

Preparation of CuS nanoparticles embedded in poly(vinyl alcohol) nanofibre via electrospinning

JIA XU, XUEJUN CUI, JINHUI ZHANG, HONGWEI LIANG[†],
HONGYAN WANG and JUNFENG LI*

College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

[†]State Key Laboratory of Inorganic Synthesis and Preparative, Jilin University, Changchun 130012, People's Republic of China

MS received 14 July 2007; revised 19 January 2008

Abstract. Poly(vinyl alcohol) (PVA)/CuS composite nanofibres were successfully prepared by electrospinning technique and gas–solid reaction. Scanning electron microscopic (SEM) images showed that the average diameter of PVA/CuS fibres was about 150–200 nm. Transmission electron microscopy (TEM) proved that a majority of CuS nanoparticles with an average diameter of about 15–25 nm are incorporated in the PVA fibres. X-ray diffraction (XRD) analyses and electron diffraction pattern also revealed the forming of CuS crystal structure in the PVA fibres.

Keywords. CuS nanoparticles; electrospinning; poly(vinyl alcohol).

1. Introduction

In the past decade, the preparation of low-dimensional semiconductor nanostructures has become a hotspot of material research because of their novel optical and electrical properties. As an important semiconductor, copper sulfides (CuS) are widely used as *p*-type semiconductors in solar cells, optical filters and superionic materials (Chivers 1996; Li *et al* 2002; Zhang *et al* 2002). A number of methods have been developed for the synthesis of CuS nanostructures including hydrothermal route (Zhang *et al* 2004a,b; Ji *et al* 2005; Zhu *et al* 2005; Roy and Srivastava 2006), organogel (Xue *et al* 2004), hydrogel-assisted synthesis (Kalyanikutty *et al* 2006), template-free chemical route (Gautam *et al* 2004), microemulsions route (Dong *et al* 2002), precursor decomposition route (Ou *et al* 2005), solid-state reaction route (Ni *et al* 2003; Wang *et al* 2006), sonochemical synthesis (Wang *et al* 2002; Xu *et al* 2006), non-aqueous solution process (Zhang *et al* 2006), pickering emulsion route (He and Li 2007), microwave irradiation techniques (Liao *et al* 2003; Ni *et al* 2004), pyrolysis of single source precursors (Larson *et al* 2003) and so on.

Electrospinning is a simple and low-cost method for preparing the nanofibres with ultra-small diameters. When a strong electrostatic force is applied to the capillary containing a polymer solution, the solution is ejected from the capillary and deposited as a nonwoven fibrous mat on a template serving as the ground for electric charges. In recent

years, there has been a growing interest in the incorporation of functional nanoparticles in the polymer nanofibres due to their uniquely promising properties and applications. The electrospinning technique has been proved to be a facile and effective method for manufacturing nanoscale polymer fibres and polymer/inorganic composite fibres (Huang *et al* 2003; Xia *et al* 2003). Wang *et al* fabricated various polymer/inorganic nanoparticle composite fibres such as PAN/Ag nanofibres (Wang *et al* 2005), PVA/ZnS:Cu nanofibres (Wang *et al* 2006) and PVP/Ag₂S nanofibres (Lu *et al* 2005).

In this paper, we prepared CuS nanoparticles that were well dispersed in polymer matrices via electrospinning technique and gas–solid reaction.

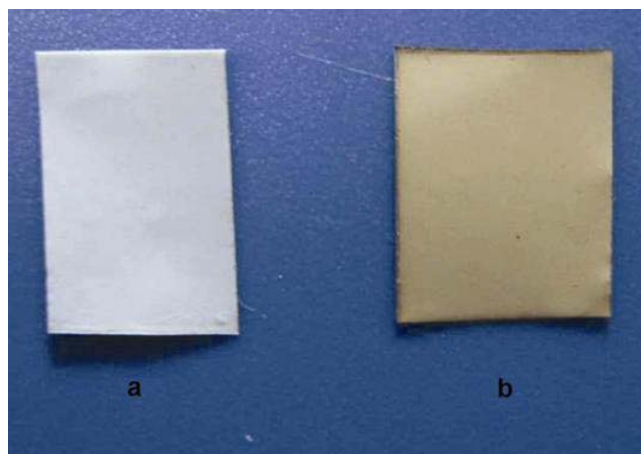


Figure 1. Photograph of (a) PVA/CuSO₄ film and (b) PVA/CuS film.

