

Fabrication of TiO₂/CdS composite fiber *via* an electrospinning method

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The electrospinning method coupled with a chemical reaction is employed to fabricate a TiO₂/CdS composite fiber. The concentration of CdS can be changed by varying the amount of CdCl₂ present as the crystal seed in the precursor sol. The DRUV-Vis spectra results show that the TiO₂/CdS composite fiber absorbs both in the UV and visible regions. The results of TEM, XRD, PL, CLSM and Raman spectra also confirm the formation of CdS in TiO₂ fibers.

1. Introduction

The photophysics and chemistry of titanium dioxide (TiO₂) has been one of the most studied topics in the literature over the past few decades.¹ A critical drawback of TiO₂, however, is that it has a large band gap (3.2 eV), which is too large to allow efficient absorption of sunlight.² To increase the absorption of long-wavelength photons of TiO₂, researchers have adopted different strategies, among which the assembling of a low band gap semiconductor material, *e.g.*, cadmium sulfide (CdS)³ or cadmium selenide (CdSe),⁴ on the surface of TiO₂ is thought to be effective. The use of low-dimensional TiO₂ nanostructures (such as nanotubes and nanofibers), is one of the most promising options to improve the photoactivity, and has attracted considerable attention from the materials science community. It is not only because the intercrystalline contacts of TiO₂ can be greatly decreased to facilitate electron transfer through the titania layer with high-BET specific surface area, but also because these one-dimensional nanostructures can act as guided electron channels in electrodes made from them.⁵ The studies of Kamat *et al.* confirmed that one-dimensional TiO₂/CdSe nanotubes have a greater conversion efficiency than TiO₂/CdSe nanoparticles.⁶ Recently, CdS-functionalized TiO₂ nanotubes⁷ have attracted a lot of attention because of their potential to harvest sunlight and their fast charge transport properties. However, the reported methods to synthesis TiO₂/CdS nanotubes are complicated and some of them require a chemical linker.

Electrospinning is a straightforward, cost-effective method to produce novel fibers with diameters ranging from nanometers to micrometers.⁸ The obtained fibers have very large continuous surface areas compared with other materials, *e.g.* spheres and slices.⁹ Herein, we present a novel and simple method to prepare TiO₂/CdS composite fibers by directly electrospinning a titanium alkoxide precursor containing a cadmium salt. After being calcined at 500 °C, the prepared fiber is directly exposed to thioacetamide (0.1 M) solution. This method avoids the adsorption step compared with the

successive ionic layer adsorption and reaction (SILAR) technique,¹⁰ and has the following obvious advantages: (a) the semiconductor particles are uniformly distributed on the TiO₂ support; (b) no extra organic bridging molecules are required, avoiding introduction of impurities; (c) the method is operated under mild conditions.

2. Experimental

2.1 Materials

N,N-Dimethylformamide (DMF), thioacetamide (TAA), absolute ethanol and acetic acid were supplied by Shanghai Chemical Reagent Co., Ltd. Poly(vinyl pyrrolidone) (PVP, MW = 1 300 000) was provided by Alfa Aesar. CdCl₂ was purchased from Sinopharm Chemical Reagent Co., Ltd. Tetraethyl titanate (Ti(OBu)₄) was supplied by Shanghai Linfeng Chemical Reagent Co., Ltd. All the chemicals were used without further purification.

2.2 Preparation of TiO₂/CdS composite fiber

The fabrication of TiO₂/CdS composite fiber was based on previously reported methods with some modifications.¹¹ A typical synthesis was as follows. Firstly, 1.0 g of Ti(OBu)₄ was mixed with 2 mL of acetic acid and 2 mL of ethanol in a beaker. After 20 min, this solution was removed from the beaker and added to 4 mL of ethanol that contained 0.4 g of PVP, 1 mL DMF, and an appropriate amount of CdCl₂, followed by magnetic stirring for 2 h. TiO₂/Cd²⁺/PVP composite fiber was then electrospun from the Ti(OBu)₄ sol at an appropriate high voltage, and the obtained fiber was calcined at 500 °C to crystallize TiO₂ and remove the PVP template. Finally, the prepared Cd²⁺/TiO₂ fiber was exposed to TAA (0.1 M) solution, and the mixture was dispersed with ultrasound. After reaction for 1.5 h, the solution turned yellow, indicating the formation of the TiO₂/CdS composite fiber. The amount of CdS can be controlled by varying the concentration of CdCl₂ in the sol.

