Study of Fluorescence Quenching and Dialysis Process of CdTe Quantum Dots, Using Ensemble Techniques and Fluorescence Correlation Spectroscopy

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Luminescence properties of quantum dots (QDs) are closely related to their surface structure and chemical properties. In this work some ensemble techniques and fluorescence correlation spectroscopy (FCS) were used to study the fluorescence quenching and dialysis process of CdTe QDs. It is found that when some heavy metal ions, such as silver ions (Ag^+), quench QDs, the free Ag^+ ions bind with bare Te atoms and form the AgTe structure on the surface. The FCS experimental results show that the quenching process is not the gradual reduction of fluorescence intensity of single QDs, but the decrease in the number of bright QDs with the addition of Ag^+ ions. In other words, the bright QDs turn into dark directly in the quenching process. It is observed that some dark QDs converse into the bright QDs in the dialysis experiments and the dialysis process can improve the brightness per QDs. Furthermore, the results of FCS and fluorescence spectroscopy illustrate that the increase of the fluorescence quantum yield (QY) is mainly attributed to the removal of excess unreacted Cd-MPA complex and the possible chemical change of the QDs surface in the dialysis process. These new results can help us to further understand the complex surface structure of water-soluble QDs, improve their surface chemical features, and expand their applications in some fields.

1. Introduction

In the two past decades, quantum dots (QDs, also know as nanocrystals) have received wide interest due to their unique physical and chemical properties, such as size-dependent tunable photoluminescence, broad excitation spectra, narrow emission bandwidths, and good photostability.[1−3] Recently, the great advances in the surface chemistry of QDs allow them to be effective in practical applications, such as multicolor biological imaging and detection.[4−6,7−11] Certain techniques (including surface modification chemistries) are developed to synthesize hydrophilic QDs with surface chemistry adaptable to various biological applications.[12−17] Luminescence properties of QDs are closely related to the nature of their surface.[18−20] Morphologically, there are certain trap sites on the QDs surface, and these trap sites can dramatically reduce the photoluminescence (PL) efficiency of QDs.[21] It is believed that during the surface modification process the enhancement of luminescence is the result of the elimination of traps sites and surface passivation.[22−24] And those surface modification techniques strongly affect other colloidal and photophysical properties of QDs, such as size and aggregation, etc. Many ensemble techniques have been used to monitor the change of their surface chemistry and colloidal properties of QDs, including UV/vis absorption and fluorescence spectroscopy, transmission electron microscopy (TEM), X-ray photoemission spectroscopy (XPS), and atomic force microscopy (AFM). But these ensemble-averaged measurements cannot reflect the interaction between individual molecules and QDs because the dynamic behavior of individual QDs has been averaged and hidden. The complexity of the surface chemistry of QDs is still not explicit.

Fluorescence correlation spectroscopy (FCS) is an ultrasensitive and noninvasive detection technique that uses statistical analysis of the fluctuations of fluorescence emitted from a small, optically well-defined open volume element.[25,26] The autocorrelation function can provide us some important information, such as the average number of luminescent particles in the volume and the coefficient of diffusion. Meanwhile, the changes of ensemble luminescence intensity and the brightness per particle (BPP) can be measured based on count rate and the number of bright particles. As a result, the use of FCS offers the unique opportunity to study luminescence quenching and the surface chemical properties of QDs. The concept of fluorescence correlation spectroscopy (FCS) emerged in the early 1970s,[27,28] but until Rigler et al. adopted the confocal detection system, this technique had not gained wide application in many fields.[29] Now FCS has been used to characterize certain parameters of water-soluble QDs, such as their concentration, brightness, hydrodynamic radius, and monodispersity.[9,30−33] The fluorescence quenching and enhancement are the results of the modification from atoms and molecules located near the surface, and their studies give new insights into the surface chemistry of QDs. Fluorescence quenching has been successfully exploited in the pursuit of understanding complex macromolecular systems in both chemical and biological fields. The quenching process of QDs can be believed as the binding of a quencher molecule to the surface of QDs and turning the "bright" QDs into the "dark" QDs. It can result from different processes, such as energy transfer, electron transfer, etc. But from the viewpoint of surface chemistry, all the quenching processes of QDs are the result of surface structure change of QDs. So the study of quenching of QDs will open a window for us to understand further the surface structure of QDs. Several groups reported the presence of a dark subpopulation of QDs in the QDs sample.[9,31,34] The "dark" QDs contain certain defect sites, and

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they can be regarded as the quenched QDs. The dialysis process eliminates some free ions and stabilizers from a sample solution, and it can also be regarded as the reverse process of quenching of QDs or possible chemical and structure change of the surface of QDs. Here we used a combination of ensemble spectroscopic methods and FCS to characterize the fluorescence quenching and dialysis processes of CdTe QDs. The relationship between the number of "bright" QDs and luminescence intensity during the quenching and dialysis process was investigated systematically by FCS.

