

# Fabrication and Characterization of CdTe Nanoparticles Attached to Poly(4-vinylpyridine) Nanofibers

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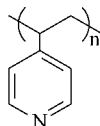
**ABSTRACT:** The major objective of this work was to characterize the status of CdTe nanoparticles attached to the surface of poly(4-vinylpyridine) (P4VP) nanofibers. Scanning electron microscopy and transmission electron microscopy images indicated that the attachment of CdTe nanoparticles enlarged the diameter of P4VP nanofibers. Moreover, the results of the energy-dispersive X-ray spectrum and the electron diffraction pattern revealed that the deposition on the surface of P4VP nanofibers was CdTe in a cubic lattice. Furthermore, CdTe existed in its

optical style according to photoluminescence spectra. X-ray photoelectron spectroscopy verified Cd in CdTe nanoparticles combined with the N atom in P4VP nanofibers. Therefore, the obtained results provide some references for preparing coaxial nanofibers attached by other nanoparticles. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 281–286, 2008

**Key words:** adsorption; fluorescence; nanolayers; nanotechnology; self-assembly

## INTRODUCTION

Because of pyridine rings in the structural unit of poly(4-vinylpyridine) (P4VP), P4VP possesses special activity to immobilize enzymes and other organic molecules. Thus, P4VP is a wonderful ligand for preparing biosensors.<sup>1,2</sup> In addition, P4VP also forms a good electroactive polymer complex with metals because of the heterocyclic groups.<sup>3,4</sup> For example, the interaction between P4VP and copper makes a special composite that behaves as an electrochemical material with a special thermal property.<sup>3,4</sup> In particular, Jones et al.<sup>5</sup> succeeded in preparing P4VP nanofibers attached by NaAuCl<sub>4</sub> and AgNO<sub>3</sub> and then reduced by sodium borohydride (NaBH<sub>4</sub>) to form Au/P4VP and Ag/P4VP nanofibers, respectively. Therefore, P4VP plays an important role in the synthesis of inorganic–organic hybrid materials:



poly(4-vinylpyridine) (P4VP)

CdTe possesses a unique size-dependent optical property that has attracted more scientific attention in imaging, chemical sensors, optical switches, display devices, and biological labels.<sup>6–10</sup> After being enwrapped by thioglycolic acid (TGA) in the process of preparing CdTe nanoparticles with the reaction between NaHTe and Cd<sup>2+</sup>, thiol-stabilized CdTe nanoparticles exhibit strong optical activity. We have wrapped thiol-stabilized CdTe nanoparticles in poly(vinyl pyrrolidone) (PVP) and detected the photoluminescence (PL) intensity of CdTe/PVP nanofibers.<sup>11</sup> This research background motivated us to adhere CdTe nanoparticles to P4VP nanofibers to investigate the PL intensity of CdTe nanoparticles on the surface of P4VP nanofibers. These composite nanofibers were potential optical nanofibers that could extend the application of CdTe.

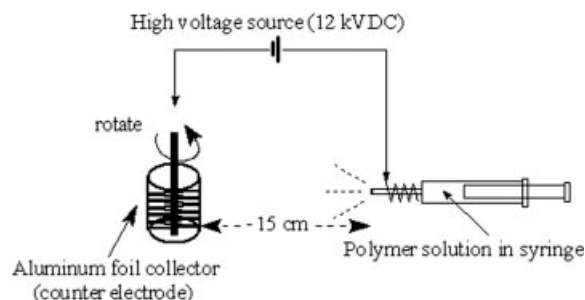
Among many methods used to fabricate nanomaterials, electrospinning plays a major role because a polymer solution splits to jet toward a grounded collector and forms nanofibers automatically in the field of a high-voltage direct current (DC).<sup>12–14</sup> The first aim of this work was to prepare P4VP nanofibers to which CdTe nanoparticles were adhered. Then, the obtained composite nanofibers were investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In addition, the attachment of CdTe nanoparticles to the surface of P4VP nanofibers was proved by the electron diffraction (ED) pattern. PL and energy-dispersive X-ray (EDX) patterns were also applied to verify the existence of CdTe nanoparticles on the surface of P4VP

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**Scheme 1** Electrospinning apparatus.

nanofibers. Moreover, X-ray photoelectron spectroscopy (XPS) spectra revealed the interaction between CdTe nanoparticles and P4VP.

