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BRIEF COMMUNICATION

Formation of ZnO within flexible polymer fibers

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Abstract In the process of fiber production from Zinc acetate and Polyvinylpyrrolidone using the electrospinning method, ZnO forms at temperature as low as 120 °C. The fibers were characterized using scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and ultraviolet–visible (UV–Vis) spectroscopy. Upon heating at 120 °C for 12 h some fibers shrink in diameter down to about 100 nm while others remain in the 400–900 nm range. Within the hybrid fibers, ZnO crystallizes in the wurtzite structure with a bang gap of 3.3 eV. The hybrid fibers exhibit the flexibility of polymer component and optical properties of ZnO phase, and promise to be very useful in various applications.

Keywords ZnO · Nanofibers · Hybrid fibers · Electrospinning · Sol–gel

1 Introduction

Zinc oxide (ZnO) is a II^b-VI compound semiconductor with a wide energy band gap in the near-UV region (3.4 eV) [1], that preferentially crystallizes in the hexagonal wurtzite-type structure. Important advantages of ZnO-based structures are non-toxicity, low cost, quantum size effects, and large exciton binding energy of 60 meV (compared, for example, to 26 meV in GaN) which allows more efficient excitonic emission at room temperature. These advantages make ZnO materials very attractive for industrial applications. Some current applications of ZnO are in solar cells [2] and UV-absorbing material in sunscreens [3]. Potential applications of ZnO structures are in UV light emitters, spin functional devices, gas sensors, and transparent electronics [4]. Nanostructures based on ZnO are promising novel materials with interesting electronic and optical properties and researchers are still searching for novel ways of preparing ZnO nanofibers [5].

Electrospun pure ZnO and doped ZnO as well as composite metal-oxide nanofibers such as ZnO–NiO and TiO_2–ZnO fibers show potential for use in sensors applications [6–10]. On the other hand, hybrid nanofibers containing both polymers and ZnO phase could be a candidate for white-light emission applications [11], and the electrospinning, as a relatively simple, straight-forward, and inexpensive method for producing continuous nanofibers with diameters from a few microns down to below 100 nm, could become a method of choice in making ZnO fibers.

ZnO generally forms above 400 °C [10]. Formation of ZnO thin film was previously observed at 200 °C using the sol–gel method [12]. ZnO/cellulose hybrid nanofibers were prepared by Ye et. al. [13] and it was reported that the solvothermal treatment in glycerol at 180 °C for 2 h induced the formation of hexagonal ZnO nanoparticles. In this letter, we report the formation of ZnO structures within hybrid fibers (ZnO/PVP) at temperatures as low as 120 °C and characterize the fibers using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and ultraviolet–visible (UV–Vis) methods.

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Formation of ZnO at such low temperature is important because these hybrid fibers preserve excellent flexibility of polymeric materials with the possibility of attaining some properties of ZnO.

2 Experimental

ZnO fibers have been prepared using a combination of a sol–gel process and electrospinning, followed by calcination of the Polyvinylpyrrolidone (PVP)/Zinc acetate mixture. Zinc oxide precursor solution was prepared by dissolving Zinc acetate (Aldrich) in distilled water at a weight ratio of 1:4. A polymer solution has been prepared by dissolving PVP (Aldrich, molecular weight: 1,300,000) in absolute ethanol at a weight ratio of 1:5. Zinc acetate solution was mixed with the ethanol solution of PVP at a weight ratio of 1:1 and the mixture was kept at 40 °C for 6 h under constant stirring to initiate the reaction between PVP and $Zn(CH3COO)_2$ resulting in a viscous gel of PVP/Zinc acetate. The sol–gel precursor was taken in a 5 ml syringe with a needle connected to the positive terminal of a high DC voltage power supply operating at 20 kV. The high electrical forces overcome the surface tension within the droplet at the tip of the syringe needle and the jet of charged precursor solution is ejected out from the needle towards the collector. The electrospun fibers were collected on the grounded aluminum foil 20 cm below the needle. The flow rate was maintained at 4 μl/min. The obtained fibers were calcined at low temperatures in a tube furnace under ambient conditions with the heating rate of 5 K/min and are kept at these low temperatures for various times until the formation of ZnO fibers was initiated.

