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Luminescent polyvinylpyrrolidone/ZnO hybrid nanofibers membrane prepared by electrospinning

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Abstract: Polyvinylpyrrolidone (PVP)/ZnO composite nanofibers were successfully prepared by a facile method called electrospinning technique. The synthetic strategy involved two steps: (1) Preparation of ZnO sol in ethanol solution. PVP molecules then added into the above sol and achieved the appropriate rheology for electrospinning; (2) Electrospun the above solution to obtain fibers of PVP/ZnO composites. Scanning electron microscopic (SEM) analysis of the composite nanofibers revealed network structures like a spider's web. Transmission electron microscopy (TEM) showed small nanoparticles of the ZnO component with an average particle size in the range of 3 — 4 nm and a good dispersion. X-Ray diffraction results showed that a pure wurtzite phase was obtained in PVP fibers. XPS spectra proved that the Zn and O elements existed in PVP/ZnO composite nanofibers. FTIR and UV-vis spectroscopy were used to characterize the structure of PVP/ZnO composite nanofibers. The photoluminescence properties of the PVP/ZnO composite nanofibers were also investigated.

Introduction

The synthesis of semiconductor nanoparticles especially with diameters in the range of 1—10 nm has gained considerable interest over the past few years because of their novel optical and electrical properties [1-4]. Size reduction entails confinement of charge carriers to the restricted volume of small particles, with a large fraction of the constituent atoms or molecules being at or near the surface. These circumstances lead to quantum size effects. These unique properties lead to appearance of many new application areas, such as their use in solar cells, photo-detectors, light-emitting diodes and switches. Among the semiconductor quantum dots, ZnO has attracted much attention owing to its wide band gap energy of 3.37 eV and a large exciton binding energy of 60 meV [5]. ZnO nanoparticles, because of their larger specific surface, higher surface activity, the superior luminescence and photoelectric properties, have become a most promising material in making of transparent electrode in display dye-sensitized solar cells, short-wavelength light-emitting and laser diodes, and piezoelectric materials, etc [6-11].

In recent years, metal/semiconductor nanoparticles immobilized in polymer matrices have generated considerable interest owing to their distinct individual and cooperative properties [12-15]. Specially, such one dimensional (1D) nanostructured composites have exhibited unique physicochemical, electrophysical, magnetic and optical properties [12, 14, 15]. Our groups have prepared conducting polymer/CdS composite microwires by introducing weak interactions such as hydrogen bonding and/or electrostatic interactions [16]. In recent times, an electrospinning method is frequently used to produce polymer fibers and polymer/inorganic composite fibers membrane [17-19]. Electrospinning was first reported in 1934 and has been receiving much attention due to its simplicity and effectivity to produce ultrafine fibers with diameter in the range of nanometer to micrometer. Up to now, the electrospun fibers have been finding a broad range of applications in membrane technology [20], tissue engineering [21], optical and biosensors [22,23], superhydrophobic surface [24,25] and drug delivery [26]. When a strong electrostatic force is applied to the capillary containing a polymer solution, it is ejected from the capillary and deposited as a nonwoven fibrous mat on a template serving as the ground for the electric charges. Using this method combined gas-solid reaction, one has prepared PbS nanoparticles and CdS nanorods dispersing in polymer fiber matrices firstly [27, 28]. However, the used H_2S gas was harmful to the environment. So we developed a two-step method to synthesize polymer/semiconductor nanoparticles composite nanofibers [29]. The synthetic strategy involved two steps: firstly, preparing a sol containing Ag_2S nanoparticles suspension combined with PVP, and achieving the appropriate rheology for electrospinning. Then electrospinning the above sol solution to obtain PVP/Ag_2S composite fibers. Shao et al. also prepared PVA/ZnO composite nanofibers using this method [30]. However, the content of ZnO in the composite was so little that XRD and TEM could not detect it. Moreover, the ZnO sol was prepared in water solution, so it could only apply to synthesize water-soluble polymer/ZnO composite fibers. In this article, firstly we prepared high content of ZnO sol in organic solvent. Then electrospun the PVP/ZnO ethanol solution to prepare PVP/ZnO composite fibers. The content of ZnO in PVP fibers could reach up to 10%—20%. This method provided a simple technique that allowed the synthesis of high content of ZnO nanocrystallines in PVP nanofibers.

