The Influence of Carboxyl Groups on the Photoluminescence of Mercaptocarboxylic Acid-Stabilized CdTe Nanoparticles

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The CdTe nanoparticles were prepared in aqueous solution using different mercaptocarboxylic acids such as 3-mercaptopropionic acid (MPA) and thioglycolic acid (TGA) as stabilizing agents following the synthetic route described in ref 9. The pH-dependent photoluminescence (PL) of MPA- and TGA-stabilized CdTe nanoparticles was systematically investigated before and after addition of poly(acrylic acid) (PAA) into the CdTe solutions. Experimental results reveal that lowering the pH can increase the PL efficiency of both MPA- and TGA-stabilized CdTe. Moreover, the PL of the CdTe can further be increased in the presence of PAA in low pH range. X-ray photoelectron spectroscopy (XPS) was employed to investigate the interaction between the carboxyl groups from PAA and CdTe nanoparticles which were assembled in polymer matrix by a layer-by-layer self-assembly method to exclude interference from other species in CdTe solutions. XPS results demonstrate that the S/Te ratio of CdTe particles decreases after the addition of PAA, which strongly suggests that PAA can strongly interact with CdTe nanoparticles via the coordination between carboxyl groups and cadmium ions on the particle surface. As a result, the PL efficiency of the mercaptocarboxylic acid-stabilized CdTe nanoparticles is enhanced in acidic range.

1. Introduction

Exploring novel materials based on semiconductor nanoparticles has become one of the most attractive areas of current research.1–4 Due to quantum confinement effects, semiconductor nanoparticles exhibit unique physical and chemical properties distinctly different from their corresponding individual molecules or bulk materials.5,6 Over the past two decades, significant progress has been achieved in controlling the size and surface of wet-chemically synthesized semiconductor nanoparticles.7–17 Water-soluble semiconductor nanoparticles with high photoluminescence (PL) quantum efficiency have shown great potentials in photonic crystals,18,19 thin-film light-emitting devices,20–22 and especially biological labels.23,24 Water-soluble semiconductor nanoparticles with high PL efficiency can be obtained mainly by two different ways. The first way is to replace the surface-capping molecules on particles prepared by TOPO method with water-soluble thiols or silica shell.23–31 The second way is to directly synthesize semiconductor nanoparticles in aqueous solutions using water-soluble thiols as stabilizing agents.32–39 In these two approaches, the water-soluble thiols play an important role and contribute greatly to the stability and the functionality of the resulting nanoparticles.9,23,24,27–31,33,34 In addition, different choices of water-soluble thiols also critically determine the PL efficiency due to the difference in the resulting particle surface structures.9,25,37 Therefore, studies of surface structure of thiol-stabilized nanoparticles continue to be of great importance in controlling the optical properties of nanoparticle materials.23,40,41

Experimentally, pH-dependent PL is observed from the colloidal CdTe nanoparticles stabilized by mercaptocarboxylic acids.9 One possible explanation is the formation of annulus complexes forming in acidic pH range from cadmium ions and mercaptocarboxylic acids around the CdTe particle core, which provides better surface passivation at low pH to the CdTe nanoparticles.9,19,33,36,37 However, more experiments are still required in order to understand the influence of the surface structure on the PL efficiency of the CdTe nanoparticles, for example whether the coordination between the carboxyl group from the particle surface-capping mercaptocarboxylic acid and cadmium ions on the particle surface can form at low pH and change the CdTe particle surface properties. In this paper, we report CdTe nanoparticles prepared in the presence of two different mercaptocarboxylic acids such as 3-mercaptopropionic acid and thioglycolic acid. The impact of the carboxyl group from the mercaptocarboxylic acids on the PL efficiency is investigated. The interaction between the carboxyl groups and the particle surface is further studied by adding poly(carboxylic) acid into the mercaptocarboxylic acid-stabilized CdTe solutions. Combining with X-ray photoelectron spectroscopic results, the
particle surface composition and the correlation between the particle surface structure and particle PL efficiency are discussed.

