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ScienceDirect

Physica E 35 (2006) 75–80

PHYSICA E

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Synthesis and characterization of SiO_2-coated mercaptoacetic acid-stabilized CdSe nanocrystals in aqueous solution

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Received 29 July 2005; received in revised form 18 April 2006; accepted 28 May 2006
Available online 26 July 2006

Abstract

Mercaptoacetic acid-stabilized CdSe nanocrystals (NCs) coated with SiO_2 shell have been prepared in aqueous solution at room temperature. The results showed that the characteristic UV–Vis absorption peak disappeared, the band-edge photoluminescent (PL) emission greatly increased and the surface state emission decreased after the CdSe core overcoating with SiO_2 shell. The absorption spectra of the CdSe/SiO_2 composites did not obviously change but the PL spectra continually varied with reaction time during, about, a month. The quantum yield of the CdSe/SiO_2 composites was enhanced compared to the CdSe cores. Transmission electron microscopy (TEM) images revealed that multiple nanocores were incorporated in the spheres ranging in diameter mainly from 50 to 100 nm. Very aggregated spheres might be caused by the further hydrolysis of tetraethyl orthosilicate (TEOS). The X-ray diffraction (XRD) patterns also implied that the CdSe NCs had been incorporated in the SiO_2 matrix.

PACS: 68.65.Hb; 78.40.Fy; 61.46.Df

Keywords: Quantum dots; CdSe/SiO_2; Optical properties; Nanostructures

1. Introduction

Comparing the methods of the decomposition of organometallic precursors in organic solvents [1–4], aqueous solution synthetic methods of semiconductor quantum dots (QDs) are appealing because of their simplicity, safety, low reaction temperature and low cost. In recent years, much work has been reported on the solution synthetic methods for the preparation of QDs [5–11]. Since the mercapto group of mercaptoacetic acid (MA), or thioglycolic acid and 3-mercaptopropionic acid (MPA) can bind to the surface of the QDs, and the polar carboxylic acid groups render the dots water-soluble [12], the QDs synthesized with these molecules as stabilizers in aqueous solution are of special interest for biomedical applications. Unfortunately, the QDs synthesized with this method often have low photoluminescence (PL) quantum yield (QY) and broad PL emission, which is not beneficial to biomedical applications. Research on the method for improving the QY and making the emission narrower is therefore necessary. Up to now, however, the control of the PL properties of the QDs is still a challenge for developing synthetic chemistry for these materials, and this issue still remains mostly unsolved [13].

It is well known that the surface properties of the QDs have significant effects on their optical properties. Therefore, passivation of the surface of the QDs is the key to any investigation of such nanocrystals (NCs). During the past decade, inorganically coated QDs, such as CdSe/ZnS [2,3], CdSe/CdS [4,8], CdSe/ZnSe [14], CdSe/ZnSe/ZnS [14,15], CdS/ZnS [16] and CdS/HgS [5], etc., have been investigated. These core–shell nanocomposites have been shown to passivate the traps that present at the surface of the QDs. However, Cd [17] and Se [18] and other elements of QDs, such as Hg, Zn, Te, etc., are toxic to many cells. The

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doi:10.1016/j.physe.2006.05.002

release of these toxic materials from the dots into the biological environment would greatly limit their biomedical applications. Passivating the QDs with the inorganic shell(s) containing toxic ions would render the clinical applications of the QDs are far way off.

Recently, SiO_2 overcoated QDs (e.g., CdS, CdSe/ZnS, CdTe, etc) [19–27] have attracted considerable attention because these composites not only exhibit novel physicochemical properties, but also reduce the release of the toxic ions. Additionally, the surface of SiO_2 is suitable for conjugating many biomolecules, and the optical active SiO_2 colloids can serve as the starting point for a variety of photonic materials such as laser media, diffraction gratings and sensing films [21]. Over the past few years, CdSe NCs are important QDs that have been used in many biomedical systems [12,19,28–31], but to our knowledge, no work is presented about SiO_2 overcoated CdSe NCs which are synthesized in aqueous solution with MA as a stabilizer.

This paper presents a relatively simple method to passivate the surface nonradiative recombination sites of CdSe NCs. The synthesis begins with the reaction of CdSe NCs in hot water containing MA molecules, and SiO_2 shells are then directly deposited at the surface of these CdSe cores at room temperature. A more interesting finding is that the optical properties of the SiO_2-coated CdSe are quite different from that of the bare CdSe dots. These resultant CdSe/SiO_2 core–shell composites may have many advantages for biomedical, electrical and optoelectronic applications.

