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Synthesis of ultra-fine α-Al_2O_3 fibers via electrospinning method

A. Mahapatra, B.G. Mishra, G. Hota *

Department of Chemistry, NIT Rourkela, Orissa 769008, India

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Abstract

Ultra-fine Al_2O_3 fibers were synthesized via electrospinning technique using PVP/ethanol polymer solution and aluminium acetate sol followed by calcinations at higher temperature. The formation, crystalline phase, surface morphology, fibers diameter and surface area of alumina ultra-fine fibers were characterized using FT-IR, TGA/DTA, XRD, SEM, TEM and BET analytical techniques. The results show that pure and crystalline α-Al_2O_3 ultra-fine fibers were formed with fiber diameter in the range of 100–500 nm and BET surface area of the fibers were found to be 40 m^2/g.

Keywords: Alumina; Ultra-fine fibers; Electrospinning

1. Introduction

One-dimensional nanostructure such as nanorods, nanotubes, nanowires, and nanofibers have attracted much interest over the past decade as they can address the needs of a wide range of advanced applications [1]. The nano-sized fiber structures are unique as compared to bulk fibers due to their high surface to volume ratio, fiber interconnectivity, micro scale interstitial space and also high porosity. These properties attract a lot of attention of present research on ceramic nanostructure, which also improves the performance for many modern applications [2]. Alumina (Al_2O_3) is one of the most excellent ceramic oxides [3] and has been studies extensively over a long period of time because of its application potential as adsorbents, catalysts and catalyst support [4–6], and reinforcements for composite materials. Alumina is also used for adsorption/chemisorptions of heavy toxic metal ions such as arsenic or arsenate. The adsorption depends on exposed surface area; therefore, nanofibers with high surface area produced by different synthetic methods might be ideal for this application. Several methods have been adopted for the synthesis of nanosized alumina materials [7] which includes mechanical milling, sol–gel method [8], hydrolysis and precipitation, hydrothermal method [9], combustion synthesis [10], and electrospinning method [11,12]. Among them, electrospinning method, a non-equilibrium electro-hydrodynamic process, is a platform technology for the production of a larger number of polymeric nanofiber materials. Recently, electrospinning is used as a novel method for preparing various inorganic and ceramic fibers with a diameter ranging from several micrometers to tens of nanometers [13–15]. The morphology of the fibers depends on the process parameters; including solution concentration, applied electric field strength, deposition distance and deposition time [16,17]. Arising out of their specific surface area and highly porous structure electrospun fibers can be used in a number of applications including membranes, tissue engineering and other biomedical applications [18]. Electrospun nanofibers have diameters 5–10 times smaller than that of melt blown fibers. Most of the recent work on electrospinning are focused to understand deeper the fundamental aspects of the process in order to gain control of nanofiber morphology, structure, surface functionality, and strategies for assembling them or on determining appropriate conditions for electrospinning of various polymers and biopolymers [19,20].

Recently, Li et al. [21] have reported a brief overview of recent progress in the preparation of ceramic nanofibers using electrospinning method. They have highlighted several unique features associated with electrospinning technique and illustrated the potential of electrospinning in ceramic nanofibers processing and applications. Similarly, the recent advances in nanostructured ceramics by electrospinning

* Corresponding author. Tel.: +91 661 2462655; fax: +91661-2462651.
E-mail addresses: garud31@yahoo.com, garud@nitrkl.ac.in (G. Hota).

