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Enhancement Effect of Illumination on the Photoluminescence of Water-Soluble CdTe Nanocrystals: Toward Highly Fluorescent CdTe/CdS Core−Shell Structure

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A strong photoluminescence enhancement effect of illumination on CdTe nanocrystals stabilized by thioglycolic acid (TGA) was observed. Under optimized conditions, the fluorescence quantum yield of CdTe nanocrystals in aqueous solution reached 85% at room temperature. Optical measurements indicated that the photodegradation of TGA rather than NCs was the main reason for the PL enhancement effect since sulfide ions released from TGA during illumination coordinated with cadmium ions on the surface of CdTe and formed a shell structure of CdS there. X-ray photoelectron spectroscopic results further proved the formation of CdS shell on the CdTe core during illumination. The colloidal solution of CdTe/CdS core−shell nanocrystals with photoluminescence quantum yield higher than 80% turned out to be very stable. Therefore, the current investigations not only reveal the PL enhancement effect of illumination, but also provide a useful synthetic route for producing water-soluble and highly fluorescent CdTe/CdS core−shell nanocrystals.

Introduction

Due to quantum confinement effects, semiconductor nanocrystals (NCs) exhibit special physical and chemical properties which are greatly different from those of their corresponding bulks.[1−4] Over the past two decades, great efforts have been put into the synthesis of highly fluorescent II−VI semiconductor nanocrystals.[5−8] Up to now, the TOP/TOPO synthetic approach has become one of the most successful and mature methods for preparing highly fluorescent II−VI NCs.[5−6,9−10] In the best case, the fluorescence quantum yield (QY) of as-prepared CdSe NCs reached 85% which could be further raised by constructing a shell structure of either ZnS or CdS around the CdSe core.[5,10] Such high fluorescence quantum yields make these NCs potentially useful in electroluminescence devices as emitting materials,[11] or in biological and biomedical research fields as fluorescent labeling materials.[12] However, the direct product of the TOP/TOPO synthetic approach is insoluble in water, which to some extent limits applications of TOPO-stabilized NCs (TOPO, trioctylphosphine oxide) as bio-labeling materials. Therefore, different post-preparative procedures have been recently developed to transfer the TOPO-stabilized NCs from organic solvent into water. The main strategy is to replace the surface-binding TOPO with molecules that have either strong polar groups such as carboxylic acid,[12−15] or reactive groups such as Si−O−R.[16] The latter type of surface

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modification allows the following construction of hydrophilic SiO_2 layer around the fluorescent NCs core. However, the photoluminescence (PL) QY greatly decreases when the NCs are transferred into water—it only reaches 40–45% in the best cases[17]—which indicates that even perfect surface passivation achieved in organic solvent is not perfect anymore after the NCs are brought into water. This is because water is a strong polar solvent that can induce various equilibriums related to the NCs, which makes their surface passivation extremely difficult in an aqueous system.

An alternative way to the above-mentioned method for producing water-soluble cadmium chalcogenide nanocrystals is to directly synthesize the NCs in water. Different types of thiols are required as stabilizing agents in this synthetic route.[8,18] The typical fluorescence QY of the as-prepared CdTe NCs synthesized by this method can reach several percent. Systematic investigations on the CdTe NCs reveal that surface Te atoms with dangling bonds are responsible for the low fluorescence QY.[19] Therefore, effectively reducing the amount of surface Te will greatly improve the fluorescence QY. Several post-preparative methods have been adopted to obtain highly fluorescent CdTe prepared by this method. For example, the size-selective precipitation technique has been proven to be an important method to separate NCs of different sizes from an ensemble.[9] It can also be used to extract NCs with better surface passivation since these NCs possess the smallest growth rate.[20] Second, the formation of a shell structure of TGA–Cd complexes on the surface of CdTe can also improve the PL quantum yield of the CdTe NCs in aqueous solution.[8] Nevertheless, the optimized fluorescence quantum yield achieved by these two methods can only reach 40% in the best case, which indicates that all these measures can only improve the fluorescence QY to a certain level. Therefore, how much room one has to further increase the fluorescence quantum yield of II–VI NCs in aqueous solution remains an open question.