Results and discussion

Fig. 1 shows the SEM photographs of hybrid fibers of PVP/ZnO. It is found that the fibers are randomly oriented on the substrate, and the individual fibers have high slenderness ratios. The diameter of the fibers is between 100 nm and 400 nm, and they are longer than several millimeters. The film has a network structure because numerous fibers interweave integrally like a spider's web. In the XRD curve of the hybrid fibers, the diffraction peak at $2\theta = 22^{o}$ corresponds to the PVP crystalline phase (Fig. 3b).

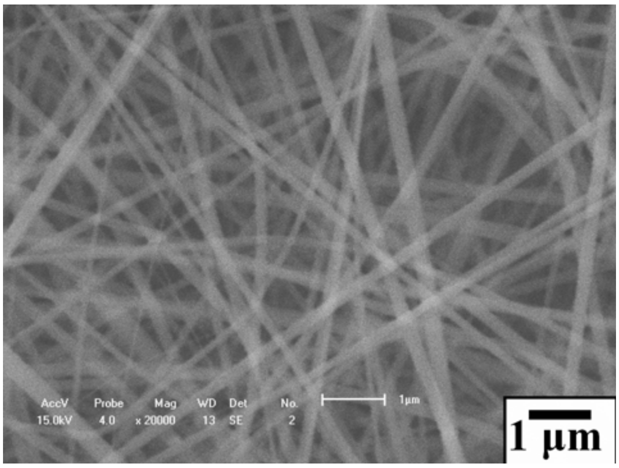

Fig. 1. SEM image of hybrid PVP/ZnO nanofibers by electrospinning.

Except the diffraction peaks of PVP, the other peaks all ascribe to the wurtzite of ZnO, which is similar to the pure ZnO nanopartilces (Fig. 3a) and the previous report [31]. According to Scherrer's equation, $D_{hkl} = \kappa\lambda \times 57.3/\beta\cos\theta$, where D is the average diameter of the crystals in angstroms, λ is the X-ray wavelength (λ = 1.5418 Å), κ is the shape factor (κ = 0.89), θ is the Bragg angle in degrees, β is the line broadening measured by half-height in radians. When the reflecting peaks of ZnO in Fig. 3 are chosen to calculate crystal size of ZnO nanoparticles, the average size of ZnO nanoparticles are in the range of 3—4 nm, which is also proved by TEM image (Fig. 2). And the TEM image also shows that the ZnO nanoparticles are dispersed in PVP fibers effectively.

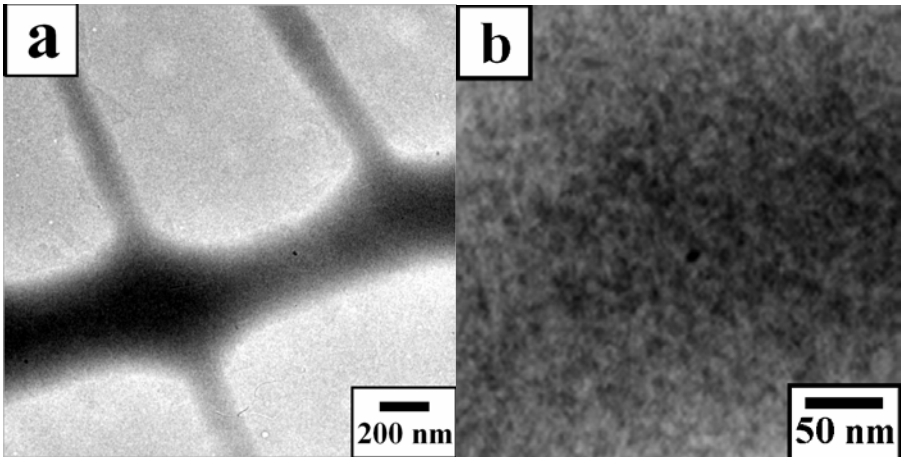

Fig. 2. TEM images of hybrid PVP/ZnO nanofibers by electrospinning: a, b) TEM images at different magnification.

