

Synthesis and characterization of CuO electrospun nanofiber using poly(vinyl acetate)/Cu(CH₃COO)₂ annealing method

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ABSTRACT

One dimensional nanofibers of organic and inorganic materials have been used in filters, optoelectronic devices, sensors etc. It is difficult to obtain ultra fine fibers of inorganic materials having lengths in the order of millimeter as they tend to break during formation due to thermal and other mechanical stresses. In this study, we have investigated the mechanism to prevent the defect formation and the breaking of CuO nanofibers by using optimized heat flow rates. CuO nanofibers were obtained by heat treating the poly(vinyl acetate) PVA composite fibers formed by electrospinning. The morphology and structural characteristics of prepared samples were investigated by Scanning electron microscopy, Transmission electron microscopy and X-ray diffraction. It was found that the morphology of the composite and annealed nanofibers could be influenced by the concentration of the polymer content. A lower concentration favors the formation of defects along the fiber and the number of defects reduces when the concentration is increased. Copyright © 2013 VBRI press.

Keywords: CuO nanofiber; electrospinning, SEM; TEM; FTIR.



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Introduction

Nanoscale one-dimensional materials, such as nano-wires, nanorods, nanowhiskers, and nanofibers, have stimulated great interest due to their importance in basic scientific research and potential technology applications [1–3]. They are expected to play an important role as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices. Many unique properties have already been proposed or demonstrated for this class of materials, such as superior mechanical toughness [4], higher luminescence efficiency [5],

enhancement of thermoelectric figure of merit [6], and a lowered lasing threshold [7]. Metal oxide nanofibers have attracted increasingly interests for both fundamental and practical reasons. It has shown to be an industrially important material that can be widely used in applications such as gas sensors, magnetic storage media, solar energy transformation, semiconductors and catalysis. In order to obtain these materials, various preparation methods have been developed including arc discharge [8], laser ablation [9], template [10, 11], precursor thermal decomposition [12], and other methods [13–15]. Recently, inorganic nanofibers or superfine fibers have been produced by using electrospun fibers of polymer/inorganic composite as the precursor [16, 17]. Electrospinning is considered as a simple and convenient method for preparing fibers with extremely high aspect ratio, from their corresponding solution which can be used for different industrial applications. Enormous effort has been put in to understand and optimize the morphology of electrospun fibers by controlling the processing parameters like viscosity, surface tension, concentration of the solution, electric field and flow rate. There has been a significant progress on the fabrication of electrospun fibers and the effect of various parameters on fibers morphology [18–23].

Electrospinning method involves the following steps: (1) Preparation of a sol with suitable inorganic precursor and polymer content, and achieving the right rheology for electrospinning. (2) Spinning of the solution to obtain fibers of polymer/inorganic composite. (3) Cal-cinations of the composite fibers to obtain final oxide fibers. It is important, however, to control all of the above three stages in order to obtain high quality fibers with the desired final properties. CuO nanofibers are important materials for their use in various industrial application.

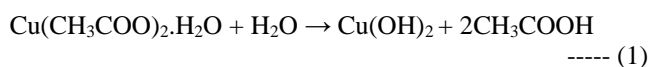
Not many investigations have been reported on the reasons behind defect formation in the fibers and breakage of fibers during thermal treatment; methods to control the formation of defects have also not received much attention. The main aim of this study is to investigate the effect of heat flow rate and inorganic precursor content/concentration on CuO-PVA fiber morphology and the possible mechanism behind such structural changes in fibers. In this communication, we present a study of the structural & microstructural properties of CuO nanofibers.

Table 1. Optimized parameters of the CuO nanofibers.

Electrospinning Parameters	Optimized Values
Applied electric field	1.4kV/cm
Distance between electrodes	14cm
Size of the needle opening	25G
Conductivity of the sol	15.6 m S/cm
Temperature of the sol	303K
Viscosity of the sol	1.03 Pa.s
Calcination temperature	823K
Time of the calcining	5hr
Average diameter of the fiber after calcining	200nm

Experimental

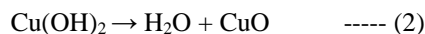
Copper acetate (99%), zinc acetate(99%), polyvinyl alcohol PVA (Mw = 80 – 124 kD) and 100% pure acetic acid were purchased from Aldrich and used as received without any further purification. 0.5g of the copper acetate (Cu(CH₃COO)₂·H₂O) was dissolved in 4.5ml of 10wt% aqueous PVA solution. This solution was then stirred for 24h at room temperature for the formation of pale blue colored copper hydroxide. Eq. (1) represents the chemical reaction depicting the hydrolysis of the employed precursor to the formation of Cu(OH)₂. Later, as-prepared solution was introduced in 10ml syringe with a hypodermic needle (dia. 2 mm) in a controlled electrospinning setup.



