

Characterization and photoluminescence studies of CdTe nanoparticles before and after transfer from liquid phase to polystyrene

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Abstract. The major objective of this work was to detect the change of photoluminescence (PL) intensity of CdTe nanoparticles (NPs) before and after transfer from liquid phase to polystyrene (PS) matrix by electrospinning technique. Thio-stabilized CdTe NPs were first synthesized in aqueous, then enwrapped by cetyltrimethylammonium bromide (CTAB), and finally, transferred into PS matrix to form CdTe/PS nanofibres by electrospinning. Then, CdTe/PS nanofibres were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) to observe their morphology and distribution, respectively. The selective area electronic diffraction (SAED) pattern proved that the CdTe NPs were cubic lattice. The PL spectrum indicated that CdTe NPs have been transferred into PS nanofibres, and the PL intensity of CdTe NPs in the nanofibres was even higher than that before CdTe NPs were introduced into PS nanofibres. Moreover, X-ray photoelectron spectra (XPS) revealed that thiol-stabilized CdTe NPs were enwrapped by CTAB, and PS acted as a dispersant in the process of electrospinning.

Keywords. CdTe; CTAB; electrospinning; nanofibre; nanoparticle; photoluminescence intensity.

1. Introduction

CdTe nanoparticles (NPs) have attracted greater attention because of their unique optical properties, especially their potential applications in the manufacture of chemical sensors, optical switches, display devices and biological labels (Li *et al* 2005; Poznyak *et al* 2005). Up to now, self-assembled CdTe NPs in different solutions have been obtained. Because the Te^{2-} is sensitive to the oxygen in the process of preparing CdTe NPs, it is necessary to utilize thioglycolic acid (TGA), as a preservative agent, to modify the surface of CdTe NPs, resulting in the surface of the thio-stabilized CdTe NPs with electronegative charges (Gaponik *et al* 2002; Zhang *et al* 2003a). To further protect Te^{2-} in CdTe NPs against oxidization, and to transfer CdTe NPs from aqueous solution into organic solvent, cetyltrimethylammonium bromide (CTAB) as cationic surfactant was introduced. It was proved that the PL intensity of CdTe NPs enwrapped by CTAB enhanced remarkably (Wang *et al* 2007a). Moreover, polystyrene (PS), an inert polymer, is utilized in many research works. Then, it may be an attractive topic to disperse CdTe NPs into PS matrix in order to generate a novel fluorescent nanocomposite (Chen *et al* 2001; Li *et al*

2006; Wang *et al* 2007b). In addition, among many methods to fabricate one-dimensional nanomaterials, electrospinning plays such a major role that is applied to prepare nanofibres composing of inorganic or organic NPs (Ji *et al* 2006; Ostermann *et al* 2006).

Presented here is a convenient and efficient way to fabricate CdTe/PS nanofibres, in which lipophilic CdTe NPs dispersed in PS nanofibres homogeneously. The morphologies of the obtained nanofibres were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The crystal state of CdTe NPs in PS nanofibres was detected by selective area electron diffraction (SAED) pattern. The optical state of CdTe NPs in PS nanofibres was characterized by the photoluminescence (PL) spectra. In addition, X-ray photoelectron spectra (XPS) revealed that thiol-stabilized CdTe NPs were enwrapped by CTAB, and CdTe NPs only dispersed in PS nanofibres rather than interaction with PS by a chemical bond.

2. Experimental

2.1 Materials

Sodium borohydride (NaBH_4), tellurium powder (200 mesh, 99.8%) and thioglycolic acid (TGA, 97%) were

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purchased from Aldrich. $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (99%) and cetyltrimethylammonium bromide (CTAB) were purchased from Beijing Chemicals Co., China. All the other chemicals were of analytical grade and used as received.

2.2 Synthesis and assembly of CdTe NPs

Thiol-stabilized CdTe NPs were synthesized following literature (Zhang *et al* 2003b; Li *et al* 2004). In brief, NaBH_4 (80.0 mg) and tellurium powder (127.6 mg) were mixed in a 5 mL flask under nitrogen atmosphere. One mL of ultrapure water was added into the flask to initiate the reaction. The reaction system was cooled by ice in the next 8 h, then the black tellurium powder disappeared and white sodium tetraborate precipitated on the bottom of the flask. The NaHTe was formed in clear supernatant. At the same time, after 456.8 mg of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 0.42 mL of TGA were dissolved under stirring in 200 mL of ultrapure water (deaerated by N_2 for 30 min) in another flask, the pH of the solution was adjusted to 10.5 with 1 mol/L NaOH dropwise. After the freshly prepared NaHTe solution was transferred to the latter mixture under N_2 , the mixture was refluxed and stirred vigorously for 4 h to form thiol-stabilized CdTe NPs solution.