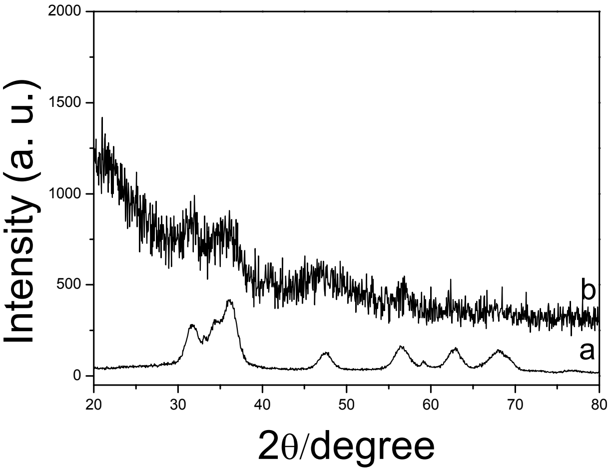

Fig. 3. XRD patterns of (a) ZnO nanoparticles and (b) hybrid PVP/ZnO nanofibers by electrospinning.

Fig. 4 shows the typical XPS spectra of hybrid fibers of PVP/ZnO. The C (1s) peak appears at about 284.4 eV, the N (1s) peak is observed at about 399.6 eV, which proves the existence of PVP polymer in the composite fibers. The O (1s) peaks are observed at 530.8 and 533.3 eV, the former is ascribed to the oxide ions in ZnO, and the latter is attributed to the C=O in PVP molecules. The Zn (2p3/2) for ZnO is shown in Figure 4b. The Zn (2p3/2) XPS peak which appears at 1020.5 eV coincides with the findings for ZnO. These results clearly indicate that the hybrid fibers are composed of PVP and ZnO.

