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White-light emission of polyvinyl alcohol/ZnO hybrid nanofibers prepared by electrospinning

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Polyvinyl alcohol/ZnO (PVA/ZnO) hybrid nanofibers were prepared by the electrospinning technique. The structural and spectral information of the nanofibers was characterized by scanning electron microscopy, x-ray diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry, resonant Raman, and photoluminescence (PL). The results indicate that ZnO were successfully embedded in the one-dimensional hybrid fibers via chemical interactions between ZnO and PVA. PL results show the PVA/ZnO nanofibers have an intense white-light emission, which originates from the simultaneous emission of three bands covering from the UV to visible range. A possible PL mechanism was proposed accordingly. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2048808]

One-dimensional (1D) nanomaterials, such as nanowires, nanorods, nanobelts, and nanotubes, have been the subject of intensive research due to their large specific surface areas and quantum confinement effects. They are expected to play an important role as both interconnects and functional units in the fabrication of nanoscale electronic, optoelectronic, electrochemical, and electromechanical devices.[1,2] 1D organic-inorganic composites are particularly challenging, because they could sustain the advantages of mixing the organic materials, such as flexibility, processability, and light weight, and the inorganic materials such as attractive modulus, hardness, heat, and chemical resistance, and optical function.

Up until now, a large number of methods have already been demonstrated for preparing 1D nanostructures, including chemical vapor deposition,[3] vapor-liquid-solid[4,5] solvothermal,[6] solution phase,[7] and so on, but these methods were mostly applied for generating 1D inorganic materials, such as nonmetal,[3] semiconductors,[4,6] metal,[7] and metal oxides.[5] These methods seem impuissant when comes down to organic-inorganic materials.

Notably, electrospinning (a drawing process based on electrostatic force) was developed in recent decades to fabricate 1D nanomaterials. Electrospinning provides a simple way to prepare nanofibers with both solid and hollow interiors that are long in length, uniform in diameter, and diverse in composition.[8,9] Several groups had used polyvinyl alcohol (PVA), polyethylene oxide, and other polymers as an electrospinning template to load inorganic precursors.[10,11]

In the present letter, we introduced the fabrication of PVA/ZnO hybrid nanofibers by electrospinning. The hybrid fibers show surprisingly intense white emission with broad emission bands covering from the UV to visible range. Könenkamp and co-workers[12] had reported white electroluminescence in vertically oriented ZnO nanowires grown in a low-temperature process on SnO_2-coated glass substrates. But, to the best of our knowledge, there was no report on the white luminescence properties of 1D organic-inorganic hybrid materials related to ZnO, which will have potential applications for white-light nanodevices, such as light-emitting diodes (LEDs) and flat panel displays.

The preparing procedure consists of two steps: (1) Preparing of a gel containing ZnO quantum dots (QDs) suspension and PVA, and achieving the appropriate rheology for electrospinning, and (2) spinning the solution to obtain fibers of PVA/ZnO composites. The synthesis of ZnO QDs was similar to that described by Spanhel *et al.*[13] The concentration of the QDs was 0.1 M. The UV-visible absorbance spectra showed that the average radius of the colloids was about 4 nm.[14] ZnO colloids were added droplet to PVA solution ($Mn=80\,000$, about 10 wt %) with the volume raio of 1:8, then a viscous solution of PVA/ZnO composite was obtained. The electrospinning process was similar to our previous result.[11] A voltage of 20 kV was applied to the solution and a sprayed dense mat of fibers was collected. In order to investigate the structural effect, a control experiment was conducted on a PVA/ZnO film by spin casting the PVA/ZnO solution on a silicon slice.

Scanning electron microscopy (SEM) investigation was performed on a JSM-6700F. X-ray diffraction (XRD) patterns of the samples were recorded by a Siemens D5005 Diffractometer, scans were ranged from 4° to 70° (2θ) at the speed of $2°\ \mathrm{min}^{-1}$, using Ni-filtered Cu $K\alpha$. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on Magna 560 FT-IR spectrometer with a resolution of $1\ \mathrm{cm}^{-1}$. Resonant Raman and photoluminescence (PL) were performed on LabRam HR-800 confocal Raman microscope excited by a 325 nm He–Cd laser at room temperature. The differential scanning calorimetry (DSC) was carried out on a

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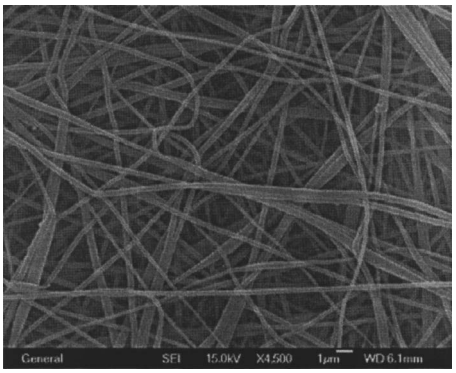

FIG. 1. SEM images of PVA/ZnO hybrid fibers with average diameter about 300 nm. (scale bar=1 μm).