*Author for correspondence (jfli@jlu.edu.cn)

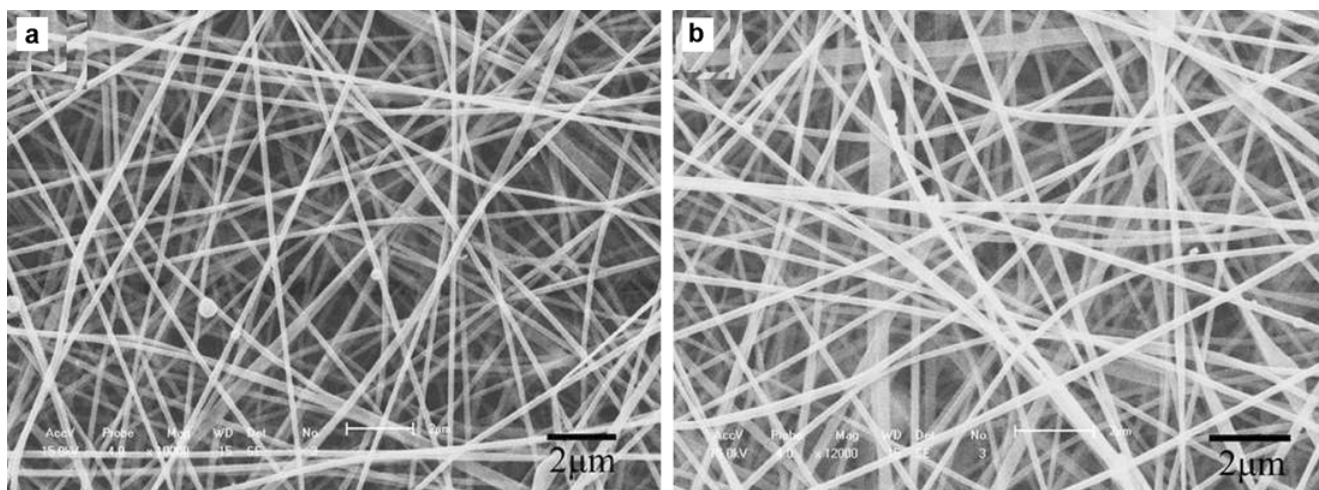


Figure 2. SEM images of (a) PVA/CuSO₄ film and (b) PVA/CuS film.

2. Experimental

2.1 Materials

Poly(vinyl alcohol) (PVA, Mn = 77,000, 97%, Tianjin Guang Fu Fine Chemical Research Institute), sodium lauryl sulfate (SDS, Shanghai San Pu Chemical plant Limited) and copper sulfate pentahydrate (CuSO₄·5H₂O, 99%, Tianjin Xin Tong Fine Chemical plant Limited) reagents were used without further purification. Sulfurated hydrogen (H₂S) was prepared in our laboratory. Distilled water was used as a solvent.

2.2 Instruments

The scanning electron microscopic (SEM) measurements were recorded on a SHIMADZU SSX-550 microscope. The transmission electron microscopic (TEM) images were recorded on a JEM-2000EX microscopy. XRD patterns were obtained with a Siemens D5005 diffractometer using Cu K α radiation. FT-IR spectra were recorded on a Nicolet Instruments Research series 5PC Fourier transform infrared spectrometer.

2.3 Preparation of PVA/CuS composite nanofibres

For preparing the PVA/CuS composite nanofibres, 0.0868 g of copper sulfate pentahydrate (CuSO₄·5H₂O) and 0.0051 g of sodium lauryl sulfate (SDS) were dissolved in 10 ml distilled water under vigorous stirring for 1 h. Then, 0.5001 g PVA (4.72 wt.%) was dissolved in the above-mentioned solution. The mixture was heated at 90°C for 6 h under continuous stirring. And then, the mixed solution was cooled down to room temperature under stirring for 24 h. By pouring the solution in a glass syringe with a tip inner diameter of 1 mm and then adjusting the distance from the tip of the spinning nozzle to

the aluminium foil collector of 25 cm, the electrospinning was completed under a direct current voltage of 12 kV. The film of PVA/CuSO₄ fibres formed on the aluminium foil. And then, the film was placed into a chamber and exposed to H₂S atmosphere for 24 h. Therein, H₂S gas was prepared by the reaction of Na₂S with diluted H₂SO₄. The film of PVA/CuS fibres was obtained.