2. Experimental Section

2.1. Materials and Reagents. In experiments, all chemicals used were of the highest purity commercially available. Rhodamine green and Rhodamine 6G were purchased from Molecular Probes (Eugene, OR). Mercaptopropionic acid (MPA) was acquired from Aldrich-Chemie (Steinheim, Germany). The 12 000 molecular weight cutoff dialysis membrane tubing (Thomas Scientific, Philadelphia, PA) was used in the dialysis experiments. All solutions were prepared with ultrapure water purified on Millipore Simplicity (Millipore), and filtered through 0.22 μm membrane filters (Shanghai Bandao Co., China) prior to use.

2.2. Synthesis of Water-Soluble CdTe QDs. Water-soluble CdTe QDs were prepared as described.[35] Briefly, Cd precursor solutions were prepared by mixing a solution of $CdCl_2$ in the presence of MPA, and were then adjusted to pH 8–9 with 1 M NaOH. The solution was deaerated with N_2 for 30 min. Under vigorous stirring, the oxygen-free NaHTe solution prepared according to the reference was injected.[5] The typical molar ratio of Cd^{2+}:NaHTe:MPA was 4:1:10 in our experiments. The mixture solution was heated under microwave irradiation and the size of the prepared QDs could be tuned by changing reaction temperature and reaction time. The prepared CdTe QDs solutions were purified by precipitating with isopropyl alcohol, centrifuging, and then drying in a vacuum.

2.3. Characterization of CdTe QDs with Ensemble Techniques. UV/vis absorption spectra of CdTe QDs were obtained by using a Lambda 20 UV/vis spectrophotometer (Perkin-Elmer, USA). Photoluminescence spectra were recorded on a Varian Cary fluorescence spectrophotometer. All optical measurements were carried out at room temperature. The quantum yield (QY) of CdTe QDs was measured according to the method described in ref 42. Rhodamine 6G (ethanol as solvent) was chosen as a reference standard (QY = 95%). X-ray powder diffraction (XRD) spectra were taken on a Bruker AXS D8-advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$Å).

2.4. Fluorescence Correlation Spectroscopy. Fluorescence Correlation Spectroscopy (FCS) measurements were performed with a home-built FCS system.[36] In brief, the 488 nm laser line from an argon ion laser (43 Series, Melles Griot, CA, USA) was attenuated to 40 μW by a circular neutral density filter, and then expanded to underfill the back aperture of the objective lens. The expanded laser line was focused with a water immersion objective (UplanApo, 60×NA1.2, Olympus, Japan) to a small volume within the diluted sample. The resulting excitation volume is on the order of 1 fL. The excited fluorescence signal collected by the objective passed through the dichroic mirror (505DRLP, Omega Optical, USA) and then was filtered by a band-pass filter (530DF30, Omega Optical, USA) to block scattering laser light. Finally, the fluorescence was coupled into a 35-μm pinhole at the image plane in front of the single-photon counting module (SPCM-AQR16, Perkin-Elmer EG&G, Canada). The fluorescence fluctuations were

correlated with a correlator card (ALV-5000/EPP, ALV-GmbH, Germany). All raw FCS data were analyzed with the standard equation for particles diffusing in a three-dimensional Gaussian volume element and nonlinearly fitted with the Microcal Origin 6.0 software package based on the Levenberg–Marquardt algorithm.

$$G(\tau) = \frac{1}{N} \frac{1}{\left(1 + \dfrac{\tau}{\tau_D}\right)} \frac{1}{\sqrt{1 + \left(\dfrac{\omega_0}{z_0}\right)^2 \dfrac{\tau}{\tau_D}}} \tag{1}$$

The number of bright QDs was acquired by taking the inverse of the correlation amplitude, and the brightness per particle (BPP) was calculated on the basis of the acquired number of bright QDs and average count rate.

2.5. Quenching Procedures. Into a 10-mL calibrated test tube was successively placed 2 mL of 1 mg/mL purified CdTe QDs and different amounts of quencher, then the solution was diluted to the mark with ultrapure water and mixed thoroughly. The solution was measured with ensemble spectroscopic methods and FCS after the same waiting time.