2. Experimental Section

3-Mercaptopropionic acid (MPA) (Aldrich, 99+%), thiol-glycolic acid (TGA) (Aldrich, 97+%), poly(acrylic acid) (PAA) (Aldrich, M_\text{w} ca. 450 000), poly(methacrylic acid, sodium salt) (PMAA) (Aldrich, M_\text{w} ca. 9500, 30 wt % solution in water), poly(diallyldimethylammonium chloride) (PDDA) (Aldrich, M_\text{w} ca. 100000–200000, 20 wt % solution in water), CdCl\_2 (99+%), NaBH\_4 (99%), and tellurium powder (Aldrich, -200 mesh, 99.8%) are commercially available products.

a. Preparation of Sodium Hydrogen Telluride. By a molar ratio of 2:1, sodium borohydride was used to react with tellurium in water to produce sodium hydrogen telluride (NaHTe). Briefly, 80 mg of sodium borohydride was transferred to a small flask; then 1 mL of ultrapure water was added. After 127.5 mg of tellurium powder was added in the flask, the reacting system was cooled by ice. During the reaction, a small outlet connected to the flask was kept open to discharge the pressure from the resulting hydrogen. After approximately 8 h, the black tellurium powder disappeared and sodium tetraborate white precipitation appeared on the bottom of the flask instead. The resulting NaHTe in clear supernatant was separated and used in the preparation of CdTe particles.

b. Preparation of CdTe Nanoparticles. A series of aqueous colloidal CdTe solutions were prepared by adding freshly prepared NaHTe solution to 1.25 \times 10^{-3} \text{ N} \text{N}_2\text{-saturated CdCl}_2 solutions at pH 9.0 in the presence of mercaptocarboxylic acids as a stabilizing agent. The molar ratio of \text{Cd}\text{Cl}/stabilizer/HTe was fixed at 1:2.4:0.5. The resulting mixture was then subjected to a reflux that controlled the growth of the CdTe nanocrystals. In brief, CdTe particles with their size ranging from 2.8 to 4.0 nm were obtained. HCl and mercaptocarboxylic acid were used in the investigation of the pH-dependent photoluminescence of the CdTe nanoparticles obtained.

c. Preparation of CdTe Solutions Containing PAA. 2.9 nm CdTe nanoparticles were chosen to prepare the PAA-containing CdTe solution. The concentration of carboxyl groups from PAA was controlled the same as that from mercaptocarboxylic acid in the CdTe solution (standard PAA concentration). Typically, 3 mL of 0.1 N PAA aqueous solution (pH 9.0) was added to 100 mL of CdTe stock solution.

d. Fabrication of CdTe Nanoparticle/PDDA Multilayer Films. Freshly cleaned substrates (quartz slides and single-crystal silicon wafer) were first covered by one thin layer of PDDA by immersing the substrates into the PDDA solution (0.9 vol %). Then the PDDA-modified substrates were alternately dipped into CdTe aqueous solution and the PDDA solution for 20 min, respectively, interrupted by water-washing and \text{N}_2\text{-dry}ing processes after the deposition of each layer of CdTe/PDDA.

e. Characterization. UV-Vis absorption spectra were obtained by using a Shimadzu 3100 UV–Vis–near-IR spectrophotometer. Fluorescence experiments were performed with the help of a Shimadzu RF-5301 PC spectrofluorimeter. All optical measurements were performed at room temperature under ambient conditions.

X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MK II spectrometer with a Mg K\alpha excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) were recorded by a JEOl-2010 electron microscope operating at 200 kV. X-ray powder diffraction (XRD) was carried out using a Siemens D5005 diffractometer.

3. Results and Discussion

a. Characterization of Mercaptocarboxylic Acid- Stabilized CdTe Nanoparticles. Figure 1 presents typical evolutions of both absorption and photoluminescence spectra of MPA-stabilized CdTe nanoparticles as a function of particle size. The average particle size of samples shown in Figure 1 was derived from the 1s–1s electronic transition in the absorption spectra based on a theoretical model from a previous report. The size and size distribution of the CdTe nanoparticles were further confirmed by TEM. Under TEM, the CdTe appear as spherical particles with crystalline structures. On average, the particle size distribution is around 15%.