Perkin–Elmer thermal analysis DSC system. Measurements were conducted from 20 to 700 °C, at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

Figure 1 shows the SEM photographs of hybrid fibers of PVA/ZnO. It can be seen that the fibers align in random orientation because of the bending instability associated with the spinning jet. The average diameter of fibers is about 300 nm, and the length can even reach to decimeter grade. ZnO QDs cannot be observed on the fiber surface, suggesting that the ZnO QDs are embedded in the PVA fibers. In the XRD curve of the hybrid fibers, a broad peak around 20° appears, corresponding to the (101) plane of PVA semicrystalline in the hybrid fibers. But, the signals of ZnO are not observed; may be owing to its low content in the hybrid fibers of PVA/ZnO.

The existence of ZnO and the interactions between PVA and ZnO in the hybrid fibers are confirmed by FT-IR and resonant Raman spectra. Figures 2(a) and 2(b) show the FT-IR spectra of pure PVA and hybrid fibers, respectively. For the PVA fibers [Fig. 2(a)], the bands at about 3320, 2940, 1437, 1093, and 850 cm^{-1} are assigned to the vibrations of –OH, $–CH_2$, C–C, and C–O groups of PVA, respectively.[15] However, for hybrid fibers [Fig. 2(b)], besides the vibration bands of PVA, a new intense broadband between 400 and 750 cm^{-1} assigned to the Zn–O vibration of ZnO apears,[16] indicating that the hybrid fibers are composed of PVA and ZnO.

More evidence of the existence of ZnO in the hybrid fibers is provided by resonant Raman spectra (Fig. 3). The UV resonant Raman scattering at room temperature was performed to investigate the vibrational properties of the hybrid

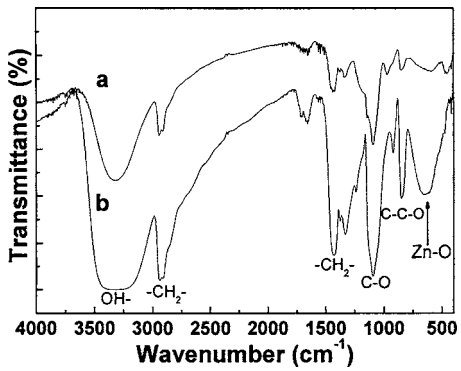

FIG. 2. IR spectra of PVA (a) and PVA/ZnO (b) hybrid fibers. The arrow indicated the vibration band of Zn–O.

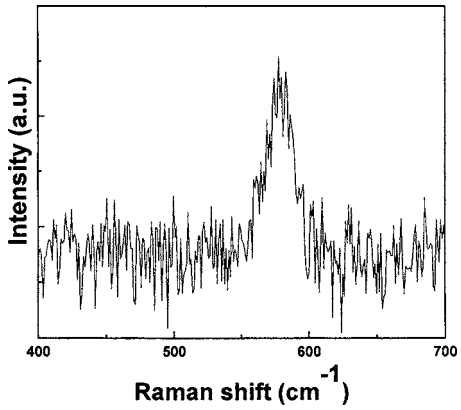

FIG. 3. Resonant Raman spectra of PVA/ZnO hybrid fibers at room temperature using 325 nm line of a He–Cd laser as the excitation source. This band, centered at 586 cm^{-1}, was attributed to the Raman E_1-LO phonon scattering of ZnO.

fibers. The energy of the He–Cd laser line (325 nm) is 3.82 eV, which is higher than the band gap of ZnO (3.37 eV). In Fig. 3, a significant Raman band centered at 586 cm^{-1} with the bandwidth of 25 cm^{-1} is observed, which is attributed to the Raman E_1-longitudinal optical (LO) phonon of nanosized ZnO.[17]

To determine the interactions between PVA and ZnO, DSC of pure PVA and PVA/ZnO hybrid fibers were conducted. For the pure PVA fibers [Fig. 4(a)], the endothermic peak below 100 °C is attributed to the loss of absorbed water. The peaks around 250 °C corresponds to the loss of water which form a H bond between PVA molecules. The two exothermic peaks at about 305 and 500 °C are associated with the degradation of side chain (the scission of C–O) and main chain (the scission of C–C) with the delta enthalpy of 3760 and 1188 J g^{-1}, respectively.[18] For the hybrid fibers [Fig. 4(b)], the exothermic peak below 450 °C is not observed, while the peak around 500 °C is sharp and strong with delta enthalpy of 3305 J g^{-1}, suggesting that the degradation of PVA is remitted. The effect of ZnO on the degradation of polymer was also described by other groups.[19] The above results demonstrate the existence of some interactions between a PVA molecule and ZnO via forming a H bond and an O–Zn–O bond. These interactions could be responsible for novel luminescent properties of hybrid fibers of PVA/ZnO.