2.6. Dialysis Procedures. Ten milliliters of the unpurified CdTe QDs were placed into the dialysis tubing, and then the solution was dialyzed against the ultrapure water. Ensemble spectroscopic and FCS measurements were done every 3–5 h during dialysis.

2.7. Element Analysis by ICP-AES. The solutions of CdTe QDs were quenched with different amounts of Ag^+ ions and dialyzed in the ultrapure water to eliminate free Ag^+ ions for 12 h. Then the quenched QDs solutions were precipitated with isopropyl alcohol, centrifuged, and then dried in the vacuum heater. ICP-AES performed by IRIS Advantage 1000 (Thermo Jarrell Ash Co.) was to characterize the contents of some elements. The purified CdTe powder (identified as crude CdTe sample) was characterized by ICP-AES directly.

3. Results and Discussion

3.1. Study of Fluorescence Quenching with Ensemble Spectroscopy. Our preliminary experimental results showed that some heavy metal ions, such as Cu^{2+}, Hg^{2+}, and Ag^+, had fluorescence quenching of CdTe QDs. Of these ions, Ag^+ ions possessed the strongest fluorescence quenching effect, and therefore it was chosen as a model quencher in the steady state quenching experiments. Figure 1A displayed the typical fluorescence spectra as functions of the quencher concentration. It was observed that the emission intensity reduced successively with the increasing of the Ag^+ ion concentration and decreased to approximately one-fifth of the initial intensity in this study. Meanwhile, the spectral wavelength maximum was red-shifted for 15 nm. It is indicative that the Ag^+ ions are bound to the surface of QDs and the surface state of QDs is changed. Fluorescence quenching of CdTe QDs was best described by the well-known Stern–Volmer equation

$$\frac{I_0}{I} = 1 + K_{sv}C \tag{2}$$

where I_0 and I are the intensity in the absence and presence of the quencher (Ag^+ ions), K_{sv} is the Stern–Volmer quenching constant, and C is the concentration of the quencher. In Figure 1B, K_{sv} is found to be 2.8×10^5 mol^{-1}.

According to Langmuir law, the surface of QDs consists of a finite number of binding sites. Each site can link with one Ag^+ ion in the solution. So the rate of ions binding to the surface

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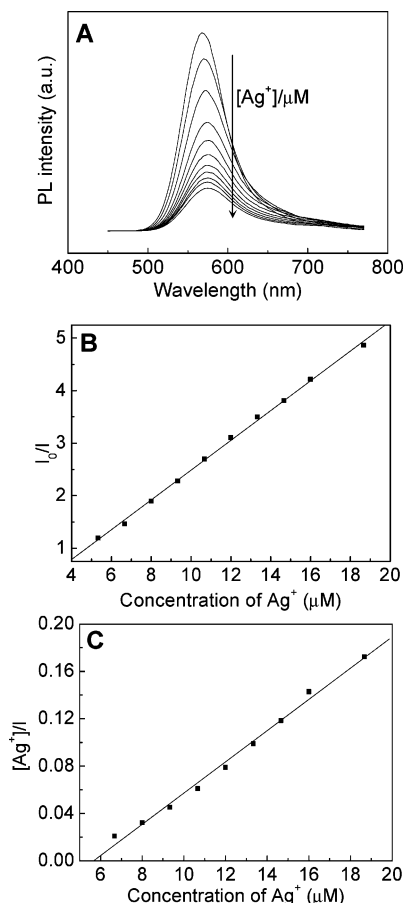
Figure 1. (A) PL measurements of CdTe QDs solution (200 μg/mL) as titrated with aliquots of Ag$^+$ ions (2 × 10^{-4} mol/L). (B) Stern–Volmer plot of the fluorescence of CdTe QDs vs the Ag$^+$ ion concentration. The straight line is the best fit of the data to eq 1. (C) Langmuir binding isotherm description of CdTe QDs quenched with Ag$^+$ ions. The straight line is the best fit of the data to eq 2.

of QDs is proportional to the concentration of Ag$^+$ ions in the solution. Chen and Rosenzweig believed that there was the following relationship between the quencher concentration and fluorescence intensity:[37]

$$\frac{C}{I} = BI_0 \frac{C}{I_0} \qquad (3)$$

where I_0 and I are the intensity in the absence and presence of the quencher, respectively, C is the concentration of quencher, and B is the binding constant. In the quenching experiments of CdTe QDs, the plot of C/I as a function of C is shown in Figure 1C. A good linearity (correlation coefficient was higher than 0.995) was obtained in the wide range of Ag$^+$ ion concentration, which suggested that binding of the Ag$^+$ ion with QDs complied with the Langmuir law.

