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Short Communication

Optical Properties Investigation of Core/Shell Quantum Dots by Low Temperature Synthesis

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The core/shell structure semiconductor nanoparticle CdTe/CdS was synthesized in aqueous solution using thioglycolic acid as a stabilizer. UV-vis spectra, the fluorescence spectra of the series of CdTe, CdS QDs samples were also analyzed in detail, and the result indicates that the intensity of flourescence was increasing and the absorption and emission peaks had redshift regularly with the increasing of the reaction time. The XRD patterns proved that the CdS did not to form single core in the process of CdTe/CdS synthesis. The synthesized quantum dots(QDs) exhibit strong and stable band-edge luminescence. The optical properties of QDs can be improved when CdTe as a core was coated with CdS as a shell to form a core/shell QDs.

Keywords: core/shell; fluorescence; CdTe/CdS

1. INTRODUCTION

In recent years，luminescent water-soluble semiconductor nanocrystals or quantum dots (QDs) have attracted tremendous attention in both of fundamental studies and technical applications, such as lasers[1], biomedical fluorescence labels[2-4], and light-emitting diodes[5], because of their unique optical and electronic properties, such as high chemical stability, broad excitation spectrum, narrow emission spectrum, good tune and neglectable optical bleach phenomenon etc[6, 7].

Synthesis of high quality quantum dots has been an important topic in the field of materials chemistry[8]. Currently, the highly luminescent Ⅱ-Ⅳ QDs is also prepared by the organometallic synthetic route using trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) as stabilizing reagents, which has lots of advantages, such as narrow FWHM (Full Wave of Half Maximum), high fluorescent quantum yield, and good monodispersity[9]. However, the QDs which are obtained in this method are hydrophobic and insoluble in water, which limits their biological applications. Furthermore these QDs synthesized through organometallic routes need undergo surface modification with hydrophilic capping agents in aqueous solution. This process is often problematic and the as-prepared QDs are often associated with several drawbacks such as limited stability and low emission quantum yield[10, 11].

Therefore, directly synthetic route to produce QDs in aqueous solution which is using the small molecular thiols as stabilizing agents is improved highly[12]. Water-soluble QDs is better than the QDs synthesized in organic phase in some aspect, such as asepsis, lower cost, simple operation, and good repeatability and more controllable at the electron and surface quality. Moreover, the excellent biocompatibility is most important character. But, some disadvantages are still existent: lower QY, broader FWHM, and no-uniform particle size.

It is well known that optical absorption of nanocrystals shift to higher energy as the size decrease, while the emission at the absorption band is always too weak to be investigated in details due to much nonradiative recombination at nanoparticle surface. To eliminate the surface defects, some kinds of materials such as organic molecules, polymers and inorganic compounds are used to overcoat the nanoparticles. It has been found that nanocrystals which overcoated with high band gap inorganic materials formed core/shell type nanocrystals exhibit high photoluminescence intensity at band edge due to effective elimination of surface nonradiative recombination[13]. However the effect of CdS shell on the electronic characteristics and the luminescence of CdTe core and The forming mechanisms are fewly reported.

In this paper, core/shell quantum dots were fabricated by an aqueous solution using thioglycolic acid as a stabilizer. Effect of the growth parameters on the optical and structure properties of quantum dots were investigated by fluorescence spectra and XRD. The mechanisms of the forming of quantum dots were further analyzed.

2. EXPERIMENTAL

All chemicals were used directly without any further purification unless otherwise stated. Tellurium powder (99.9 %), $CdCl_2·2.5H_2O$ (99.0 %), $Na_2S·9H_2O$ (≥98 %) and thioglycolic acid (TGA,≥ 98 %) were purchased from Tianjin Chemical Reagents Company. Distilled water was used throughout.

Te precursor solutions were prepared by mixing Te powder (0.0638 g) and $NaBH_4$ (0.0674 g) in distilled water (5 ml). The solution was treated by N_2-saturating for 30min in room temperature.

Cd precursor solutions were prepared by mixing $CdCl_2$ (0.228 g) and stabilizer of TGA (0.15 ml) in distilled water (50 ml). Then the pH value of the mixed solution was adjusted to 10 by dropwise addition of 1 mol/L NaOH solution. The solution was stirred and defeated by N_2 bubbling for 30min.

The freshly prepared NaHTe solution as quickly added into the mixture with vigorous stirring, then the resulting solution was refluxed at 100 °C for 2 h under nitrogen atmosphere. (Then anhydrous methanol and ether was added to precipitate the CdTe and excess TGA were removed.)

The method of synthesizing CdTe/CdS core/shell water-soluble quantum dots as follows: The Cd precursor solution (0.2 mol/L) was prepared by dissolving $CdCl_2 \cdot 2.5H_2O$ (0.228 g) in distilled- water (5 ml).The sulfur precursor solution (0.2 mol/L) was obtained by dissolving $Na_2S \cdot 9H_2O$ (0.240 g) in distilled water (5 ml).