It has been demonstrated that using inorganic semiconducting materials with broader band-gap to form a shell structure on the surface of fluorescent NCs with narrower band-gap is an effective approach to reduce the surface traps of the core NCs.[5] One of the most successful systems is the CdSe/CdS core–shell nanocrystals prepared by the TOP/TOPO method, whose fluorescence quantum yield can reach nearly 100%.[5b] Many analogous works have been done in recent years following this strategy. But in aqueous systems, there are only a few successful examples toward such core–shell structure for II–VI fluorescent nanocrystals.[21,22]

Recently, it has been reported by different groups that illumination shows fluorescence enhancement effects on many II–VI semiconductor NCs.[20,23–26] Due to the complexity of the photochemistry for inorganic nanocrystals, so far most investigations were only concentrated on the understanding of the PL enhancement effects. Here we report preparation of water-soluble CdTe nanocrystals with fluorescence QY up to 85% at room-temperature achieved by illuminating the as-prepared CdTe NCs stabilized by TGA. These NCs turned out to be very stable in aqueous solution after illumination and no decrease in fluorescence QY was observed several months after they had been kept in a refrigerator. To our best knowledge, this is the highest QY for II–VI NCs in aqueous solution. Systematic investigations revealed that the PL enhancement effect achieved by illumination was strongly related to the photodegradation of TGA rather than CdTe nanocrystals themselves. Since sulfide ions were released during illumination, a highly fluorescent CdTe/CdS core–shell structure was constructed.

Experimental Section

Chemicals. Thiolglycolic acid (TGA) (Aldrich, 97+ %, product 475343), 3-mercaptopropionic acid (MPA) (Aldrich, 99+ %, product M5801), polyethylenimine (PEI) (Aldrich, product 181978), tellurium powder (Aldrich, −40 mesh, 99.997%, product 264865), $CdCl_2 \cdot 2.5H_2O$ (99+ %), and $NaBH_4$ (99%) are commercially available products and were used as obtained.

Synthesis of Fluorescent CdTe Nanocrystals. The colloidal CdTe solutions were prepared using a synthetic route reported earlier.[8] Tellurium powder was chosen as a starting material to prepare NaHTe aqueous solution. Briefly, it was reduced by slightly excessive sodium borohydride in water in an ice-bath. After Te was completely reduced, 0.5 M H_2SO_4 was introduced to generate H_2Te gas that was discharged by a N_2 flow into another flask containing 0.05 M NaOH aqueous solution. Finally, an aqueous solution of 0.05 M NaHTe was obtained. Then a certain volume of the NaHTe solution was injected into a $CdCl_2$ solution containing thioglycolic acid (TGA). The pH value of latter solution was fixed at 11.2. The molar ratio of $Cd^{2+}/Te^{2-}/RSH$ was set to 1:0.5:2.4. The reaction between cadmium ions and NaHTe took place immediately after the injection of NaHTe solution and changed the mixture from colorless to orange. Then the orange solution was heated till boiling. After being refluxed for 20 min, TGA-stabilized CdTe nanocrystals exhibiting green fluorescence were obtained. In similar way, CdTe nanocrystals stabilized by 3-mercaptopropionic acid (MPA) were synthesized.

Illumination of CdTe Nanocrystals. It was observed that the fluorescence of the TGA-stabilized CdTe nanocrystals in N_2-saturated aqueous solution can be greatly enhanced by illumination under room light of low-pressure mercury-rare-gas discharge lamps. Normally more than 20 days was required to bring the fluorescence quantum yield to its maximum. The final fluorescence quantum yield for the TGA-stabilized CdTe reached 85% at room temperature. After illumination, the highly fluorescent CdTe nanocrystals obtained presented excellent stability in aqueous solution. No

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evident change was observed so far with respect to both absorption and fluorescence 8 months after the illuminated CdTe aqueous was obtained.

Measurements of Fluorescence Quantum Yield. The fluorescence QY of the CdTe nanocrystals was carefully measured using Rhodamin 6G as fluorescence standard. In detail, Rhodamin 6G was dissolved in anhydrous alcohol with its absorbance around 0.018 at the excitation wavelength, normally 475 nm, where the diluted CdTe solutions showed the same absorbance. By comparing the integrated areas of emissions from Rhodamin 6G and CdTe, respectively, the fluorescence quantum yield of CdTe was calculated taking 95% for Rhodamin 6G in diluted solution.[27]

Fabrications of CdTe/PEI Multiplayer Films. To investigate both compositive and structural changes happening to CdTe nanocrystals during the illumination, the electrostatic layer-by-layer self-assembly method was adopted to deposit CdTe nanocrystals on silicon wafers in combination with polyethylenimine (PEI).[8b] CdTe nanocrystals and PEI were deposited in an alternating fashion. Normally films of 20 bilayers were prepared for X-ray photoelectron spectroscopy measurements.

