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Synthesis and characterization of PVB/silica nanofibers by electrospinning process

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ABSTRACT

This paper describes PVB/silica nanofibers which were fabricated by electrospinning. Although electrospinning has developed rapidly over the past few years, electrospinning nanofibers are still at a premature research stage which is a process by which polymer nanofibers can be formed when a droplet of viscoelastic polymer solution is subjected to high voltage electrostatic field. PVB/silica nanofibers were obtained when the PVB/silica precursor ratio was 15% and the average diameters ranged from 100 to 200 nm and increased with increasing solution concentration and electrospinning synthesized at 12 kV of the applied voltage. The morphologies and structures of PVB/silica nanofibers were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analyzer (TGA), Fourier transform infrared spectrometer (FTIR), energy dispersive spectrometer (EDS).

1. Introduction

One-dimensional (1D) nanostructures such as nanofibers, nanorods, nanotubes and nanobelts are receiving increasing attention because of their large length to diameter ratio, as we have learned from natural materials such as inorganic/organic materials may be simultaneously hard. Polymer nanofibers can be produced by traditional vapor growth method [1] or chemical vapor depositing method, which was developed at the beginning of this century [2]. The jet grows longer and thinner due to bending instability or splitting occasionally [3] until it solidifies or collects on the collector.

Nanoscale size wires can be generated by electrospinning, in which high voltage is applied to the capillary droplet of polymer or solution overcome the liquid surface tension to form and draw the jet down to considerably finer fibers [4–9]. In a typical electrospinning process, when a strong electrostatic field is applied to a capillary containing a polymer solution, it is ejected from the capillary and deposited as a non-woven fibrous mat on a template, which serves as the ground for the electric charges. Wire formation was observed at above certain concentrations, where the specific viscosity increased significantly [10]. Electrospinning has the unique ability to produce nanofibers of different materials in various fiber assemblies. In the basic process of electrospinning, we need to consider parameters of factors, which include flow rate, concentration, viscosity, surface tension, conductivity and distance between the capillary and collector, it is possible to get some variations in the morphologies of the nanofibers.

Since the polymer/silica nanocomposites not only can improve the physical properties such as the mechanical properties and thermal properties of the materials, but can also exhibit some unique properties, they have attracted strong interest in many industries. The fibers have also been demonstrated and have many potential applications in various areas such as tissue engineering, catalysis, sensing, as well as fabrication of composite materials, supercapacitors, and tubular structures [11–14]. The potential application of nanofiber devices for a variety of sensor applications including detection of cells, viruses, and biochemicals [15–17]. These materials have been proven to be the promising catalysts that combine the advantage of shape selectivity with the efficient mass transport [18,19]. The presence of silica has improved catalytic activities and selectivity significantly as compared to conventional silica catalysts in a series of catalytic reactions.

The commonly used polyvinylbutyral (denoted as PVB) acts as mesopore template. PVB is a nontoxic, odorless, and environment friendly polymer, and it is widely used as functional materials in various fields. Also, because of its good compatibility with inorganic materials, PVB is an excellent organic component for the fabrication of organic/inorganic hybrid composites.

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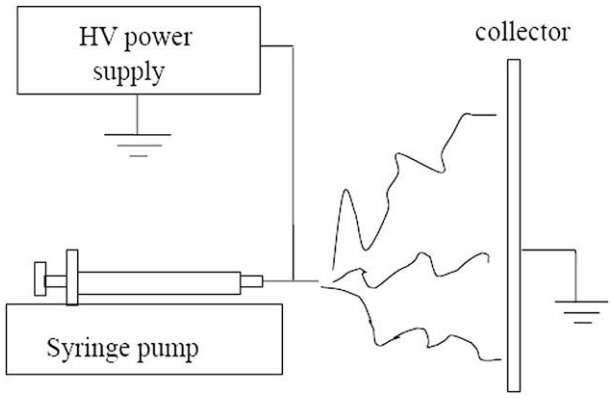

Scheme 1. Schematic diagram of electrospinning device.