2.3 Characterization

Wide-angle (0–80°, 40 kV/200 mA) X-ray powder diffraction (XRD) data was recorded on a Rigaku D/max 2550 VB/PC diffractometer using nickel-filtered CuKα radiation with a

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wavelength of $\lambda = 1.5406 \text{ \AA}$. Transmission electron microscopy (TEM, JEOL JEM-2100F) measurements were performed on TiO_2/CdS fiber samples which were drop-cast onto a carbon-coated Cu grid. The optical absorption spectra of the composite fibers was recorded using a UV-Visible spectrophotometer (Varian, Cary 500). The fluorescence experiment was carried out on a RF-5301PC spectrometer. Confocal laser scanning microscopy (CLSM) images of TiO_2/CdS fiber were obtained using a confocal laser scanning microscope (LSM 510, Carl-Zeiss Inc.). Raman spectra was collected using a Via + Reflex Lan Ram spectrometer with a 785 nm excitation source.

3. Results and discussion

Fig. 1A depicts the Diffuse Reflectance Ultraviolet and Visible (DRUV-Vis) spectra of TiO_2/CdS composite fiber and pure TiO_2 fiber. We observed that pure TiO_2 fiber absorbs in the UV region with a band edge of approximately 400 nm (band gap, $E_g = 3.2 \text{ eV}$). On the other hand, the spectrum of the TiO_2/CdS composite fiber absorbs both in UV as well as the visible region with a band edge of 530 nm ($E_g = 2.34 \text{ eV}$), which confirms the formation of a CdS semiconductor. The studies show that the TiO_2/CdS composite fiber thus prepared absorbs in the visible as well as in the UV region of the solar spectrum, and that the absorption peak intensity increases with the increasing concentration of CdCl_2 in the $\text{Ti}(\text{OBu})_4$ sol.

Fig. 1B shows the photoluminescence (PL) spectra of TiO_2/CdS composite fibers and $\text{Cd}^{2+}/\text{TiO}_2$ fibers recorded

with 450 nm excitation. The PL spectra of TiO_2/CdS fibers exhibited a sharp emission band at 495 nm that did not shift with increasing concentration of CdCl_2 . The band at 495 nm is attributed to the typical excitonic band-to-band radiative emission of CdS because of its location near the absorption edge (approximately 500 nm, as determined from the absorption spectra of Fig. 1). However, $\text{Cd}^{2+}/\text{TiO}_2$ fibers (Fig. 1B (e)) did not show any emission under the 450 nm excitation, which confirms that the sharp emission band at 495 nm belongs to CdS nanoparticles. In general for semiconductors, the optical properties mainly depend on the particle size, shape and the nature of the semiconductor surface.¹² According to Fig. 1A and B, both the absorption peak and emission peak of sample (a) showed a minor blue-shift, which indicates that the increasing concentration of CdCl_2 leads to the growth of the reaction center, and the prepared CdS nanoparticles becoming smaller. Thus we chose sample (a) in Fig. 1, for further studies.

X-ray diffraction (XRD) was used to identify the crystalline phases of the pure TiO_2 fiber and TiO_2/CdS composite fibers. From the XRD results in Fig. 2a, it is evident that a mixed anatase/rutile crystal structure was formed. The XRD patterns of pure TiO_2 fiber show that the peaks at 2θ values of 25.2, 37.9, 48.2 and 62.9° correspond to the anatase TiO_2 structure, whereas the peaks at 2θ values of 27.5, 36.1, 41.4, 54.3, 68.8 and 75.0° correspond to the rutile structure. Meanwhile, as shown in Fig. 2b and c, there is an additional broad peak at $2\theta = 30.9^\circ$, which is attributed to the (200) plane of cubic phase CdS. The XRD peak corresponding to small CdS particles was broad and reflected the dispersion of small CdS nanocrystallites in TiO_2 fibers. The $\text{Cd}^{2+}/\text{TiO}_2$ fibers were also investigated, and the result (Fig. 2d) indicates that doping TiO_2 with Cd^{2+} affects the anatase-to-rutile phase transition temperature.