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. Powder X-ray diffraction was taken with a Regaku D/Max-2500 diffractometer under Cu Kα radiation ($\lambda = 1.54056$ Å).

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB 220i-XL spectrometer. All binding energies for different elements were calibrated with respect to C1s line at 284.6 eV from the contaminant carbon. A combination of 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.

Results and Discussion

The evolutions of both absorption and fluorescence spectra of CdTe nanocrystals as functions of illumination time are presented in Figure 1a. Illumination leads to increases of absorbance in the whole absorption range. In the meantime, the 1s–1s excitonic transition becomes sharper with a red shift for the absorption onset. The fluorescence reacts accordingly to the changes in absorption. The photoluminescence intensity is simply enhanced as illumination is prolonged and shifts to lower energy side only by 15 nm along with the redshift for the absorption onset. Details are shown in Figure 1b. For comparison, a CdTe aqueous solution was prepared in exactly the same way but kept in dark. However, similar measurements revealed that there was nearly no change observed with respect to both absorption and fluorescence spectra. Therefore, it is reasonable to attribute the above observations to photorelated effects.

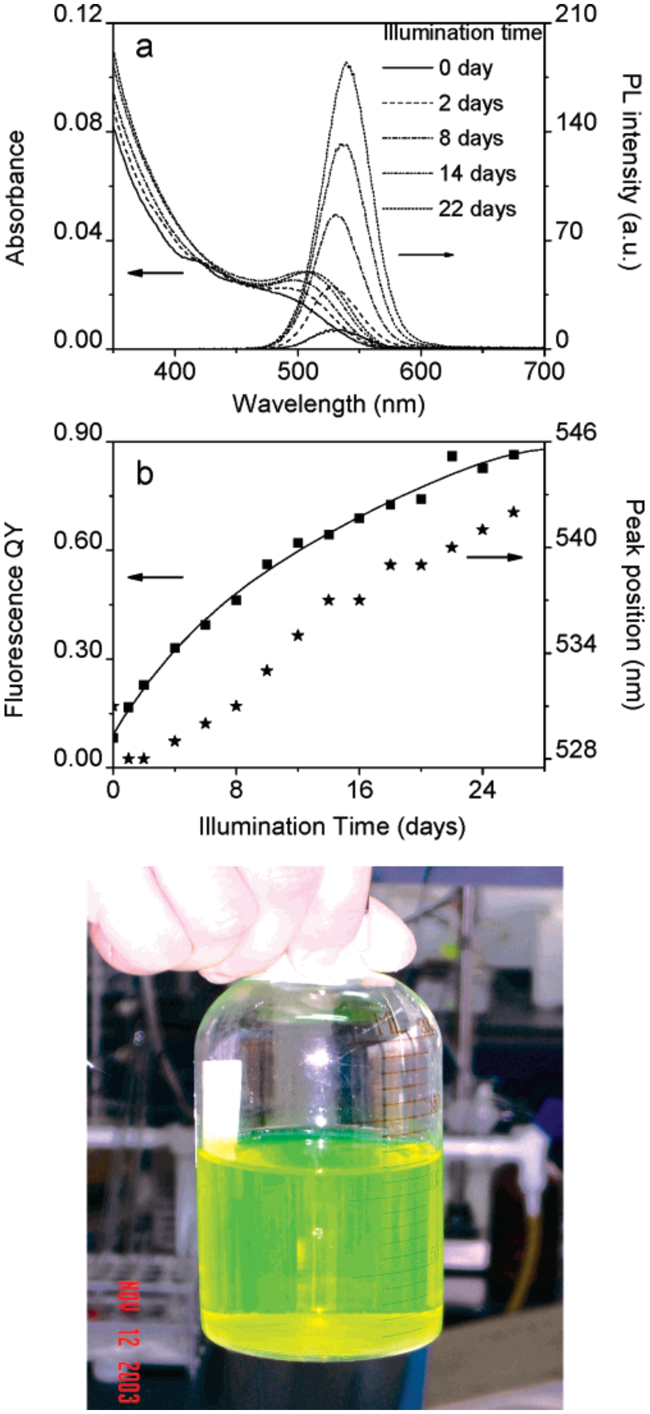

Figure 1. (a) Temporal behavior of absorption and PL spectra of the TGA-capped CdTe NCs recorded during illumination. The excitation wavelength for fluorescence measurements was 400 nm. (b) Fluorescence quantum yield (QY) and the PL peak position as functions of illumination time. The solid line is a guide for eye. The photograph at the bottom is an aqueous solution of CdTe NCs with fluorescence QY up to 85%. It was taken under normal room light without using additional excitation light source. The yellow-green color is from the fluorescence of CdTe NCs.