Scanning electron microscopy images of as-spun and heated fibers were taken using a Hitachi S—2460N instrument under the same conditions with 3000× magnification and a voltage of 15 kV. A powder X-ray diffractometer (Rigaku D/Max-2000T) operating at 40 kV and 40 mA and with Cu K_α radiation ($\lambda = 0.154$ nm) was used for monitoring phase changes of the electrospun fibers at low temperatures. FTIR measurements were conducted on a Bruker IFS 66v/s spectrometer. UV–Vis spectra were acquired using a Cary 300 visible–UV spectrophotometer made by Varian.

3 Results and discussion

SEM image of as-spun fibers (before heating) is shown in Fig. 1a. The fibers are flexible and have uniform thickness with the diameter in the 400–900 nm range. Figure 1b is the SEM image of the electrospun fibers subsequently heated at 120 °C for 12 h. Upon heating at 120 °C a fraction of the fibers have diameters in the same range as as-spun fibers (400–900 nm) whereas the other fraction shrinks in diameter down to around 100 nm. Although the decrease in diameter of the fibers upon exposure to heat is expected, and is generally attributed to the removal of polymers and organics, our measurements show that shrinking of the fibers can occur at temperatures as low as 120 °C. Fig. 2 displays thermogravimetric analysis (TGA) of the fibers. According to TGA measurements, at this temperature polymers constitute 67 % of the hybrid fiber structure.

Figure 3 shows XRD results for as-spun fibers, those heated at 120 °C for 2 h, and fibers heated at 120 °C for 12 h. The major XRD peaks correspond to the (100), (002), (101), (102), (110), (103), and (112) planes of ZnO. It can be seen that even heating for 2 h at 120 °C shows some evidence of formation of hexagonal wurtzite ZnO phase, and further heating for 12 h allows growth of the crystals. The fibers are hybrid and contain large quantities of polymeric material as can be seen in the broad amorphous

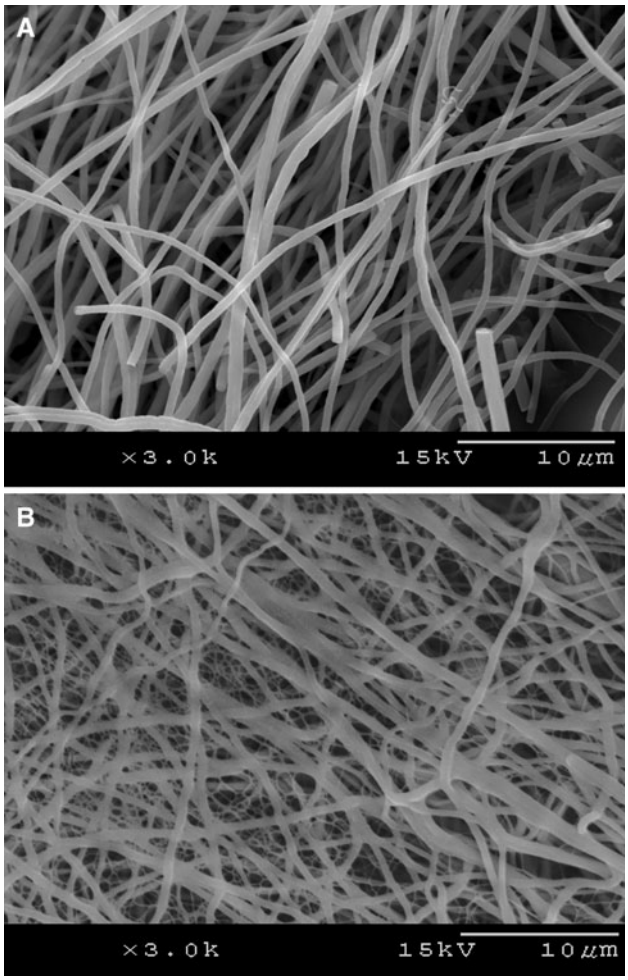

Fig. 1 Representative SEM images of as-spun fibers (**a**), and fibers heated at 120 °C for 12 h (**b**)