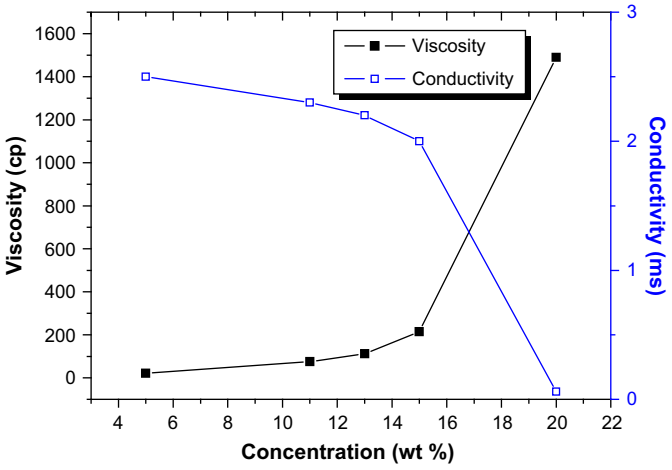

Fig. 2. Viscosity and conductivity changes of PVB/silica precursor with various concentration ratios.

2. Experimental

2.1. Materials and methods

TEOS (high-purity tetraethyl silicate) and ethanol absolute were from PA Panreac. Hydrochloric acid was from Panreac. Poly-(vinylbutyral) (PVB) (average $M_v \sim 40$ kDa) was obtained from ChangChun Group Company.

2.2. Preparation of electrospinning solution and PVB/silica nanofibers

The schematic setup of the electrospinning process used in the study is shown in Scheme 1. Amorphous silica precursor was dissolved in solvent mixtures of TEOS/ethanol/water/HCl with the ratios

