

Electrospinning Mediated Synthesis of α Alumina using different Organometallic precursors

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Abstract:

Ultra-fine α -alumina fibers were prepared via electrospinning technique using PVP polymer solution and aluminum isopropoxide / aluminium acetate as alumina precursors followed by calcinations at higher temperature. The formation, crystalline phase, surface morphology, fibers diameter and surface area of alumina nanofibers were characterized using FT-IR, XRD, SEM, TEM and BET analytical techniques. Effect of alumina precursor's loading on the formation of nanofibers and annealing temperature on the crystalline nature of alumina nanofibers has been discussed here. The results show crystalline phase and fiber morphology largely influenced by calcinations temperature.

Key Words: Alumina, nanofibers, electrospinning.

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1. INTRODUCTION

One dimensional nanostructure such as nanorods, nanotubes, nanowires, nanofibers etc have attracted much interest over the past decade as they can address the needs of a wide range of advanced applications [1]. Among them, nano-sized fibrous structures are unique as compared to normal fibrous structures is due to their high surface to volume ratio, fiber interconnectivity, micro scale interstitial space and also high porosity. Alumina (Al_2O_3) is one of the most excellent oxide precursors and has been studied extensively over a long period of time because of their potential for broad applications in adsorbents, catalysts and catalyst support [2-4], and reinforcements for composite materials. Alumina is also used for adsorption /chemisorptions of heavy toxic metal ions such as arsenic or arsenate. Several methods have been adopted for the synthesis of nanosized alumina [5] materials which includes mechanical milling, sol-gel method [6], hydrolysis & precipitation, hydrothermal method [7], combustion synthesis [8], electrospinning method [9] etc. Among them, electrospinning, a non-equilibrium electrohydrodynamic process, is a platform technology for the production of a range of nanofibrous materials. Most of the recent work on electrospinning has focused either on trying 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 [10]. More recently, Yang et al. [11] synthesized composite $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ 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 fabrication of nanosized $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ composite fibers. Panda et al. [12] has successfully prepared alumina nanofibers by electrospinning method using different precursors from a combination of PVA and PEO polymer precursor, aluminum acetate and alumina nitrate as alumina precursor.

In this study, we have reported the synthesis of $\alpha\text{-Al}_2\text{O}_3$ nanofibers using different organometallic precursors such as aluminium acetate (AlAc) and aluminium isopropoxide (AIP) by electrospinning method. The effect of organometallic precursors and calcination temperature on the formation, morphology and crystallization of nanofibers has been discussed here.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The polymer poly vinyl pyrrolidone (PVP; $M_n = 1300\ 000$) was obtained from Sigma-Aldrich (USA). Aluminium Isopropoxide, (AIP; $C_9H_{21}O_3Al$) & Ethanol was obtained from Merck, Germany, Aluminium sulphate 16 hydrate (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 & 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 isopropoxide & aluminium acetate were used as aluminium precursors. The polymer to aluminium precursor's weight ratio was maintained at 3:1. The resulting PVP-aluminium isopropoxide or PVP-aluminium acetate solutions were 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 1.5 ml/hr. 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.

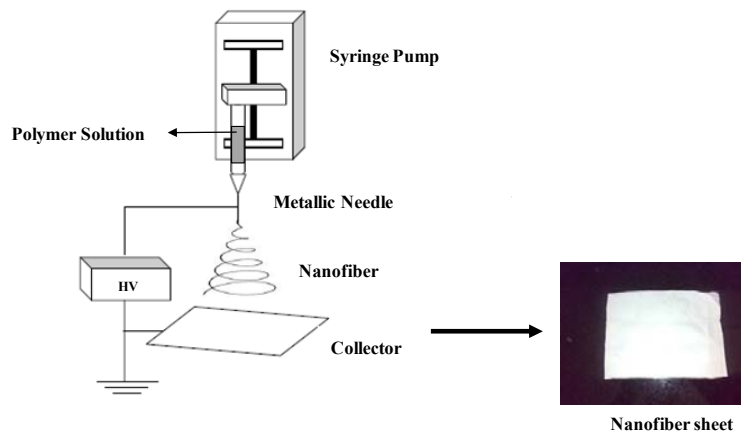


Figure 1: Schematic diagram of electrospinning setup

3. RESULTS AND DISCUSSION.

The preparation of α -Al₂O₃ using electrospinning method has been reported earlier. [13]