Na_2S and $CdCl_2 \cdot 2.5H_2O$ solutions were added sequentially to a solution of CdTe QDs. The mixture was stirred and refluxed for 2 h at 100 °C under a N_2 atmosphere, cooled to room temperature, and then precipitated using acetone and diethyl ether. The precipitate was separated by centrifugation (1000 rpm for 10 min) and dried to afford the QDs[14].

The crystal phase and crystallinity were analyzed at room temperature by XRD using Cu Kα radiation. The fluorescent spectra of the as-prepared quantum dots samples were measured using a Xe lamp with an certain excitation wavelength. The UV-vis absorption spectra of the samples were recorded on a New Century T6 photospectrometer.

3. RESULTS AND DISCUSSION

Several techniques were utilized to monitor the shell growth and characterize the structure, crystallinity, and composition of the prepared particles.

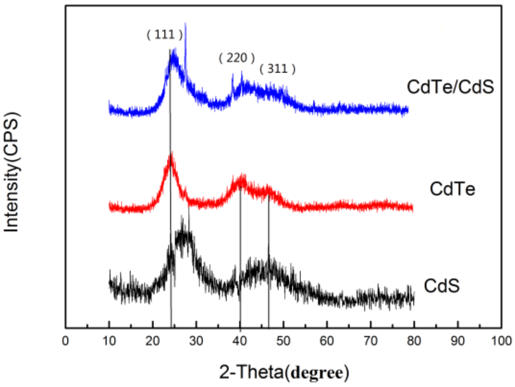

Figure 1. XRD patterns of CdS, CdTe and CdTe/CdS QDs

To identify the core/shell structure, the crystallographic properties were investigated by powder X-ray diffraction (XRD). Figure 1 compares the XRD patterns of several samples to the theoretical peak positions of the powder materials of CdTe, CdS, and CdTe/CdS, respectively. The diffraction peaks of CdTe/CdS core/shell were located 25.4°, 41.7°, 49.9°. Basically, the peak positions of the CdTe sample match quietly the theoretical values of the wurzite structure of CdTe. By contrast, the diffraction pattern of CdTe/CdS matches those of bulk CdTe much better than CdS. In addition, the peak positions of the CdTe/CdS move slightly toward a higher angle to CdS (but shapes being nearly unchanged) due to formation of the CdS shell on CdTe core. A homogeneous alloy, which would show a significant narrowing of XRD peak widths with increasing size, and the distribution of bond lengths resulting from intrinsic strains is a possible explanation for why. Similar changes in diffraction pattern were observed during the growth of CdS shell on CdTe core of previous reports as well.

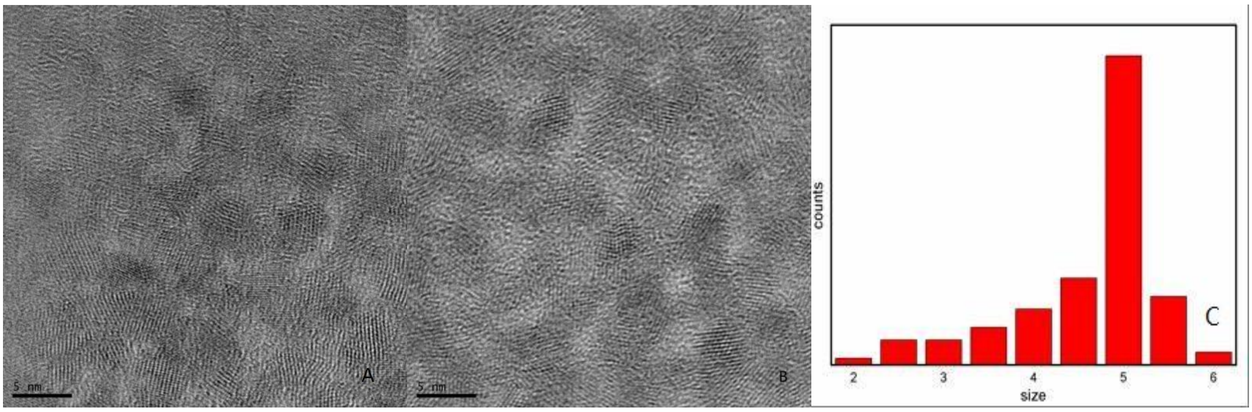

Figure 2. TEM image of CdTe/CdS (A), CdTe (B) and size histograms of CdTe/CdS QDs (C)

Figure.2 shows transmission electron microscopy (TEM) image of the CdTe-core nanocrystals and core/shell nanocrystals and size distributions. In particular, the images show the CdTe-core nanocrystals appear as spherical particles with crystalline structures and possess excellent monodispersity. In addition, the size of CdTe/CdS increases to 4.7nm in comparison with the CdTe-core size of 3.5 nm, which indicates that the optimal shell thickness of the CdS is 1.2 nm. Furthermore, the size of distribution also reveals the excellent monodispersity of the sample.