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methods have been reviewed by Ramaseshan et al. [22]. In this review they have reported the electrospun mediated synthesis of various ceramics nanofibers in details along with their many useful applications. The fabrication of transparent alumina nanofiber by electrospinning method has been reported by Azad [23]. This author has used aluminium 2,4-pentanedionate and PVP polymer solution to prepare inorganic–organic composite fibers which upon sintering at high temperature yield high-purity and crystalline α-alumina nanofibers. Dia et al. [24] have prepared ultra-fine alumina-borate oxide fiber via sol–gel mediated electrospinning method. The average diameter of the alumina-borate fiber was found to be 550 nm and upon crystallization, the surface of the fibers became rough due to the development of the grain boundaries. The authors have also reported that the alumina-borate phase was unstable and was formed at calcination temperature 1000–1200 °C. However, a new stable crystalline phase of α-alumina was formed at 1400 °C. More recently, Yang et al. [25] synthesized composite Cr_2O_3/Al_2O_3 nanofibers with the fiber diameter in the range of 50–100 nm, after calcination of PVA/chromium nitrate/aluminium nitrate composite fibers at certain temperature. They have adopted a modified sol–gel method followed by electrospinning method for the fabrication of nanosized Cr_2O_3/Al_2O_3 composite fibers. Panda and Ramakrishna [26] has successfully prepared alumina nanofibers by electrospinning method using different precursors from a combination of PVA and PEO polymer precursor, and alumina nitrate as alumina precursor. Maneeratana and Sigmund have reported direct synthesis of continuous hollow alumina fibers via sol–gel mediated electrospinning method using aluminium alkoxide precursors [27]. Very recently, Kang et al. have synthesized alumina nanofibers with average diameter 100–800 nm by electrospinning $AlCl_3$/PVP solution followed by calcinations at high temperature [28].

In this study, we have reported the synthesis of α-Al_2O_3 ultra-fine fibers using organometallic aluminium acetate (AlAc) sol precursor and PVP/ethanol polymer solution by electrospinning method. The commercially available aluminium acetate is found to be either boric acid stabilized form or basic acetate form, which is sparingly soluble in water and alcohol. Therefore, direct synthesis of alumina fiber by electrospinning method using commercially available acetate precursors is a tedious task. Hence, we have prepared aluminium acetate aqueous sol, by co-precipitation method and have used the prepared sol as a precursor for alumina fiber synthesis.

2. Experimental procedure

2.1. Materials

The polymer poly vinyl pyrrolidone (PVP; Mn = 1,300,000) was obtained from Sigma–Aldrich (USA). Ethanol was obtained from Merck, Germany, aluminium sulphate hydrated ($Al_2(SO_4)_3{\cdot}16H_2O$; GR) was purchased from Merck India. Barium acetate ($Ba(Ac)_2$, AR grade) was supplied by S.D. Fine Chem Ltd., India. Acetic acid (AA) was purchased from Rankem, India. All the chemicals were used without further purifications. Double distilled water and 25 ml neat and cleaned glass bottles were used throughout the experiments.

2.2. Fabrication of alumina nanofibers

The PVP solution (10 wt%) was prepared by dissolving PVP polymer powder in absolute ethanol under constant and vigorous stirring. Aluminium acetate was used as aluminium precursors and was prepared by mixing saturated solution of barium acetate and aluminium sulphate. The aluminium precursor sol was mixed with the previously prepared PVP/ethanol solution followed by the addition of 1–2 drops of acetic acid. The polymer to aluminium precursor's weight ratio was maintained at 3:1. The resulting PVP–aluminium acetate solution was loaded into a 3 ml plastic syringe fitted with a metallic needle. The polymer solution was pushed to the needle tip using the syringe pump and the feed rate was kept at 1.0 ml/h. The positive terminal of a variable high voltage (Glassman, Japan) power supply (14 kV) was applied to the metallic needle, whereas the negative terminal was connected to the grounded collector which was covered with the aluminium foil served as counter electrode. The distance between the needle tip and collector was maintained 10 cm. All the experiments were conducted at room temperature with a relatively low humidity (45–50%) condition.

After electrospinning, the as-spun PVP/aluminium acetate composite fibers were calcined in air for 2 h at higher temperatures (1000 °C) at a heating rate of 20 °C/min in order to obtain pure Al_2O_3 nanofibers.