The flow rate and applied electric field was varied to obtain the optimal conditions for the electrospun fibers. The obtained optimal condition was as follows: flow rate of 0.2ml/h and the applied electric field of 1.25kV/cm. High electric field strength (1.4kV/cm) was employed to enable

for the high stretch rates of the electrospun jet. The distance between the needle tip and the collector against the applied electric field was set as 14cm. The longer distance between the needle tip and the collector aided the stretching of the jet due to the increase in the distance covered by the spiralling electrospun jet before being deposited on the collector. **Table 1** shows the optimized parameters for the preparation of CuO nanofibers.

The fiber mesh obtained was then annealed to obtain CuO nanofibers. Annealing of the electrospun fibers at 550–650 °C for 4-5h at different heat flow rates caused the elimination of water molecules from the copper hydroxide and resulted in the formation of copper oxide (CuO) as given in Eq (2). The heating and cooling rates employed were kept at 1, 2 and 5 °C/min, respectively,



The fine calcined powders were used to characterize the structural and microstructural properties of the compound. The X-ray diffraction pattern of the compounds were recorded at room temperature using X-ray powder diffractometer with CuK α ($\alpha = 1.5418\text{\AA}$) radiation (Rigaku Miniflex, Japan) in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 70^\circ$) at a scanning rate of 2°min^{-1} . The morphology of the electrospun nanofibers was observed using field emission scanning electron microscopy (FE-SEM, JOEL JSM-6340F; Japan) with an EDAX attachment. Spectroscopic characterization has been investigated by a Fourier-transform infrared (FT-IR) spectrophotometer supplied by Perkin Elmer, USA.

Results and discussion

Fig 1(A) shows the characteristic diffraction peaks of PVA and Copper acetate composite (as spun). **Fig 1(B)** gives the XRD curves for calcined fiber samples. These x-ray diffraction patterns indicate the formation of monoclinic structure of CuO. After calcining at 550 and 650 °C, the semicrystalline peak for PVA around $2\theta = 20^\circ$ corresponding to (101) plane disappeared. XRD spectra of the fibers after calcinations at 550°C and 650°C showed peaks at $32.3^\circ(110)$, $35.4^\circ(002)$, $38.5^\circ(111)$, $48.5^\circ(-202)$, $53.1^\circ(020)$, $57.9^\circ(202)$, $61.1^\circ(-113)$ and $67.5^\circ(220)$ corresponding to CuO and they agreed very well with the literature [24]. The XRD pattern corresponds to monoclinic copper oxide phases which are in very good agreement with reported values in the literature JCPDS – 5 – 0661. No characteristic peaks of impurity and intermediate products were observed.

Fig. 2, shows the EDAX spectrum of the calcined CuO nanofibers at 550° C. It confirms the presence of the elements in CuO. From the EDAX measurements, it was obtained that Cu and O are present in the weight percentages of 92.33 and 7.67 respectively.

Fig. (3) shows the SEM micrographs of the composite nanofibers for various PVA-polymer concentrations (6, 8, 10 and 12wt%). The formation of fibers could be conveniently controlled by optimizing the polymer concentration. At low concentrations, formation of defects such as beads along the fibers were observed (**Fig. 3a**) which is due to the capillary breakup of the spinning jet

because of surface tension [25]. As the concentration of the polymer in the solution increases (Fig. 3A-3D), the number of defects was found to decrease, resulting in the formation of uniform fibers with increase in diameters.