Both absorption and PL spectra shown in Figure 1 exhibit “quantum size effects”. The excitonic peak position in absorption shifts from 494 to 611 nm when the particle size increases from 2.8 to 4.0 nm by reflux. In the meantime, PL peak position shifts from 522 to 655 nm. The relative PL quantum yields (QY) of four different CdTe samples with particle diameters of 2.8, 3.3, 3.6, and 4.0 nm are estimated to be 18%, 38%, 17%, and 2%, respectively, using Rohdamine 6G as PL reference. CdTe nanoparticles (3.6 and 4.0 nm) were obtained by a size selective precipitation procedure using 2-propanol as bad solvent to narrow the particle size distribution.

The XRD and SAED of 2.9 nm CdTe nanoparticles are presented in Figure 2. The SAED pattern appears as broad diffuse rings due to the small particle size. The powder XRD
profile of the nanoparticles shows broad peaks typical for nanocrystals. The lattice parameters derived from SAED and XRD measurements for MPA-stabilized CdTe nanoparticles fit to the cubic zinc blende structure of bulk CdTe crystal. Therefore, the cubic crystalline structure is adopted to estimate the surface coverage of sulfur for any given S/Te ratio.

b. The pH-Dependent PL of Mercaptocarboxylic Acid-Stabilized CdTe Nanoparticles. To use mercaptocarboxylic acid as a stabilizer in the syntheses of CdTe nanoparticles is very important to gain both the stability and the functionality of the resulting particles. Similar to the thioglycolic acid-stabilized CdTe, the 3-mercaptopropionic acid-stabilized CdTe nanoparticles also show pH-dependent photoluminescence. Figure 3 presents fluorescent intensity of CdTe-MPA and CdTe-TGA vs pH value. Solutions of 0.1 N MPA and TGA were used to decrease the pH of the corresponding CdTe solutions. The fluorescent intensity of the TGA-stabilized CdTe increases gradually with the decrease of pH. Then it stops increasing until the pH of solution reaches 4.5. Similarly, the fluorescent intensity of the MPA-stabilized CdTe increases until the pH reaches 6.0, then it decreases drastically upon further decrease of pH. Comparing MPA with TGA, the main difference in chemistry is pH-dependent photoluminescence. Figure 3 clearly tells that the MPA-stabilized CdTe reaches its PL maximum at a higher pH than TGA-stabilized CdTe. Therefore, it is reasonable to partly attribute the pH-dependent PL behaviors of MPA- and TGA-stabilized CdTe to the protonation of carboxylate groups from particle surface-binding thiol. A previous report has proved the existence of a secondary coordination between the carboxylate oxygen from Cd(SCH$_2$COOCH$_2$CH$_3$)$_2$ and primary thiol-binding cadmium.

It can then be deduced that a secondary coordination between the carbonyl O atom of free acid and the Cd atom at the CdTe particle surface exists, which in return provides better surface passivation and consequently higher PL efficiency. In fact, the PL of CdTe is not solely determined by the interaction between carboxyl groups from mercaptocarboxylic acids and particle surface in the acidic range. Lowering the pH value also changes the CdTe surface complexes formed by excess of mercaptocarboxylic acids and cadmium ions which remain in the CdTe solutions. According to previous reports, complexes of mercaptocarboxylic acid and cadmium ions contribute to the PL enhancement and the stability of the CdTe solution at low pH.

Table 1: The $pK_{\text{COOH}}$ and $pK_{\text{SH}}$ of a Series of Compounds Containing Carboxyl Groups

