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Polymeric nanofiber composites with aligned ZnO nanorods

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ABSTRACT

ZnO nanorods with high aspect ratio were synthesized and were dispersed in poly(vinyl alcohol) (PVA)–water, PVA–water-N,*N*-dimethylforamide (DMF) and poly(acrylonitrile) (PAN)–DMF systems. These mixtures were electrospun to understand their spinning behaviour. It was found that only PAN–DMF system could result in formation of nanofiber composites reinforced with aligned ZnO rods. PAN nanofibers reinforced with ZnO rods up to 50 wt% on the weight of polymer could be readily electrospun. The presence of aligned ZnO rods inside PAN nanofibers was confirmed using scanning electron microscopy (SEM) and scanning/transmission electron microscopy (STEM). Raman analysis revealed that such reinforced nanocomposites are enabled only when ZnO rods could interact with both the dispersant as well as the polymer. Both random and aligned ZnO–PAN reinforced nanofibers could be successfully produced to suit different applications.

1. Introduction

ZnO has attracted remarkable attention in research because of its wide range of potential applications such as catalysis [1], solar cells [2,3], optoelectronic devices [4,5], and chemical and biological sensors [6]. Various methods have been employed to prepare different morphologies of ZnO structures including spheres, star, flower [7], rods [8–11], etc.

Aligned ZnO nanofibers or hollow nanotubes have also been produced using template assisted synthesis for optoelectronic applications [12]. Also, vertically aligned ZnO rods on various substrates have been produced for field emission and super hydrophobic properties [13,14] and increased interfacial strength [15]. One-dimensional tubular ZnO nanostructures have been produced using electrospinning of polymer solution with zinc precursor followed by calcination [16].

For many applications, it is important to produce composites of ZnO nanostructures in order to incorporate properties that are absent with ceramic materials. Composites of ZnO nanoparticles with polymers such as poly(ethylene terephthalate), poly(phenylene vinylene) have been reported either by in situ synthesis of ZnO particles in polymer matrix [17] or by incorporating ZnO isotropic nanoparticles into films [18,19] or electrospun fibers [20,21] to impart multifunctionalities.

Composites of ZnO rods are expected to have enhanced properties, especially when they are made to align inside a composite structure. However, presence of aggregates and inhomogeneous distribution of nanostructures is a major obstacle in polymer nanocomposites. Their dispersion and inclusion in aligned form has never been investigated, and therefore, remains an important area for exploration. Incorporation of long ZnO nanorods inside a nanofiber is a greater challenge in this direction.

Interaction of nanostructures with polymer chains and solvent is likely to play a crucial role in determining their dispersion and alignment along the nanofibers axis. In the present study, feasibility of orienting high aspect ratio ZnO nanorods along the axis of nanofibers has been investigated in poly(vinyl alcohol) PVA/H_2O, PVA/H_2O–DMF and poly(acrylonitrile) PAN/DMF systems.

2. Experimental methods

2.1. Materials

Fiber grade commercial acrylic terpolymer, with M_w of 75,000 was procured from Pasupati Acrylon, India. The terpolymer had about 8% methyl acrylate and 1% 2-acrylamido 2-propane sulfonate as comonomers in addition to acrylonitrile. Zinc acetate dihydrate, Sodium hydroxide (NaOH), N,*N*-dimethylforamide (DMF), and ethanol were procured from Merck, India. Poly(vinyl alcohol) PVA, (cold) of M_w 1,25,000 and degree of hydrolysis 86–89% was obtained from CDH, India.

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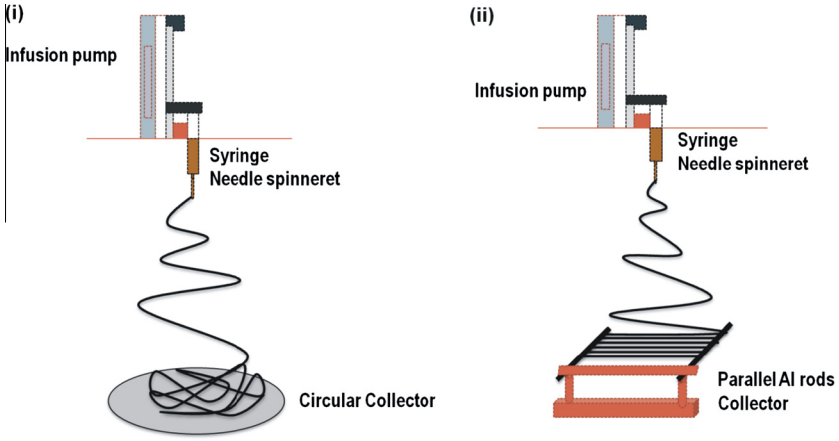

Fig. 1. Electrospinning set up for making: (i) random and (ii) aligned nanofiber web.