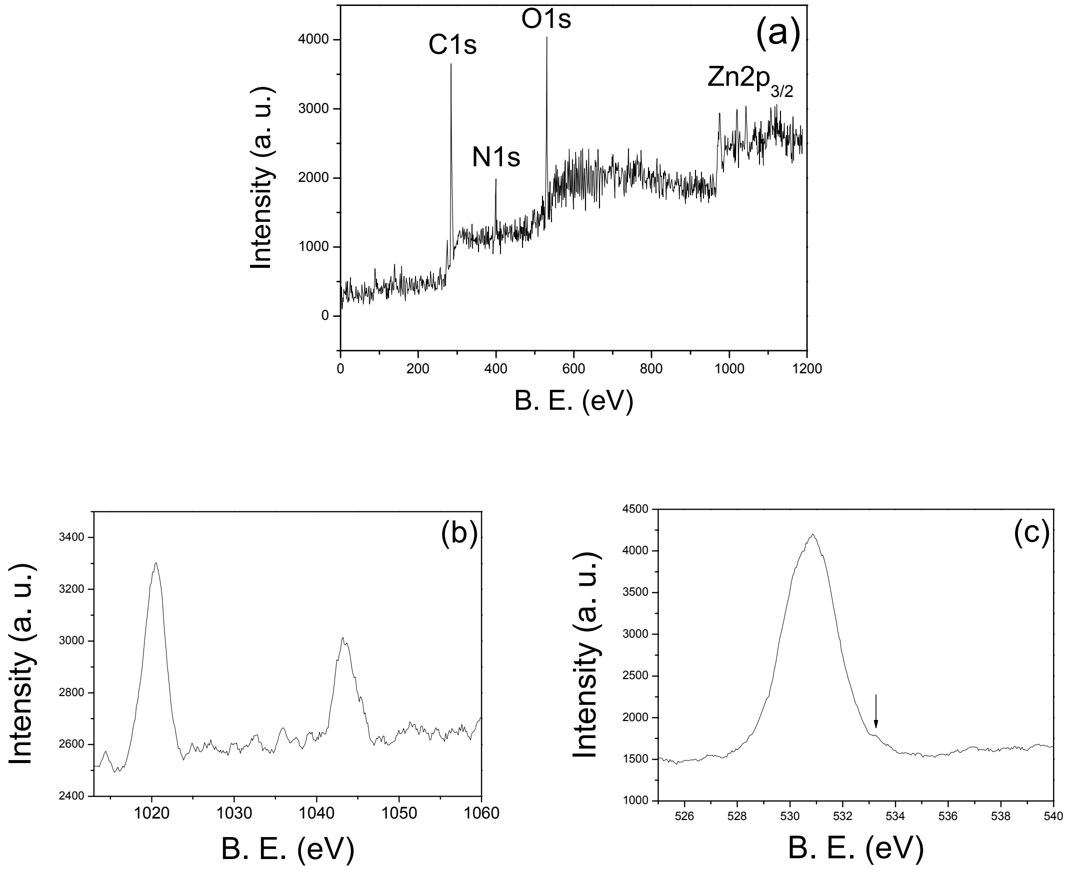

Fig. 4. XPS data of hybrid PVP/ZnO nanofibers: (a) full spectrum, (b) Zn2p, (c) O1s.

FTIR spectra are also used to characterize the molecular structure of PVP/ZnO composite nanofibers. Figs. 5a and 5b show the FTIR spectra of pure PVP and hybrid PVP/ZnO fibers, respectively. From Fig. 5a, it is found that characteristic peaks of pure PVP at around 1656 (C=O stretching), 1423 (C-C stretching), 1286 cm^{-1} (C-N stretching), are observed. For hybrid fibers in Fig. 5b, all of the PVP peaks appears, and the C=O band shifts towards lower frequency (from 1656 to 1652 cm^{-1}), which indicate that the ZnO nanoparticles are combined with PVP fibers. Besides the vibration bands of PVP, a new intense band at about 619 cm^{-1} assigned to the Zn–O vibration of ZnO appears, indicating that the hybrid fibers are composed of PVP and ZnO.

The optical properties of the ZnO particles in ethanol solution and hybrid PVP/ZnO fibers membrane are shown in Fig. 6. The UV–vis absorption spectrum of ZnO nanoparticles in ethanol solution typically resembles those of nanoparticles prepared in alcohol solutions [31, 32]. From the correlation of the absorption spectrum with the size diameter as used by Meulenkamp [32], we estimate the diameter of ZnO particles to be between 3 and 4 nm, which is also proved by XRD spectra and TEM in the former discussion. And for hybrid fibers, the UV–vis absorption spectrum is similar with that of pure ZnO nanoparticles in ethanol solution, indicating the ZnO nanoparticles are dispersed in PVP fibers.

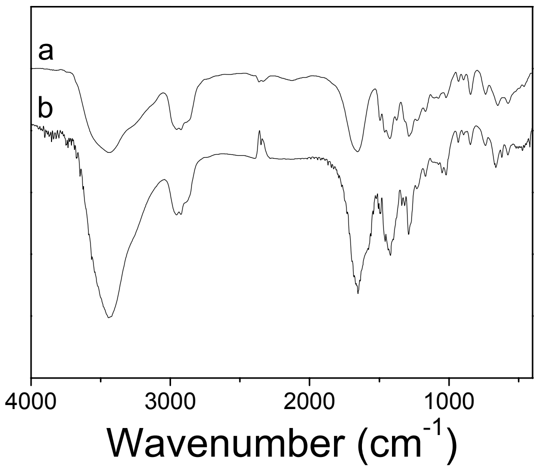

Fig. 5. FTIR spectra of (a) pure PVP and (b) hybrid PVP/ZnO nanofibers.