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>$pK_{\text{SH}}$</th>
<th>$pK_{\text{COOH}}$</th>
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<tr>
<td>TGA</td>
<td>10.05</td>
<td>3.53</td>
</tr>
<tr>
<td>MPA</td>
<td>10.20</td>
<td>4.32</td>
</tr>
<tr>
<td>PAA</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>PMAA</td>
<td>5.65</td>
<td></td>
</tr>
</tbody>
</table>

c. The Influence of Carboxyl Groups on the PL of CdTe Nanoparticles. To avoid the interference of thiol groups from mercaptocarboxylic acids, PAA was chosen to check the PL enhancement effect solely originated from carboxylic acids. Figure 4 shows the influence of PAA on the pH-dependent PL of MPA-stabilized CdTe nanoparticles. Diluted HCl and MPA solutions were used to tune the pH of the CdTe solution to the acidic range. Upon addition of 3 mL 0.1 N (referring to carboxylic acid group) PAA into 100 mL of CdTe stock solution in the basic range, no obvious PL enhancement was observed. The PL intensity increases gradually with the decrease of pH until the pH becomes 6.0, then it rises dramatically. During this process, the absorption spectra of the CdTe solution remains nearly unchanged, providing evidence that no particle growth occurs. The PL intensity reaches its maximum at pH 5.0, and then decays rapidly upon further decrease of pH. Compared with the maximum PL intensity achieved in the absence of PAA, the PL intensity obtained in the presence of PAA is increased by a factor of 1.5. Similar pH-dependent PL is also observed from the TGA-stabilized CdTe in the presence of PAA (Figure 5).

Along with the decrease of pH, a red-shifted PL was observed from the MPA-stabilized CdTe in the low pH range. The red-shift in PL is attributed to an additional sulfuration reaction taking place on the CdTe surface during the decrease of the pH value. It is also demonstrated that the red-shift greatly depends on the decrease of pH.
PAA concentration of 3 solutions versus pH values obtained by using HCl (circle), HCl with a PAA concentration of 3 × 10⁻³ N (snow), HCl with a PAA concentration of 1.2 × 10⁻² N (triangle).

Figure 6. Fluorescence peak position of MPA-stabilized CdTe solutions versus pH values obtained by using HCl (circle), HCl with a PAA concentration of 3 × 10⁻³ N (snow), HCl with a PAA concentration of 1.2 × 10⁻² N (triangle).

on the concentration of PAA (Figure 6). In the absence of PAA, the PL exhibits a gradual red-shift up to 14 nm before precipitation of CdTe appears at pH 4.5. In contrast, there is no precipitation observed in the same pH range for the PAA nanoparticles is strong enough to complex PAA with CdTe.

Figure 7. Schematic illustration of the surface structure of CdTe nanoparticles modified with MPA and PAA. The coil represents the PAA alkyl chain. R represents a carboxylic acid group. The coordination between the carboxyl oxygen and cadmium on the particle surface is represented as dot line. The naked sulfur species in the particle resulted from the decomposition of thiols.

The pH-dependent interaction between PAA and the CdTe nanoparticles is whether the coordination between the PAA carboxyls and CdTe particles in the acidic range, which contributes to the PL enhancement effect due to the strong interaction between PAA and the CdTe particles.

Figure 8. X-ray photoelectron spectra from (CdTe/polyelectrolyte)⁺³ layer thin films, assembled layer-by-layer on a clean single-crystal silicon substrate precoated with PDDA, then CdTe. (a) Cd 3d spectrum, and (b) Te 3d, S 2p spectrum.

Table 2: The Calculated Number of S Atoms per nm² of CdTe Particle Surface. Cubic Zinc Blende Model Is Employed for 2.9 nm CdTe Nanoparticles. The S/Te Ratios Used in the Calculation Were Obtained by XPS Measurements

