PREPARATION OF Al_2O_3 NANOFIBERS BY THERMAL CALCINATION WITH LOW TEMPERATURE PLASMA PRE-TREATMENT

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Abstract

Inorganic submicron fibers (ISF) are nowadays widely studied material. Usually, they are produced by 2-step process. First, the composite metal-organic fibers are produced from polymer matrix and metallic precursor, typically alkoxides or salts by standard spinning techniques. After this, prepared composite fibers are thermally calcinated to remove polymer and form ceramic fibers. In this study, we used low temperature plasma generated at atmospheric pressure using Diffuse Coplanar Surface Barrier Discharge (DCSBD) to eliminate organics from the composite fibers before thermal treatment to reduce the time required for thermal calcination of Al_2O_3 fibers. This plasma pre-treatment enables using significantly higher heating rates compared to standard calcination without damaging the fiber structure.

Keywords: Plasma assisted calcination, inorganic fibers, DCSBD, alumina fibers

1. INTRODUCTION

In recent years, there is an ongoing research on the use of ISF for various applications, such as insulations, filters, photocatalysts, or biomedicinal applications [1-4]. Nowadays most of the ISF are produced by thermal calcination of electro-spun metal-organic fibers [5]. For Al_2O_3, thermal calcination is conducted at temperatures varying from 500 °C - 1200 °C, with heating rates usually up to 5 °C/min [6]. Time and temperature affect morphology and crystal phase of final product. While electrospinning is fast and relatively cheap method, calcination is much more energetically demanding and time consuming. With increased popularity of these materials, many researchers started to focus on developing alternative methods of production. In our work, we studied the possibility of base polymer removal from polyacrylonitrile/$Al(NO_3)_3{\cdot}9H_2O$ composite submicron fibers by low temperature plasma before thermal treatment. Low temperature plasma is chemically active environment with high amount of reactive oxygen (ROS) and nitrogen (RNS) species. We used plasma generated by Difuse Coplanar Surface Barrier Discharge (DCSBD) at atmospheric pressure in laboratory air. This type of plasma source was previously described in details in work [7,8]. We compared effects of power supplies with different frequency and input power for polyacrylonitrile (PAN) decomposition. In previous research, DCSBD plasma was successfully used in preparation of TiO_2 fibers [9].

2. EXPERIMENTAL SETUP

Polymer/precursor submicron fibers (SF) were prepared by needleless spinning method using *Nanospider™ (Elmarco, Czech Republic)* from solution of polyacrylonitrile (PAN, *Sigma-Aldrich, Slovakia*), N,N-dimethylformamide (DMF, *Acros Organic*, 99.8%), and aluminium nitrate nonahydrate $Al(NO_3)_3.9H_2O$ (*Centralchem, Slovakia*). SF samples used in this study were prepared by Institute of Materials Research, Slovak Academy of Sciences, Košice, SR. Low-temperature plasma was generated by DCSBD at atmospheric pressure in laboratory air. In our experiments, discharge was fed by 2 different AC power supplies with sinusoidal signal (*Lifetech, Czech Republic*). Source A supplied 400 W at frequency 14.6 kHz and voltage 10 kV (peak-to-peak), Source B supplied 600 W at 26.9 kHz and 20 kV (peak-to-peak). Samples were held by movable holder 0.5 mm above the surface of dielectric plate during the treatment.

3. DIAGNOSTIC METHODS

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to identify the changes in chemical bonds during treatment. Spectra were collected on *Bruker Vector 22 FT-IR* with *Pike MIRacle*^{TM} accessory, in the interval 4000 - 500 cm^{-1} averaging 20 scans with resolution of 2 cm^{-1}. Scanning electron microscopy (SEM) *Mira 3* (*TESCAN*) at acceleration voltage of 5 kV was used to observe morphological changes on the surface of fibers. Samples were coated with 30 nm layer of Au/Pd. Energy-dispersive X-ray spectroscopy (EDX) detector (*Oxford Instrument*, UK) was used to measure changes in chemical composition of samples. Spectra were obtained by averaging 3 scans in integral regime with magnification 1 kx at 13 kV acceleration voltage. Samples were coated with 20 nm Au/Pd layer. For identification of crystal phase we used X'Pert Pro MRD high resolution diffractometer (PANalytical B.V., Netherlands) with static X-ray source of characteristic Cu Kα radiation (45 kV, 40 mA, λ = 0.15418 nm). Measurements were realized in Brag-Brentano configuration or grazing incident small angle X-ray scattering (GIXRD) arrangement.