2.3. Characterization

The powder X-ray diffraction patterns were recorded on a PAN analytical diffractometer (PAN-PW1830) using Ni filtered Cu Kα (λ = 1.541 Å) radiation. The surface morphology of Al_2O_3 ultra-fine fibers was characterized using Karl Ziess scanning electron microscope and were operated at 10 and 20 kV. The sample powders were deposited on a carbon tape before mounting on a sample holder for SEM analysis. The IR spectra of the samples were recorded using a PerkinElmer infrared spectrophotometer (Spectrum RX-1) with a resolution of 4 cm^{-1}, in the range of 400–4000 cm^{-1}. The BET surface area of the fibers was measured using AUTOSORB-1 equipment. The samples were degassed at 120 °C for 2 h prior to the surface area measurement.

Thermal decomposition of alumina precursor membrane was studied with thermogravimetric and differential thermal analysis (TG–DTA) using SHIMADZU (TA-60 WS) model. The data were obtained by heating the sample at 20 °C/min in air atmosphere. A Philips 200 TEM equipment was used to characterize the Al_2O_3 nanofibers and was operated at 200 kV. The Al_2O_3 nano-fibers were dispersed in ethanol and then a drop of the above dispersion was taken on a carbon coated copper grid (300 meshes) for TEM imaging.

3. Results and discussion

The preparation of α-Al_2O_3 using electrospinning method has been reported earlier. In these reports, α-Al_2O_3 has been prepared using organometallic precursors such as aluminium acetate stabilized boric acid, aluminium acetyl acetonate and inorganic precursors such as aluminium nitrate and aluminium chloride [17,23,24,26,28]. However, the use of above precursors for the preparation of alumina in electrospinning method has many disadvantages. For example the formation of aluminium borate ($Al_4B_2O_9$) fibers was observed when aluminium acetate stabilized boric acid was used as precursor. In some cases aluminium acetyl acetonate is used as precursor which is highly carcinogenic in nature. Similarly, in case of inorganic salt precursors, due to their hygroscopic nature and highly charge species; the formation of homogeneous and large scale production of fibers is extremely difficult. Hence, in order to overcome the above difficulties and for large scale production of alumina nanofibers, we have reported here the use of aluminium acetate aqueous sol as aluminium precursors and PVP as polymer.

In this work, PVP/aluminium precursor's composite fibers were prepared by electrospinning of aluminium acetate sol mixed PVP–ethanol solution. Upon calcinations of above composite fibers in air, pure Al_2O_3 ultra-fine fibers were obtained. The saturated solution of aluminium acetate was freshly prepared using aluminium sulphate and barium acetate salts. The chemical reactions occur in this process are presented below. (*Note*: Ac → CH_3COO^-)

$$Al_2(SO_4)_3 + 3Ba(Ac)_2 \rightarrow 2Al(Ac)_3 + 3Ba(SO_4)_2 \downarrow$$

$$Al(Ac)_3 \xrightarrow{\Delta} Al_2O_3$$

The barium sulphate precipitate obtained was filtered out and the filtrate containing the aluminium acetate aqueous solution was mixed with PVP–ethanol solution to prepare PVP–aluminium acetate composite fibers. We have maintained the PVP to alumina precursor weight ratio 3:1 in this case. In order to obtain the pure alumina nanofibers, the PVP/alumina precursor's composite fibers were calcined in air at two different temperatures, i.e., 500 °C and 1000 °C for 2 h.

XRD analysis has been used to determine the structure and purity of the electrospun alumina nanofibers. Fig. 1 shows the XRD curve for the calcined alumina fibers that are prepared using aluminium acetate solution. Diffraction peaks corresponding to single phase α-Al_2O_3 have been found for the sample sintered at 1000 °C for 2 h. The XRD patterns indicate that pure and highly crystalline α-Al_2O_3 is formed. No other peaks associated with the presence of impurities are observed. All the observed diffraction peaks be indexed to α-Al_2O_3 structure and are matching well with the literature value (JCPDS Card No.: 42-1468).

