within the first 32-day storage time, as shown in Figure 5b. One possible explanation for the blue shift of PL peak is due to the formation

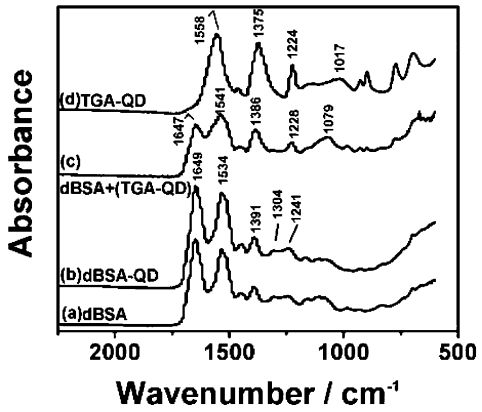

Figure 7. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra of denatured bovine serum albumin (dBSA) (a), dBSA-coated QDs (b), mixture of dBSA and thioglycolic acid (TGA)-coated QDs (c), and TGA-coated QDs (d).

of the complex shell $CdTe_x(dBSA)_{1-x}$, which leads to a decrease in the size of the inner CdTe "core". After CdTe QDs were incubated in the dBSA solution and the resultant solution was heated, the dBSA could take on a linear structure, and subsequently coat the surface of the QDs through ligand exchange, whereby a complex shell of $CdTe_x(dBSA)_{1-x}$ should form. In other words, the multi-thiol-group dBSA could substitute the native capping agent TGA through ligand exchange, generating a thin $CdTe_{1-x}(dBSA)_x$ shell on the QD surface, as shown in Figure 6.

Attenuated Total Reflectance Fourier Transform Infrared (ATR−FT-IR) has been used to prove the substitution of TGA with dBSA on CdTe QD surfaces. Figure 7 shows the ATR-FTIR spectra of dBSA (a), dBSA-coated QDs (b), mixture of dBSA and TGA-coated QDs (c), and TGA-coated QDs (d). The primary bands of interest for dBSA include the amide I band at 1649 cm^{-1} and the amide II band at 1534 cm^{-1}. For TGA, asymmetric and symmetric stretching bands of $-COO^-$ located at 1558 and 1375 cm^{-1}, respectively, are the most distinctive bands. The C−O stretch vibrational mode at ~1224 cm^{-1} is also observed in the IR spectrum of TGA-QD. When dBSA and TGA-coated CdTe QD are simply mixed (molar ratio of dBSA to QD is about 6:1), IR spectra show the peaks from the overlap result of two separate samples. Although the molar ratio of dBSA to TGA-coated QDs in this mixture is more than that in dBSA-coated QDs (molar ratio of dBSA to QD is 4:1), one

can still observe the C−O peaks from pure TGA-coated QDs, i.e., the peaks at 1228 and 1079 cm^{-1}. Eventually, when the dBSA-coated CdTe QD is formed, only the IR spectrum (b) identical to that of dBSA (a) is observed, suggesting that the TGA molecules on the CdTe QD surfaces have almost completely been replaced by dBSA molecules. However, at a higher pH value (i.e., 12), the desorption of dBSA from the QD surface may occur, resulting in the formation of QD aggregate and a decrease of PL QY (see Figure 2). The possible reason is that, under the basic condition, most of the thiol groups in dBSA are converted into thiolate anions, which easily generate thyil radicals due to the electronic transfer to the holes existing in the system (e.g., noncoordinated metallic cations, excessive ligand dBSA, or residual oxygen in the solution). As a result, the noncoordinating disulfide groups form in dBSA molecules due to the radical coupling reaction.[29,30]

Mattoussi et al. found that dihydrolipic acid (DHLA) could replace TGA to provide more stable interactions with CdSe/ZnS QD surfaces due to the bidentate chelate effect afforded by the dithiol groups.[9] Such substitution from monothiol to dithiol ligand greatly improved the long-term stability of the QDs, suggesting a more effective inference for polydentate thiolated ligands.[9,31] In our recent work, we also found that, besides dBSA, some multi-thiol-group biomacromolecules we synthesized had a similar effect on the enhancement of the QD's PL QY, and the CdTe QDs coated with these new compounds could indeed exhibit a brighter fluorescence than the original ones. An obvious blue shift of PL peak also occurred in these systems (Q. Huang and G. Shin et al., unpublished results).

In fact, after dBSA is added into the TGA-coated CdTe QD solution, the dissociation of some of Te atoms from QD surface and the attachment of dBSA at the defect site should simultaneously occur, resulting in both an enhancement of PL QY and a blue shift of PL peak. Due to high surface-to-volume ratio, the small-sized QDs have higher defect density and more Te atoms with dangling bonds on their surface.[26] The dissociation of Te atoms from the surface of small-sized QDs and the formation of $CdTe_x(dBSA)_{1-x}$ complex structure lead to a larger decrease in QD size, which is responsible for a greater blue shift of PL peak. It needs a longer time to reach saturation for the passivation of the QD surface. Due to the formation of the mixed CdTe(S) shell, there are less Te atom defects and dangling bonds on the QD surface of the large-sized QDs. Therefore, the passivation of QD surface with dBSA can easily reach saturation. As a result, it is likely that a combination shell of CdTe(S) and complex $CdTe_x(dBSA)_{1-x}$ layers forms around the "core" for the large-sized CdTe QDs. Of course, the nonlinear relationship between the QD sizes and their corresponding PL wavelength may be one of the reasons why the small-sized QDs have a larger peak shift than the larger sized ones.[32]

As discussed above, dBSA indeed plays an important role in the improvement of both chemical stability and PL QY of water-soluble CdTe QDs. However, either too low or too high dBSA/CdTe QD ratio (r) results in a lower PL intensity. When the ratio is too low, the surface defects and dangling bonds cannot be passivated well due to the lack of sufficient quantity of dBSA. Therefore, the CdTe QDs become unstable, showing a lower PL QY and a tendency toward agglomeration. For example, at dBSA/QD ratio r equal to 0.11, the PL intensity is far lower than that of the original TGA-coated QDs, while the PL peak shifts to red accompanied by a broadening of bandwidth due to poor stability of QDs. If the ratio r is too high, the excessive dBSA generates an additional trap state, which is the center of nonradiative recombination. In other words, once these defect sites are saturated, the additional dBSA plays a role of hole traps, resulting in a lower PL emission.[29]

Conclusions

In summary, the biomacromolecules with multi-thiol groups, such as denatured bovine serum albumin (dBSA), have been used as capping agents to modify the surface of water-soluble CdTe QDs and render CdTe QDs more stable. Due to its cooperative and amplifying effects of the multiple binding sites, dBSA provides enhanced coordinated interactions between CdTe surface and sulfur atoms through the formation of shell-like $CdTe_x(dBSA)_{1-x}$ complex. Such a shell structure results in not only the removal of dangling bonds of Te atoms from the CdTe surface but also the formation of a thermodynamically stable core−shell-like structure, leading to a better confinement of photogenerated charge carriers. Therefore, the dBSA-coated CdTe QDs exhibit a higher stability and photoluminescence quantum yield (PL QY) than the original TGA-coated CdTe QDs. In addition, the blue shifts of emission spectra of the dBSA-coated CdTe QDs with the storage time offer an alternative to conventional synthetic strategies for achieving different emission colors. This study provides CdTe QDs with more opportunities for applications in either biological or medical fields.

Acknowledgment. We thank Dr. Karen Schaich for the use of UV/Vis spectrometer and Dr. Richard Ludescher for the use of fluorescence spectrophotometer. This work was supported by ACS-PRF (41333-G7).

References and Notes

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