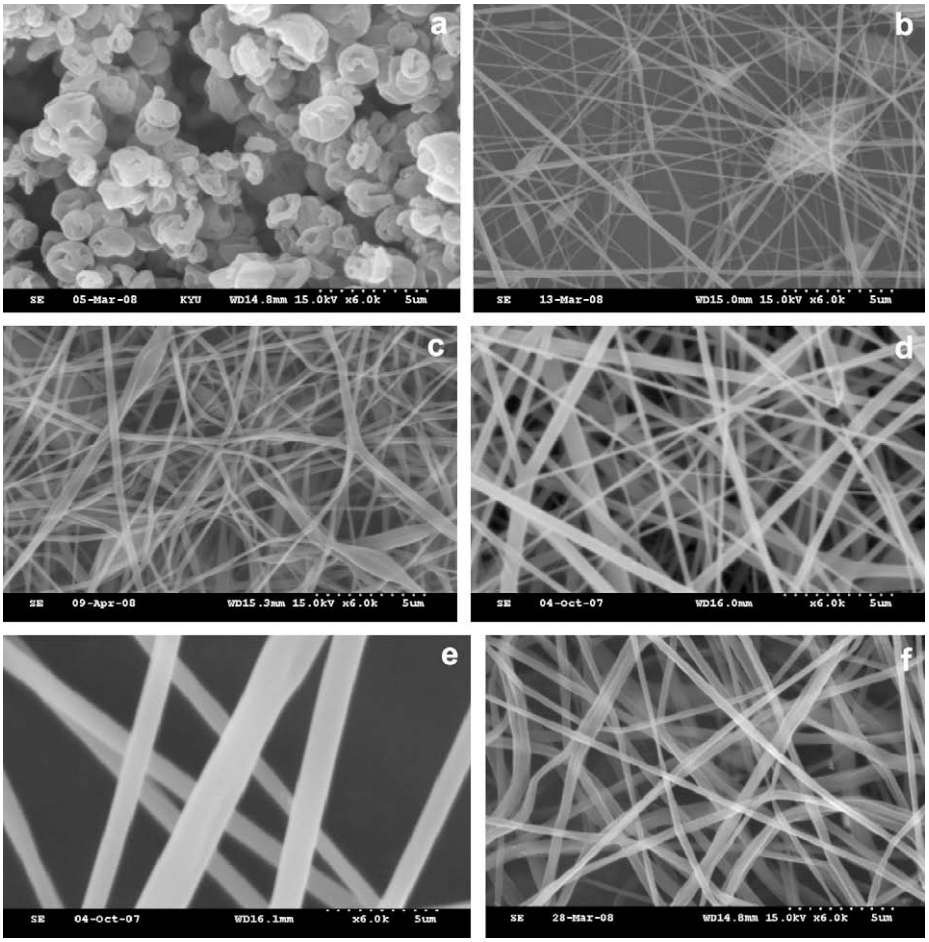

Fig. 1. SEM images of PVB/silica fibers (bar = 5 μm) electrospinning from (a) 5 wt%, (b) 11 wt%, (c) 13 wt%, (d) 15 wt%, (e) 20 wt% aqueous solutions at 12 kV; and (f) pure PVB fibers.