## EXPERIMENTAL

### Materials

TGA (97%), tellurium powder (200 mesh, 99.8%),  $\text{NaBH}_4$  (99%), and P4VP were purchased from Acros. *N,N*-Dimethylformamide (DMF), cadmium chloride ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , 99.8%), and *i*-propyl alcohol were supplied by Beijing Chemicals Co. (Beijing, China). All reagents were analytical-grade and were used without further purification.

### Preparation of CdTe nanoparticles and P4VP nanofibers

Thiol-stabilized CdTe nanoparticles were synthesized according to the literature with a little modification.<sup>15,16</sup> Briefly,  $\text{NaBH}_4$  (160 mg) was mixed with tellurium powder (255.2 mg) in a 5-mL flask deaerated with  $\text{N}_2$  in advance. Then, 2 mL of ultrapure water was added at room temperature to initiate the reaction. After approximately 8 h, the black tellurium powder disappeared, and white sodium tetraborate precipitated on the bottom of the flask. The  $\text{NaHTe}$  was formed in a clear supernatant. At the same time, 91.36 mg (0.2 mmol) of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  was dissolved in 66 mL of ultrapure water in another 100-mL, three-necked flask. After the addition of 0.6 mmol of TGA to aqueous  $\text{CdCl}_2$  under stirring, the solution was adjusted to pH 11 with 1M  $\text{NaOH}$  dropwise and then deaerated by  $\text{N}_2$  for 30 min. Finally, after 0.1 mL of a freshly prepared  $\text{NaHTe}$  solution was transferred to the latter mixture under  $\text{N}_2$ , the mixture was then refluxed and stirred vigorously to form a solution of thiol-stabilized CdTe nanoparticles. Then, an equivalent volume of *i*-propyl alcohol was added to the solution of thiol-stabilized CdTe nanoparticles to precipitate CdTe nanoparticles, which could be separated by centrifugation. The obtained deposition was dispersed in

2 mL of ultrapure water under ultrasound. Thus, the concentrated CdTe solution was obtained for the following experiment.

As for the preparation of P4VP nanofibers, 0.4 g of P4VP powder was dissolved in 1 mL of DMF under magnetic stirring to form a 0.4 g/mL P4VP solution at room temperature. As shown as Scheme 1, the P4VP solution was filled in a plastic syringe, whose needle (the internal diameter was 0.8 mm) was connected to a 12-kV positive voltage with regulated DC. A piece of aluminum foil wrapped on a grounded rotating cylinder (10 cm  $\times$  20 cm) was applied to collect the nanofibers. The distance between the needle tip and the foil was  $\sim$  15 cm. After the power was switched, the ejection rate of the solution from the syringe was 1.2 mL/h, and the electrospinning was carried out in air. The nanofibers could be collected on the foil at the ambient temperature. The majority of the solvent was volatilized in air during electrospinning. The obtained samples were preserved in a vacuum desiccator for several days before characterization to eliminate the residual solvent.<sup>17,18</sup>

### Assembly of CdTe nanoparticles to P4VP nanofibers

The P4VP nanofibers were dipped in the concentrated CdTe nanoparticle solution, which was deaerated by  $\text{N}_2$  for 2 h in advance, were then taken out and washed thoroughly with ultrapure water, and were finally dried for 3 h in a vacuum desiccator.