The fact that illumination can increase the PL of semiconductor nanocrystals has been reported by several groups.[20,23–26] Due to the large surface/volume ratio, nanoparticles have lots of surface dangling bonds which become reactive upon illumination. Up to now, illumination-assisting PL enhancement effects were generally explained by the photochemical degradations of nanoparticles themselves. In one of the recent publications from Gaponik, they reported quite similar photoenhancing PL from TGA-capped CdTe nanocrystals.[20a] Their explanation is the dissolution of nanocrystals induced by photochemical etching. Experimental results supporting this photochemical etching mechanism generally showed clear blueshifts for both fluorescence and absorption.[20,23] A different explanation is the ligand rearrangement induced by illumination for TOPO-capped CdSe nanocrystals. However, in this latter example, Asami and co-workers also observed a clear

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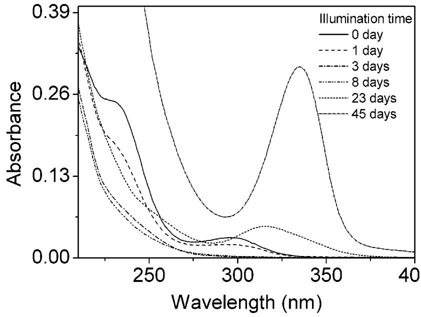


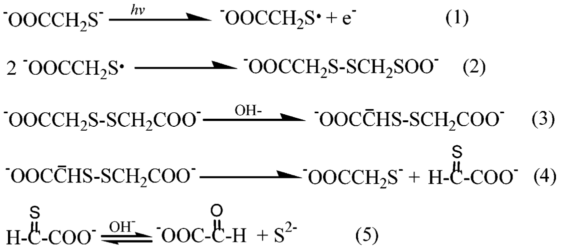
Figure 2. Evolution of absorption spectrum of thiolglycolic acid (TGA) in N_2-saturated aqueous solution recorded during illumination. The pH value of the TGA solution was 10.

blue shift in PL during the photobrightening process.[25] Nonetheless, all these mechanisms do not fully explain the spectroscopic changes shown in Figure 1.

In Figure 1a, only very slight blue shift with respect to fluorescence is presented after the first 2 days of illumination. During this period of time, the 1s−1s excitonic transition starts to become sharper. According to the mechanism proposed by Weller et al., the crude solution of CdTe contains nanocrystals of different qualities. The lower quality nanocrystals possessing more surface defects and lower photostability will be dissolved primarily upon illumination.[20] The resultant monomers of Cd and Te ions will fuse to higher quality nanocrystals that have the intermediate size in ensemble and the smallest growth rate as well. As a result of such selective photochemical etching process, the particle size distribution is narrowed, which on one hand sharpens the 1s−1s excitonic transition in absorption, and on the other hand gives rise to a blue shift in PL. But in the current experiment, the blue shift in PL is only several nanometers. This is because the CdTe NCs were kept in the N_2-saturated aqueous solution during illumination. The photodegradation of CdTe NCs was therefore much slower than that observed in ambient conditions by Weller.[20]