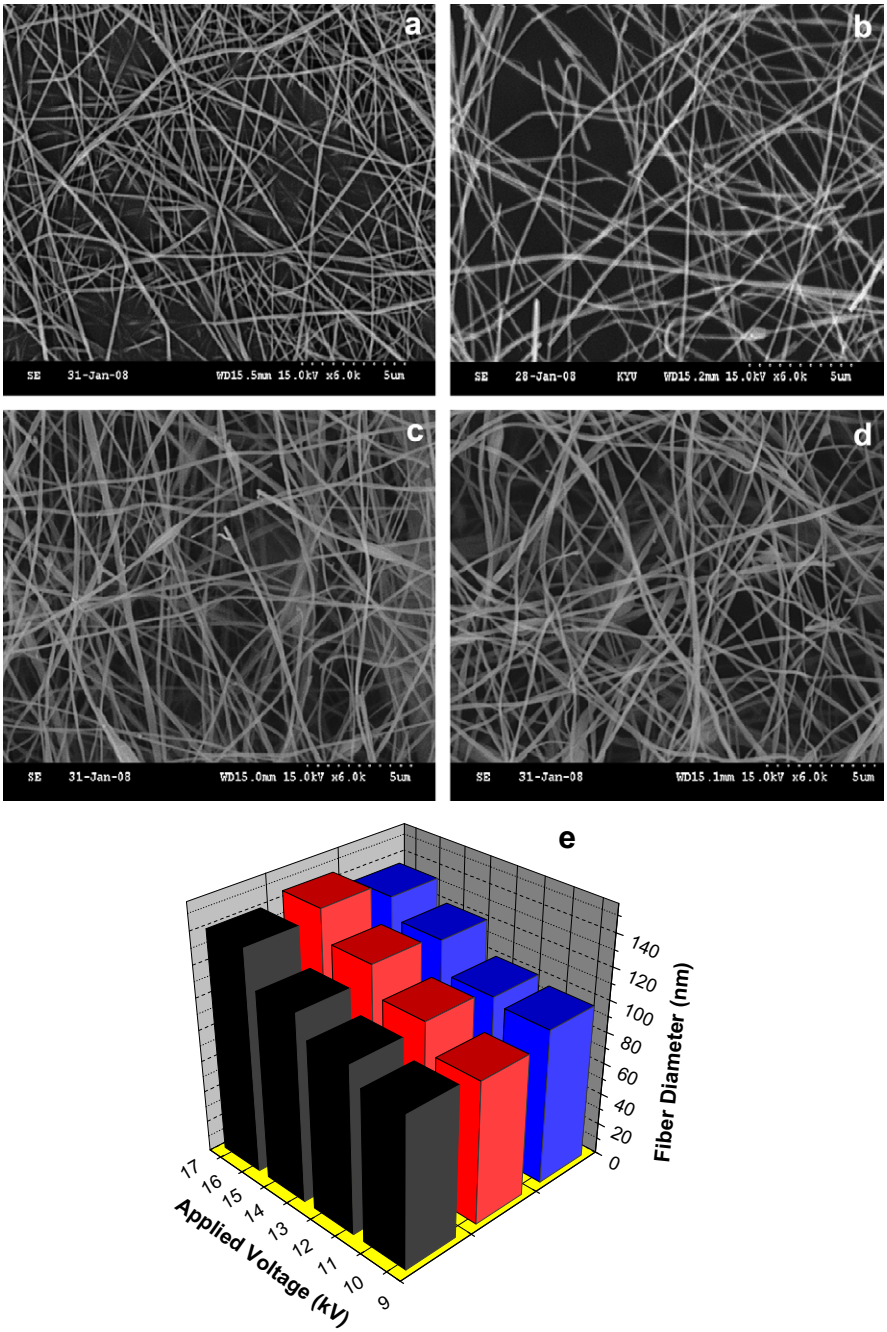

Fig. 3. SEM images of PVB/silica fibers (bar = 5 μm) electrospinning from different voltages are 10 kV (a), 12 kV (b), 14 kV (c), 16 kV (d) and dependence of PVB/silica nanofibers size on voltages (e).

of 1/4/4/1 (w/w). In electrospinning of polymer solutions, the fiber formation process can be characterized by the formation and thinning of the liquid jet to the solidification and deposition of fibers on the collecting target. Fibers were electrospinned as reported in literature [20,21]. A stainless steel electrode was connected to a high voltage power supply (You-Shang Technical Corp.), which can generate DC voltage up to 30 kV. The supplied voltages between the tip and collector were set at 16 kV with a tip-to-collector distance of 8 cm. The applied voltage first overcomes the liquid surface tension to form a jet, which then bend, and spiral into a larger looping path as the jet thins into finer fibers and solidifies. Homogeneous solutions of silica were prepared and added PVB at 15 wt% concentrations with gentle magnetic stirring at ambient temperature for 1–2 h. The solutions were prepared and used immediately for electrospinning. About 1 ml of solution was placed in a glass tube with a 0.21 mm inner diameter tip. Aluminum foil was used as the collector and connected to the ground. The concentration dependence of solution viscosity was higher for the PVB solutions than the aqueous solutions. This may be due to the more expanded conformation of silica in the aqueous media caused by the electrostatic repulsion between partially charged silica molecules.

2.3. Morphologies of PVB/silica nanowires

The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric

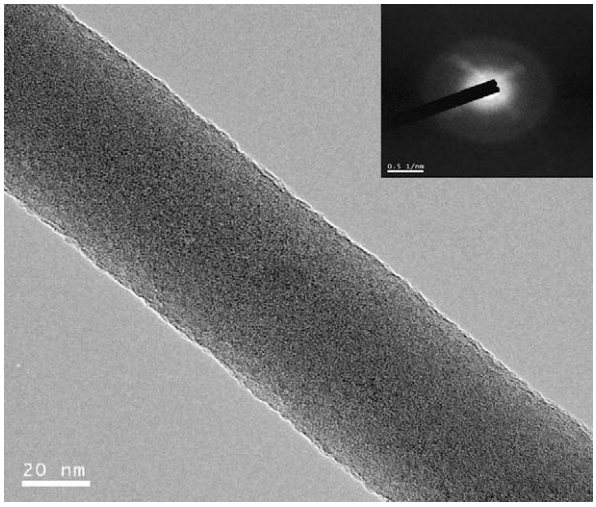

Fig. 4. TEM images of silica nanofibers by electrospinning (scale bar is 20 nm). The inset is the SAED pattern recorded from the same nanofibers.