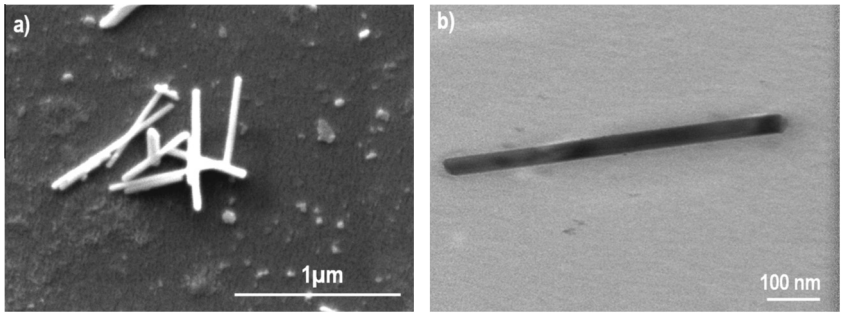

Fig. 2. SEM (a) and TEM (b) images of ZnO nanorods.

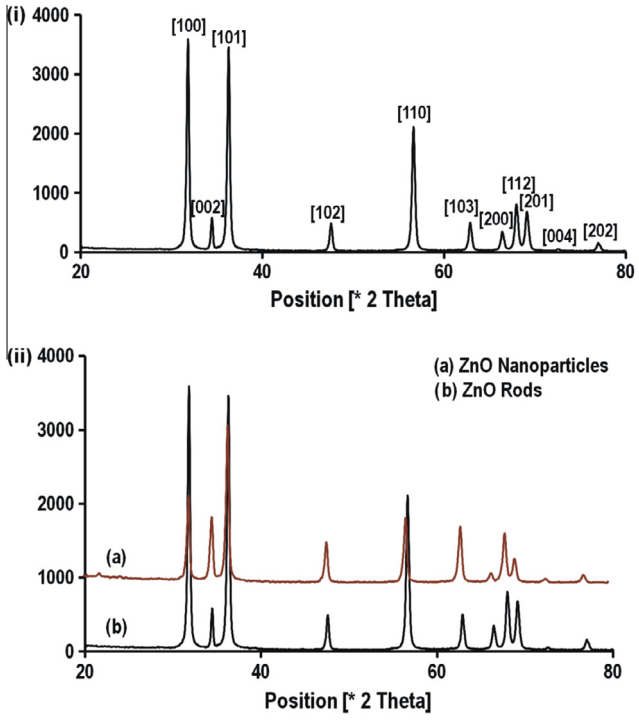

Fig. 3. X-ray diffraction patterns of: (i) ZnO nanorods (ii) ZnO nanorods and nanoparticles.

2.2. Methods

2.2.1. Synthesis of ZnO rods

The nano sized, ZnO rods were synthesized using hydrothermal non stirred vessel as reported in the literature [8,10,22]. Zn^{2+}/OH^{-} ratio was kept 1:10 and ethanol was used as solvent for the synthesis. In a typical procedure, Zinc acetate dihydrate ($Zn(Ac)_2{\cdot}2H_2O$) (0.002 mol) was added in 20 ml ethanol. In the above dispersion, 0.02 mol of NaOH dissolved in 40 ml ethanol were added drop wise. This mixture was then transferred to a non-stirred hydrothermal vessel and kept for 12 h at 150 °C. Precipitates obtained were washed several times with water, finally with ethanol and then dried.

2.2.2. Dispersion of ZnO rods

2.2.2.1. ZnO–PVA/water. 10 wt% of ZnO rods on the weight of PVA were dispersed in water by stirring for 15 min followed by ultrasonication for 30 min in sonication bath (Elma, at 100% power and frequency of 35 kHz). ZnO–PVA composite solution was prepared by adding required amount of PVA (from a stock solution of 16 wt%) to the above dispersion. Additional water was added to adjust the total solid content to 8 wt%. The final mixture was constantly stirred for 5 h at 50 °C, followed by sonication for 30 min at 100% power and frequency of 35 kHz. The sample was coded as 10 ZnO–PVA/H_2O.

2.2.2.2. ZnO–PVA/water:DMF(60:40). 10 wt%, 20 wt% and 50 wt% of ZnO rods on the weight of PVA were dispersed in the solvent i.e. water:DMF (60:40) using the method described above. The total solid content was maintained at 8 wt% for all compositions. These