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Preparation and Optical Properties of CdTe/CdO·nH$_2$O Core/shell Nano-composites in Aqueous Solution[†]

Xiao Zhang[a, b], Xing-ping Zhou[a*], Si-yu Ni[a], Guo-liang Dai[c*], Yin-sheng Wang[a]

a. *Institute of Biological Sciences and Biotechnology, Donghua University, Shanghai 201620, China;*
b. *College of Material Science and Engineering, Donghua University, Shanghai 201620, China;*
c. *National Microgravity Laboratory, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China*

The deposition of CdO·nH$_2$O on CdTe nanoparticles was studied in an aqueous phase. The CdTe nanocrystals (NCs) were prepared in aqueous solution through the reaction between Cd^{2+} and NaHTe in the presence of thioglycolic acid as a stabilizer. The molar ratio of the Cd^{2+} to Te^{2-} in the precursory solution played an important role in the photoluminescence of the ultimate CdTe NCs. The strongest photoluminescence was obtained under 4.0 of [Cd^{2+}]/[Te^{2-}] at pH~8.2. With the optimum dosage of Cd(II) hydrous oxide deposited on the CdTe NCs, the photoluminescence was enhanced greatly. The photoluminescence of these nanocomposites was kept constant in the pH range of 8.0-10.0, but dramatically decreased with an obvious blue-shifted peak while the pH was below 8.0. In addition, the photochemical oxidation of CdTe NCs with cadmium hydrous oxide deposition was markedly inhibited.

Key words: CdTe, Cadmium hydrous oxide, Optical properties, Surface modification, pH, Stability

I. INTRODUCTION

Recently, colloidal semiconductor nanocrystals (NCs), also known as quantum dots (QDs), have attracted considerable attention as novel biological luminescent labels [1,2]. Compared with traditional labels, they have some unique and fascinating physical and chemical properties, such as sharp and symmetrical emission spectra, high quantum yield, good chemical and photo stability, readily tunable spectral proper ties and so on [2-4].

Cadmium telluride (CdTe) is one of substances providing very high photoluminescence (PL) quantum efficiency among II-VI semiconductor materials, which could be synthesized in aqueous solution with simplicity and high reproducibility. Especially for fluorescent label applications, the water-soluble NCs are needed [2,5-7]. Besides, the surface chemistry plays a great role concerning the properties of the NCs, such as the quantum yield and photo-stability. The high quantum yield of CdTe NCs was accomplished when thioglycolic acid (TGA), 3-mercaptopropionic acid, 1-thioglycerol, L-cysteine, thiolactic acid, mercaptosuccinic acid, or 2-mercaptoethylamine were used as the capping ligands [8-10]. However, the photoluminescence is unstable under ambient air conditions. Although thiol-capped CdTe NCs prepared directly in aqueous solution

show much better stability, their surface properties also changed and a clear blue-shifted emission and absorption caused by photo-oxidation was observed [11].

It has been reported that the growth of an inorganic shell with a broader band gap on the surface of lumines-cent NCs is an effective way to improve the spectral properties of the NCs [11]. Most of the properties of these "core/shell" systems are dependent on both core and shell materials. Some successful systems of core-shell nanocomposites have been reported, such as silica encapsulated CdSe [12,13], CdTe/SiO$_2$ [14,15], CdTe/CdS [11,16], CdTe/Co(OH)$_2$ [17], etc. Besides, the hydroxide ions played an important role in the preparation of CdTe NCs in aqueous phase. It has been found that deposition of Cd (II) hydrous oxide on CdS and CdSe NCs increased markedly the PL intensity of these NCs, respectively [18,19]. The formation of Cd (II) hydrous oxide shell on the quantum dots improved luminescence quantum yields, increased fluorescence lifetimes, and had other benefits related to the tailoring of relative band gap positions between the shell and core [20]. However, the tangible results of Cd (II) hydrous oxide on the photoluminescence intensity of CdTe NCs have not been gotten. There is no information on the effects of some important factors such as reactant concentrations, pH of suspension, and oxygen on the photoluminescence of CdTe/CdO·nH$_2$O core/shell composites. The investigation of such effects is of great important for preparing strongly luminescing CdTe NCs and their practical applications.

In this work, CdTe NCs and CdTe/CdO·nH$_2$O core/shell nanocomposites were prepared in aqueous solution. The introduction of CdO·nH$_2$O can effectively passivate the core surface to protect it from oxidation

and improve the PL yield as well as the photo-stability.