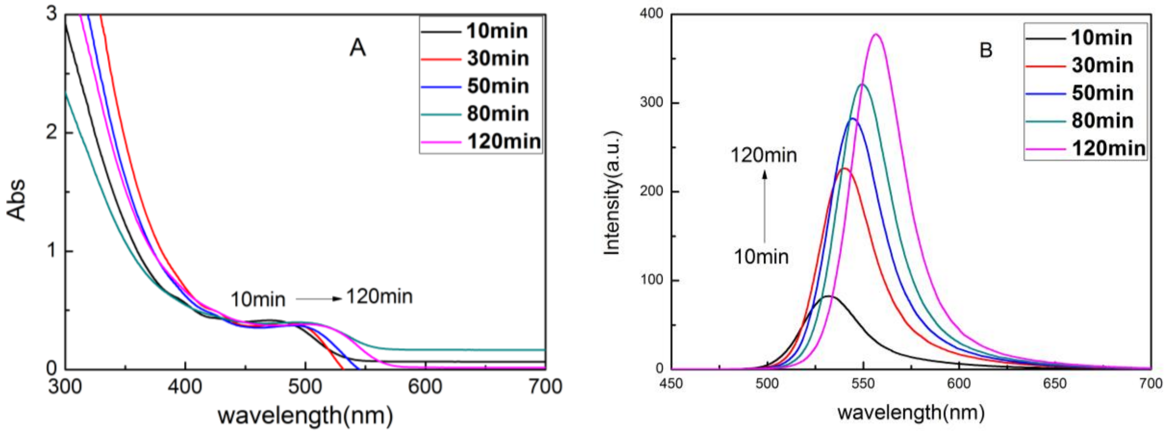

Figure 3. Normalized UV/Vis absorption spectra (A) and PL emission spectra (B, λ_{ex}=400nm) of plain CdTe cores with different reaction times.

Figure.3(A) and (B) show normalized UV/V is absorption spectrum and typical photoluminescence spectrum (PL) of CdTe QDs measured ina broad range of time frames. (with different reaction time). From the figure.3 (A), it could be seen that the absorption peak strongly dependent on the reaction time. With increasing reaction time the maximum absorption peak of samples had an evident redshift. From the figure.3 (B), it was seen that only one emission band is observed at a fixed excitation wavelength of 400nm. In addition, the emission maximum peaks systematically shifts toward lower energies and the PL band gets broader with the increasing of reaction time[15]. The above results could prove that the reaction time controls the diameter of CdTe QDs obviously. That is to say the absorption and fluorescence emission peaks shifted to lager energy with decreasing size.

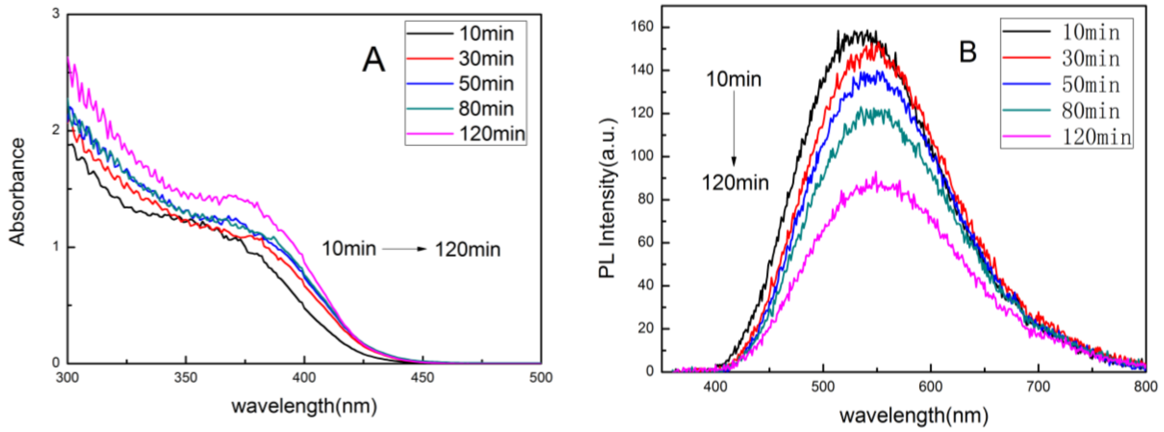

Figure 4. Normalized UV/Vis absorption spectra (A) and PL emission spectra (B, λ_{ex}=340nm) of plain CdS cores with different reaction times.