In order to enwrap CdTe NPs by CTAB, 40 mL of CdTe solution was separated from the above mixture and transferred into another 100 mL of flask under nitrogen atmosphere at 50°C, to which 1.7348 g of CTAB was added slowly. CdTe NPs enwrapped by CTAB precipitated at the bottom of the flask while CTAB was dissolved completely, then cooled to room temperature. The precipitate was separated by centrifugation, and 20 mL of chloroform was added to dissolve the precipitate. The solution of the obtained CdTe NPs enwrapped by CTAB was red-brown. This solution (20 mL) was concentrated with N_2 stream to 2.0 g for usage in further experiment.

2.3 Transferring CdTe NPs to PS nanofibres by electrospinning

PS (0.6 g) was dissolved in 2.4 g of *N,N*-dimethylformamide (DMF) under stirring to form a homogeneous PS/DMF solution, to which the aforementioned 2.0 g of CdTe/chloroform solution was added and stirred for 6 h.

The CdTe/PS mixture was filled to an acutilingual glass tube wrapped with copper wire, which was connected with a 12 kV positive d.c. A grounded aluminum cylinder with a surface area of 10×20 cm was applied to collect the nanofibres after the power was switched on. Electrospinning was carried out at room temperature (25°C) and the distance from the tip of the glass tube to the surface of the aluminum cylinder was 15 cm (Lu *et al* 2005a; Matsumoto *et al* 2006).

2.4 Characterization of liquid and solid samples

The morphologies of the nanofibres were observed by a scanning electron microscopy (SEM, Shimadzu SSX-550, Japan) and a transmission electron microscope (TEM, Hitachi S-570, Japan). Selective area electronic diffraction (SAED) was utilized to determine the lattice of CdTe NPs. X-ray photoelectron spectra (XPS, VG-Scientific ESCALAB 250 spectrometer with a monochromatic Al $K\alpha$ X-ray source at 1486.6 eV) revealed the interaction between CdTe NPs and PS. Moreover, the variations in PL intensities of CdTe NPs in different states were investigated on Shimadzu RF-5301 PC spectrofluorimeter (Japan). All these measurements were performed at room temperature.

3. Results and discussion

3.1 Characterization of CdTe/PS nanofibres by SEM, TEM and SAED

The morphologies of the obtained CdTe/PS nanofibres were observed by SEM and TEM as shown in figure 1. The SEM image (shown as panel A) indicates a smooth surface of CdTe/PS nanofibres with an average diameter around $\sim 370 (\pm 38)$ nm. Panel B is a TEM image to show CdTe NPs dispersing in PS nanofibres homogeneously. Whether CdTe exists in PS nanofibres can be detected by analysis of elements within a selective area *via* SAED. The inset chart in panel B indicates the diffraction cycle of the elements within the PS nanofibres, whose radii, r , were 0.54 cm, 0.91 cm and 1.08 cm, respectively. Thus, the distance between the CdTe wafers, d , can be expressed as follows

$$d = L\lambda/r, \quad (1)$$

where $L = 0.8$ m, $\lambda = 0.00251$ nm. The values of d were calculated as 0.372, 0.221 and 0.186 nm, respectively. By assigning the elements to Cd and Te in PCPDFWIN software, the h , k , l results were (111), (220) and (311), indicating that CdTe NPs existing in PS nanofibres are cubic lattice. This result is in agreement with the previous report (Lu *et al* 2004).

3.2 Determination of PL intensity of CdTe NPs in different states

The aim of preparing CdTe/PS nanofibres is to investigate the PL property of CdTe NPs before and after transferring them from the liquid phase to PS nanofibres by electrospinning. At present, the PL intensities of CdTe NPs in various states were collected in figure 2. As line **a** in figure 2 shows, the maximum PL intensity (696 a.u.) of thiol-stabilized CdTe NPs locates at 572 nm. After CdTe NPs are enwrapped by CTAB (line **b**), the PL