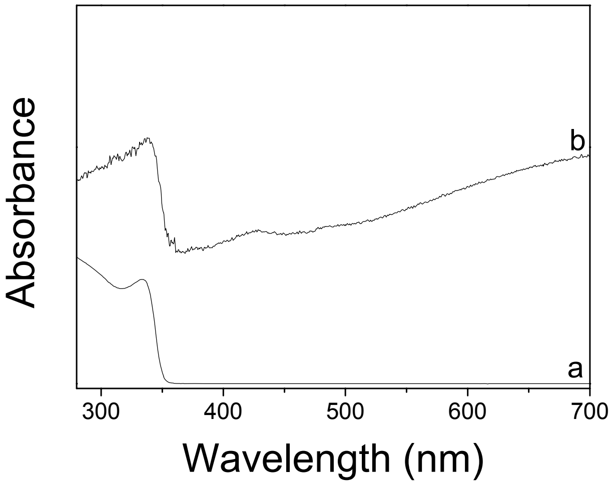

Fig. 6. UV/Vis spectra of (a) ZnO nanoparticles in ethanol solution and (b) hybrid PVP/ZnO nanofibers by electrospinning.

The room-temperature photoluminescence (PL) spectra of the above-mentioned ZnO nanoparticles in ethanol solution and hybrid PVP/ZnO fibers are shown in Fig. 7. For only ZnO nanoparticles, an emission band at around 514 nm is observed, which is attributed to the transition between the electron close the conduction band and the deeply trapped hole at the V0** center (oxygen vacancy containing no electrons). This emission is also attributed to the transition between the electron at V0* [electron], or V0** [two electrons], and the hole at vacancy associated with the surface defects. In the hybrid ZnO/PVP fibers, the PL spectrum shows the similar emission bands of ZnO nanoparticles, only the emission band red-shifted a little (from 514 to 518 nm). A new weak emission band at about 386 nm, which may originate from the combined action of the organic functional groups of PVP fibers and the exciton combination of ZnO, is also observed in ZnO/PVP fibers. The spectra results indicate that the emission bands of PVP/ZnO hybrid fibers membrane are composed of that of PVP and ZnO nanoparticles.

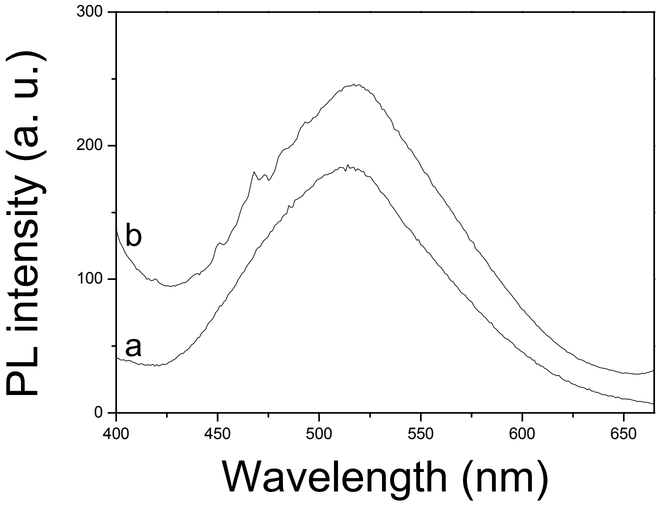

Fig. 7. Room-temperature photoluminescence spectra of (a) ZnO nanoparticles in ethanol solution and (b) hybrid PVP/ZnO nanofibers by electrospinning.

Conclusions

In summary, we demonstrate a method to synthesize hybrid nanofibers of PVP/ZnO by electrospinning. SEM image shows that the morphology of the composite is nanofibers which are randomly oriented on the substrate. TEM images prove that ZnO nanopaticles are embedded in the composite fibers. XRD, XPS and FTIR characterize the molecular structure of PVP/ZnO composite nanofibers. The optical properties of the PVP/ZnO hybrid nanofibers are also studied by UV-vis absorption spectra and photoluminescence spectra.