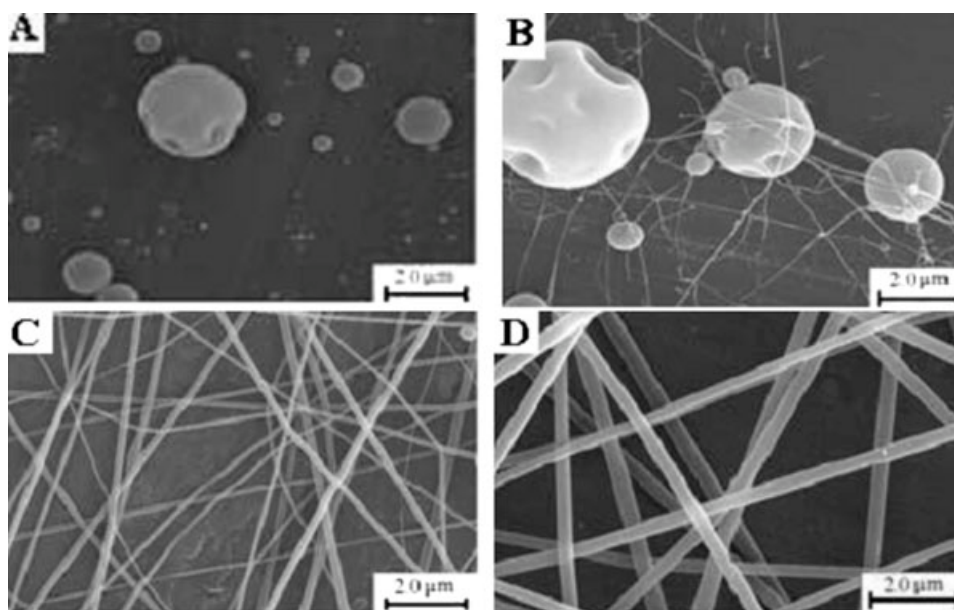
### Characterization of the nanofibers

The morphologies of the obtained P4VP nanofibers before and after combination with the CdTe nanoparticles were observed with a scanning electron microscope (XL30 ESEM, FEI, Japan) with a function of EDX to characterize the distributive status of elements in the field of vision. The ED of the sample was measured on a transmission electron microscope (S-570, Hitachi, Japan). The PL intensities of the CdTe nanoparticles and CdTe/P4VP nanocomposites were measured with a steady-state fluorescence spectrometer (FS920, Edinburgh Instruments, United Kingdom). In addition, P4VP nanofibers and CdTe/P4VP nanocomposites were determined by XPS (Escalab 250, VG-Scientific) to explore the interaction between the CdTe and P4VP.

## RESULTS AND DISCUSSION

### Characterization of the morphology of P4VP nanofibers by SEM

The morphology of the nanofibers obtained by electrospinning was affected by the viscosity and surface



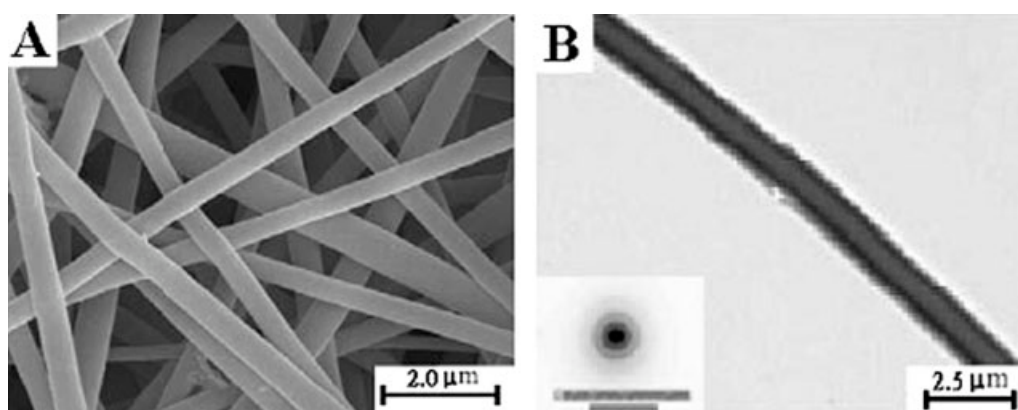
**Figure 1** SEM images of P4VP nanofibers electrospun from P4VP/DMF solutions with concentrations of (A) 0.1, (B) 0.2, (C) 0.3, and (D) 0.4 g/mL.

tension of the polymer solution. Although there was a nonlinear relationship between the aforementioned parameters and the concentration of the polymer solution, the optimal nanofibers could be obtained with a certain concentration of the polymer solution. Therefore, the appropriate concentration of the P4VP/DMF solution for obtaining nanofibers was investigated first. Figure 1 outlines the morphologies of the obtained species when the concentrations of P4VP were 0.1, 0.2, 0.3, and 0.4 g/mL. As shown as Figure 1(A), only some spherules were obtained when the concentration for the P4VP/DMF solution was 0.1 g/mL. With the increase in the concentration of P4VP/DMF solution to 0.2 g/mL, some P4VP nanofibers with an average diameter of 132 nm appeared among the spherules. The spherules disappeared as the concentration of the P4VP/DMF solu-