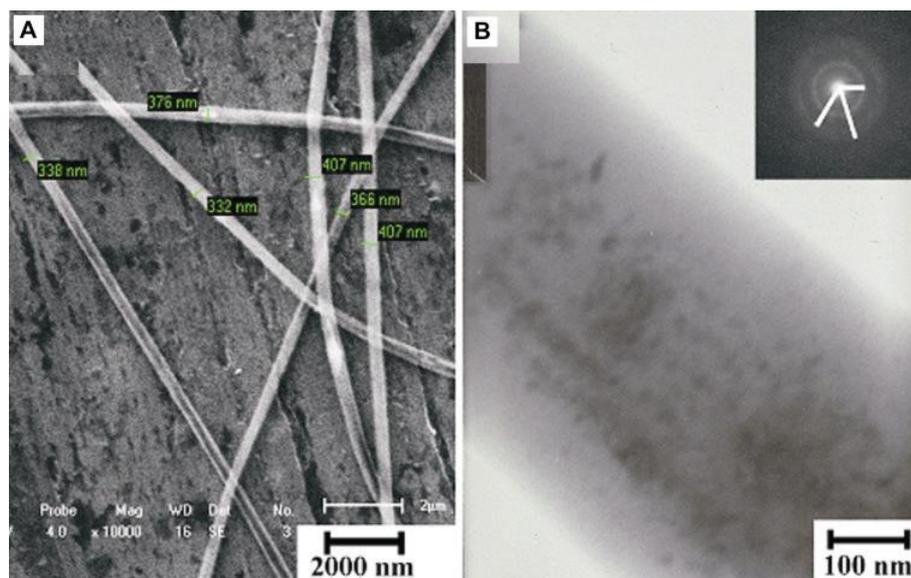


Figure 1. SEM image of CdTe/PS nanofibres (A), TEM image of CdTe/PS nanofibres (B) and CdTe SAED pattern (inset).

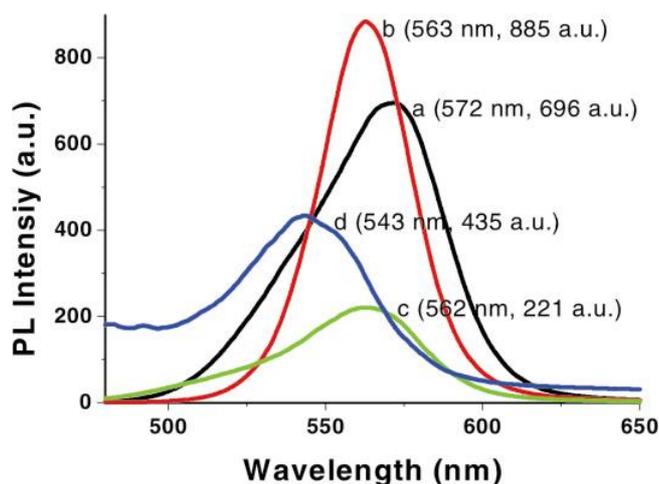


Figure 2. PL spectra of CdTe NPs aqueous (a), CTAB wrapped CdTe NPs solution (b), CdTe/PS mixed solution before electrospinning (c) and CdTe/PS nanofibres (d).

intensity of CdTe NPs increases to 885 a.u., together with the wavelength shift to 563 nm. Moreover, the emission peak of CdTe NPs wrapped by CTAB is narrow as well. This can be attributed to the uniform granularity of CdTe NPs, and to the fact that the disfigurement on the surface of CdTe NPs is modified by CTAB. When PS matrix is introduced into the above-mentioned solution, as line **c** shows, the PL intensity decreases remarkably (221 a.u.), and almost no shift of the peak is found in this case (562 nm). The decrease in PL intensity of CdTe is due to the introduction of the PS matrix, leading to the decrease of the transmittance of light through CdTe NPs

solution, which is composed of PS. Although the PL intensity (line **d**, 435 a.u.) of CdTe/PS nanofibres decreases remarkably compared with those of aforementioned solutions (lines **a** and **b**), it still increases significantly compared with line **c**. It is also found that the wavelength of the peak of CdTe/PS nanofibres shifts to 543 nm (line **d**). This phenomenon indicates that the surface of CdTe NPs is wrapped with too much polymer matrix, resulting in PL quench of CdTe NPs.