Figures 5(a)–5(d) show the PL spectra of ZnO QDs, pure PVA fibers, spin cast film of PVA/ZnO, and hybrid fibers of PVA/ZnO at room temperature, respectively. As shown in

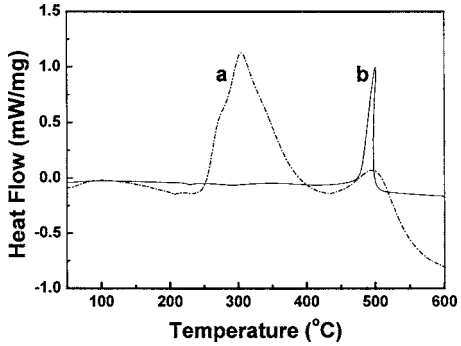

FIG. 4. DSC curves of PVA (a) and PVA/ZnO (b) fibers, showing that PVA was stabilized by ZnO until heating to 450 °C.

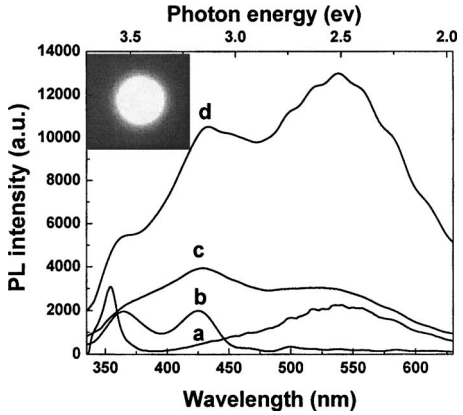

FIG. 5. PL spectra of ZnO QDs (a), PVA fibers (b), PVA/ZnO spin cast film (c) and PVA/ZnO hybrid fibers (d) at room temperature using the 325 nm line of a He–Cd laser as the excitation source. Insert is the luminescence photograph of the PVA/ZnO hybrid fibers taken by using UV filter (325 nm) and charge coupled device camera (color online).

Fig. 5(a), ZnO QDs have two emission bands at around 355 and 550 nm. The former mainly comes from the emission of a mixture of free exciton and bound exciton related to impurity or defects.[20] The green emission at about 550 nm is the transition between the electron close the conduction band and the deeply trapped hole at the V_0^{**} center (oxygen vacancy containing no electrons).[21] This emission is also attributed to the transition between the electron at $[V_0^*$, electron] or $[V_0^{**}$, two electrons] and the hole at vacancy associated with the surface defects.[22] Two emission bands appear at about 364 and 440 nm in the PL spectra of PVA fibers [Fig. 5(b)], which may originate from the organic functional groups of PVA. In the PVA/ZnO film [Fig. 5(c)], the PL spectrum shows the emission bands of both ZnO and PVA. The UV emission may originate from the combined action of the organic functional groups of PVA fibers and the exciton combination of ZnO. The band at about 440 nm comes from PVA, which overlaps with the visible emission band of ZnO. The spectra results indicate that the emission bands of PVA/ZnO hybrid film are composed of that of PVA and ZnO. However, for the hybrid fibers, though the positions of the emission bands are similar to that of hybrid film, the intensity of these bands, especially the visible emission, has a significant increase. This may be attributed to two aspects. First, in the solution of the composite of PVA/ZnO, the interaction between PVA and ZnO is not strong enough to confine the aggregation of ZnO QDs, thus there may exist large particles of ZnO in the matrix of PVA. This situation also exists in the hybrid film. However, the high electric field induces the polarization and orientation of ZnO QDs, thus, the ZnO QDs can be well-dispersed in the composite. By considering the above factors and below situation, i.e., in the hybrid fibers, the diameter of the fiber (about 300 nm) is much larger than the diameter of ZnO (about 8 nm), the hybrid fibers can be regarded that the ZnO QDs is dispersedly embedded in and aligned along the PVA matrix fiber. Thus, the interaction between ZnO QDs and PVA molecules is enhanced. Second, the visible luminescence related to surface defects becomes strong due to the high surface to volume ratio of the electrospun hybrid fibers.[23] These results also imply that the smaller the diameters of the hybrid fibers, the higher the surface to volume ratio, and the stronger the intensity of visible emission. As a result, the simultaneous emission of three wide bands covers from the UV to visible range, and an intense white luminescence signal is observed. The luminescence spot on the sample is inserted in Fig. 5.