Fig. 3 shows the Raman spectrum of the TiO_2/CdS composite fibers. The Raman lines at 400, 517 and 637 cm^{-1} can be assigned as the B_{1g} , A_{1g} or B_{1g} , and E_g modes of the anatase phase, respectively, while for the rutile phase the band located at 242 cm^{-1} is observed.¹³ The Raman peaks located around 320 cm^{-1} correspond to the first-order transverse optical phonon mode (TO) of CdS. As compared to previous

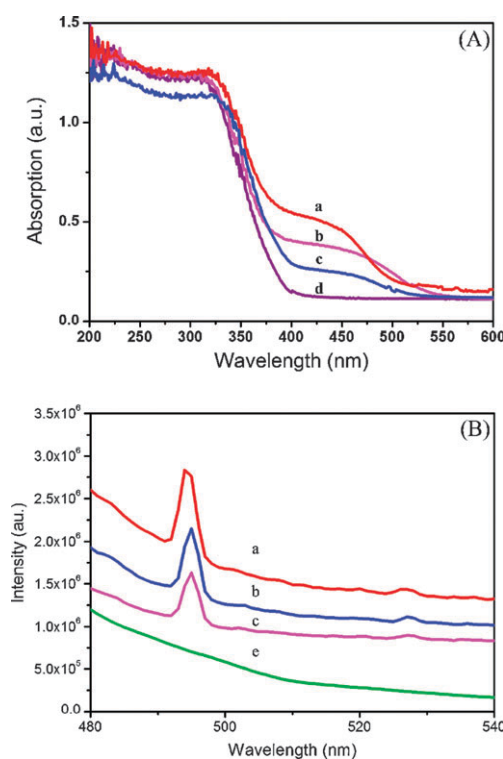


Fig. 1 (A) DRUV-vis spectra and (B) photoluminescence spectra of: TiO_2/CdS composite fibers, with (a) 7.2 wt%, (b) 4.8 wt% and (c) 2.4 wt% CdS: TiO_2 ; (d) pure TiO_2 fibers; (e) $\text{Cd}^{2+}/\text{TiO}_2$ fibers.

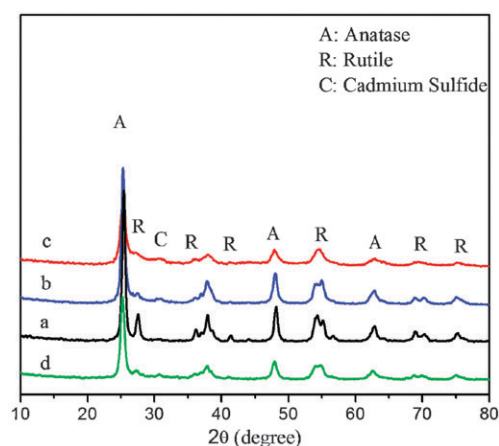


Fig. 2 XRD spectra of: (a) pure TiO_2 fibers; (b) 2.4% and (c) 7.2% TiO_2/CdS composite fibers; (d) $\text{Cd}^{2+}/\text{TiO}_2$ fibers.

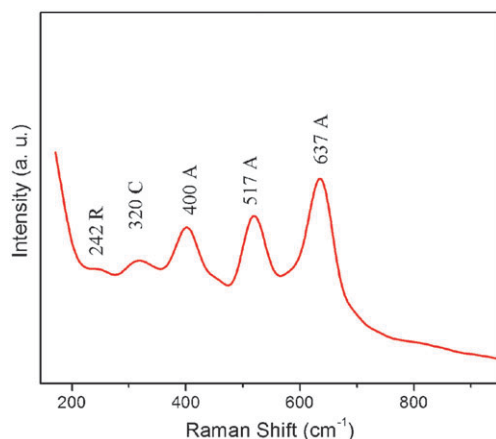


Fig. 3 Raman spectrum of TiO_2/CdS composite fibers (7.2%).