During the following stage of illumination, the most evident change is a drastic increase in PL. The selective photochemical etching mechanism proposed by Weller cannot explain this PL behavior because the heavy photochemical etching will cause strong blue shift in both absorption and fluorescence.[20] In contrast, the PL starts to shift slightly to red after the first 2 days of illumination. Therefore, it can be deduced that the following PL enhancement is not caused by further photodecomposition of CdTe itself. In the solution of the as-prepared CdTe, apart from CdTe NCs, there are excessive thioglycolic acid and cadmium ions. The latter do not react upon the illumination of room light. Therefore, photochemical decomposition of thioglycolic acid becomes the key to understanding the whole changes. It is known that thiol molecules can be oxidized and form disulfide upon illumination even in the absence of oxygen. Systematic research revealed that the oxidation of thiols is done via a radical mechanism.[28] The temporal evolution of absorption spectrum of thioglycolic acid is presented in Figure 2. A N_2-saturated TGA solution of 2.0×10^{-3} M was prepared and subject to illumination for different periods of time at a pH value of 10. Then it was diluted by 10× for UV−Vis absorption measurements. In Figure 2, two absorption peaks from TGA are shown before illumination. The first peak at 234 nm is attributed to the transfer of sulfur nonbonded electrons to C−S antibonding orbit.[29] The second peak at 295 nm appearing at pH value around 10 may be associated with the deprotonation of −SH since pK_a of RSH is 10.0. In alkaline range, the α-carbon may also be deprotoned,[30] as a result, *p* electrons delocalize throughout the molecule, which gives rise to the strong absorption at 295 nm. As illumination goes on, the absorption peaks at 234 and 295 nm start to decrease till the peak at 295 vanishes. Meanwhile, the characteristic odor of thiols becomes faint and finally disappears. This indicates the formation of dithiodiglycolic acid since it exhibits featureless absorption in the investigated wavelength range.[30] As illumination is further prolonged, the solution color changes to yellow and a new absorption peak appears at 313 nm. In addition to further increase in intensity, the newly developed peak at 313 nm finally shifts to 335 nm which is the characteristic absorption for thioglyoxylic acid. This is very well consistent with the results on cleavage of the disulfide bonds reported by Norman.[30] The overall reactions are listed in Scheme 1. In fact, to analyze the photodegradations of saturated aliphatic thiols is rather difficult.[29] We are not intending to depict all possible reactions for the photodecomposition of thioglycolic acids using Scheme 1. But what are certain of, from the spectroscopic changes in Figure 2, are the formations of dithiodiglycolic acid and thioglyoxylic acid. The following degradation of the thioglyoxylic acid took place in alkaline range and then released sulfide ions into the system (see eq 5 in Scheme 1). In the presence of CdTe and excessive cadmium ions in the system, sulfide ions may react with them in three different ways: (1) sulfide ions react with cadmium ions and form independent clusters in the solution; if this is the dominant process, it will only lead to increases in absorbance below 508 nm with characteristic absorption of CdS clusters,[5b] (2) sulfide ions may also incorporate into the lattice of CdTe nanocrystals and form alloy structures, but it should result in an obvious blue shift in PL[7b] (this is not observed in Figure 1a), and (3) sulfide ions may react with cadmium ions on the CdTe particle surface and form a shell structure of CdS. The last possibility seems to be most relevant to explain the PL changes in Figure 1a. Because CdS has broader band-gap than CdTe, the formation CdS shell on the

Scheme 1. Overall Reactions Initiated by Illumination for TGA in Alkaline Solution



$$^{-}\mathrm{OOCCH_2S}^{-} \xrightarrow{h\nu} {}^{-}\mathrm{OOCCH_2S}^{\bullet} + e^{-} \qquad (1)$$

$$2\ {}^{-}\mathrm{OOCCH_2S}^{\bullet} \longrightarrow {}^{-}\mathrm{OOCCH_2S\text{-}SCH_2SOO}^{-} \qquad (2)$$

$$^{-}\mathrm{OOCCH_2S\text{-}SCH_2COO}^{-} \xrightarrow{\mathrm{OH-}} {}^{-}\mathrm{OOC\bar{C}HS\text{-}SCH_2COO}^{-} \qquad (3)$$

$$^{-}\mathrm{OOC\bar{C}HS\text{-}SCH_2COO}^{-} \longrightarrow {}^{-}\mathrm{OOCCH_2S}^{-} + \mathrm{H\text{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{\text{-}COO}^{-} \qquad (4)$$

$$\mathrm{H\text{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{\text{-}COO}^{-} \overset{\mathrm{OH}^{-}}{\rightleftharpoons} {}^{-}\mathrm{OOC\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{\text{-}H} + \mathrm{S}^{2-} \qquad (5)$$

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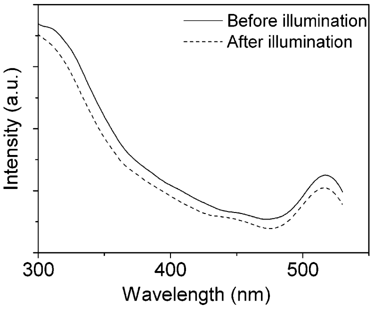

Figure 3. PL excitation spectra of the TGA-capped CdTe NCs recorded before and after illumination while PL was detected at 530 nm.