Experimental part

Materials

PVP (Aldrich, weight-average molecular weight, Mw = 1300,000), Zinc acetate ($C_4H_6O_4Zn{\cdot}2H_2O$ from Shantou Xilong Chemical Factory Guangdong, China), absolute ethanol, and lithium hydroxide ($LiOH{\cdot}H_2O$ from Tianjin Kermel Chemical Reagents Development Centre, China) were used as received without further purification.

Instruments and measurements

FTIR Spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR22 Spectrometer. Transmission spectra of ZnO nanoparticles in ethanol solution and hybrid PVP/ZnO nanofibers membrane were recorded on a Shimadzu UV-2501 PC Spectrometer. X-ray diffraction patterns (XRD) were obtained with a Siemens D5005 diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) measurements were performed on a SHIMADZU SSX-550 microscope.

Transmission electron microscopy (TEM) experiments were performed on a JEOL 2010F electron microscope with an acceleration voltage of 200 kV. Analysis of the X-Ray photoelectron spectra (XPS) were performed on an ESCLAB MKII using Mg as the exciting source. Photoluminescence spectra of ZnO nanoparticles in ethanol solution and hybrid PVP/ZnO fibers membrane were recorded on a Shimadzu RF-5301 PC spectrofluoro-photometer.

Synthesis of ZnO sol in ethanol solution

In a typical procedure, a 0.1 L ethanolic zinc acetate solution (0.1 M) was placed into a distillation flask fitted with a condenser and refluxed for a short time in order to dissolve all zinc acetate sample. Then the obtained solution was cooled rapidly to room temperature. A desired amount of lithium hydroxide powder was added to the diluted, cooled precursor solution (the concentration of LiOH is 0.14 M). The mixture was then hydrolyzed in an ultrasonic bath at about 0 ^{o}C for 20 min. Finally, the ZnO solution was filtered to remove dust and any undissolved lithium hydroxide. Thus, a transparent and stable colloidal solution 0.1 M was yielded.

Preparation of PVP/ZnO composite fibers by electrospinning

To electrospin PVP/ZnO composite fibers, the combination of PVP/ZnO sol in ethanol solution was prepared. In a typical procedure, 0.6 g of PVP (Aldrich, Mw = 1300, 000) was mixed with 9.4 g of the above ZnO ethanol sol solution, followed by magnetic stirring for 2 h to ensure the dissolution of PVP. Then the mixture was loaded into a plastic syringe equipped with a 14 cm long needle made of copper. The needle was connected to a high-voltages supply that is capable of generating DC voltages up to 30 kV. In our experiment a voltage of 12 kV was applied for electrospinning. A piece of flat aluminum foil was placed 20 cm from the tip of the needle to collect the nanofibers. The electrospinning was conducted in air.

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References

[1] Michael, H. H.; Samuel, M.; Henning, F.; Hao, Q.Y.; Yi, Y.W.; Hannes, K.; Eicke, W.; Richard, R.; Pei, D.Y.; *Science* **2001**, *292*, 1897.
[2] Weller, H.; *Angew. Chem. Int. Ed.* **1993**, *32*, 41.
[3] Henglein, A.; *Chem. Rev.* **1989**, *89*, 1861.
[4] Henglein, A.; *Top. Curr. Chem.* **1988**, **143**, 113.
[5] Reynolds, D. C.; Look, D. C.; Jogai, B.; Hoelscher, J. E.; Sherriff, R. E.; Harris, M. T.; Callahan, M. J.; *J. Appl. Phys.* **2000**, *88*, 2152.
[6] Gerischer, H.; Tributsch, H.; *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 437.
[7] Cao, H.; Xu, J. Y.; Zhang, D. Z.; Chang, S. H.; Ho, S. T.; Seelig, E. W.; Liu, X.; Chang, R. P. H.; *Phys. Rev. Lett.* **2000**, *84*, 5584.
[8] Bagnall, D. M.; Chen, Y. F.; Zhu, Z.; Yao, T.; Koyama, S.; Shen, M. Y.; Goto, T.; *Appl. Phys. Lett.* **1997**, *70*, 2230.
[9] Yang, T. L.; Zhang, D. H.; Ma, J.; Ma, H. L.; Chen, Y.; *Thin Solid Films* **1998**, *326*, 60.