Several mechanisms have been proposed to explain the process of some heavy metal ions (such as Cu^{2+} and Hg^{2+}) quenching QDs. Liang and co-workers found that Ag$^+$ ions could replace the surface Cd(II) ions of CdSe QDs and release Cd(II) into the solution because of the extremely low solubility of Ag$_2$Se compared with that of CdSe.[38] Kim and co-workers believed that carboxyl groups were important for coordinating with quenching ions.[39] In our quenching experiments, to further investigate the reaction mechanism of Ag$^+$ ions with CdTe QDs, the CdTe QDs were characterized by ICP-AES and XRD. In the experiment, the solutions of CdTe QDs were first quenched with different amounts of Ag$^+$ ions, and then extensively

TABLE 1: The Molar Ratios of Cd, S, and Ag to Te of CdTe QDs Samples Characterized by ICP-AES

molar ratio[a]	Cd/Te	S/Te	Ag/Te	Te[b]
sample A	3.00	3.54	N/A	1
sample B	2.99	2.67	N/A	1
sample C	2.95	2.78	0.37	1
sample D	3.06	3.04	0.83	1
sample E	2.98	3.35	1.50	1

[a] Sample A: crude CdTe QDs sample. Sample B: dialyzed CdTe QDs sample. Sample C: 1/2 quenched CdTe QDs sample. Sample D: 3/4 quenched CdTe QDs sample. Sample E: completely quenched CdTe QDs sample. [b] Te is set as 1.
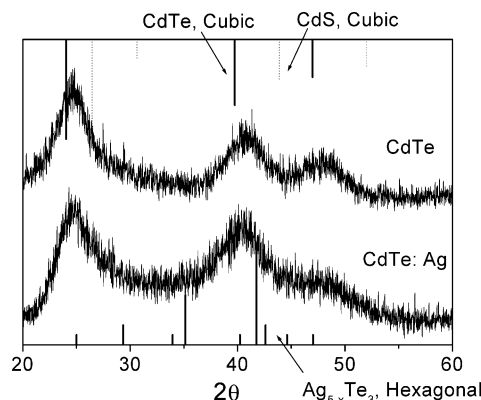
Figure 2. The powder X-ray diffraction patterns of the CdTe QDs and quenched CdTe QDs.

dialyzed against the ultrapure water to remove free Ag$^+$ ions for 12 h. The dry powder samples of quenched CdTe QDs for ICP-AES and XRD were prepared according to the purification process of CdTe QDs. The crude and dialyzed CdTe QDs samples were used as the references. To make clear the content change of elements of the quenched QDs sample, Te content is set as 1 and the molar ratios of Cd, Ag, and S versus Te were calculated and given in Table 1. It was found that the molar ratios of Cd/Te of samples were almost unchangeable with the addition of quencher Ag$^+$ ion. So the assumption of ion exchange between Cd ion and Ag ion in our experiment seems to be unreasonable according to this result. QDs have a very large surface-to-volume ratio and about 10−50% of total atoms are exposed on their surfaces. Systematic investigations on the CdTe QDs have also revealed that Te atoms on the surface of QDs affect fluorescence QY greatly.[20] Since the extensive dialysis experiment can eliminate the effect of the content of Ag due to the physical absorption of Ag ions on the surface, the increase of content of Ag should mainly be attributed to the formed bonds between Ag and the bare surface atoms of QDs. The XRD spectra as shown in Figure 2 confirmed the existence of AgTe besides CdTe and CdS. CdS was attributed to the thiol group on the surface of CdTe. It was obvious that thiol groups of the dialyzed sample had dissociated from the surface of QDs on the basis of the decrease of S/Te compared with the crude sample. The molar ratio of S/Te increased with the addition of Ag$^+$ ion from zero to completely quenched CdTe; however, they were all less than the value of the crude CdTe sample. This result indicated that while the added Ag$^+$ ions were bound to the surface of QDs, they could stabilize the ligand MPA on the surface of QDs further. On the basis of the above-mentioned results, the change of the particle surface structure in the fluorescence quenching was illustrated in Figure 3. When the quenching happens, Ag$^+$ ions enter the bare Te atom sites and form the AgTe structure, which is responsible for the red shift and quenching phenomenon. The Ag$^+$ ions on the surface