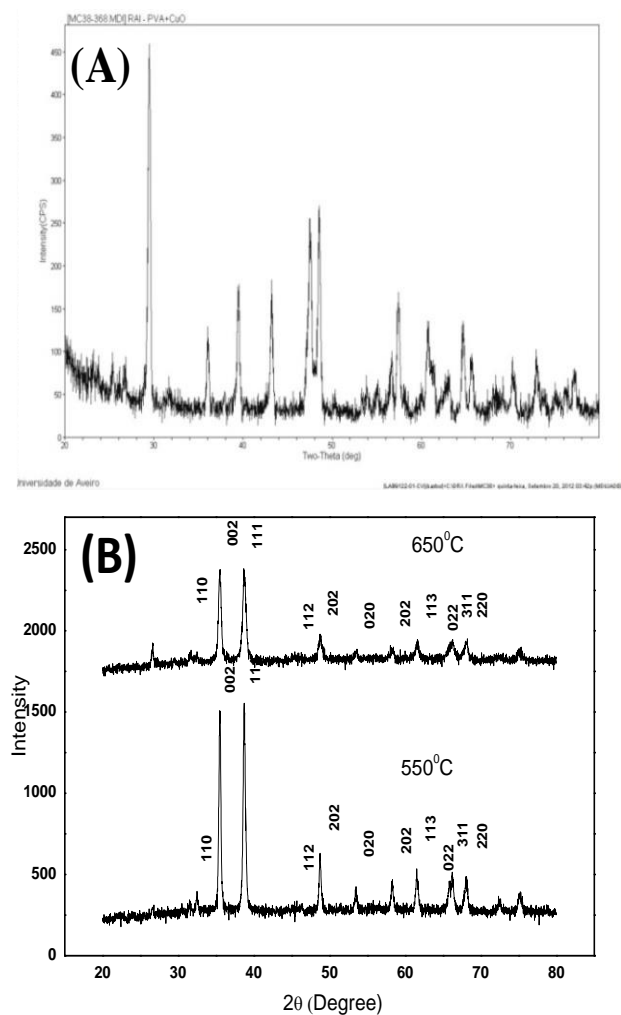


Fig. 1. (A) XRD patterns of PVA/copper acetate composite fibers (as spun), (b) XRD patterns of PVA/copper acetate composite fibers calcined at 550 & 650 °C.

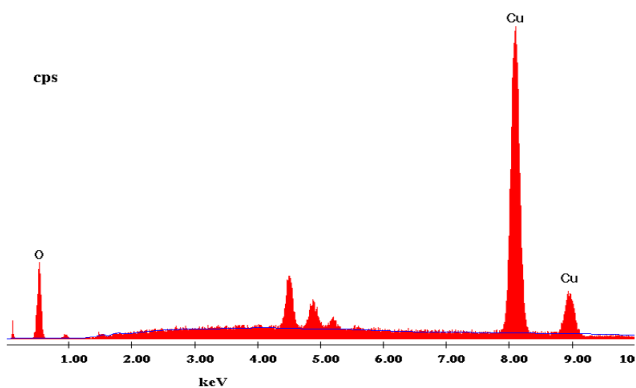


Fig. 2. EDAX spectrum of the calcined CuO nanofibers.

This suppression of defects during the fiber formation can perhaps be understood as follows: Increasing concentration of solution helps to raise the viscoelastic forces which might have resulted in reducing the influence

forces due to surface tension. The result obtained is similar to those observed earlier in the case of polystyrene [26]. The obtained results illustrate that the morphology of the composite fibers were optimized with minimal defects when the concentration of the gel reached 12 wt%. It can be seen from the SEM images that a random mesh of nanofibers was obtained. This randomness of the fiber mesh obtained was the direct consequence of the bending instability associated with the electrospun jet [27].

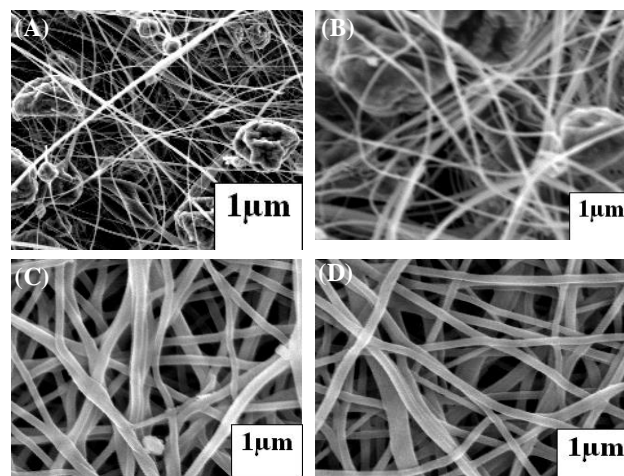


Fig. 3. SEM photograph for PVA/copper acetate composite fibers for various concentrations (A) 6, (B) 8, (C) 10, (D) 12wt%.

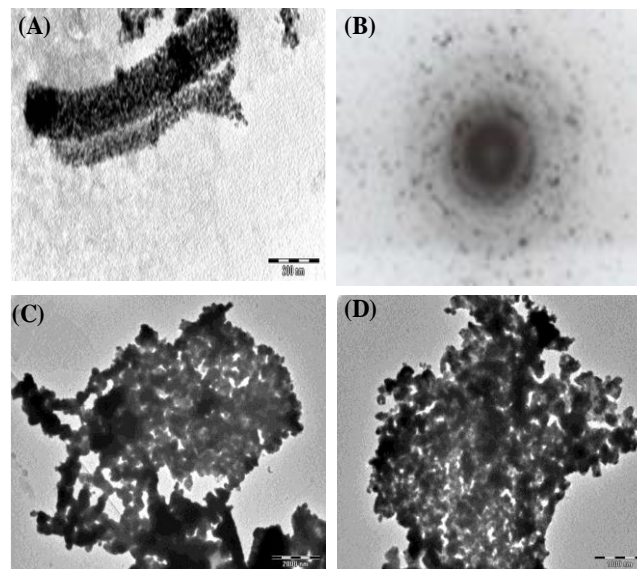


Fig. 4. (A) TEM photographs for PVA/copper acetate composite fibers at heating rate 1⁰/min., (B) SAED pattern PVA/copper acetate composite fibers at heating rate 1⁰/min., TEM photographs for PVA/copper acetate composite fibers at heating rate (C) 2⁰/min. and (D) 5⁰/min.