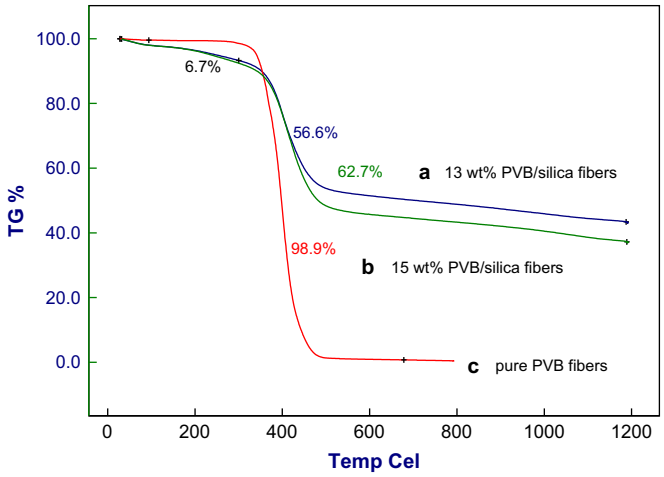

Fig. 5. Thermogravimetric analysis (TGA) curve of electrospinning 13 wt% PVB/silica fibers (a), 15 wt% PVB/silica fibers (b) and pure PVB fibers (c) synthesized at 12 kV of the applied voltage.

analyzer (TGA), and Fourier transform infrared spectrometer (FTIR), respectively, XRD was carried out on a D/MAX-500 X-ray powder diffraction with Cu Kα radiation ($\lambda = 1.5418$ Å). The scanning rate of 0.02 s^{-1} was applied to record the patterns in the 2 Theta range of 15–70°. TEM characterization was taken on a JEM-2000EX, using an accelerating voltage of 160 kV. Hitachi S-4200A scanning electron microscopy (SEM) at an acceleration voltage of 5 kV was employed to characterize the morphologies. The X-ray energy dispersive spectroscopy (EDS) was recorded on an EX220, HORIVA spectroscopy, which was attached to the SEM for composition analysis.

3. Results and discussion

3.1. Morphologies of electrospinning PVB/silica fiber formation

Electrospinning fibers were obtained from 15 wt% PVB/silica mixture solution at 12 kV with a tip-to-collector distance of 8 cm with various concentrations. In electrospinning of polymer solutions, the fiber formation process can be characterized by the formation and thinning of the liquid jet to the solidification and deposition of fibers on the collecting target. Fig. 1 shows a series of SEM images of PVB/silica nanofibers from precursor solutions with different concentrations ratios of 5%, 11%, 13%, 15% and 20%. As can be seen in Fig. 1(a) no fibers were obtained when the ratio was 5%. With the concentration of PVB increased, bead-on-string structures were observed as shown in Fig. 1(b)–(e) and the bead density decreased. PVB/silica nanofibers with smooth surface were obtained when the PVB/silica ratio was 20%. It can be increased that the concentration of PVB was a key factor in preparation of smooth PVB/silica nanofibers. PVB acted as the fiber template, which in the PVB/silica fibers exists states is adsorbed polymer chains induce not only steric repulsion but also bridging attraction. In addition to affecting the electrostatic and Van Der Waals interaction. Pure PVB fibers were observed as shown in Fig. 1(f), which the morphology is smooth than other different concentration PVB/silica.

To illustrate the effect of parameters of solutions on the morphology of resulting viscosity and conductivity of PVB/silica fibers with different ratios were examined as shown in Fig. 2. With the ratio increased, both parameters of PVB/silica fibers decreased, and bead-on-string structures appeared. When the ratio further increased, the beads on fibers decreased. The results showed that low conductivity preferred electrospinning. The wires size was increased with the increase in PVB concentration as shown in Fig. 2.

Fig. 3(a)–(d) shows SEM micrographs of the electrospinning PVB/silica fibers at four different applied voltages, 10 kV, 12 kV, 14 kV and 16 kV. The electrospinning silica fibers obtained at 10 kV are, on the whole, thicker than those obtained at 12 kV. The results are summarized in Fig. 3(e). It is observed that the diameter distribution of the silica fibers is shifted to the smaller size as the applied voltage decreases. This trend of reduction in size with the applied voltage has been reported in various electrospinning organic fibers [22]. The most population is in the range of 100–200 nm for the silica fibers synthesized at 10–16 kV. One hundred silica fibers were selected from ten spots of 60 × 60 μm^2 to measure the distribution of the diameters.

