Preparation and characterization of ZnS:Cu/PVA composite nanofibers via electrospinning

Haiying Wang, Xiaofeng Lu, Yiyang Zhao, Ce Wang *

Alan G. MacDiarmid Institute, Jilin University, Changchun, 130012, PR China

Received 8 October 2005; accepted 12 January 2006
Available online 3 February 2006

Abstract

ZnS:Cu/Poly(vinyl alcohol) (PVA) composite nanofibers have been successfully prepared by electrospinning technique. The formation of ZnS:Cu/PVA nanofibers were carried out by reacting H2S with Zn(AC)2:Cu/PVA nanofibers, which were electrospun from the mixture aqueous solution of Zn(AC)2, Cu(AC)2 and PVA. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray-diffraction (XRD) analyses revealed that the morphology of the ZnS:Cu/PVA nanofibers consists of the dispersion of ZnS:Cu nanoparticles with cubic structure in PVA nanofibers. The coordinations between –OH and Zn2+:Cu were characterized by infrared spectroscopy. The photoluminescence spectroscopy studies showed the significant difference between the ZnS/PVA fibers and the ZnS:Cu/PVA fibers. The luminescence decay time measure further invested that the Cu was doped in the ZnS crystal.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Electrospinning; ZnS:Cu nanoparticles; Poly(vinyl alcohol); Nanofibers

1. Introduction

Research on semiconductor nanoparticles stimulated great interest in recent years because of their unique optical and electrical properties. Among the semiconductor nanoparticles, zinc sulfide as an important II–VI semiconductor has been researched extensively because of its broad spectrum of potential applications such as in catalysts, electronic and optoelectronic nanodevices [1,2]. Particularly, copper-doped zinc sulfide phosphors show interesting properties that are different from those of un-doped matrix materials, such as the emission spectra and decay time of doped samples can be varied which create new opportunities for luminescent study and are widely used for cathodoluminescent devices [3–7].

Some people consider that incorporating nanoparticles into polymer matrices is a meaningful method to allow nanoparticles to be used in electroluminescent devices [8]. Therefore, much work about preparation of hybrid organic/inorganic films has been done. For instance, Xiong et al. fabricated polymer/Cu2S nanoparticles film through layer-by-layer assembly method [9]. Meldrum et al. deposited PbS on self assembled monolayers of 16-mercaptohexadecanoic acid [10]. Wang et al. fabricated nanoparticles/polymer composite thin film by a surface-initiated atom transfer radical polymerization (ATRP) method [11]. In this paper, we successfully dispersed copper-doped zinc sulfide nanoparticles incorporated in PVA fiber matrices using electrospinning technique and gas/solid reaction.

Electrospinning is a simple and low-cost method for making the nanofibers with ultra-small diameters. Since the first patent on this process was issued in 1934 [12], many materials have been prepared using this method [13–21]. In recent years, there has been a growing interest in the incorporation functional nanoparticles in the polymer nanofibers due to their uniquely promising properties and applications. We dispersed silver nanoparticles into PAN nanofibers to increase the electronic conductivity of the fibers [22]. Recently we also prepared PVP/Ag2S composite fibres and PVP/CdS composite fibres via electrospinning [8,23]. Here, using electrospinning technique and gas/solid reaction we first obtained ZnS:Cu/PVA composite...
fibers which copper-doped zinc sulfide nanoparticles with a
diameter of about 3 nm well dispersed in PVA fiber matrices.

2. Experimental procedures

2.1. Materials

Poly(vinyl alcohol) (PVA, Mw = 80,000, 97%, Beijing Yi Li
Chemical Factory), zinc acetate (Zn(Ac)₂·2H₂O, 99%, Shantou
Xi Long Chemical Factory), copper acetate (Cu(Ac)₂·H₂O,
99%, Shantou Xi Long Chemical Factory). These reagents were
used without further purification. Sulfureted hydrogen (H₂S)
was prepared by us. Distilled water was used as solvent.