Figure.4 (A) and (B) showed normalized UV/Vis absorption spectra and typical photoluminescence spectrum (PL) of CdS QDs with different reaction time. From the figure.4, the law was the same as the CdTe QDs which showed in the figure.3.

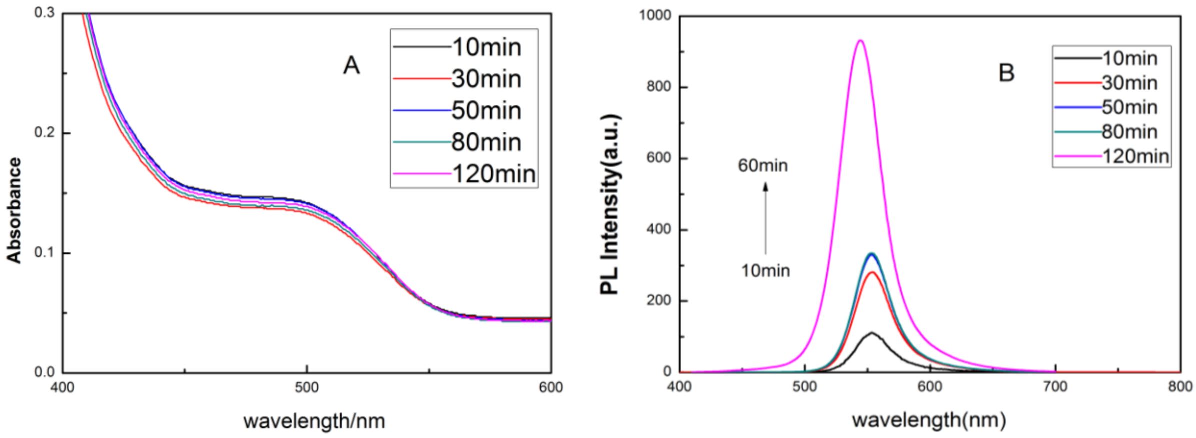

Figure 5. Normalized UV/Vis absorption spectra (A) and PL emission spectra (B, λ_{ex}=340nm) of CdTe/CdS core/shell with different reaction times.

The emission peaks had a redshift with the reaction time increasing. It indicated that the QDs size increased with the reaction time. The lines were not such smoothly because the reaction condition was alkaline which favored the growth of CdTe but not the CdS. The crystal form of CdS was unsatisfactory which lead to the not smoothing lines.

Figure.5 (A) and (B) showed normalized UV/Vis absorption spectrum and typical photoluminescence spectrum (PL) of CdTe/CdS QDs with different reaction time. Obviously, a wide bandgap shell (CdS) was epitaxially grown on the targeted core nanocrystals (CdTe). The emission peaks of core/shell QDs kept unanimous with the increasing reaction time, but the quantum yields are higher. These phenomena as a result of the surface of CdTe core/shell QDs took place a further passivation which made the surface defect of CdTe/CdS decreasing but the fluorescence intensity increasing. With advancing reflux time the absorption edge and emission peak did not change obviously which indicated that diameter of CdTe/CdS did not change too much but adjust crystal form mainly[16].

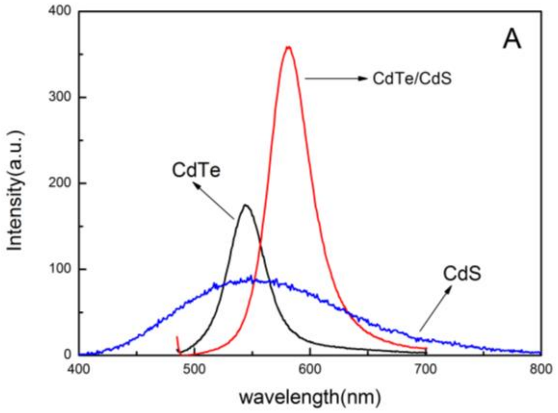

Figure 6. PL emission spectra (A) of CdTe, CdTe/CdS and CdS.

As shown in figure.6, compared with single CdTe and CdS, the fluorescence intensity of CdTe/CdS was increased obviously, and the emission peak of CdTe/CdS was red-shifted with a decrease in FWHM. The excitated electron but not the hole in CdTe could enter into CdS shell because of its big effective mass. The binding energy of CdTe/CdS decreased after combination of electrons and holes. The FWHM of core/shell QDs was narrow down because of the modified of crystal form and the distribution of diameter evenly[13, 17, 18].

4. CONCLUSION

In summary, we prepared the wide band-gap material CdS capped on the surface of CdTe QDs under the conditions of aqueous phase and low temperature. The experiments revealed that the optical properties of CdTe QDs can be improved with adding into the Cd and S precursor. CdTe/CdS QDs exhibited a significant red shift of absorption edge and emission peak, fluorescence intensity increasing as the time increasing, which proved that surface defect has been enhanced further more.

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