3. Results and discussion

Figure 1 shows PVA/CuSO₄ and PVA/CuS films. After reacting with H₂S gas, the PVA/CuSO₄ film (figure 1a) turned from white to brown (figure 1b). This proves that the CuS has been obtained by the reaction between CuSO₄ and H₂S. Figure 2 shows the SEM images of the PVA/CuSO₄ and PVA/CuS films. We can see that the fibres morphology of PVA/CuS which reacted with H₂S gas (figure 2b) hardly changed compared with the PVA/CuSO₄ fibres (figure 2a) and their diameters ranged from 150–200 nm.

Figure 3 shows TEM image of the PVA/CuS nanofibres. From bright field image (figures 3a, b), we can see that the nanoparticles are well dispersed in the PVA fibre matrix. These nanoparticles are separated from each other and their average diameter ranged between 15 and 25 nm. The dark field image (figure 3c) further proves that these nanoparticles were crystal-like. The electron diffraction pattern indicates that these nanoparticles are roughly consistent with CuS hexagonal crystal (inset of figure 3b) (Thongtem *et al* 2007).

The CuS nanoparticles may be bound by the chemical interactions between CuS and –OH units of PVA, which can prevent the CuS nanoparticles from aggregation in the nanofibres. It can be proven by the FTIR spectrum. Figure 4A shows absorption peak of –OH group of the PVA located at 3319 cm⁻¹ (curve a). In the PVA/CuS fibres,

this peak is shifted to 3303 cm^{-1} (see figure 4A (curve b)). This result indicates the interaction between $-\text{OH}$ group and CuS nanoparticles.