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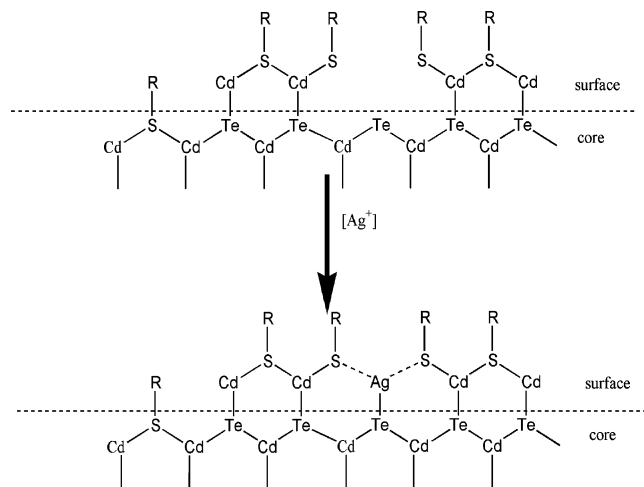
Figure 3. Schematic illustration of the surface structures of CdTe QDs and CdTe QDs quenched by Ag^+ ions. R represents a carboxylic acid group.

of QDs can also interact with the near thiol group, which could explain the results in Table 1.

3.2. Study of Fluorescence Quenching with FCS. In the FCS experiment, the fluctuation of fluorescence ($I(t)$) is recorded in real time and the correlation function is calculated as a function of time. These fluctuations are the results that fluorescent molecules diffuse in or out of the optically well-defined open volume element. The fluctuations are also induced by the change of fluorescence intensity of fluorescent molecules, for example, fluorescent molecules transform to nonfluorescent