II. EXPERIMENTS

A. Materials

NaBH$_4$(A.R. 96%), tellurium powder (99.8%), CdCl$_2 \cdot$2.5H$_2$O(A.R. 99%), NaOH, and HCl were purchased from Sinopharm Co. (China). Thioglycolic acid (TGA) was purchased from A. J. Matthey Company (Germany). Water was purified with Milli-Q (18.2 MΩ) water system.

B. Preparation of CdTe nanocrystals

The synthesis of CdTe NCs was performed according to the modified previous methods [21]. First, excess sodium borohydride was used to react with tellurium powder in water to generate sodium hydrogen telluride (NaHTe). Briefly, sodium borohydride (2.6 mmol) and 2 mL N$_2$-saturated ultra-pure water were added to a small flask. After tellurium powder (0.5 mmol) was added into the flask, the reacting system was cooled by ice. About 8 h later, the black tellurium powder disappeared and a white precipitation of sodium tetraborate appeared on the flask instead. NaHTe in the clear supernatant was separated and used for the preparation of CdTe NCs.

The aqueous colloidal CdTe solution was prepared by adding freshly prepared NaHTe solution to N$_2$-saturated CdCl$_2$ solution in the presence of thioglycolic acid (TGA) as a stabilizing agent. The molar ratio of Cd^{2+} to TGA was fixed at 1/2.4 in the precursory solution. Then the system was heated to 100 °C and the stable reflux distillation was maintained with stirring for 3 h. Nitrogen was used as the protective gas during the reacting. The standard conditions were established at 4.0 of [Cd^{2+}]/[Te^{2-}] and pH$\sim$8.2 with 0.625 mmol/L Te^{2-}.

For the investigation of effect of [Cd^{2+}]/[Te^{2-}], [Cd^{2+}]/[Te^{2-}] ratio was also controlled at 6.0, 3.0, and 2.0, respectively.

C. Formation of CdTe/CdO·nH$_2$O core/shell nano-composites

To 12 mL of the fairly stable CdTe suspension prepared under the standard conditions, 0.01 mol/L NaOH and 0.01 mol/L CdCl$_2$ were drop-wisely added with vigorous agitation at room temperature. The NaOH was used for maintaining pH at 8.8. The photoluminescence was checked for every addition of 67 μmol/L CdCl$_2$ and addition of the CdCl$_2$ stopped after the PL intensity no longer increased. Finally, 45 mL of the mixture was obtained.

In order to investigate pH effect on the photoluminescence of Cd(II) hydrous oxide deposited CdTe NCs, the pH was adjusted with 0.1 mol/L NaOH or HCl solution. This CdTe/CdO·nH$_2$O solution was aged at room temperature for 8 h. Then the UV and PL spectra under different pH value were measured for comparison [19].

D. Optical measurements

UV-Vis absorption spectra of CdTe NCs in suspension before and after deposition of Cd(II) hydrous oxide were conducted with an ultraviolet-visible spectrophotometer (Jasco V-530, Japan) and the PL of these particles was measured with an F-4500 Spectrofluorometer (Hitachi, Japan) equipped with Xe lamp. The excitation wavelength was 400 nm.

III. RESULTS AND DISCUSSION

A. Optical properties of CdTe nanocrystals

In order to explore the reason for changes in optical properties of CdTe suspensions, the absorption and photoluminescence (PL) spectra of TGA-stabilized CdTe sols with different [Cd^{2+}]/[Te^{2-}] ratios were examined and the outcome was shown in Fig.1. Figure 1(a) displays the UV-Vis spectra of CdTe NCs prepared under different [Cd^{2+}]/[Te^{2-}] ratios with 0.625 mmol/L tellurium ion at pH$\sim$8.2 at 100 °C. It was observed that with an increase in [Cd^{2+}]/[Te^{2-}] from 2.0 to 4.0, absorption shoulders were blue-shifted from 520 nm to 514 nm, which revealed a series of nanosized CdTe crystalline was successfully produced. However, with the further increase in the ratio of [Cd^{2+}]/[Te^{2-}] to 6.0, a fairly unstable sol was obtained. This is in a good agreement with the results for preparation of CdSe NCs [18]. Figure 1(b) shows the PL spectra (Excitation wavelength 400 nm) of the corresponding samples in Fig.1(a). A series of PL peaks was observed in the range of 564-547 nm. Obviously, the PL intensity increased with increasing [Cd^{2+}]/[Te^{2-}]. The promotion of PL intensity probably was related to a thin shell of cadmium hydrous oxide around the CdTe cores formed with highly excessive Cd^{2+} in the weak alkaline system, analogous of the formation of CdSe sol [18].