Fig. 2 shows the FT-IR spectra of PVP–aluminium acetate as spun composite fibers and alumina fibers obtained after calcination of composite fibers at 1000 °C. The spectrum of the as-spun ultra-fine fiber (Fig. 2a) shows the characteristic peaks at 1283, 1433 and 1647 cm^{-1}, corresponding to the stretching and bending vibrations of PVP [12]. The broad band observed around 3400 cm^{-1} indicates the O–H stretching frequency of acetate precursors. When the fibers were calcined at 1000 °C, the characteristic peaks of PVP and O–H stretching band disappeared as shown in Fig. 2b. This is because of removal of polymer and decomposition of acetate precursors at higher calcination temperature. However, appearance of new peaks in the range of 565–880 cm^{-1} may be attributed to the presence of alumina [3], which is also supported by XRD results.

Thermal behavior of the PVP–aluminium acetate as-spun ultra-fine fiber membrane was studied by TGA–DTA analysis in air up to 1000 °C at a heating rate of 10 °C/min. Fig. 3 represents the TGA–DTA curve of PVP–aluminium acetate as-spun ultra-fine fibers. It could be observed from the figure that the fibers have four major weight losses, represented by four peaks in DTA curve. An endothermic peak is observed in DTA

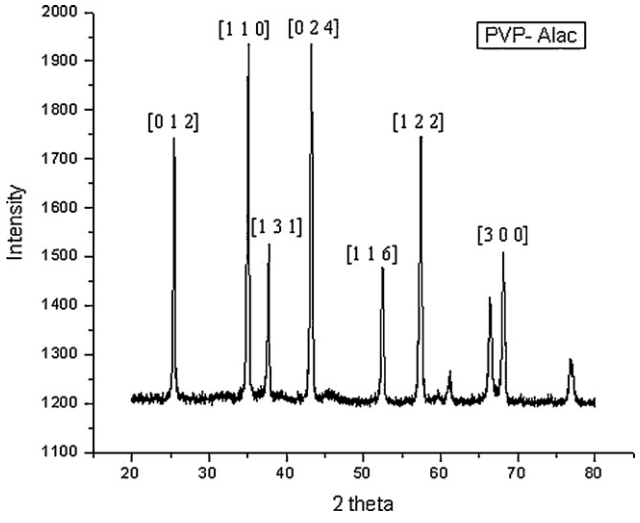

Fig. 1. XRD pattern of α-Al_2O_3 prepared by electrospun (a) PVP–aluminium acetate nanofiber; sintered at 1000 °C.

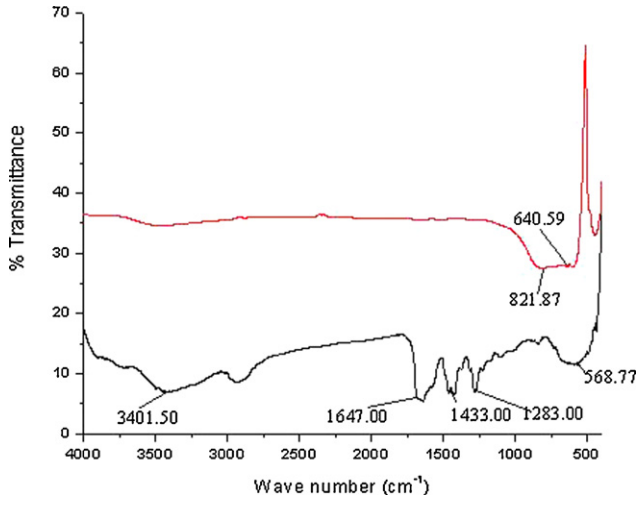

Fig. 2. FTIR of (a) as spun composite fiber and (b) fiber sintered at 1000 °C.