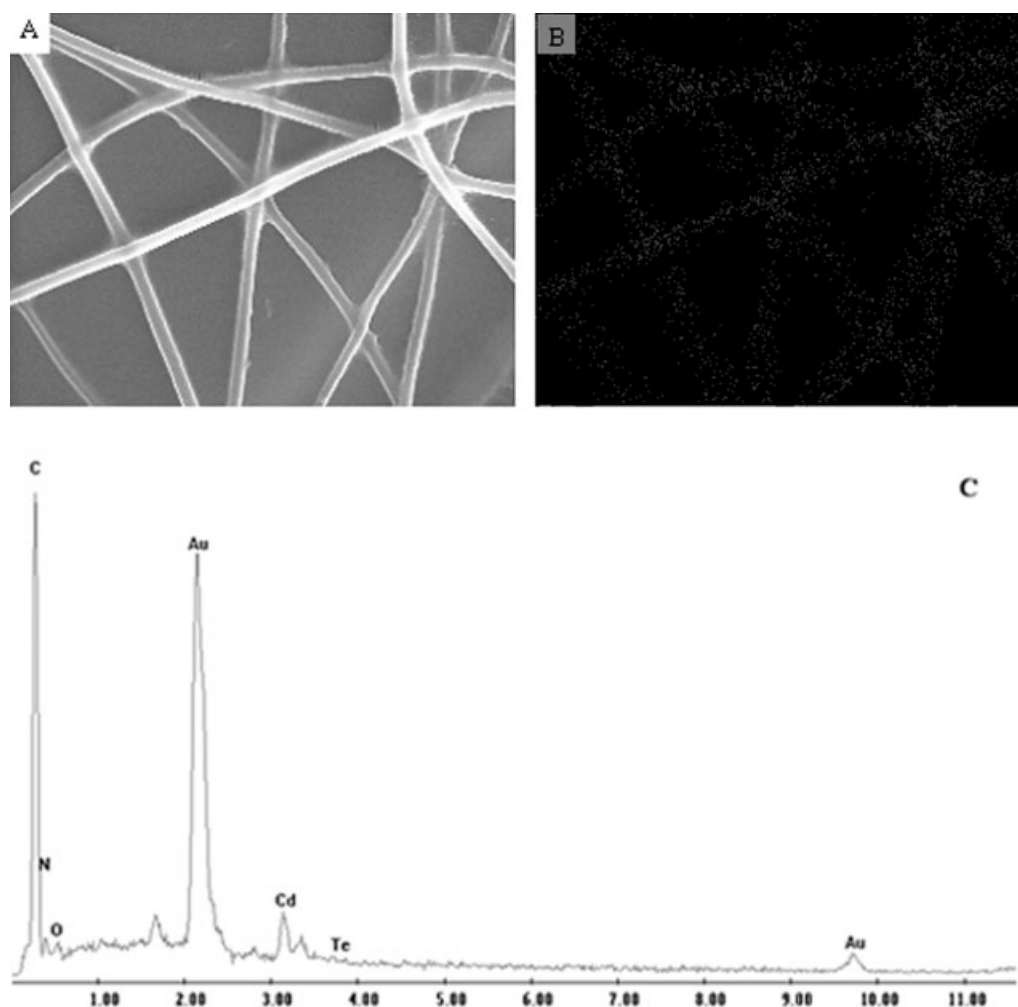
tion increased to 0.3 g/mL. Finally, homogeneous and smooth P4VP nanofibers with a diameter of approximately 360 nm were derived from a 0.4 g/mL P4VP/DMF solution, and they were suitable for preparing CdTe/P4VP nanocomposites. The obtained results indicated that the morphology of the P4VP/DMF solution was related to the concentration of the P4VP/DMF solution. Herein, P4VP nanofibers with a diameter of approximately 360 nm were selected for assembly with thio-stabilized CdTe nanoparticles.

#### Observation of the CdTe/P4VP nanocomposites by SEM, TEM, ED, and EDX

P4VP nanofibers were prepared successfully from the solution of 0.4 g/mL P4VP/DMF, and then the



**Figure 2** (A) SEM and (B) TEM images (and an ED pattern in the inset) of CdTe/P4VP nanocomposites.



**Figure 3** (A) SEM image of a selected area of CdTe/P4VP nanocomposites, (B) elemental distribution of CdTe nanoparticles, and (C) EDX spectrum of CdTe nanoparticles.