2.2. Instruments

The Scanning electron microscopy (SEM) measurements
were recorded on a SHIMADZU SSX-550 microscope. The
transmission electron microscopy (TEM) images were recorded
on a Hitachi S-570 microscopy. UV–Vis absorption spectra were
recorded on a UV-2501 PC Spectrometer (SHIMADZU). XRD
patterns were obtained with a Siemens D5005 diffractometer
using Cu Kα radiation. FT-IR spectra of KBr powder-pressed
pellets were recorded on a BRUKER VECTOR 22 spectrometer.
Fluorescence measurements were performed with an Eidingberg
pectrometer. Luminescence lifetime of ZnS:Cu nanocrystals was
recorded on a Spex 1934D-phosphorescence spectrophotometer.

2.3. Preparation of ZnS:Cu/PVA composite nanofibers

In a typical procedure, PVA aqueous solution (10 wt.%) was
prepared by dissolving PVA powder in distilled water at 80 °C
under magnetic stirring for 1 h, followed by cooling to room
temperature with continuation of stirring for another 12 h. Thirty
grams PVA aqueous solution thus obtained was dropped
slowly into the Zn(Ac)₂ and Cu(Ac)₂ aqueous solution (0.76 g
Zn(Ac)₂·2H₂O, 0.0175 g Cu(Ac)₂·H₂O and 7 g H₂O) under
vigorous stirring in a water bath at 80 °C. After stirring for 5 h,
the mixture was held in a spinning nozzle with a tip diameter of
1 mm. A copper pin connected to the anode of a high-voltage
generator was placed in the solution. A voltage of 20 kV was
applied to the solution and dense webs of fibers were collected
on an aluminum foil, at a distance of 12 cm from the tip of the nozzle. Finally, the film attached on the aluminum foil was separated from the aluminum foil and exposed in H$_2$S gas at 50 °C to prepare ZnS:Cu nanoparticles in situ.

3. Results and discussion

Fig. 1a shows SEM image of the electrospinning Zn(Ac)$_2$:Cu/PVA nanofibers. The morphology of the fibers is smooth and uniform. They are longer than several millimeters, with diameters about 300 nm and without the presence of any beads. Furthermore, the morphology of the fibers does not change after reaction with H$_2$S gas (see Fig. 1b).

TEM images of the composite fibers are presented in Fig. 2. It is found that the particles with average diameter of about 3 nm are rather evenly distributed in the PVA fibers. The electron diffraction pattern (inset) indicated that these nanoparticles were roughly consistent with those obtained from the β-ZnS crystal. The rings corresponded to $d$ (111)=3.118 Å, $d$ (220)=1.9115 Å, $d$ (311)=1.6059 Å, respectively [24], which are in good agreement with the values calculated from the XRD pattern. In the FT-IR spectra of the fibers [Fig. 3(1)], the band at around 3426 cm$^{-1}$ is attributed to O–H stretch vibration of PVA. However, in the curve of Zn(Ac)$_2$:Cu/PVA and ZnS:Cu/PVA fibers, this peak changed to 3405 cm$^{-1}$. This date demonstrated that there is coordination link between –OH and Zn$^{2+}$ [25], which prevented the ZnS:Cu nanoparticles from aggregation in the nanofibers. The X-ray patterns of the ZnS:Cu/PVA nanofibers are presented in Fig. 3(2). The peak at $2\theta$=20° corresponds to the (101) plane of crystalline PVA in the ZnS:Cu/PVA nanofibers. The diffraction angles at $2\theta$=28.08, 48.36 and 57.43 degrees can be assigned to (111), (220), and (311) planes [26] of the cubic structure of ZnS, respectively. According to Scherrer’s equation [27]:

$$\beta = k\lambda/D\cos\theta$$

where $\lambda$ is the X-ray wavelength, $k$, the shape factor, $D$, the average diameter of the crystals in Angstrom, $\theta$, the Bragg angle in degree, and $\beta$ is the line broadening measured by half-height in radium. $k$ is often assigned a value of 0.94 and $\lambda$ is often assigned a value of 1.5405. When the reflecting peaks at $2\theta$=28.08, 48.36 and 57.43 degrees are chosen to calculate the average diameter, the average size of the ZnS:Cu nanoparticles is about 3.4 nm, which is consistent with the results of TEM. From XRD analysis, no characteristic peaks of impurity

Fig. 3. (1) FT-IR spectra of (a) pure PVA, (b) 2.5% Cu-doped Zn(Ac)$_2$/PVA nanofibers, (c) 2.5% Cu-doped ZnS/PVA nanofibers; (2) XRD pattern of 2.5% Cu-doped ZnS/PVA nanofibers.