Electrospinning fibers obtained from 15 wt% PVB/silica mixture solution at 16 kV with a tip-to-collector distance of 8 cm with various concentrations. In electrospinning of polymer solutions, the fiber formation process can be characterized by the formation and thinning of the liquid jet to the solidification and deposition of fibers on the collecting target. Fig. 4 shows TEM images of porous silica nanofibers from precursor solutions with parameter conditions of including the smallest available needle of inner diameter of 0.16 mm, low volume feed rate of 0.1 ml/h, applied voltage of 12 kV and tip collector distance of 8 cm. Fig. 4 shows a TEM image of a selected area from a amorphous silica nanofibers. The surfaces of these nanofibers are smooth and porous structure. Both the morphology and size determined by SEM are similar to the TEM results.

3.2. Thermal behavior of electrospinning PVB/silica fibers

Fig. 5 shows TGA thermogram of the silica fibers obtained at 12 kV. It is observed that the weight decreases substantially at the low temperature region and decreases continuously. 13 wt% PVB/silica fibers (Fig. 5(a)) showed three steps and a total loss of ca. 56.6%. The first step of ca. 6.7% from 100 to 310 °C could be attributed to the desorption of the water, and the second significant weight loss of ca. 38% between 320 and 460 °C was assigned to the decomposition of PVB. From 460 to 680 °C, there was a weight loss of ca. 11.9%, which was assigned to the release of water formed from the condensation of silanols in the silica framework. 15 wt% PVB/silica fibers (Fig. 5(b)) showed three steps and a total loss of ca. 62.7%. The first step of ca. 6.7% from 100 to 310 °C could be attributed to the desorption of the water, and the second significant weight loss of ca. 45% between 320 and 460 °C was assigned to the

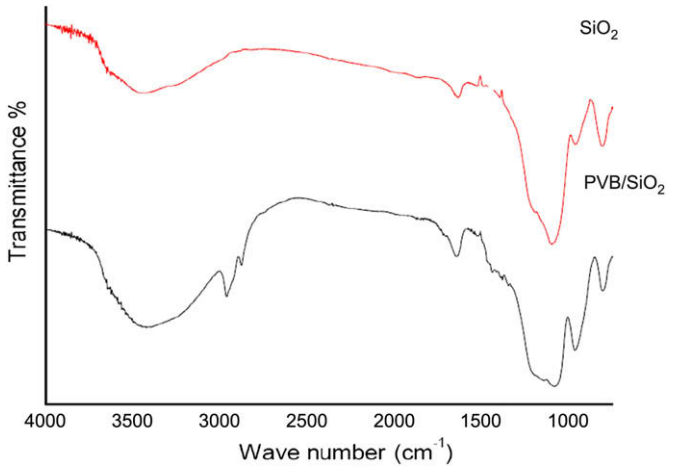

Fig. 6. FTIR spectrum of silica fibers (a) and PVB/silica fibers synthesized at 12 kV of the applied voltage.

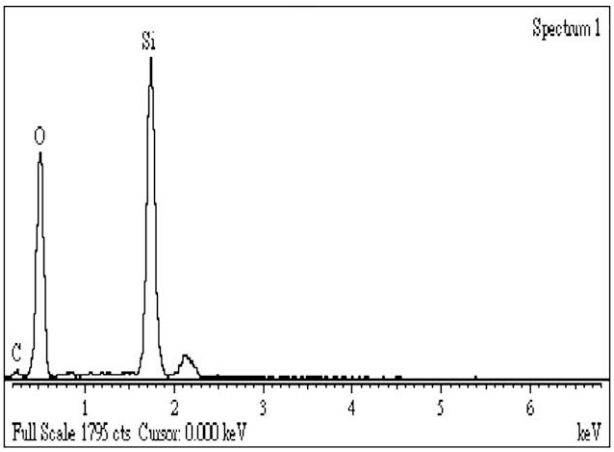

Fig. 8. EDS images of silica nanofibers by electrospinning process at 12 kV of the applied voltage.

decomposition of PVB. From 460 to 680 °C, there was a weight loss of ca. 11%, which was assigned to the release of water formed from the condensation of silanols in the silica framework. PVB fibers (Fig. 5(c)) showed that weight loss began to occur at approximately 340 °C and was complete at about 460 °C. The temperatures corresponding to peak maxima were near 400 °C for ions representing aliphatic species and near 410 °C for alkyl aromatics.