results obtained for CdS crystals,¹⁴ the Raman peak of the as-prepared CdS particles in TiO_2 fibers is downshifted by approximately 20 cm^{-1} . This feature likely arises from the confinement of optical phonons in the nanometer-sized samples, as demonstrated by a spatial correlation model.¹⁵ Nevertheless, the local increase in temperature caused by laser heating during the Raman measurements may also give rise to a shift and asymmetric broadening of the Raman signals.¹⁶

The hybrid structure of the resulting composite of TiO_2/CdS fiber was characterized by transmission electron microscopy (TEM) and confocal laser scanning microscopy (CLSM). As shown in Fig. 4A, the $\text{Cd}^{2+}/\text{TiO}_2$ fiber had a smooth surface, whereas in Fig. 4B, the TiO_2/CdS composite fiber had a relatively rough surface, which seems to be beneficial to the formation of CdS nanoparticles. The average diameters of $\text{Cd}^{2+}/\text{TiO}_2$ fibers and CdS/TiO_2 composite fibers are equal (approximately 180 nm). Fig. 4C shows the high-resolution

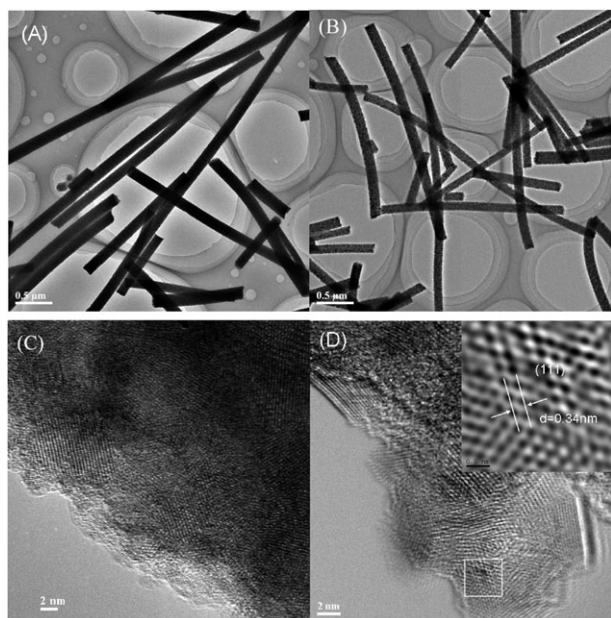


Fig. 4 TEM image of: (A) $\text{Cd}^{2+}/\text{TiO}_2$ fibers; (B) TiO_2/CdS composite fibers (7.2%); (C) HRTEM of $\text{Cd}^{2+}/\text{TiO}_2$ fibers; (D) TiO_2/CdS composite fibers (7.2%).

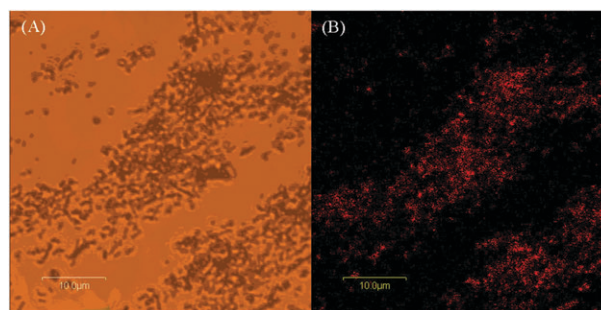


Fig. 5 CLSM image of TiO_2/CdS composite fibers (7.2%) in (A) light field and (B) fluorescent field (488 nm excitation).

TEM (HRTEM) image of $\text{Cd}^{2+}/\text{TiO}_2$ fibers, in which we can only find the lattice fringes of TiO_2 , and Fig. 4D shows the corresponding HRTEM image of the TiO_2/CdS composite fiber. The lattice fringes of 0.34 nm, corresponding to the (111) plane of CdS in a cubic crystal system, confirms the uniformity of the CdS nanoparticles.

The uniform distribution of CdS particles on TiO_2 fiber was further confirmed by a CLSM image. The result shows that the light image (Fig. 5A) and the fluorescent image (Fig. 5B) match well. The images reveal that the CdS particles exhibited strong fluorescence and a good dispersion, whereas the $\text{Cd}^{2+}/\text{TiO}_2$ didn't show any fluorescence under the same conditions (488 nm excitation).