4. RESULTS

4.1. Effect of DCSBD plasma treatment

To measure the decomposition of PAN in dependence on exposure time, we treated the samples for up to 30 minutes in plasma generated with Source A in ambient air at atmospheric pressure. The O-H stretching and bending from hydrated precursor and absorbed water can be visible [10]. The stretching and deformation of C-H bonds is attributed to the presence of PAN and residues of dimethylformamide [10]. Characteristic vibration of CN and C-CN originating from PAN were detected [10]. Several peak between 1750 cm^{-1} - 1550 cm^{-1} are caused by O-N=O stretching of nitrate part of precursor and O-H bending of adsorbed water [11][12]. On the FTIR spectra (**Figure 1**), with increasing time we observed decrease of the peaks associated with PAN.

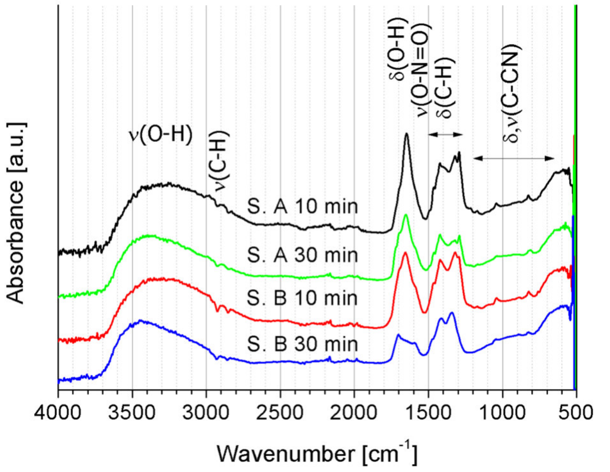

Figure 1 - FTIR spectra of ($Al(NO_3)_3$)/PAN SF after 10 and 30 minute plasma treatment with A and B source compared to untreated sample

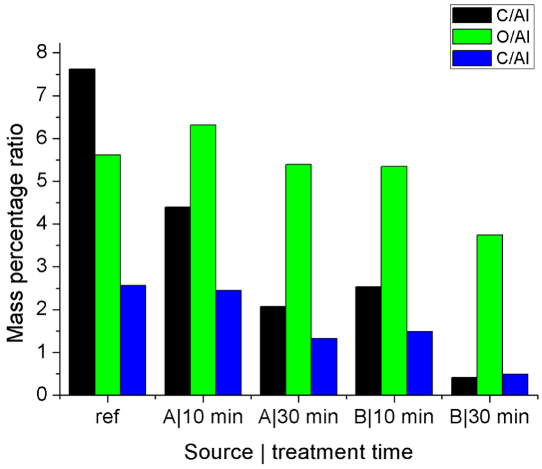

Figure 2 Mass percentage ratio of C, O and N in ($Al(NO_3)_3$)/PAN SF after 10 and 30 minute plasma treatment with A and B source compared to untreated sample

Chemical composition of the samples was measured by EDX. Aluminium does not create any gaseous products during plasma treatment and the mass in fibers remains constant. The mass percentage of aluminium was used as a reference to obtain relative change of mass of other elements. Relative mass of carbon, oxygen and nitrogen to aluminium is shown in **Figure 2**. During a short treatment, we can see decrease in carbon and slight increase in oxygen and nitrogen in samples, which might be caused by binding of ROS and RNS, but after longer treatments, we can see decreasing trend.

Comparison of the effects of plasma calcination with discharge fed by source A and B shows higher decrease of absorption peaks characteristic for PAN when using source B. Decrease in relative mass of carbon, oxygen and nitrogen was also higher with source B after the same treatment time. Comparing the ratio of relative mass decrease to supplied energy shows higher energy efficiency of source B compared to source A. None of these treatments resulted in morphological changes visible under SEM (**Figure 3**).