3.3. Structures of electrospinning PVB/silica fibers

The chemical structure of resulting nanofibers at 12 kV was characterized with an FTIR spectrometer, as shown in Fig. 6. It is seen that the peaks at 790, 935, and 1043 cm^{-1} are assigned to Si–O–Si vibration and the broad band near 3416 cm^{-1} is assigned to O–H vibration. It should be noted that there is no peak of methyl (CH_3) or methylene (CH_2) of ethoxy group ($-OCH_2CH_3$) in the FTIR spectrum: typical IR bands of CH_3 or CH_2 are several strong peaks at 2800–3000 and 1400–1800 cm^{-1} regions. This implies that most of the TEOS is hydrolyzed and the ethoxy group is changed to the silanol group (Si–OH). The broad band peak at 3416 cm^{-1} results from intra- and intermolecular hydrogen bonds of the silanol groups. Therefore determine an obtained silica nanofibers after passing through 500 °C the heat treatment the PVB polymer by to overflow completely disperses the evaporation. The results indicated that the resulting fibers are PVB/silica nanofibers.

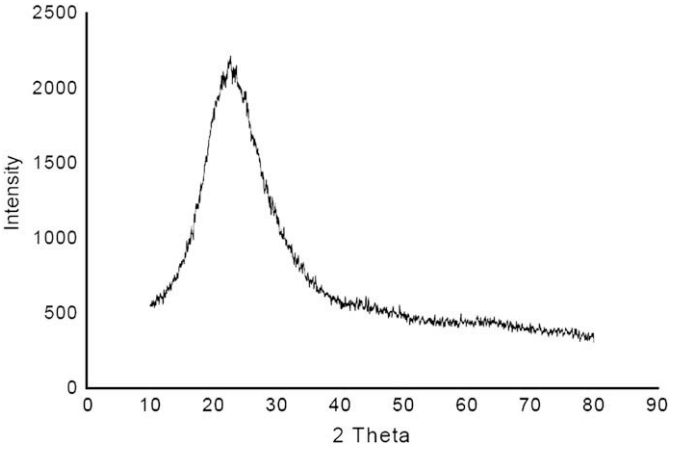

Fig. 7. XRD images of silica nanofibers by electrospinning process at 12 kV of the applied voltage.

We investigated crystalline structure of the silica fibers with X-ray diffraction pattern. The X-ray diffraction pattern of silica fibers obtained at 12 kV is shown in Fig. 7. This X-ray diffraction pattern exhibits the characteristics of amorphous silica. X-ray diffraction patterns of silica nanofibers shown one equatorial peak at $2\theta = 23°$. EDS analyses of silica nanofibers by electrospinning process reveal the presence of Si and O as shown in Fig. 8. When the probe was focused on rod areas, Si and O peaks were detected and quantitative analysis demonstrated that the atomic ration of Si:O is about 1:2. Most nanofibers obtained by electrospinning are in non-woven form. So it is difficult to find whether the molecular chains are oriented or not with the conventional measurements. Fiber average sizes calculated from the Scherrer equation were 102 nm at 12 kV.

4. Conclusions

The significant advantage of electrospinning is that long and continuous nanofibers can be produced in cost effective way, which makes it a potential application for nanoscale reactors. This technique can be used with a variety of polymers to produce nanoscale fibrous membranes. It is expected that this large amount of available surface area has the potential to provide unusually high sensitivity and fast response time in sensing applications. The sensors used in these studies operate with high sensitivity by monitoring the change in physical properties of the nanostructures resulting from interactions with specific species of interest.

PVB/silica nanofibers were successfully fabricated by electrospinning. PVB/silica nanofibers with smooth surface were obtained when the PVB/silica precursor ratio was 15%. Their diameter varies from few nanometers to 100–200 nm. Increasing the PVB concentration the homogeneity increases while the beads disappear. However increasing polymer concentration increases the diameter of nanofibers. Wire sizes were strongly dependent on the concentrations and voltages in both solution series and averaged from 100 to 200 nm.

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