molecules or inversely. In the fluorescence quenching of CdTe QDs, the "bright" QDs change into the "dark" and the intensity of fluorescence decreases gradually with the adding of Ag^+ ions into the solution. FCS is well suitable for the characterization of fluorescence quenching since the amplitudes of FCS curves can reflect the number change of the bright QDs. The FCS curve of CdTe QDs titrated with standard Ag^+ ion solution is shown in Figure 4A. It was observed that with the increase of the Ag^+ ion concentration, the number of "bright" CdTe QDs decreases and the diffusion time remains almost constant. When the Ag^+ ion concentration was more than 4 μM, it was observed that the fitting curves were not properly fit anymore with the autocorrelation curves. This was probably attributed to the partial aggregation between the brighter QDs and quenched QDs driven by heavy-metal ion recognition and binding for a high concentration Ag^+ ions.[39] Meanwhile, Figure 4D shows that the change of the brightness percent particle (BPP) is very small (negligible) although the determined count rate reduces to only about 10% of the initial value. That is to say, when the majority of QDs was quenched, in the solution there were still a few "bright" QDs. This result demonstrated that when the quenching ions were bound to the surface of QDs, the "bright" QDs turned directly into the "dark" QDs, and the brightness of the unquenched QDs did not decrease. To demonstrate the applicability of the Stern−Volmer description for the binding of Ag^+ ions to QDs with FCS data, the plots of N_0/N and CR_0/CR as a function of concentration of Ag^+ ions are obtained in Figure 4B and Figure 4C. N and CR are the number and count rate of bright QDs at a given number of Ag^+ ions, respectively. $K_{sv,occupany}$ and $K_{sv,CR}$ are found to be 7.4×10^5 mol^{-1} and
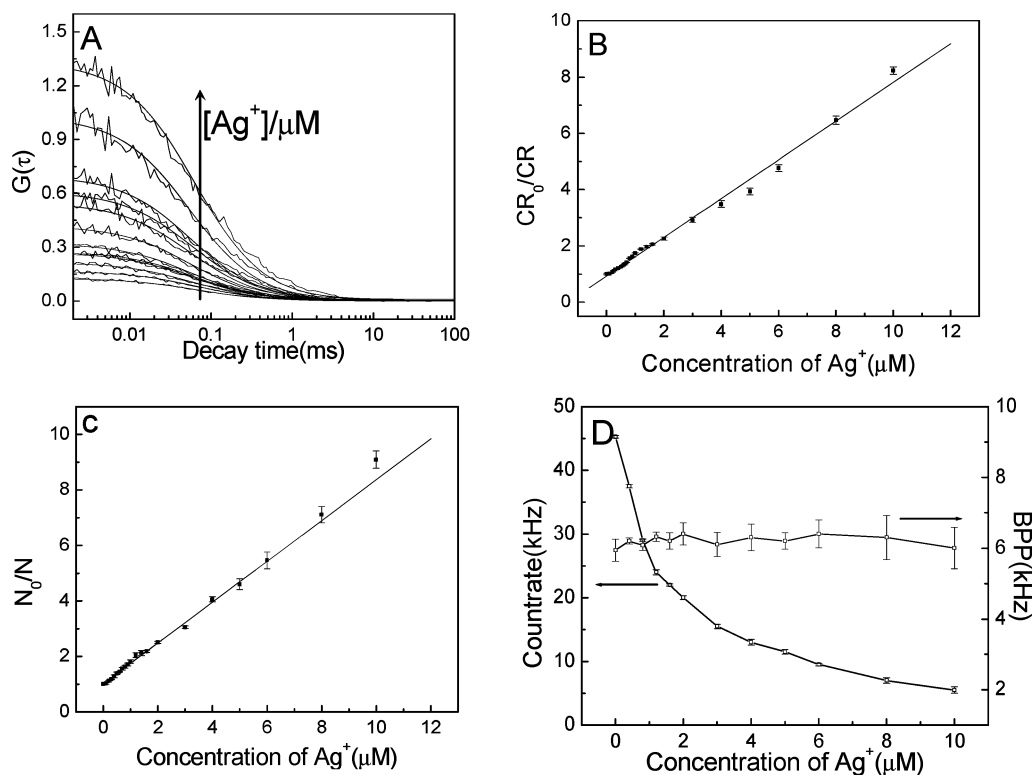
Figure 4. (A) Typical FCS curves of CdTe QDs solution quenched with different concentrations of Ag^+ ions. The concentration of CdTe QDs solution was 100 μg/mL. The smooth lines were the Levenberg−Marquardt nonlinear fitting curves. (B) Stern−Volmer plot of the count rate (CR) of CdTe QDs vs the Ag^+ ion concentration obtained from FCS data. CR is the count rate of CdTe QDs at a given number of Ag^+ ions. The straight line is the best fit of the data to eq 1. (C) Stern−Volmer plot of the count rate of CdTe QDs vs Ag^+ ions concentration obtained from FCS data. N is the number of bright CdTe QDs at a given number of Ag^+ ions. The straight line is the best fit of the data to eq 1. (D) Silver ion concentration dependence of count rate and BPP of the bright QDs. The count rate (CR) decreased with the addition of Ag^+ ions, but the BPP remains almost constant. The acquisition time of each FCS measurement is 30 s and the error bars are calculated according to 10 repeated measurements. N is obtained from the reverse of fitted $G(0)$ and CR is the mean of the count rate of each FCS measurement.