In addition, this blueshift (lines **b**, **c** and **d**) phenomenon of all the aforementioned CdTe samples compared with CdTe aqueous solution (line **a**) can also be understood by the relationship between the energy level, ΔE , and the absorbance of wavelength, λ , as follows

$$\Delta E = (hc)/\lambda, \quad (2)$$

in which h stands for Planck constant and c stands for light velocity. Equation (2) reveals the inverse proportional relationship between ΔE and λ . With the addition of CTAB, CdTe NPs (line **a**, 572 nm) are wrapped by CTAB so perfectly that the distance of CdTe NPs (line **b**, 563 nm) gets large, resulting in an increase of the emissive energy, ΔE , and a decrease of the wavelength, λ . Thus, it is reasonable to observe the blue shift in the PL spectra. Moreover, no remarkable blue shift appears in the solution after PS matrix was introduced, demonstrating that the PS matrix does not affect the emissive energy of CdTe, but the decrease of transmittance of the solution leads to a decrease of the PL intensity of the solution. It can be found from TEM image that CdTe NPs dispersed randomly in PS matrix and the PL spectra of CdTe/PS nanofibres is detected from the diffuse reflection of the CdTe/PS nanofibres. Thus, CdTe NPs in PS nanofibres

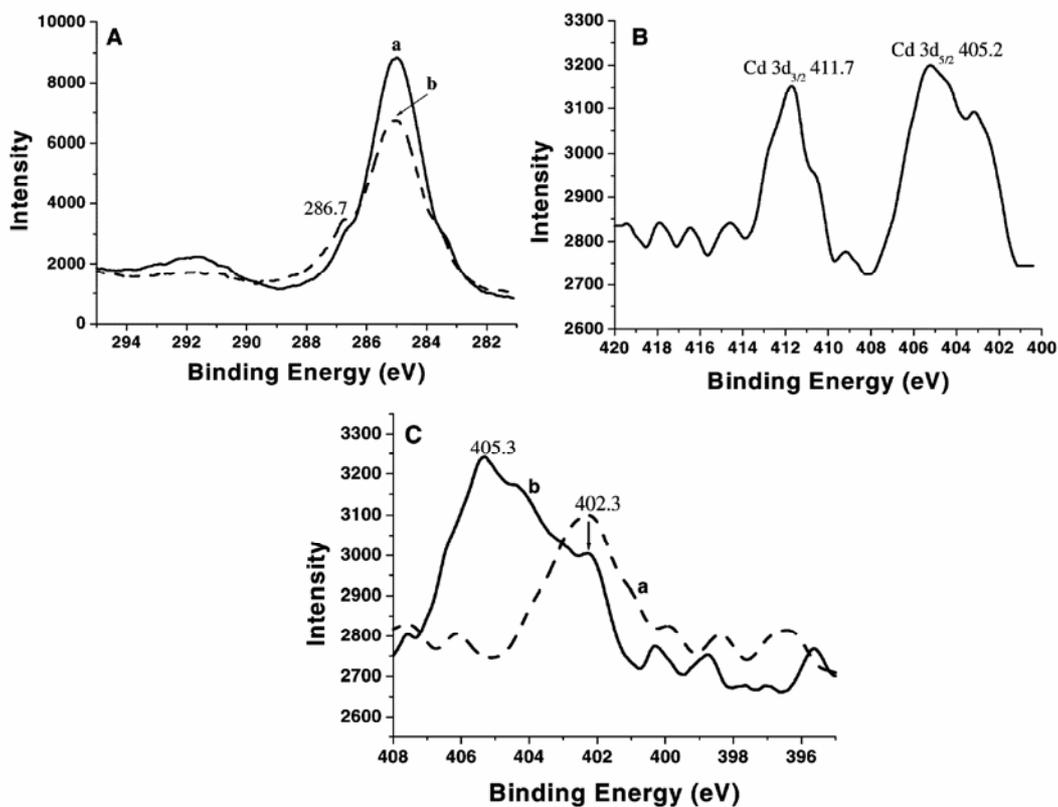
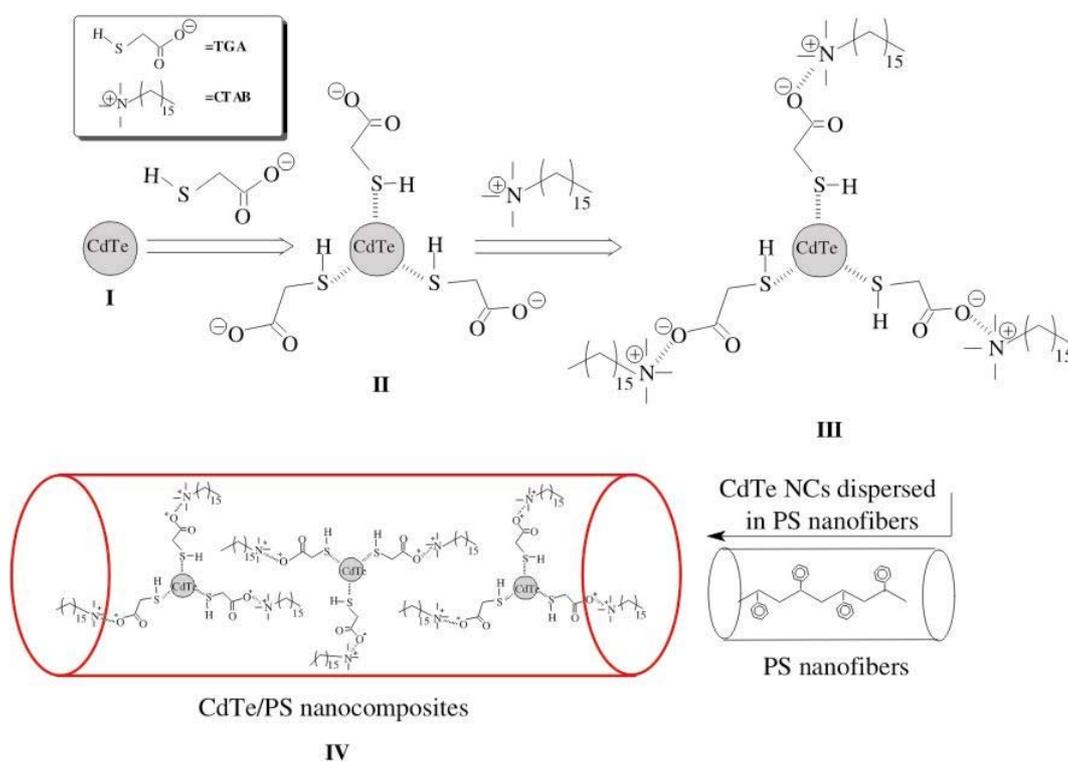