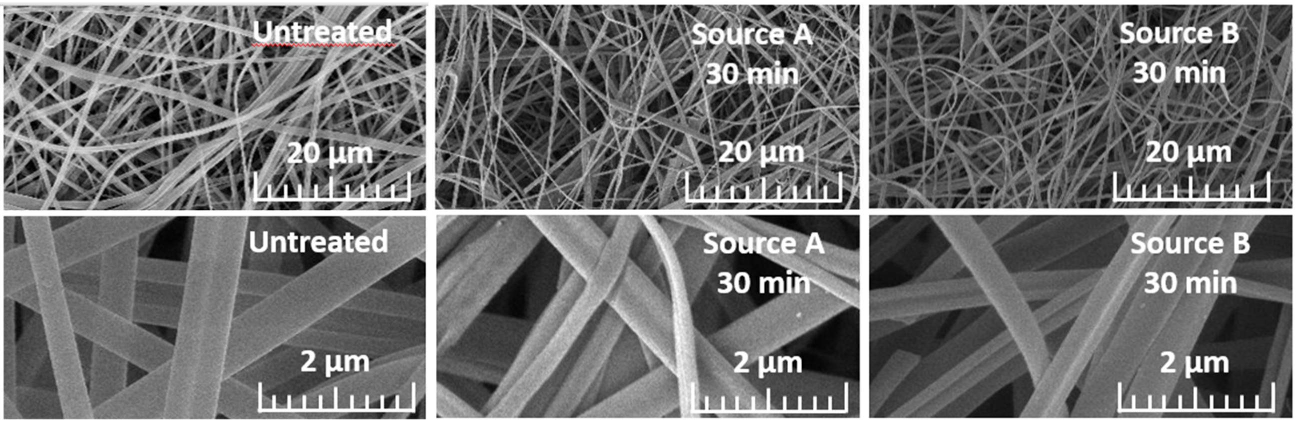

Figure 3 SEM images of $(Al(NO_3)_3)$/PAN SF 30 minute plasma treatment with A and B source compared to untreated sample

4.2. Thermal calcination of plasma pre-treated samples

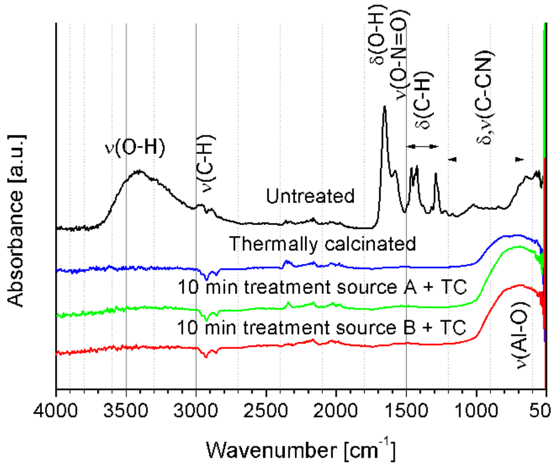

Figure 4 FTIR spectra of (Al(NO3)3)/PAN SF after 3 hours of thermal calcination

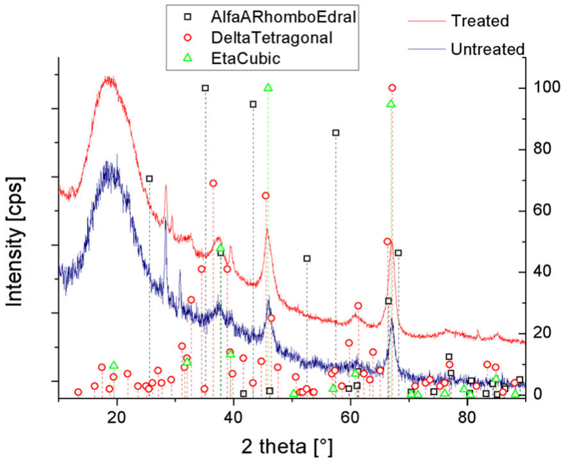

Figure 5 XRD spectra of SF with and without plasma pre-treatment after thermal calcination at 920 °C