In this work, we have used aluminium acetate and aluminium iso-propoxide sol in PVP-ethanol solution to prepare PVP/aluminium precursors composite fibers. Upon calcinations of above composite fibers in air, pure Al₂O₃ ultra-fine fibers were obtained. XRD analysis has been used to determine the structure and purity of the electrospun alumina nanofibers. Figure 2 shows the XRD curve for the calcined alumina fibers that are prepared using aluminum isopropoxide (Fig. 2) as aluminium precursors respectively. . The XRD patterns of Fig 2a indicate that pure & highly crystalline α -Al₂O₃ is formed. No other peaks associated with the presence of impurities are observed. All the observed diffraction peaks be indexed to α - Al₂O₃ structure and are matching well with the literature value (JCPDS Card No: 42-1468). Figure 3 shows the FT-IR spectra of PVP-aluminium acetate as spun composite fibers and alumina fibers obtained after calcination of composite fibers at 1000⁰ C. The spectrum of the as spun nanofiber (Fig 3b) shows the characteristic peaks at 1292, 1423 and 1660 cm⁻¹, corresponding to the stretching and bending vibrations of PVP [17]. The broad band observed around 3400 cm⁻¹ indicates the O-H stretching frequency of acetate precursors. When the fibers were calcined at 1000⁰ C, the characteristic peaks of PVP and O-H stretching band disappeared as shown in Fig 3c. The FeSEM micrographs of the PVP-Aluminium isopropoxide as spun composite nanofibers and fibers calcined at 1000⁰C are shown in Fig. 4. It is observed from the figure that the fibrillar structure in the as spun composite is fully retained in the sintered sample, with considerable decrease in fiber diameter. The fibers obtained are appears to be porous structure and have rough surfaces morphology. It is observed from the figures that ultra-fine cylindrical fibers having diameter in the range of 200-500 nm can be successfully prepared using aluminium acetate as precursors. Pure alumina nanofibers with smooth surface morphology have been obtained by sintering the above composite fibers as shown in Figure 4. The SEM elemental detection X-ray analysis (SEM-EDAX) clearly suggest that the presence of aluminium and oxygen elements (Fig 4). This result indicates the formation of pure alumina nanofibers. The surface area of the alumina fibers are found to be 40 m²/gm and are nonporous in nature as observed by BET studies.

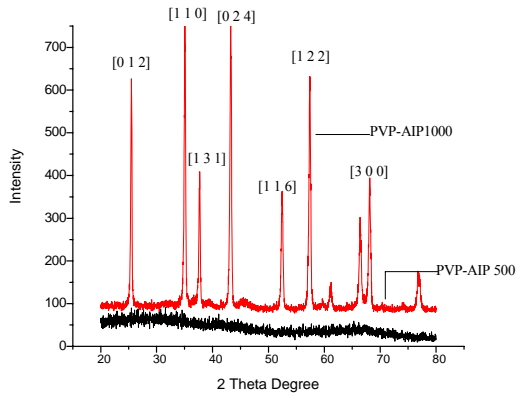


Figure 2: XRD pattern of α - Al_2O_3 prepared by electrospun PVP-AIP nanofiber sintered at 1000°C and 500°C .