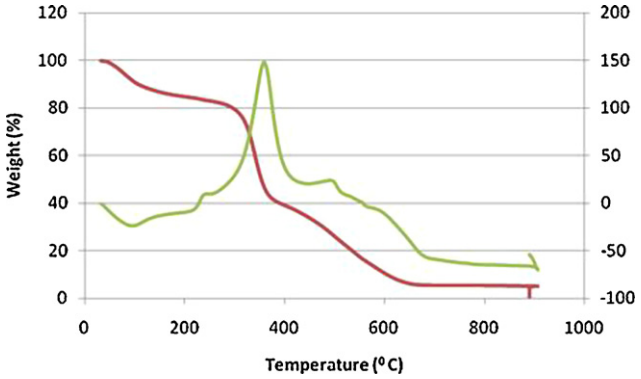

Fig. 3. TGA/DTA curve of the PVP–aluminium acetate as spun nanofiber membrane.

curve with maxima at 98 °C, and three exothermic peaks are observed between 260 °C and 500 °C. It is believed that the first weight loss of 9 wt% was because of evaporation of residual moisture and ethanol molecules in the fibers. The second weight loss starting at 260 °C, with a weight loss of 11% resulted from decomposition and burning of PVP polymer fibers. The third and fourth weight loss, observed between 350 and 650 °C, with a loss of 73 wt%, corresponds to complete combustion of PVP polymers and organometallic aluminium acetate. When the temperature exceeds 650 °C, the TGA graph is nearly horizontal, which indicates the complete burning of polymer, and organic matters resulting the formation of pure aluminium oxide fibers.

The SEM micrographs of as-spun PVP–aluminium acetate composite fibers and fibers sintered at 1000 °C have been shown in Fig. 4. It is observed from the figures that ultra-fine cylindrical composite fibers having diameter in the range of 200–600 nm can be successfully prepared using aluminium acetate as precursors (Fig. 4a). Pure Al_2O_3 ultra-fine fibers with smooth surface morphology have been obtained by sintering the above composite fibers as shown in Fig. 4b. It is observed from the figure that the fiber like structure in the as-spun composite membrane is fully retained in the sintered sample, with considerable decrease in fiber diameter. The SEM elemental detection X-ray analysis (SEM-EDAX) clearly suggest that the presence of aluminium and oxygen elements (Fig. 4c). This result indicates the formation of pure alumina fibers.

In order to obtain more information about the formation of individual Al_2O_3 ultra-fine fibers, we have carried out the TEM analysis. Fig. 5a shows the TEM micrograph of Al_2O_3 ultra-fine fibers after calcination at 1000 °C for 2 h at a heating rate of 20 °C/min. TEM micrograph (Fig. 5a) clearly indicates the formation of nano-sized fibers. Furthermore, it is observed from the TEM studies that the diameters of nanofibers were not uniform, instead a broad range of fibers were formed (100–500 nm), which is also consistent with the fibers diameter observation by the magnified SEM micrographs. Fig. 5b shows the selected area electron diffraction pattern of alumina nanofibers. The corresponding diffraction rings and bright spot on the electron diffraction pattern suggest that the alumina fibers obtained are highly crystalline in nature, which is also consistent with XRD results.

The surface area of the alumina fibers are found to be 40 m^2/g and are nonporous in nature as observed by BET studies.