Fig. 4. (1) UV–Vis spectra and (2) photoluminescence spectrum under different concentration of Cu-doped ZnS/PVA nanofibers. (a) Un-doped; (b) 0.5% Cu-doped; (c) 1.5% Cu-doped (d) 2.5% Cu-doped.
phases have been observed. This implies that minor amount of additional Cu does not influent the planes of cubic crystalline ZnS [28].

Fig. 4(1) shows UV–Vis spectra of the Cu-doped ZnS and undoped ZnS nanocrystals in the fibers. The absorption peak at 315 nm in the curve of un-doped sample is attributed to the absorption of ZnS nanoparticles. With the Cu doping concentration increased from 0, 0.5%, 1.5% to 2.5% the absorption edge showed a blue shift from 315, 313, 310, to 306 nm. The curve of 0.5% Cu-doped sample was essentially similar to that of the un-doped sample as the concentration of doping material was so small that was not effective in the quantum particle size under similar synthesis conditions [29].

The emission spectra of un-doped ZnS/PVA nanofibers and ZnS:Cu/PVA nanofibers were showed in Fig. 4(2). Their excitation wavelength is at 315 nm. The emission spectra varied with increasing of Cu doping concentration. The emission peaks of Cu-doped samples red shifted slightly from 474, 476 to 480 nm with the Cu doping concentration increased from 0.5%, 1.5% to 2.5%, but were quite different from the un-doped one which emission peak was 445 nm. At the same time, the relative fluorescence intensities increased insignificantly. Generally speaking, the emission spectra of Cu-doped ZnS were reported quite-different by different authors because of different quantum particle size, surface or impurity defect levels in the band gap, caused by different synthesis techniques. In this paper, we observe the emission peaks of Cu-doped sample at about 480 nm, which was very close to the value by the report of Khosravi et al. [29]. The blue luminescence observed for the un-doped sample in our paper is associated with defect-related emission of the ZnS host. In case of the Cu-doped samples, the green luminescence is due to transition from defect level to the copper induced $t_2$ level.

In order to demonstrate that the Cu was doped in the ZnS crystal effectively, we measured the luminescence decay of un-doped ZnS/PVA nanofibers and ZnS:Cu/PVA nanofibers. (see Fig. 5) Here, we used the excitation wavelength at 315 nm, the emission of un-doped sample was at 445 nm, while the emission of Cu-doped sample was at 480 nm. For un-doped sample, one decay time at 70 ns was obtained. Whereas in the case of 2.5% Cu-doped sample, two exponential decay times were observed. The fast one was 68 ns and the slow one was 335 ns. We attributed the decay time of about 68 ns to defect-related ZnS emission existed in both the un-doped sample and the Cu-doped samples [30]. The slow decay time of 335 ns only in the Cu-doped samples was associated with the $t_2$ level of Cu impurity.

4. Conclusions

We have successfully prepared ZnS:Cu/PVA nanofibers with various concentration of Cu doping by electrospinning method. The Cu-doped ZnS nanocrystals with diameter about 3 nm were well-dispersed in PVA nanofibers through the coordination between –OH and Zn$^{2+}$:Cu, which prevented the ZnS:Cu nanoparticles from aggregation in the nanofibers. Furthermore, the PL measurement and luminescence decay time measurement demonstrated that the luminescence properties of Cu-doped samples changed significantly compared with the un-doped sample, which was caused by the influence of copper induced $t_2$ level. Therefore, we anticipate that this ZnS:Cu/PVA composite nanofibers with good photo luminescence property can be exploited for fabrication of optoelectronic nanodevices.

Acknowledgements

The work has been supported in part by the National 973 Project (No. 2001CB610505), by the National Natural Science Foundation of China (NSFC Nos. 50473008 and 20320120169) and by DuPont Company through a Young Faculty Grant Award to C. Wang. We thank Dr. Wenping Jian for useful help.

References