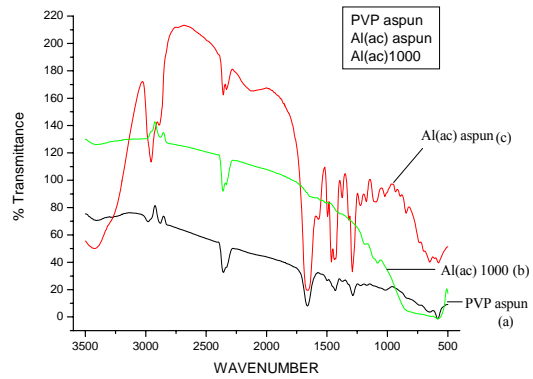


Figure 3: FTIR of (a) as spun PVP fibre (b) as spun composite fiber of Aluminium acetate and (c) fiber sintered at 1000°C

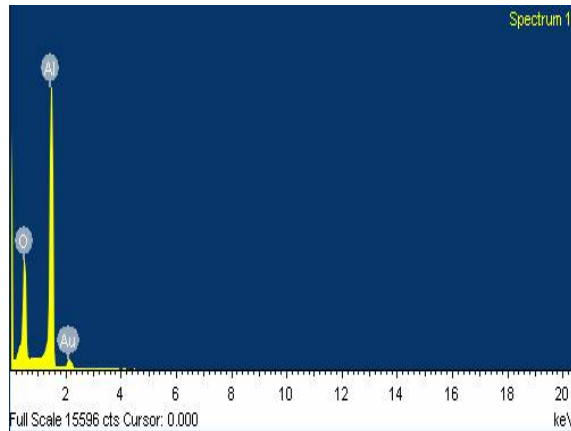
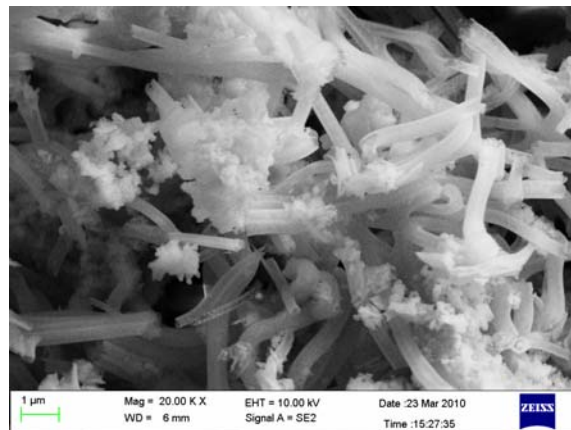
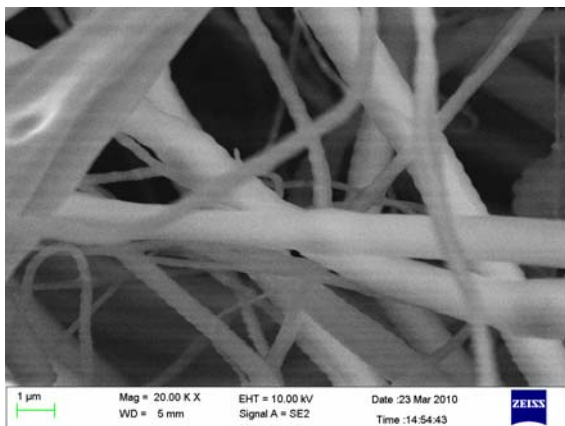


Figure 4: FeSEM images of as spun nanofiber of (a) PVP-Aluminum isopropoxide precursor & (b) sintered at 1000°C (d) SEM-EDAX of sintered alumina.

4. CONCLUSION:

α - Al₂O₃ nanofibers were successfully prepared by sol-gel processing & electrospinning method using aluminium isopropoxide and aluminium acetate as alumina precursors. XRD analysis of the calcined fiber at 1000⁰ C confirms the formation of pure alpha alumina phase. SEM images showed the as spun fibers morphology is smooth and formation of continuous fiber mats, whereas the fibers sintered at 1000⁰ C have rough surfaces and smaller diameter. The elemental detection x-ray analysis of sintered fibers suggests the presence of Al & O elements, indicates the formation of alumina nanofibers.

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