2. Experimental section

$CdCl_2 \cdot 2.5H_2O$, Na_2SO_3, Se powder, $NH_3 \cdot H_2O$, MA, Tetraethyl orthosilicate [TEOS, $Si(OEt)_4$], Rhodamine 6G and absolute ethanol were purchased from Shanghai Chemical Regent Co., Ltd. Riboflavin (high purity grade) was purchased from Genebase Gene-Tech Co., Ltd. Na_2SeSO_3 solution was prepared freshly by dissolving Se powder in Na_2SO_3 solution under nitrogen atmosphere at 358 K for at least 24 h. All the reagents and solvents were analytical grade, and were used without further purification. The water used in all experiments was prepared by a Millipore Milli-Q Plus purification system.

For a typical synthesis of CdSe NCs, the desired amount of $CdCl_2$ powder was added to thoroughly degassed MA aqueous solution of 50 ml, followed by addition of $NH_3 \cdot H_2O$ until the pH value was 11.0. The mixture solution was heated to 368 K. The concentration of $CdCl_2$ and MA were 1 and 8 mM, respectively. Then 0.8 mM Na_2SeSO_3 solution of 50 ml was added to the $CdCl_2$ solution under continuous vigorous stirring at N_2 atmosphere at 368 K. After stirring for about 30 min, the reaction solution was cooled naturally to room temperature.

Four kinds of CdSe/SiO_2 core–shell composites were synthesized in this work. For the typical experiment, TEOS solution containing 27% (v/v) absolute ethanol was added to the aforementioned CdSe solution with vigorous stirring at room temperature. The volume of the CdSe solution was retained at 15 ml, and the TEOS mixture solution was 170, 340, 700 μl and 1.4 ml, respectively. From each sample 1 ml of reaction solution was withdrawn at 2, 7, 14 and 28 days, followed by centrifugation, washing three times with absolute ethanol and water. The precipitates were then redispersed in water. The residual reaction solutions (28 days) were centrifugated and washed in the similar way as mentioned above, and freeze-dried at 203 K for 24 h taking on a ALPHA-2-4 freeze-dryer (MARTIN CHRIST Gefriertrocknungsanlagen Gmbh, Germany).

For preparation of pure SiO_2 colloids, 340 μl of TEOS containing 27% (v/v) absolute ethanol was added into 15 ml of water ($pH = 10.7$) with vigorous stirring at room temperature. The collecting, washing and drying processes of the SiO_2 precipitates were in a similar way as that of CdSe/SiO_2 described above.

UV–Vis absorption spectra of the CdSe NCs, pure SiO_2 and CdSe/SiO_2 composites were taken on a diode array spectrophotometer (UV-2102PC, Unico (Shanghai), USA) with a Deuterium lamp source. The PL spectra excited by 400 nm were taken on a fluorescence spectrometer (F-2500, Hitachi, Japan) with a Xenon lamp source. The QY of the CdSe and CdSe/SiO_2 in aqueous solution were determined by comparing the integrated emission to that of Rhodamine 6G in ethanol, and the riboflavin was used as calibration reagent, which was according to the procedure described in Ref. [11]. For the above optical measurements, dilute solutions of the CdSe in water were placed in 1 cm quartz cuvettes, and the absorbance of all solutions below 0.5 at excitation wavelength was used. All the measurements were taken at room temperature. The color fluorescent images (excitation: 488 nm) of the CdSe/SiO_2 composites were recorded on a digital color camera (COOLPIX4300, Nikon, Japan) that was attached to an upright fluorescence microscope (Leica, DME, Germany). For the morphology evaluation, the suspensions were dispersed via ultrasound irradiation, and then air dried onto carbon coated grips and observed by transmission electron microscopy (TEM, JEOL-1230, Japan). X-ray diffraction (XRD) patterns were performed on a D8 DICOVER GADDS diffractometer (Bruker, German) using a graphitic-filtered Cr Kα ($\lambda = 0.22898$ nm) radiation.

3. Results and discussion

Fig. 1 shows the UV–Vis absorption and PL spectra of the CdSe NCs, pure SiO_2 and CdSe/SiO_2 composites synthesized with different amount of TEOS withdrawn at 2 days. We observe that the resolved lowest exciton transition of the CdSe NCs locates at 438 nm, which pronounced blue shifts from 716 nm of bulk CdSe band gap [1]. After overcoating with SiO_2, the characteristic absorption peak of the CdSe NCs disappeared. No pronounced difference