B. Enhancing photoluminescence of CdTe nano-crystals by surface deposition of cadmium (II) hydrous oxide

Figure 2(a) displays the effect of the CdCl$_2$ addition at pH$\sim$8.8 on the PL of the CdTe sol ([CdTe]: $\sim$0.171 mmol/L) prepared under 4.0 of [Cd^{2+}]/[Te^{2-}] ratio. Figure 2(b) shows the relationship between PL intensity and the amount of the added CdCl$_2$. With
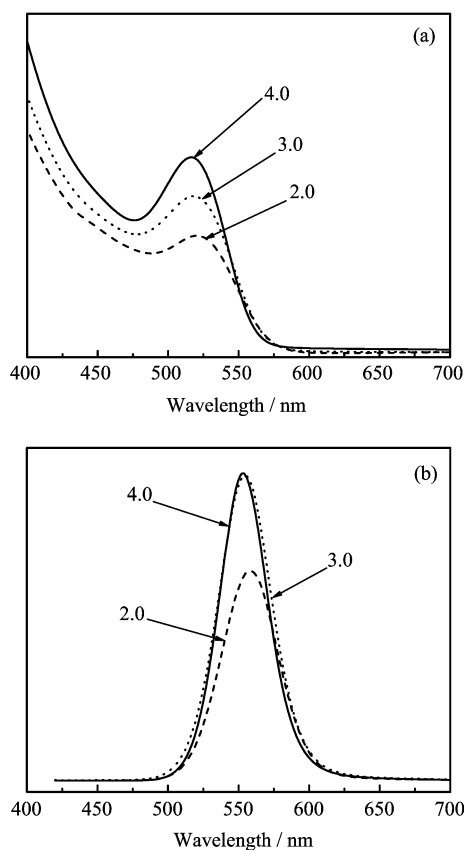
FIG. 1 PL spectra (a) and UV-Vis spectra (b) of CdTe NCs prepared at pH~8.2 under the ratios of [Cd^{2+}]/[Te^{2-}] with 0.625 mmol/L Te^{2-}.
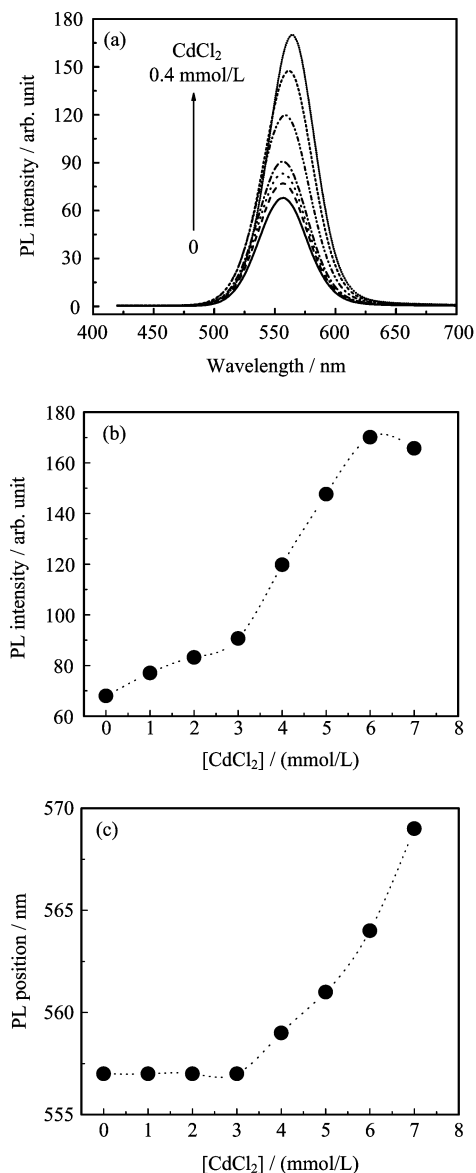

FIG. 2 (a) Effect of Cd(II) hydrous oxide deposited on the CdTe surfaces on their photoluminescence. (b) Effect of the added CdCl$_2$ on PL intensity. (c) Effect of the added CdCl$_2$ on PL position.

the increasing dosage of CdCl$_2$ added, the PL was enhanced greatly until the concentration of CdCl$_2$ reached to 0.4 mmol/L. Then, there was no longer PL intensity increase at CdCl$_2$ concentration lager than 0.4 mmol/L. The enhanced PL intensity may result from the formation of core-shell structure since the CdO·nH$_2$O shell was of a higher band gap than the CdTe core. The shell has the extra benefit that it may possibly remove the defect sites on the surface produced in the formation process of the CdTe NCs. Figure 2(c) shows the relationship between PL position and the amount of the added CdCl$_2$. The PL peak position was red-shifted from 557 nm to 564 nm while the CdCl$_2$ concentration increased from 0 to 0.4 mmol/L. This suggests that the CdO·nH$_2$O shell is thick enough to remove the defect sites existing on CdTe surfaces.