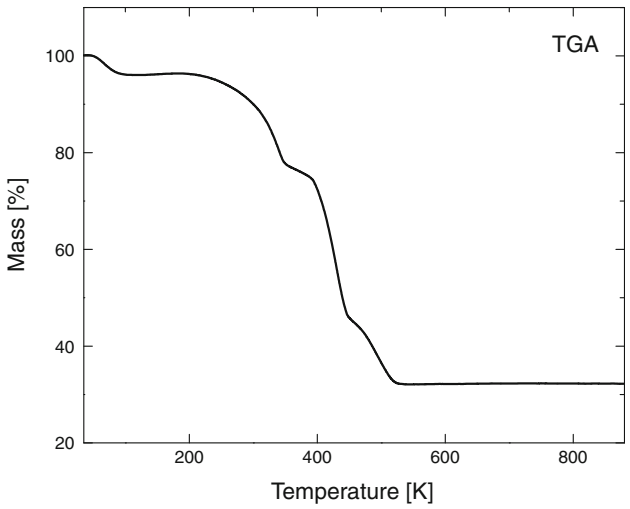

Fig. 2 Thermogravimetric analysis of as-spun hybrid fibers

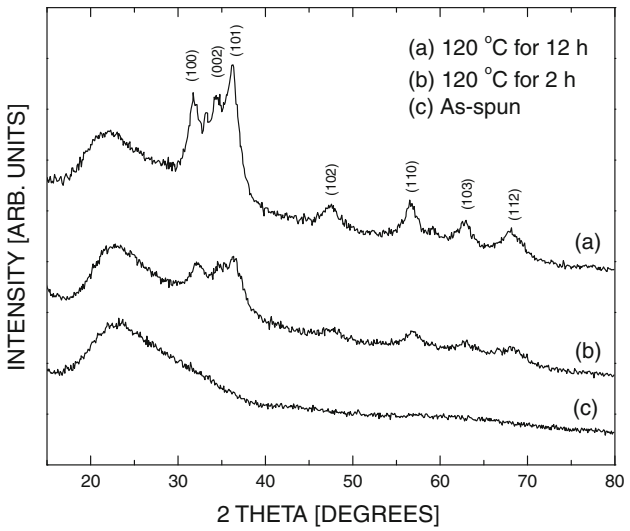

Fig. 3 XRD spectra of as-spun fibers, fibers heated at 120 °C for 2 h and fibers heated at 120 °C for 12 h. ZnO starts to form at 120 °C, and the broad feature indicates that large portion of the fibers has amorphous form. Formation of ZnO occurs in the presence of amorphous phase

feature around $2\theta = 22^{o}$. Therefore, the formation of ZnO phase within the fibers occurs in the presence of large quantities of polymeric materials. TGA experiments reveal that these low calcination temperatures cause removal of solvents whereas removal of polymers starts above 300 °C.

FTIR spectra of the as spun and fibers heated at 120 °C for 12 h are displayed in Fig. 4. All of the organic groups including C–C and C–O bonds are in the 700–1,700 cm^{-1} range and are due to PVP. The band near 3,500 cm^{-1} is due to the presence of water in the as spun fibers. The band slightly below 500 cm^{-1} is seen in the spectra of fibers heated at 120 °C and is assigned to ZnO [14, 15].