obtained P4VP nanofibers were immersed in the concentrated CdTe solution. After P4VP nanofibers were taken out from the CdTe solution, the morphology of the nanofibers was observed with SEM and TEM. As shown as Figure 2(A), the SEM image indicates that the diameter of the P4VP nanofibers enwrapped with CdTe nanoparticles enlarged to 452 nm. The TEM image [Fig. 2(B)] exhibits a compact layer enwrapping the P4VP nanofibers. Moreover, ED was performed to detect the compact layer on the surface of P4VP nanofibers. The inset chart in Figure 2(B) shows that the radius of the ED cycles ( $r$ ) was 0.55, 0.88, and 1.05 cm, respectively, revealing that the distance between the CdTe wafers ( $d$ ) was 3.65, 2.28, and 1.91 Å according to eq. (1):<sup>11</sup>

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

where  $L$  is 0.8 m and  $\lambda$  is 0.0251 Å. By assignment of the elements to Cd and Te in PCPDFWIN software (version 2.1),<sup>19</sup> the  $h$ ,  $k$ , and  $l$  values were (111), (220), and (311) planes, indicating that CdTe nano-

particles existed in a cubic lattice on the surface of P4VP nanofibers. This result was in agreement with a previous report.<sup>20</sup>

EDX equipped in SEM can be used to observe the element distribution in the field of vision of SEM. A field of vision in SEM of CdTe/P4VP nanofibers was selected, as shown as Figure 3(A), and then the function of EDX was carried out in this region to detect Cd and Te. As shown as Figure 3(B), a homogeneous distribution of Cd and Te was found. When the image of Figure 3(B) was converted into the peak form, as shown in Figure 3(C), the content of Cd was larger than that of Te in these nanocomposites. To obtain a clear morphology of the nanofibers, the sample for the observation of electron microscopy was sprayed with gold; thus, the peak of gold is exhibited in Figure 3(C).

#### PL characterization of the CdTe/P4VP nanofibers

Although Figure 3(C) shows the existence of Cd and Te on the surface of P4VP nanofibers and the calcu-



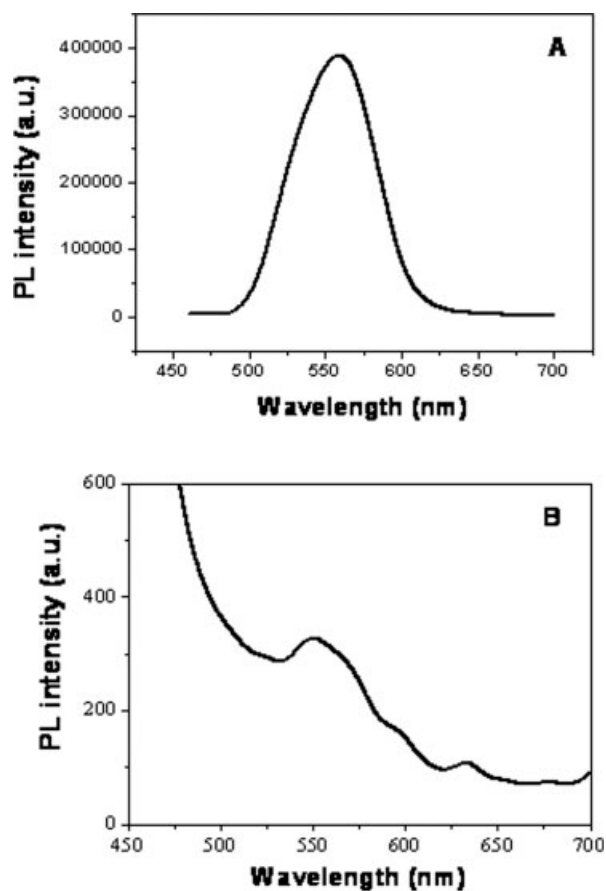


Figure 4 PL spectra of (A) thio-stabilized CdTe nanoparticles and (B) CdTe/P4VP nanocomposites.

lation of  $h, k, l$  revealed that CdTe existed in a cubic lattice, it still cannot confirm that Cd and Te existed in optical CdTe. Therefore, the CdTe/P4VP nanocomposites were characterized with PL spectra because only thio-stabilized CdTe nanoparticles can generate PL intensity at 559 nm, as shown in Figure 4(A). As can be seen in Figure 4(B), a peak around 550.8 nm was also found in CdTe/P4VP nanocomposites, indicating that the compound enwrapping the surface of P4VP nanofibers consisted of optical CdTe nanoparticles.