For thermal treatment, we selected samples that were treated under the same conditions (10 min in plasma generated at atmospheric pressure in laboratory air) with different power sources. Samples were calcinated at

700°C for 3 hours with heating rate up to 50 °C/min. On FTIR spectra (**Figure 4**), weak absorption band can be seen in the 1700 cm^{-1} - 1400 cm^{-1}, which can be attributed to water molecules bonded to aluminium ions and adsorbed on the surface [13]. On treated samples, compared to untreated, absorbance is increased in 1000 cm^{-1} - 500 cm^{-1} interval, which corresponds to deformation of Al-O-H and stretching of Al-O bonds [14]. For X-ray diffraction (**Figure 5**), we used samples treated with plasma generated by source B for 30 minutes and calcinated at 920 °C for 3 hours. The temperature was chosen for reaching measurable crystal phase. At the same condition during annealing, samples treated by plasma before heating exhibit in XRD spectra higher and more sharp peaks attributed to δ- and η-alumina phase. On the SEM images, untreated SF are twisted and often broken as a result of rapid heating, which caused thermal stress. In comparison, treated samples appear to be straight and number of breaks is reduced, thanks to removal of part of the polymer before thermal calcination (**Figure 6**).

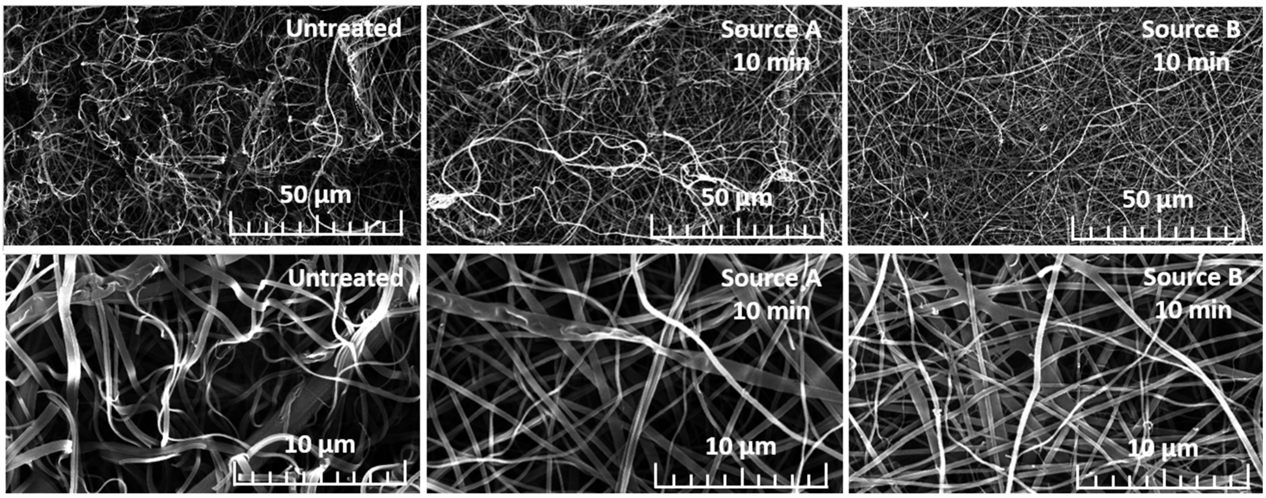

Figure 6 SEM images of (Al(NO3)3)/PAN SF after 3 hours of thermal calcination

5. CONCLUSION

The observed fast removal of base polymer by DCSBD plasma appears to be beneficial low-temperature approach for preparation of inorganic submicron fibers. PAN is one of the relatively resistant base polymers. We can reach significant removal at short exposure time during first 10 min of plasma treatment. As pre-treatment method, plasma can significantly decrease the time and energy required for obtaining of inorganic fibers. Plasma can eliminate the need of slow heating rate and the final product is characterized by improved crystallinity while retaining the fiber structure.

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