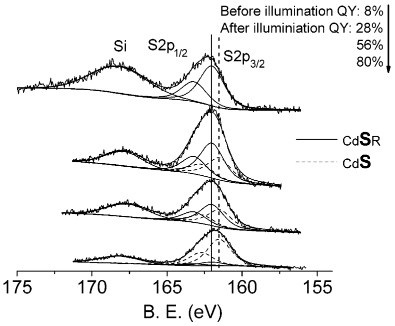

Figure 4. XPS spectra of S2p recorded from TGA-capped CdTe NCs incorporated in PEI matrixes by the electrostatic layer-by-layer self-assembly method. The vertical lines are guides for positions of $S2p_{3/2}$ from TGA-Cd and CdS, respectively. Their positions are 162.0 eV (Cd**S**R) and 161.5 eV (Cd**S**).

CdTe will effectively passivate the CdTe surface and gives rise to a great increment in PL intensity. The general increase in absorption and slight red shift near the absorption onset also support the epitaxial growth of CdS on CdTe.[5,21−22,31] Further experiment supporting this hypothesis was obtained from PL excitation measurements. Nearly no difference is presented between the spectra recorded before and after the illumination with respect to the shape of the spectrum (see Figure 3), which suggests that illumination did not alter the fluorescent center. This further proves that the CdS forms a shell structure on CdTe.

To further demonstrate this conclusion, XPS technique was used to examine the changes on the surface of TGA-capped CdTe nanocrystals induced by illumination. Different portions of CdTe solutions were extracted during illumination. Then the CdTe NCs were incorporated into PEI matrix by the electrostatic layer-by-layer self-assembly method as described in the Experimental Section. In this way, interference of small molecules in the solution could be excluded.[8b] Four CdTe samples with typical illumination periods of time were examined and the corresponding S2p spectra are shown in Figure 4. The peaks at around 162 eV comes from S. The peak centered at 168 eV is attributed to the energy loss peak of Si.[32] Due to the spin−orbit splitting, a typical S2p spectrum has a doublet structure, corresponding to $S2p_{1/2}$ and $S2p_{3/2}$ that are separated by 1.2 eV. The typical intensity ratio between $S2p_{1/2}$ and $S2p_{3/2}$ is 1:2.[33]

Table 1. Molar Ratios of Cd/Te and S/Te for CdTe Nanocrystals Extracted at Different Periods of Illumination Time; the PL Quantum Yields as well as $Te3d_{5/2}$ Binding Energies Are Given[a]

PL QY (%)	Cd/Te	S_t/Te	S_{Cd-SR}/Te	S_{CdS}/Te	$Te3d_{5/2}$ binding energy (eV)
8	1.1	0.4	0.4	0	572.7
28	6.2	4.1	2.5	1.6	572.6
56	8.3	4.9	2.7	2.2	572.4
80	5.9	3.3	0.4	2.9	572.4

[a] S_t,total content of S; S_{Cd-SR},S content from TGA-Cd complex; S_{CdS},S content from CdS.