Internal crystal structure of the CuO nanofibers sintered at 550°C at a heating rate of 1⁰/min, 2⁰/min & 5⁰/min were studied by transmission electron microscopy (TEM) and are presented in Fig. 4 (A-D). It is evident from the TEM image that the continuous fibers comprise of nanosized CuO particulates. From the TEM images, the crystal size of CuO particles was found to vary from 5 to 10 nm, whereas the grains were found to be almost in uniform shape. CuO nanofibers sintered at 550°C at a heating > 1⁰/min led to the

breakage of the nanofiber into nano particles (Fig. 4C & D). The reason why different morphologies were obtained with different heat flow rates during annealing can be understood as follows. At the initial stage of heat treatment, the polymer molecules in the composite fibers acts as a kind of template around which CuO nanoparticles are formed and held together. As the calcination temperature increases, the polymer molecules escaped along with the other residuals leaving behind CuO nanoparticles which tend to agglomerate due to Vander Waals forces and crystallize. The selected area electron diffraction (SAED) pattern of CuO nanofibers displays several concentric diffraction rings and some regular diffraction high-lighted spots on the rings (Fig. 4B), indicating the well-defined crystalline nature of an assembly of nanofibers which accords well with XRD analysis.

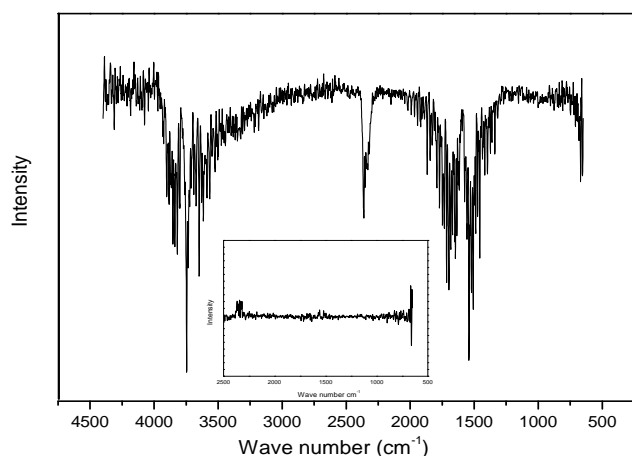


Fig. 5. FTIR results for PVA/copper acetate composite fibers (as spun), inset FTIR Spectra for copper oxide fibers calcined at 550 °C.

Fig. 5 shows the characteristic IR bands PVA and CuO recorded by FTIR spectrophotometer. All major peaks related to hydroxyl and acetate groups were observed. The large band observed between 4000 cm^{-1} and 3500 cm^{-1} is linked to the stretching O-H from the inter molecular and intra molecular hydrogen bands [28-30]. The vibration band observed between 2800 cm^{-1} and 2200 cm^{-1} refers to the stretching C-H from the alkyl groups and the peaks between 1700 cm^{-1} and 1680 cm^{-1} are due to the stretching C=O and C-O from acetate groups remaining from PVA. Fig (inset) shows the IR bands which results for the PVA/Copper acetate composite fiber calcined at 550°C for 5 hr. A peak around 570 cm^{-1} assigned to $\nu_{\text{Cu-O}}$ of copper oxide [31] appeared, indicating that the fiber obtained at this temperature has pure inorganic CuO species.

Conclusion

Defect free CuO nanofibers were synthesized through electrospinning technique. Phase formation and morphological features were analyzed by X-ray diffraction, TEM and SEM, respectively. It was found that the morphology of the composite and annealed nanofibers could be influenced by the concentration of the polymer content and heat flow rate during thermal treatment respectively. A lower concentration favors the formation of defects along the fiber and the number of defects reduces

when the concentration is increased. The reasons for the formation of defects and their reduction, and the observed structural changes of CuO nanofibers during heat treatment are also discussed. This is the first study of its kind carried out to obtain Copper oxide nanofibers without defects. These defect-free, CuO nanofibers with very few breakages can be exploited to fabricate gas sensing devices.

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