<table>
<thead>
<tr>
<th>pH</th>
<th>MPA-stabilized CdTe</th>
<th>TGA-stabilized CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>5.4</td>
<td>5.5</td>
</tr>
<tr>
<td>6.0</td>
<td>10.2</td>
<td>6.0</td>
</tr>
<tr>
<td>5.0</td>
<td>8.5</td>
<td>5.9</td>
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Preliminary results show a shift in the carboxyl stretching vibration band after PAA is mixed with CdTe in solution. However, it is difficult to quantitatively characterize the IR shift since absorptions of MPA carboxyls and PAA carboxyls are difficult to clearly differentiate. Another problem in investigating the existence of the association between PAA and CdTe nanoparticles is how to maintain the surface structure of nanoparticles and exclude interference from small molecules in solution. To solve this problem, a layer-by-layer self-assembly method was adopted to embed CdTe nanoparticles in polymer matrix utilizing cumbic interactions between negatively charged CdTe and positively charged PDDA. The elemental composition of the CdTe/PDDA multilayer films was analyzed by XPS. The appearance of a characteristic Cd 3d₅/₂ peak at 404.5 eV, S 2p peak at 161.8 eV, and Te 3d₅/₂ peak at 571.9 eV shown in Figure 8 confirms the existence of cadmium, tellurium, and sulfur species in the film. In addition, XPS data from Figure 8 also allow the determination of atomic ratios between S and Te from the particles which were originally kept in solutions of different pH. The S/Te ratio is very important for studying the change of surface-binding thiols upon addition of PAA. Using a cubic zinc blende model, the surface coverage of thiols on the CdTe surface is estimated. As shown in Table 2, the maximum number of surface-binding S on MPA-stabilized CdTe nanoparticles is located around pH 6.0 in the absence of PAA, whereas the number of surface-binding S on TGA-stabilized CdTe nanoparticles keeps increasing in the absence of PAA until the pH arrives at 5.0. This result further confirms the previous proposed mechanism on the PL enhancement caused by the formation of Cd[(S-COOH)₃]–mercaptocarboxylic acid complexes on the particle surface at low pH and also explains the pH-dependent PL of MPA-stabilized CdTe in the absence of PAA. However, in the presence of PAA the surface coverage of the S atom remains nearly unchanged in the investigated pH range of 9.0–5.0 for the MPA-stabilized CdTe, which suggests that the pH-dependent interaction between PAA and the CdTe particle critically determines the PL of the CdTe nanoparticles.
In addition, generally smaller S surface coverage of the CdTe—PAA system than that of the pure CdTe system indicates that some of the surface-binding thiols are replaced by PAA, which further proves the strong interaction between PAA and CdTe nanoparticles (Table 2). The following experiment also provides more evidence on this interaction. To exclude possible interference from the excess MPA and Cd²⁺ in CdTe stock solutions, the MPA-stabilized CdTe nanoparticles were purified by precipitation in 2-propanol and then redissolved in water. As shown in Figure 9, the PL intensity of this purified CdTe particle solution become less pronounced at pH 5.1 compared to that given in Figure 3. In the absence of excess MPA and Cd²⁺, the PL intensity decrease with the decrease of pH as a result of the deconstruction of the complexes annulus due to the protonation of the surface-binding thiolates. However, the PL of the purified CdTe solution can still be enhanced by a factor of 2 in the presence of PAA after the pH is tuned to 5.1. Since there is no excess mercaptocarboxylic acid existing in the CdTe solution, it can be concluded that the observed PL enhancement purely originates from the combination between nanoparticles and carboxyl groups. This result further supports our model proposed in Figure 7.

d. Other Chemicals Terminated with Carboxyl Groups.

When poly(methacrylic acid) (PMAA) is adopted instead of PAA, no PL enhancement will be observed. This can be explained by the spatial hindering effect of the methyl group preventing the carboxylic acid groups from binding the Cd ions on the particle surface. It should be mentioned that no direct effect from the molecular weight of polycarboxylic acid was observed on the enhancement effect.

Conclusions

Systematic pH-dependent photoluminescence and XPS studies have demonstrated that carboxyl groups have a great influence on both photoluminescence and stability of the mercapto-carboxylic acid-stabilized CdTe nanoparticles. The coordination between the carboxyl groups and cadmium ions can effectively improve the PL efficiency of the CdTe nanoparticles. But this enhancement effect is only observed in a certain acidic range, which suggests that the interaction between carboxyl groups and the CdTe particle surface can effectively diminish the radiative annulus for electron–hole recombination. However, two important questions remain open: (1) the details of pH-dependent chemical interaction between the carboxyl groups and cadmium ions on the particle surface, and (2) physical explanations of the PL enhancement effect involving PAA. Nonetheless, the PL enhancement effect from the carboxyl groups will provide useful instructions on chemical syntheses of highly fluorescent CdTe in aqueous solution.

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References and Notes