### Investigation of the complex of CdTe and P4VP nanofibers by XPS

To further investigate the interaction between P4VP and CdTe, the CdTe/P4VP nanocomposites were analyzed by XPS. As shown in Figure 5(A), the two peaks of Cd 3d were observed at 412.3 and 405.6 eV in accordance with Cd 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies, respectively. This was in agreement with the previous report.<sup>21</sup> Moreover, Figure 5(B) shows that the binding energy of N 1s in the P4VP nanofibers (line a) was observed at 399.3 eV, whereas it was located at 400.1 eV in the CdTe/P4VP nanocompo-

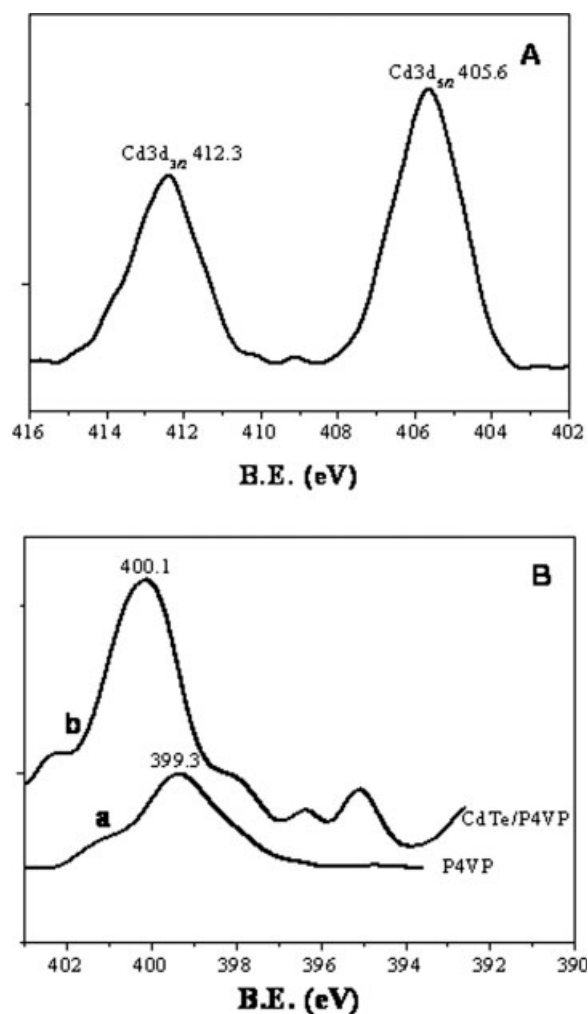
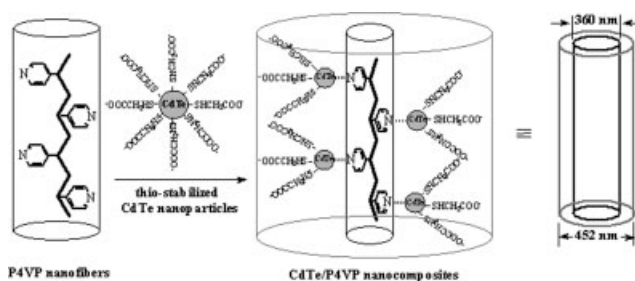


Figure 5 XPS of (A) Cd 3d nanoparticles on the surface of P4VP nanofibers and (B) N 1s of (a) pure P4VP and (b) CdTe/P4VP nanocomposites.

sites (line b), indicating that Cd was complexed by the N atom in CdTe/P4VP nanocomposites. Thus, Scheme 2 suggests a mechanism for the generation of CdTe/P4VP nanocomposites. CdTe was complexed by TGA first. When thiol-stabilized CdTe nanoparticles lost some TGA ligands to expose Cd, the Cd atom in CdTe nanoparticles combined with



Scheme 2 Mechanism of the generation of CdTe/P4VP nanocomposites.

the N atom in P4VP to form coaxial nanofibers. Therefore, the diameter of CdTe/P4VP nanocomposites (452 nm) was larger than that of P4VP nanofibers (360 nm).

### CONCLUSIONS

SEM and TEM revealed that the obtained CdTe/P4VP nanocomposites were nanofibers. EDX and PL determination proved that CdTe nanoparticles on the surface of P4VP nanofibers were optical. Furthermore, XPS verified the complexation between Cd in CdTe nanoparticles and N in P4VP nanofibers. The obtained results may provide useful information for other researchers preparing nanocomposites in which inorganic nanoparticles are attached to polymer nanofibers.

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