In conclusion, the hybrid nanofibers of PVA/ZnO with an average diameter about 300 nm were successfully prepared. The as-prepared fiber mats showed strong white emission with three bands covering from UV to visible spectral range, and a possible mechanism of white luminescence was proposed. This kind of materials is expected to be applied for white-light devices such as white LEDs and white flat panel displays.

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[1] X. Duan, Y. Hang, Y. Cui, J. Wang, and C. M. Lieber, Nature (London) **409**, 66 (2001).
[2] C. J. Lee, T. J. Lai, S. C. Lyu, Y. Zhang, H. Ruh, and H. J. Lee, Appl. Phys. Lett. **81**, 3648 (2002).
[3] C. J. Otten, O. R. Louire, M. F. Yu, J. M. Cowley, M. J. Dyer, R. S. Ruoff, and W. E. Buhro, J. Am. Chem. Soc. **124**, 4564 (2002).
[4] J. Zhang, X. S. Peng, X. F. Wang, Y. W. Wang, and L. D. Zhang, Chem. Phys. Lett. **345**, 372 (2001).
[5] Y. J. Chen, J. B. Li, Y. S. Han, X. Z. Yang, and J. H. Dai, J. Cryst. Growth **245**, 163 (2002).
[6] J. R. Heath and F. K. LeGoues, Chem. Phys. Lett. **208**, 263 (1993).
[7] F. Y. Sun, B. Gates, B. Mayers, and Y. Xia, Nano Lett. **2**, 165 (2002).
[8] D. Li and Y. Xia, Adv. Mater. (Weinheim, Ger.) **16**, 1151 (2004).
[9] E. Zussman, A. Theron, and A. L. Yarin, Appl. Phys. Lett. **82**, 973 (2003).
[10] P. Viswanathamurthi, N. Bhattarai, H. Y. Kim, D. R. Lee, S. R. Kim, and M. A. Morris, Chem. Phys. Lett. **374**, 79 (2003).
[11] X. Yang, C. Shao, Y. Liu, R. M, and H. Guan, Thin Solid Films **478**, 228 (2005).
[12] R. Könenkamp, R. C. Word, and C. Schlegel, Appl. Phys. Lett. **85**, 6004 (2004).
[13] L. Spanhel and M. A. Anderson, J. Am. Chem. Soc. **113**, 2826 (1991).
[14] N. S. Pesika, K. J. Stebe, and P. C. Searson, Adv. Mater. (Weinheim, Ger.) **15**, 1289 (2003). The average radius of the ZnO colloids were calculated according to the following equation:

$$E^* \cong E_g^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2er^2}\left(\frac{1}{m_e m_0} + \frac{1}{m_h m_0}\right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 r}.$$

[15] Y. Liu, W. Ren, L. Y. Zhang, and X. Yao, Thin Solid Films **353**, 124 (1999).
[16] S. C. Liufu, H. N. Xiao, and Y. P. Li, Polym. Degrad. Stab. **87**, 103 (2005).
[17] J. F. Scott, Phys. Rev. B **2**, 1209 (1970).
[18] N. Koji, Y. Tomonori, I. Kenji, and S. Fumio, J. Appl. Polym. Sci. **74**, 133 (1999).
[19] I. C. McNeil and M. H. Mohammed, Polym. Degrad. Stab. **48**, 189 (1995).
[20] W. Shan, W. Walukiewicz, J. W. Ager III, K. M. Yu, H. B. Yuan, H. P. Xin, G. Cantwell, and J. J. Song, Appl. Phys. Lett. **86**, 191911 (2005).
[21] A. V. Dijken, E. Meulenkamp, D. Vanmaekelbergh, and A. Meijerink, J. Phys. Chem. B **104**, 1715 (2000).
[22] Y. C. Liu, X. T. Zhang, J. Y. Zhang, Y. M. Lu, X. G. Kong, D. Z. Shen, and X. W. Fan, Chin. J. Lumin. **23**, 563 (2002).
[23] I. Shalish, H. Temkin, and V. Narayanamurti, Phys. Rev. B **69**, 245401 (2004).