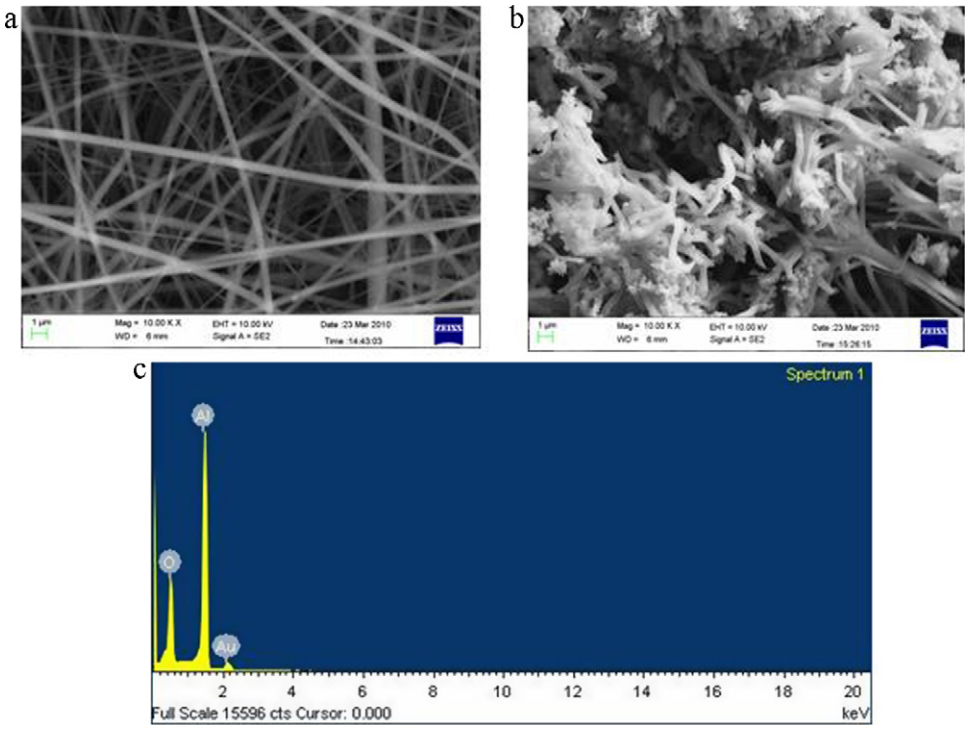

Fig. 4. SEM images of as spun nanofiber of (a) PVP–aluminium acetate precursor, (b) sintered at 1000 °C and (c) SEM-EDAX of sintered alumina.

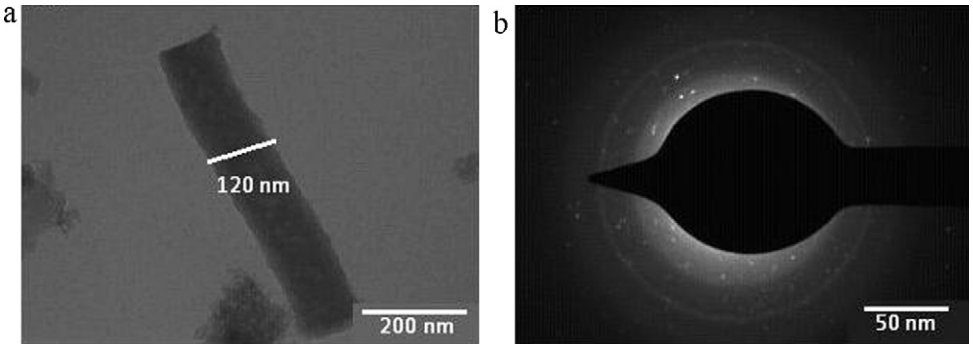

Fig. 5. TEM analysis of aluminium acetate precursor (a) after sintering at 1000 °C and (b) electron diffraction pattern.

4. Conclusion

α-Al_2O_3 ultra-fine fibers were successfully prepared by electrospinning of aluminium acetate sol and PVP polymer solution. The diameters of the fibers are found to be in the range of 100–500 nm by TEM study. XRD analysis of the calcined fiber at 1000 °C confirms the formation of pure α-alumina phase. SEM images show that the as-spun fiber morphology is smooth and formation of continuous fiber mats. However fiber like structure in the as-spun composite membrane is fully retained in the sintered sample, with considerable decrease in fiber diameter. The elemental detection X-ray analysis of sintered fibers suggests the presence of Al and O elements, indicates the formation of alumina nanofibers.

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