4. Conclusions

In summary, we have reported a novel route to prepare TiO_2/CdS composite fibers by electrospinning. This is the first report of the successful *in situ* growth of CdS nanoparticles on TiO_2 fibers. The particles dispersed well on the surface of the fiber without any aggregation, and the composite fiber was more responsive to visible sunlight.

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References

- 1 S. V. Chong, N. Suresh, J. Xia, N. Al-Salim and H. Idriss, *J. Phys. Chem. C*, 2007, **111**, 10389; D. Pan, N. Zhao, Q. Wang, S. Jiang, X. Ji and L. An, *Adv. Mater.*, 2005, **17**, 1991.
- 2 H. Jia, H. Xu, Y. Hu, Y. Tang and L. Zhang, *Electrochem. Commun.*, 2007, **9**, 354.
- 3 J. C. Yu, L. Wu, J. Lin, P. Li and Q. Li, *Chem. Commun.*, 2003, 1552; Y. Tachibana, K. Umekita, Y. Otsuka and S. Kuwabata, *J. Phys. Chem. C*, 2009, **113**, 6852; T. Kiyonaga, T. Akita and H. Tada, *Chem. Commun.*, 2009, 2011.
- 4 I. Robel, V. Subramanian, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2006, **128**, 2385.
- 5 J. H. Jang, K. S. Jeon, S. Oh, H. J. Kim, T. Asahi, H. Masuhara and M. Yoon, *Chem. Mater.*, 2007, **19**, 1984; A. Kumar, R. Jose,

- K. Fujihara, J. Wang and S. Ramakrishna, *Chem. Mater.*, 2007, **19**, 6536.
- 6 A. Kongkanand, K. Tvrđy, K. Takechi, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2008, **130**, 4007.
 - 7 J. C. Kim, J. Choi, Y. B. Lee, J. H. Hong, J. I. Lee, J. W. Yang, W. I. Lee and N. H. Hur, *Chem. Commun.*, 2006, 5024; W. T. Sun, Y. Yu, H. Y. Pan, X. F. Gao, Q. Chen and L. M. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 1124; D. R. Baker and P. V. Kamat, *Adv. Funct. Mater.*, 2009, **19**, 805; S. Banerjee, S. K. Mohapatra, P. P. Das and M. Misra, *Chem. Mater.*, 2008, **20**, 6784.
 - 8 A. Greiner and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2007, **46**, 5670; M. Jin, X. Zhang, A. V. Emeline, Z. Liu, D. A. Tryk, T. Murakami and A. Fujishima, *Chem. Commun.*, 2006, 4483.
 - 9 G. Decher, J. D. Hong and J. Schmitt, *Thin Solid Films*, 1992, **210–211**, 831; F. Caruso, R. Caruso and H. Moehwald, *Science*, 1998, **282**, 1111; T. Zhu, L. Ge, X. Wang and Z. Gu, *Polymer*, 2008, **49**, 2898.
 - 10 J. J. Li, A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson and X. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 12567.
 - 11 D. Li and Y. Xia, *Nano Lett.*, 2003, **3**, 555; Y. Li, Y. Zhu, X. Yang and C. Li, *Cryst. Growth Des.*, 2008, **8**, 4494.
 - 12 S. A. Empedocles and M. G. Bawendi, *Acc. Chem. Res.*, 1999, **32**, 389.
 - 13 M. Gotic *et al.*, *Mater. Lett.*, 1996, **28**, 225.
 - 14 V. Singh and P. Chauhan, *J. Phys. Chem. Solids*, 2009, **70**, 1074; D. Xu *et al.*, *Chem. Phys. Lett.*, 2000, **325**, 340; O. Trujillo *et al.*, *Thin Solid Films*, 1996, **13**, 200–291.
 - 15 B. Cao *et al.*, *Adv. Funct. Mater.*, 2007, **17**, 1501.
 - 16 H. Scheel, S. Reich, A. C. Ferrari, M. Cantoro, A. Colli and C. Thomsen, *Appl. Phys. Lett.*, 2006, **88**, 233114.