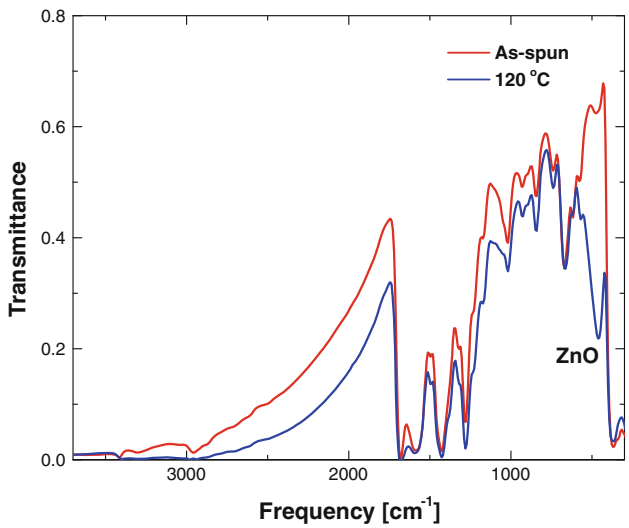

Fig. 4 FTIR spectra of as-spun (*red curve*) and fibers heated at 120 °C for 12 h (*blue curve*) (Color figure online)

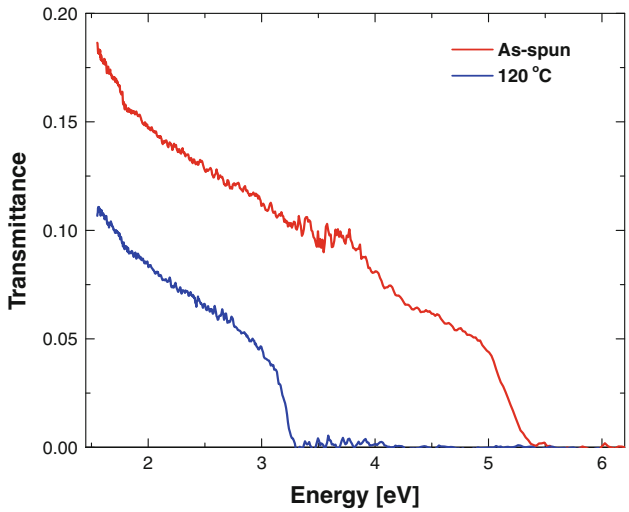

Fig. 5 Ultraviolet-visible spectra of as-spun fibers (*red curve*) and fibers heated at 120 °C (*blue curve*) (Color figure online)

UV–Vis spectra, displayed in Fig. 5, reveals that the absorption edge of polycrystalline ZnO at 3.3 eV can be observed for fibers heated at 120 °C for 12 h. This value is characteristic for ZnO. As-spun fibers show significantly larger value of the band gap which can be attributed to the presence of PVP whose band gap value we measured (results not shown) to be 4.1 eV. Heating the hybrid fibers at temperature as low as 120 °C preserves flexibility of polymeric material but at the same time results in the structure with optical properties (band gap) of ZnO. On the other hand, at temperature of 200 °C the flexibility of the fibers starts to deteriorate.

In a related study [10], the electrospun ZnO/PVP composite fibers were annealed in the 400–800 °C range to

remove PVP and to crystallize ZnO. Interestingly, in this same study the nanofibers were collected at 120 °C during the electrospinning process, the temperature at which we observe the formation of ZnO phase. We cannot completely rule out the possibility that growth of ZnO near 120 °C was overlooked in some of the earlier reports on ZnO fibers, especially since the majority of the work focuses on formation of pure ZnO fibers and since characterization is performed upon annealing at much higher temperatures [16]. These hybrid fibers produced in the work reported here have some advantages of organic polymers such as flexibility and light weight on one side and properties of ZnO on the other side. Structures like these could be considered for photocatalytic [13, 17], optoelectronic [18] as well as in chemical sensing or light emitting applications [17].

4 Conclusions

In the process of fiber production from Zinc acetate and Polyvinylpyrrolidone using the electrospinning method, the formation of ZnO is observed at strikingly low temperature of 120 °C when the fibers still contain large amounts of polymeric materials and form hybrid structures. The fibers were characterized using SEM, XRD, FTIR, UV–Vis methods. SEM shows that heating at 120 °C for 12 h significantly reduces the thickness of some of the fibers to 100 nm while the rest remains in the 400–900 nm range. Signatures of ZnO seen in XRD and FTIR are consistent with and the bang gap of 3.3 eV measured in UV–vis experiments. XRD measurements show formation of ZnO wurtzite structure. The advantage of these hybrid fibers is in combination of flexibility of the polymeric (PVP) material and optical properties of ZnO phase.

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