Figure 3. XPS spectra of C_{1s} in PS nanofibres (a) and CdTe/PS nanofibres (b) (A), Cd_{3d} in PS nanofibres (B) and N_{1s} in CTAB (a) and CdTe/PS nanofibres (b) (C).



Scheme 1. Model of the generating process of CdTe/PS nanofibres.

exhibit perfect emissive in the energy, and remarkable blue shift in the wavelength.

3.3 Detection of XPS

X-ray photoelectron spectroscopy (XPS) is used to investigate the interaction between CdTe NPs and PS nanofibres as shown in figure 3. As panel A shows, the peak of the C_{1s} of PS (line **a**) is similar to that in CdTe/PS nanofibres (line **b**), indicating that the introduction of CdTe NPs into PS nanofibres does not affect the carbon chain of PS. Furthermore, two peaks of Cd_{3d} are observed at 411.7 and 405.2 eV (shown as panel B), which are related to the binding energies of $3d_{3/2}$ and $3d_{5/2}$ of Cd, respectively. This result is in agreement with previous reports by Lu *et al* (2005b). In addition, the line **a** in panel C indicates a peak of N_{1s} at 402.3 eV in CTAB. After CdTe NPs enwrapped by CTAB is introduced into PS nanofibres, shown as line **b** in panel C, the peak of N_{1s} at 402.3 eV in CTAB decreases to be a slim shoulder peak, whereas, a strong peak locates at 405.3 eV, due to the interaction between N cation in CTAB with COO^- in TGA.

3.4 Suggestion for a model of CdTe NPs enwrapped by CTAB

The results from XPS suggest a model of formation of CdTe/PS nanofibres as shown in scheme 1. CdTe (**I**) is first stabilized by S atom in TGA to generate thio-stabilized CdTe NPs (**II**). Then CTAB (**III**) is introduced to enwrap CdTe NPs by the interaction between N^+ in CTAB and COO^- in TGA. Finally, the aforementioned CdTe NPs disperse in PS nanofibres to form CdTe/PS nanofibres (**IV**) by means of electrospinning.

4. Conclusions

To sum up, CdTe NPs are prepared in aqueous solution successfully, and enwrapped by CTAB to form lipophilic CdTe NPs. Then, lipophilic CdTe NPs are introduced into PS nanofibres by electrospinning. SEM and TEM images reveal that the obtained CdTe/PS nanofibres are nanoscale, and CdTe NPs disperse in the PS nanofibres homogeneously. The SAED pattern proves that CdTe

NPs in PS nanofibres exhibit as a cubic lattice. PL spectra indicate that CdTe NPs in PS nanofibres exist in an optical style. XPS verifies that there is no interaction between CdTe NPs and PS nanofibres. This information may be useful in further research of nanofibres involving photoluminescent CdTe NPs.

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