Figure 3 shows the UV-Vis spectra of the CdTe NCs with and without the deposition of cadmium hydrous oxide. The absorption shoulder was slightly red-shifted after the deposition. This can be attributed to the quantum confinement effect. The phenomenon could result in the red-shifted PL shown in Fig.2.

In order to confirm further the PL promotion with the deposition of cadmium hydrous oxide, the effect of Cd(OH)$_2$ particles, which could be generated with the

CdCl$_2$ addition in alkaline solution, was investigated [20]. The Cd(OH)$_2$ particles in monoclinic crystal structure were obtained by mixing CdCl$_2$ with NaOH solution [19]. Then, the Cd(OH)$_2$ paticles were mixed with the CdTe NCs and in this process no aggregation took place between the CdTe NCs and Cd(OH)$_2$ particles. Figure 4 shows the PL spectra of the pure CdTe NCs, the deposited CdTe NCs, and the mixture of CdTe NCs and Cd(OH)$_2$ particles. It was obvious that there was no increase in PL intensity of CdTe after mixed with the Cd(OH)$_2$ particles. Therefore, the cadmium hydrous oxide deposited on the surface of CdTe NCs played a decisive role in promoting the PL of the CdTe NCs.
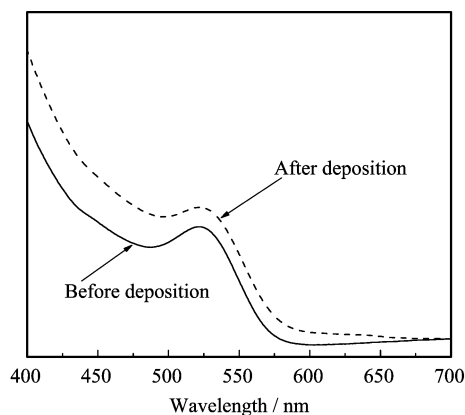
FIG. 3 UV-Vis spectra of the CdTe suspension without and with Cd(II) hydrous oxide deposition ($[Cd^{2+}]$=0.4 mmol/L).
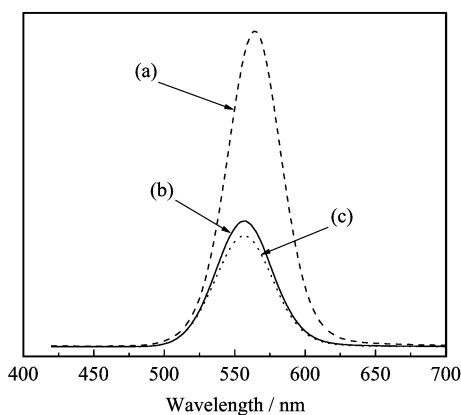

FIG. 4 PL spectra of CdTe NCs deposited with cadmium (II) hydrous oxide, the undeposited CdTe NCs, and the mixture of the CdTe NCs and the monoclinic $Cd(OH)_2$. (a) CdTe with deposition, (b) CdTe NCs, (c) Mixture of CdTe and Cd(OH)2.

C. Effect of pH on the photoluminescence of CdTe/CdO·nH₂O core/shell nanocomposites

Effect of pH on the photoluminescence of CdTe/ CdO·nH₂O core/shell nanocomposite sols was investigated. The pH of these sols was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl. Figure 5 exhibits the corresponding changes in PL intensity and PL position. Figure 5(a) displays that the PL intensity was fairly stable in pH range of 8.0-10.0. In contrast, when pH was below 8.0, the PL intensity dramatically decreased with declining pH, this may be related to the change in morphology of the cadmium hydrous oxide shell at a different pH. In Fig.5(b), the PL peak position was greatly blue-shifted with declining pH from 8.0. This may also be due to the change in morphology of the shell which made the particles smaller. In the pH range of 8.0-10.0, the peak position was constant, revealing that there was no observable effect of the adsorbed OH⁻ on the shell
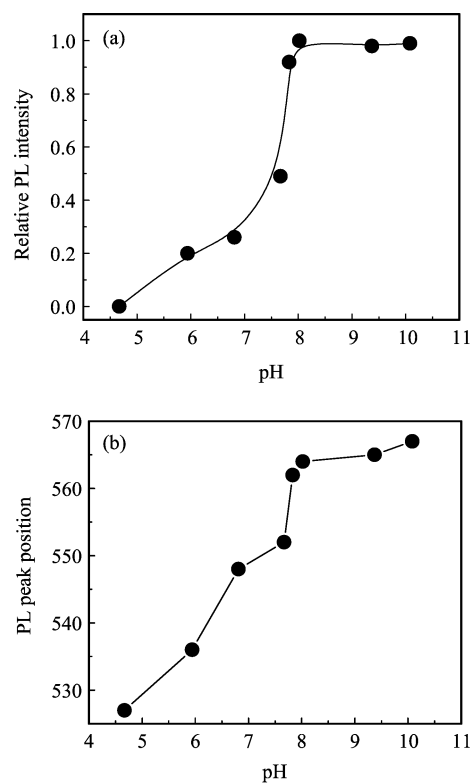