Before illumination, S2p spectrum of the TGA-capped CdTe can well be fitted with one doublet with $S2p_{1/2}$ peaking at 163.2 eV and $S2p_{3/2}$ at 162.0 eV. These binding energies are consistent with that for thiolate, which demonstrates the existence of chemical bonds between thiols and cadmium ions on the surface of CdTe nanocrystals.[31] With illumination being prolonged, the S2p doublet shifts to lower energy. This suggests that illumination caused changes to the coordination situations for S from the thioglycolic acid. Further fitting results reveal that a new doublet appears at 161.5 eV for $S2p_{3/2}$ and 162.7 eV for $S2p_{1/2}$, and increases in intensity with the increase of PL quantum yield. In the meantime, the intensity ratio between $S2p_{3/2}$ peaks at 162.0 and 161.5 eV decreases. Since the new doublet can be attributed to the S from CdS,[34] it can therefore be concluded that illumination resulted in the formation of CdS by sacrificing thioglycolic acid. More quantitative analyses on the compositions of CdTe nanocrystals were performed by comparing the integrated areas of Cd, Te, and S taking the atomic sensitivity factors of different elements into consideration. The molar ratios of Cd/Te, S_t/Te (S_t, total sulfide), S_{Cd-SR}/Te (S_{Cd-SR}, sulfide in thiolglycolic acid), and S_{CdS}/Te (S_{CdS}, sulfide in CdS) were calculated and are tabulated in Table 1 together with the corresponding PL quantum yield as well as the binding energy of $Te3d_{5/2}$. During the early stage of illumination, all molar ratios given in Table 1 present largest increments while the PL quantum yield is raised to 28%. This tells that both Cd and S increase greatly in quantity in comparison with Te. The contribution of S from CdS is less than 40% in the total increment of S/Te ratio. All these results suggest that there were at least two factors governing these changes. First, Te on the CdTe surface is gently removed by photochemical etching. But this process is not the dominant process since no blue shift was observed with respect to absorption spectrum during this stage. Second, thioglycolic acid forms a layer structure of complex in combination with cadmium ions on the surface of CdTe. Such structural changes were observed before when the pH value of as-prepared CdTe was brought into the acidic range.[8] Although the pH value of the currently investigated system was fixed in the alkaline range, the formation of TGA-Cd complex on CdTe may still become favorable upon illumination. In the alkaline range Cd ions will also coordinate with hydroxyl ions apart from thiols, and this coordination is strongly pH-dependent. Lowering the pH value will break the Cd−OH bond and

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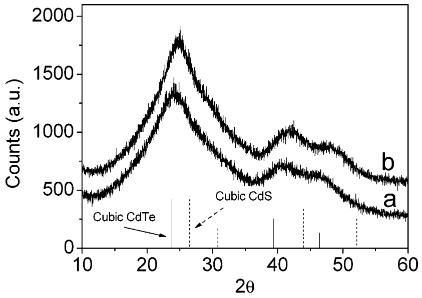

Figure 5. XRD patterns of TGA-capped CdTe NCs recorded before illumination (a), and after illumination (b). The standard diffraction lines of cubic CdTe and cubic CdS are also shown at bottom.

provide the possibility for unsaturated Cd in the TGA−Cd complex to coordinate with Te on the surface of CdTe NCs. Similarly, the photochemical degradation can detach TGA from Cd, which will offer the same possibility for the TGA−Cd complex to grow on the surface of CdTe. In addition, the early stage of illumination can increase the PL quantum yield to a level quite similar to that achieved by lowering the pH value of the CdTe colloidal solution,[8] therefore, it can be deduced that the formation of TGA−Cd complex shell on the CdTe core is the main reason for the PL increase in the early stage of illumination. But it should also be noticed that CdS already starts to form during this stage. Thereafter, till PL quantum yield reaches 56%, all molar ratios are simply increased but with different velocities. The S_{CdS}/Te increases the fastest among all molar ratios and reaches nearly the same level as S_{Cd-SR}/Te. Further prolongation of illumination gives rise to decreases to all molar ratios except for S_{CdS}/Te. This indicates that further illumination accelerates the formation of CdS by extracting sulfide ions from thioglycolic acid. It was also noticed during illumination that a white precipitate emerged when the PL quantum yield was raised to 70%. The composition of the white precipitate was analyzed by XPS. The results indicate that the precipitate is a quasi-monothio cadmium compound with the molar ratio of Cd/S/C(COOH) being equal to 1:0.85:1.[35] The appearance of the white precipitate explains the drops in the Cd/Te and S_t/Te ratios. It was also demonstrated that the CdTe/CdS colloidal solution finally obtained after illumination remained stable in a refrigerator several months after it was prepared. No drop in PL quantum yield was observed. In brief, illumination first induces the formation of the TGA−Cd complex shell on CdTe and then sulfide ions slowly generated by illumination will diffuse into the complex shell and replace thioglyic acid, and finally a CdTe/CdS core−shell structure is formed. In addition, the slight decrease in the binding energy of Te3$d_{5/2}$ also supports the formation of Cd−TGA as well as CdS shell during illumination. It has been proven that Te on the CdTe surface presents higher binding energy than that in the inner part of CdTe.[19,36]