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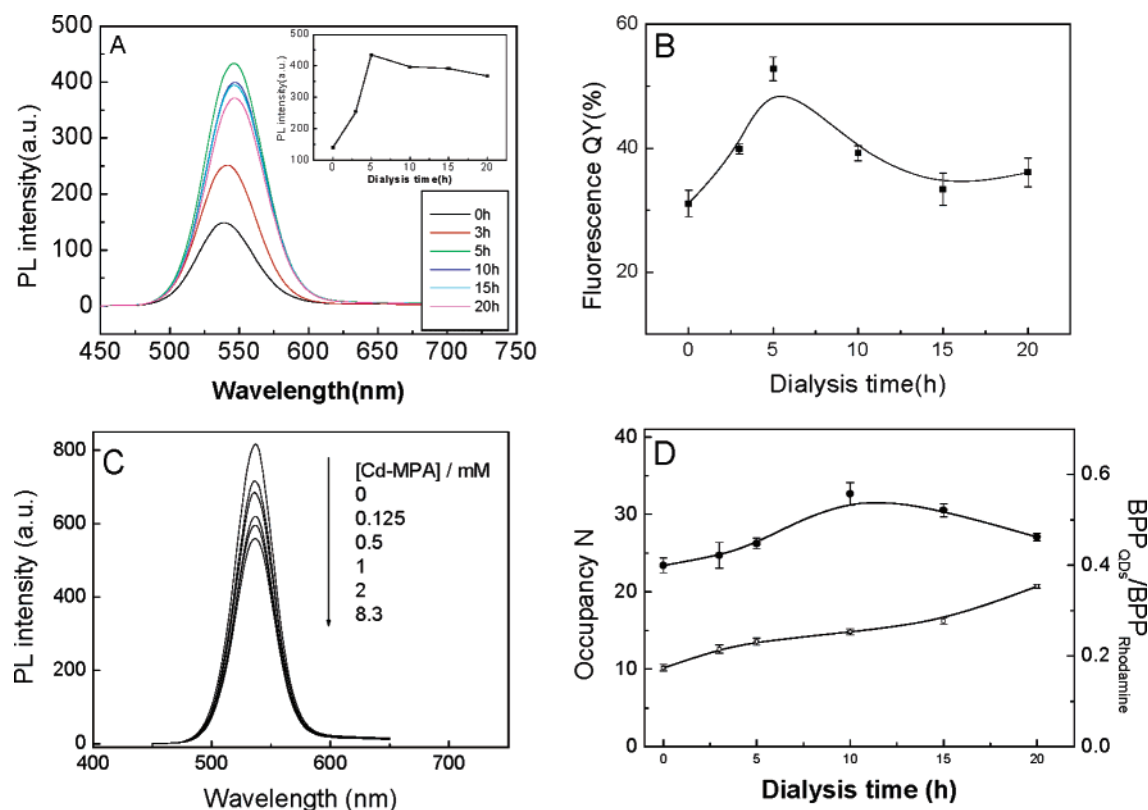
Figure 5. (A) Fluorescence spectra of CdTe QDs at the different dialysis time. Inset: the dialysis time dependence of the fluorescence intensity of CdTe QDs. (B) Plot of the fluorescence QY of CdTe QDs vs dialysis time. (C) Fluorescence emission spectra of the new dialyzed CdTe QDs in aqueous solution adding the [Cd-MPA] solutions containing the concentrations of 0.0, 0.125, 0.5, 1.0, 2.0 and 8.3 mM. (D) Dialysis time dependence of the occupancy N of the bright QDs and relative BPP using Rhodamine Green as standard. The acquisition time of each FCS measurement is 30 s and the error bars are calculated according to 10 repeated measurements. N is obtained from the reverse of fitted $G(0)$ and CR is the mean of count rate of each FCS measurement.

6.2×10^5 mol^{-1}, and both correlation coefficients of the linear fitting are higher than 0.99. This implies that in FCS the dependence of the number and count rate of "bright" QDs upon the quencher concentration can also be well described by the Stern−Volmer equation, and this equation reflects the quenching mechanism of QDs.

3.3. Effects of Dialysis on CdTe QDs. It was reported that in the synthesis of CdTe QDs, proper dialysis could significantly enhance the fluorescence intensity and QY.[40] In the prepared CdTe QDs solution, excess unreacted MPA forms Cd-MPA complexes with free cadmium ions.[38] When the prepared QDs solution (pH 8−9) was dialyzed against ultrapure water, the following processes took place, including (1) a slight increase in the acidity of the QDs solution, (2) the removal of the excess unreacted cadmium ions and MPA complex, and (3) a possible chemical change on the surface of QDs. The dissociation and association of Cd-MPA complexes on the surface are dynamic processes. As stated before, the loose-bound MPA can depart from the surface of QDs in the dialysis process. Accompanied by the dissociation of MPA from QDs surface, the free MPA can also associate with QDs. The association of MPA on the surface of QDs can remove part of the trap sites, turn the "dark" QDs into the "bright" ones, and improve the fluorescence efficiency of ensemble QDs.

Hereby the CdTe QDs were dialyzed against the ultrapure water over different periods of time, and the mechanism on fluorescence efficiency changes with dialysis was investigated systemically at the ensemble level by fluorescence spectroscopic methods and at the single molecular level by FCS. As Zhang et al. reported,[5] we also found that the fluorescence intensity of CdTe QDs reached the maximum at pH 6−7, and the change