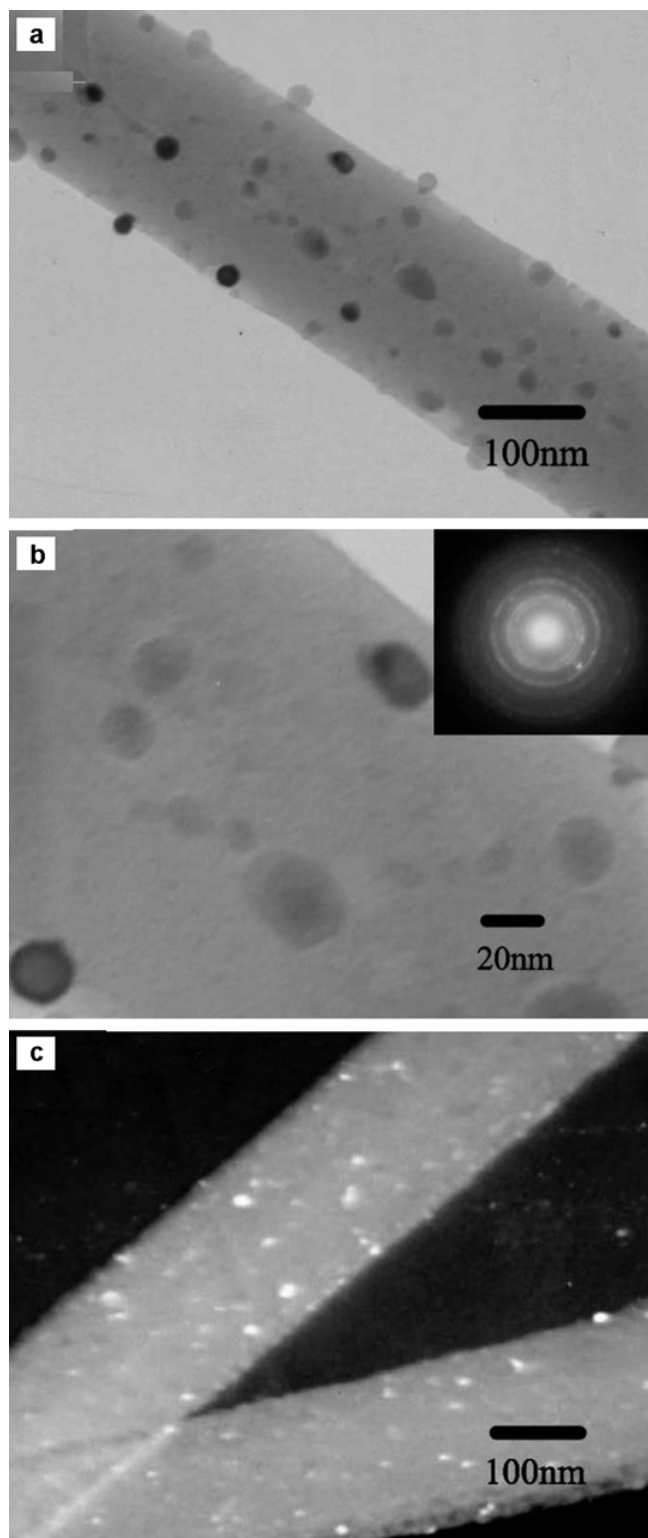


Figure 3. TEM images of PVA/CuS nanofibres: (a, b) bright field image of the fibre and (c) the dark field image of the fibre. Electron diffraction patterns of the CuS nanoparticles in the PVA fibre matrices shown in inset of (b).

Figure 4B shows an X-ray diffraction pattern of the PVA/CuS nanofibres. The peaks at $2\theta = 19.6^\circ$ and 23.4° , respectively correspond to the (101) and (200) plane of crystalline PVA (Lee *et al* 1996). Seven weak peaks are observed at 27.8° , 29.1° , 31.8° , 32.8° , 43° , 44.3° and 48.36° , which are in agreement with the standard XRD peaks of crystalline CuS and show that the CuS crystals are in the form of (101), (102), (103), (006), (106), (008) and (110) (Roy and Srivastava 2007).

4. Conclusions

PVA/CuS composite fibres were successfully prepared via the electrospinning technique and gas–solid reaction. SEM images showed that the diameter of the electrospun fibres was about 150–200 nm. X-ray diffraction results showed that a pure CuS phase was obtained in PVA fibres.

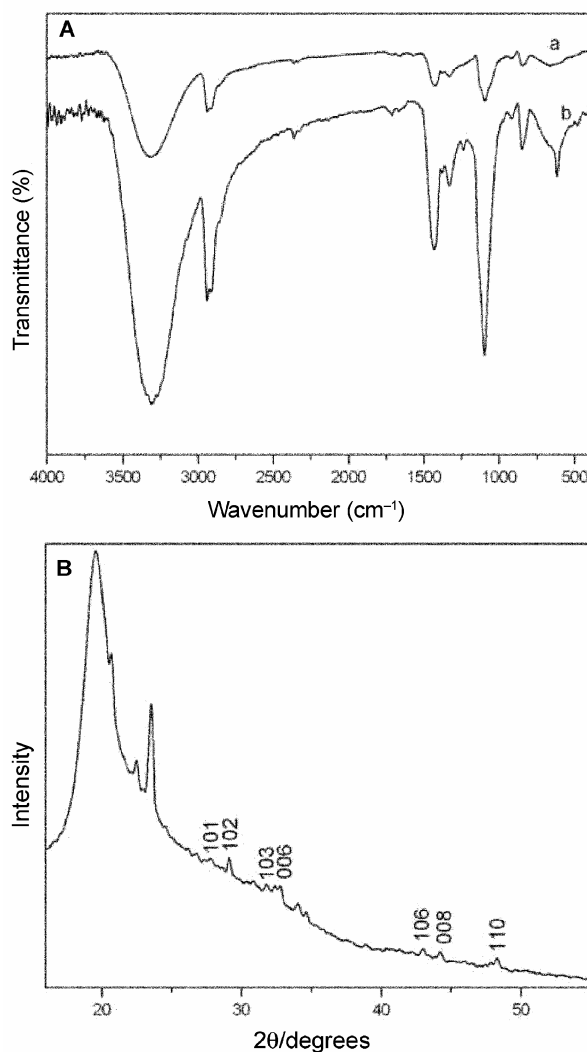


Figure 4. A. FT-IR spectra of (a) pure PVA and (b) PVA/CuS nanofibres and B. XRD pattern of PVA/CuS nanofibres.