[10] Cordaro, J.F.; Shim, Y.; May, J.E.; *J. Appl. Phys.* **1986**, *60*, 4186.
[11] Sang, B.; Yamada, A.; Konagai, M.; *Jpn. J. Appl. Phys. (Part 2)* **1998**, *37*, L1125.
[12] Woehrle D.: in ‘Macromolecule–metal complexes’, (ed. F. Ciardelli et al.); **1996**, Berlin, Springer.
[13] Trakhtenberg, L. I.; Gerasimov, G. N.; Aceksandrova, L. N.; Potapov, V. K.; *Radiation Phys. Chem.* **2002**, *65*, 479.
[14] Trakhtenberg, L. I.; Gerasimov, G. N.; Grigoriev, E. I.; *Russ. J. Phys. Chem.* **1999**, *73*, 209.
[15] Godovski, D. Yu.; *Adv. Polym. Sci.* **1995**, *119*, 81.
[16] Lu, X.; Yu, Y.; Chen, L.; Mao, H.; Zhang, W.; Wei, Y.; *Chem. Commun.* **2004**, 1522.
[17] Reneker, D.H.; Chun, I.; *Nanotechnology* **1996**, *7*, 216.
[18] Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H.; *Adv. Mater.* **2001**, *13*, 70.
[19] Dai, H.; Gong, J.; Kim, H.; Lee, D.; *Nanotechnology* **2002**, *13*, 674.
[20] Zong, X. H.; Ran, S. F.; Kim, K. S.; Fang, D. F.; Hsiao, B. S.; Chu, B.; *Biomacromolecules* **2003**, *4*, 416.
[21] Wnek, G. E.; Carr, M. E.; Simpson, D. G.; Bowlin, G. L.; *Nano Lett.* **2003**, *3*, 213.
[22] Wang, X. Y.; Drew, C.; Lee, S. H.; Senecal, K. J.; Kumar, J.; Samuelson, L. A.; *Nano Lett.* **2002**, *2*, 1273.
[23] Wang, X. Y.; Kim, Y. G.; Drew, C.; Ku, B. C.; Kumar, J.; Samuelson, L. A.; *Nano Lett.* **2004**, *4*, 331.
[24] Jiang, L.; Zhao, Y.; Zhai, J.; *Angew. Chem. Int. Ed.* **2004**, *43*, 4338.
[25] Acatay, K.; Simsek, E.; Ow-Yang, C.; Menceloglu, Y.Z.; *Angew. Chem. Int. Ed.* **2004**, *43*, 5210.
[26] Sanders, E. H.; Kloefkorn, R.; Bowlin, G. L.; Simpson, D. G.; Wnek, G. E.; *Macromolecules* **2003**, *36*, 3803.
[27] Lu, X.; Zhao, Y.; Wang, C.; Adv. Mater. **2005**, 17, 2485.
[28] Lu, X.; Zhao, Y.; Wang, C.; Wei, Y.; *Macromol. Rapid Commun.* **2005**, *26*, 1325.
[29] Lu, X.; Li, L.; Zhang, W.; Wang, C.; *Nanotechnology* **2005**, *16*,1660.
[30] Sui, S. M.; Shao, C. L.; Liu, Y. C.; *Appl. Phys. Lett.* **2005**, *87*, 113115.
[31] Lin, Y.; Wang, D.; Zhao, Q.; Yang, M.; Zhang, Q.; *J. Phys. Chem. B* **2004**, *108*, 3202.
[32] Meulenkamp, E. A.; *J. Phys. Chem. B* **1998**, *102*, 5566.