Figure 5 shows the X-ray diffraction patterns of CdTe capped with TGA before and after illumination in comparison with standard diffraction lines for cubic CdTe and CdS, respectively. Before illumination, CdTe NCs exhibit diffractions quite close to that for bulk cubic CdTe. After illumination for 20 days, the diffraction pattern of CdTe obtained slightly move toward higher angles with peak widths and shapes being nearly unchanged, which supports the formation of CdS shell on CdTe. Similar changes in diffraction pattern were observed during the growth of ZnS shell on CdSe core by Bawendi.[5c]

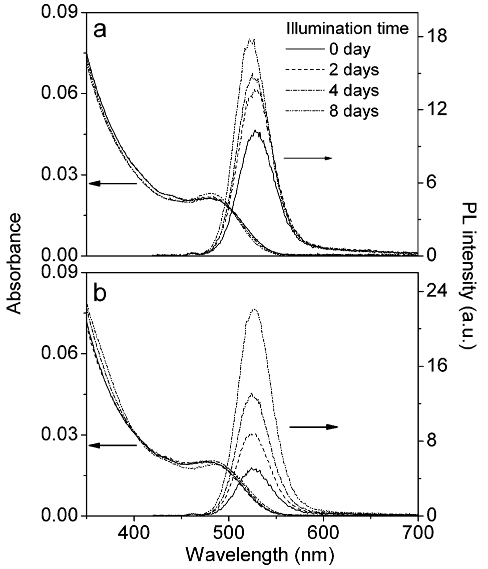

Figure 6. Temporal behavior of absorption and PL spectra of the MPA-capped CdTe nanocrystals recorded (a) with no TGA present, and (b) with an equal amount of TGA to MPA present during illumination. The excitation wavelength for fluorescence measurements was 400 nm.

To sum up, the photoenhancement effect on the PL of TGA-capped CdTe NCs is strongly related to the photodegradation of thioglycolic acid. To further verify this conclusion, similar experiments were performed with CdTe nanocrystals capped with 3-mercaptopropionic acid (MPA) in a N_2-saturated aqueous solution. MPA has a molecular structure very similar to that of TGA but quite different photodegradation behavior. It has been demonstrated that the photooxidation of 3-mercaptopropionic acids does not produce sulfide ions.[37] Figure 6a presents the absorption spectra and fluorescence spectra recorded during illumination from the MPA-capped CdTe nanocrystals in N_2-saturated aqueous solution. The illumination process was lasted for just 8 days since quite different behaviors had been observed in contrast to the TGA-capped CdTe NCs. The absorption presents a very slight blueshift near the absorption onset during illumination. This may be attributed to the photochemical etching of low quality CdTe NCs as well as the Te atoms with dangling bonds on the CdTe surface.[19,20] Moreover, the illumination just leads to a very limited increment for the PL intensity in addition to a small blueshift for the PL peak position. However, a dramatic increase was observed with respect to the PL intensity if an equal amount of TGA to MPA was present during illumination (Figure 6b). Both absorption and fluorescence spectra exhibit behaviors quite similar to that shown in Figure 1a rather than that in Figure 6a. This manifests the important role of

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thiolglycolic acid in the PL enhancement effect achieved by illumination for CdTe nanocrystals. Although the release of sulfide ions by photodecomposing TGA is very slow, it is the right point for growing CdS shell on CdTe in the current system since adding a solution of sodium sulfide directly into the system induced the formation of CdS clusters preferentially in solution rather than on the surface of CdTe. Furthermore, much less effect was observed with respect to PL after sodium sulfide was added into the solutions of CdTe capped by TGA and MPA, respectively.

In summary, the PL intensity of TGA-capped CdTe can be greatly enhanced by illumination. Different from previous research, the photodegration of TGA rather than NCs is proven to be the main reason responsible for the PL enhancement effect, although the photochemical etching of CdTe NCs also takes place and leads to the narrowing of the particle size distribution, which is reflected in the sharpening of 1s−1s excitonic transition. During the early stage of illumination, the degradation of TGA preferentially leads to the formation of TGA−Cd complex shell on CdTe, which contributes to the PL increment but only to a limited level. Further degradation of TGA produces sulfide ions which diffuse into the TGA−Cd shell and finally form a solid CdS shell structure on CdTe. As a result, the PL quantum yield is greatly enhanced and reaches more than 80% at room temperature. Since the colloidal solution of CdTe/CdS core−shell nanocrystals presents very good stability, the current investigations not only reveal the PL enhancement effect, but also provide a useful synthetic route for producing water-soluble and highly fluorescent CdTe/CdS core−shell nanocrystals.

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