TEM images showed that the dense CuS nanoparticles were roughly spherical in shape with an average diameter of about 15–25 nm and were dispersed homogeneously in the PVA fibres. So, this is a simple and feasible method for making CuS nanoparticles.

Acknowledgement

The authors gratefully acknowledge the support of the Bureau of Geological Survey of China (No. 1212101660404).

References

- Chivers T 1996 *J. Chem. Soc. Dalton Trans.* **7** 1185
- Dong X, Potter D and Erkey C 2002 *Ind. Eng. Chem. Res.* **41** 4489
- Gautam U K, Ghosh M and Rao C N R 2004 *Langmuir* **20** 10775
- He Y J and Li K S 2007 *J. Colloid Interf. Sci.* **306** 296
- Huang Z M, Zhang Y Z, Kotakic M and Ramakrishna S 2003 *Compos. Sci. Technol.* **63** 2223
- Ji H M, Cao J M, Feng J, Chang X, Ma X J, Liu J S and Zheng M B 2005 *Mater. Lett.* **59** 3169
- Kalyanikutty K P, Nikhila M, Maitra U and Rao C N R 2006 *Chem. Phys. Lett.* **432** 190
- Larson T H, Sigman M, Ghezlbash A, Doty R C and Korgel B A 2003 *J. Am. Chem. Soc.* **125** 5638
- Lee Y M, Kim S H and Kim S J 1996 *Polymer* **37** 5897
- Li H, Zhu Y, Avivi S, Palchik O, Xiong J, Koltypin Y, Palchik V and Gedanken A 2002 *J. Mater. Chem.* **12** 3723
- Liao X H, Chen N Y, Xu S, Yang S B and Zhu J J 2003 *J. Cryst. Growth* **252** 593
- Lu X F, Li L L, Zhang W J and Wang C 2005 *Nanotechnology* **16** 2233
- Ni Y, Wang F, Liu J, Miu Q, Xu Z and Hong J 2003 *Chin. J. Inorg. Chem.* **19** 1197
- Ni Y, Liu H, Wang F, Yin G, Hong J, Ma X and Xu Z 2004 *Appl. Phys.* **A79** 2007
- Ou S M, Xie Q, Ma D K, Liang J B, Hu X K, Yu W C and Qian Y T 2005 *Mater. Chem. Phys.* **94** 460
- Roy P and Srivastava S K 2006 *Cryst. Growth Des.* **6** 1921
- Roy P and Srivastava S K 2007 *Mater. Lett.* **61** 1693
- Thongtem T, Phuruangrat A and Thongtem S 2007 *J. Mater. Sci.* **42** 9316
- Wang H, Zhang J, Zhao X, Xu S and Zhu J 2002 *Mater. Lett.* **55** 253
- Wang H Y, Lu X F, Zhao Y Y and Wang C 2006 *Mater. Lett.* **60** 2480
- Wang X B, Xu C Q and Zhang Z C 2006 *Mater. Lett.* **60** 345
- Wang Y Z et al 2005 *Mater. Lett.* **59** 3046
- Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F and Yan H 2003 *Adv. Mater.* **15** 353
- Xu H L, Wang W Z and Zhu W 2006 *Mater. Lett.* **60** 2203
- Xue P C, Lu R, Li D M, Jin M, Tan C H, Bao C Y, Wang Z M and Zhao Y Y 2004 *Langmuir* **20** 11234
- Zhang H T, Wu G and Chen X H 2006 *Mater. Chem. Phys.* **98** 298
- Zhang Y, Qiao Z and Chen X 2002 *J. Mater. Chem.* **12** 2747
- Zhang Y C, Qiao T and Hu X Y 2004a *J. Cryst. Growth* **268** 64
- Zhang Y C, Hu X Y and Qiao T 2004b *Solid State Commun.* **132** 779
- Zhu H L, Ji X, Yang D R, Ji Y J and Zhang H 2005 *Micropor. Mesopor. Mater.* **80** 153