of fluorescence intensity was not apparent in the pH range of 6−8 (data not shown). The fluorescence spectra of QDs under different dialysis times are shown in Figure 5A. The change of fluorescence intensity and QY of dialyzed CdTe QDs against dialysis time is shown in Figure 5B. The fluorescence intensity and QY increased gradually with time, and the fluorescence intensity and QY reached a maximum after 5 h of dialysis. The fluorescence intensity of the QDs solution dialyzed for 5 h increased up to 3.1 times compared to that of the initial sample solution. This result suggests that other processes can also improve the fluorescence QY, such as the elimination of excess cadmium ions and MPA and possible chemical and structure change besides the adjustment of acidity. It was found thatthe Cd-MPA complex affected the fluorescence intensity of the new dialyzed QDs. As shown in Figure 5C, adding Cd-MPA complex ([Cd^{2+}]/[MPA] = 1/2.5, pH 9.0) into the new dialyzed QDs solutions can lower their fluorescence intensity but the process does not comply with the Stern−Volmer equation. And the fluorescence decline is partly due to the slight increase of pH with adding the highly concentration Cd-MPA complex into the dialyzed QDs solutions. Meanwhile, excess Cd-MPA complex induces a possible chemical and structure change on the QDs surface. Peng and co-worker believe that the surface structure of the QDs themselves plays an important role in determining the PL properties of the QDs.[43] In our experiment, the chemical and structure change is more and more evident with the dialysis time prolonged. The fluorescence decreased with increasing dialysis time. And aggregation of QDs and weak fluorescence of QDs was observed when the dialysis time was more than 30 h. This change was related to the excess dissociation of MPA as stabilizer of high surface-to-volume

ratio QDs. Although the maximum point of QY is a signature of an optimal surface structure for fluorescence of QDs in the dialysis process, the surface structure state is unstable and apt to be affected by the chemical environment. At present it is still difficult to experimentally analyze the change of surface structure of QDs in detail. Obviously, it is essential to control the dialysis time and hold the optimal concentration of Cd-MPA complex for maintaining the fluorescence of CdTe QDs.

FCS was used to further investigate the effects of the dialysis process on the QDs. Figure 5D describes the relationship between the occupancy N (the relative number of bright QDs inside the detection volume element), BPP, and the dialysis time. It was documented that the occupancy N increased with prolonged dialysis time (excess Cd-MPA removed). In theory, QDs that turn brighter will probably result in a minor change of the amplitude since the brighter QDs contribute more to the autocorrelation function than the dimmer ones. But as shown in Figure 5D, the occupancy was doubled in the dialysis process. So the increase should not be due to the minor change of amplitude for those brighter QDs. The explanation that some "dark" QDs had turned into the "bright" ones sounds more rational. And this result supported Ebenstein's report that there was a subpopulation of QDs in a long-lived dark state. Meanwhile, it illustrated that this subpopulation of QDs was not in an always-dark state and the dialysis process could turn part of the "dark" QDs into "bright" ones besides the other methods including light irradiation, optimization of inorganic coating, and optimization of organic coating. Although fluorescence QY is proportional to BPP or the occupancy N, BPP cannot be equal to QY directly. As shown in Figure 5D, at the early stage of dialysis, most of the excess MPA and cadmium ions are removed, so BPP and N increases gradually, and QY reach the maximum in a dialysis time of 5 h. But BPP decreases with the excessive removal of MPA on QDs surface although the dialysis process continues to turn the "dark" QDs into the "bright" ones with longer dialysis time. Different from those ensemble techniques, FCS implies us that two methods can be used to enhance QY of ensemble QDs, which include increasing BPP of QDs or the number of "bright" QDs.

4. Conclusions

The surface structures of water-soluble QDs are complex in solution. Its structure is apt to be influenced by the surface environment of QDs because of the very large surface-to-volume ratio and abundant bare atoms on their surfaces. Some processes, such as photoactivation and quenching, can change their surface structures and affect their fluorescence QY markedly. In this paper, ensemble techniques and FCS have been used to study the surface chemistry of CdTe QDs in the fluorescence quenching and dialysis process of QDs. The fluorescence quenching of CdTe QDs could be explained with the mechanism that the ions (Ag^+) bound with bare Te atoms and formed the AgTe structure on the QDs surface. Importantly, it was found that the quenching process did not result in the gradual reduction in the fluorescence intensity of single QDs, but the decrease in the number of bright QDs with the addition of Ag^+ ions. The enhancement of fluorescence intensity of the dialyzed QDs is the result of the removal of the Cd-MPA complex and possible chemical and structure change of the surface of QDs. And the existence of the maximal QY point confirms the change of surface structure of QDs in the dialysis process. It was observed from FCS data that the dialysis process could convert part of the "dark" QDs into "bright" QDs, and considerably improved the fluorescence intensity of single QDs. Our results further

illustrate that FCS is an effective tool for the characterization of QDs since only the bright QDs can function in the practical applications. Work is currently underway to more thoroughly reveal the surface structure of QDs.

Supporting Information Available: Plots of the residual curves at different concentrations of quencher [Ag^+]. This material is available free of charge via the Internet at http://pubs.acs.org.

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