FIG. 5 Effect of pH on the (a) PL intensity and (b) PL peak position of CdTe/CdO·nH₂O core/shell nano-composites.

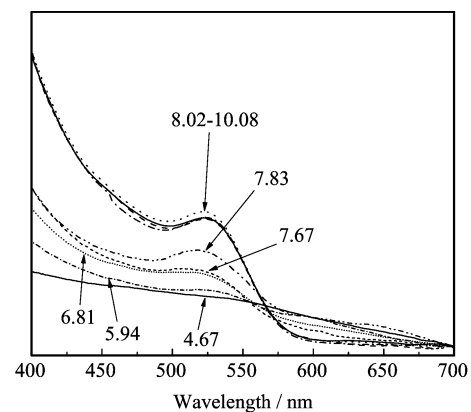

FIG. 6 UV-Vis spectra of CdTe/CdO·nH₂O core/shell nanocomposites aged under different pH.

of the composite particles on their PL in such a system with excessive hydroxide ions.

Figure 6 displays the UV spectra of CdTe/CdO·nH₂O core/shell nanocomposite sols under different pH, which further confirmed the above description.
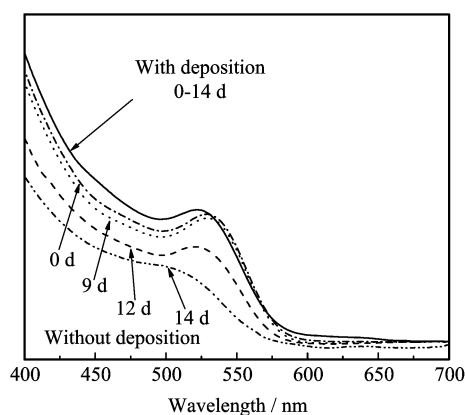
FIG. 7 UV-Vis spectra at different times after preparing and two weeks' aging of CdTe NCs and the NCs deposited with cadmium hydrous oxide.

D. Stabilization of CdTe/CdO·nH$_2$O core/shell nano-composites against photo-degradation

In order to investigate the stabilization of CdTe NCs and CdTe/CdO·nH$_2$O nanocomposites respectively, they were aged at room temperature for about two weeks. The freshly prepared CdTe NCs showed an increased absorbance within about two weeks. However, after about two weeks, the CdTe NCs without deposition of cadmium hydrous oxide exhibited a continuously decreased and blue-shifted absorption. FIG.7 illustrates the time evolution of UV absorbance of the CdTe NCs and that of CdTe/CdO·nH$_2$O nanocomposites after these sols have been aged at room temperature for two weeks. With the deposition of cadmium hydrous oxide on the particle surfaces, the absorbance was kept constant all the time. It is evident that CdTe/CdO·nH$_2$O nanocompo-sites show excellent stability.

In the other words, the findings revealed the deposition of cadmium hydrous oxide prevented O$_2$ from touching Te^{2-} on the surface of CdTe NCs. With the shell, CdTe NCs showed higher luminescence quantum yield.

IV. CONCLUSION

The molar ratio of Cd^{2+} to Te^{2-} of the precursors was found to play a crucial role in determining PL properties of water-soluble CdTe nanocrystals. The strongest photoluminescence of the stable CdTe nanocrystal suspension was obtained under 4.0 of [Cd^{2+}]/[Te^{2-}] at pH~8.2. The photoluminescence of CdTe nanoparticles was greatly promoted by the surface deposition of cadmium hydrous oxide and only the cadmium hydrous oxide existing on the surfaces of CdTe nanoparticles can promote their optical properties. The photoluminescence of core-shell structured CdTe/CdO·nH$_2$O

nanocomposites was kept stable in the pH range of 8.0-10.0.

The shell of cadmium hydrous oxide was rigid enough to prevent O$_2$ from oxidizing Te^{2-} existing on the surfaces of the CdTe nanoparticles, thus the stabilized CdTe nanoparticles were immune to photo-degradation.

V. ACKNOWLEDGMENT

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