PLASMA INDUCED REMOVAL OF BASE POLYMER MATRIX BY PREPARATION OF INORGANIC SUBMICRON FIBERS

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Abstract

In presented work we compare the influence of low-temperature plasma generated in ambient air by Diffuse Coplanar Surface Barrier Discharge on three types of most commonly used polymers - polyvinylpyrrolidone, polyvinyl alcohol and polyacrylonitrile with suitable precursors. Samples were studied in terms of chemical composition (ATR-FTIR, EDX) and surface morphology (SEM). The method was studied as a separate treatment or pretreatment procedure before thermal calcination. Thanks to the high power density of generated plasma and related high density of active particles, a significant removal of the organic part of the hybrid fiber without the damage of the fibrous structure was observed in the first 30 minutes. Plasma treatment before sintering decreases the time and temperature needed to complete removal of organics, does not require slow temperature rise and so decreases the cost and simplifies the preparation of metal oxide fibers.

Keywords: Inorganic nanofibers, plasma assisted calcination, atmospheric pressure plasma, diffuse coplanar surface barrier discharge

INTRODUCTION

Inorganic micro- and nanofibers are one of the most studied materials [1,2]. The most used method for preparation of inorganic fibers are annealing of hybrid fibers containing base polymer and precursor in the process of *thermal calcination*. During this process the fibers prepared by spinning procedures are exposed to high temperature in the order of 100°C for several hours [3]. The base polymer is removed and hybrid fibers are transformed to inorganic material. Because of high-temperature and long duration process, the fabrication of inorganic structures is considerably time-demanding, economically, environmentally and technically challenging.

One of the alternative approaches in the preparation of submicron structures by polymer-template techniques is the use of low-temperature, non-equilibrium plasma generated in a gas with high oxidative activity. Plasma suitable for so-called *plasma assisted calcination (PAC)* should be low temperature, with high oxidative capacity and sufficiently homogeneous to avoid damage of the submicron structure. This type of plasma can be easily generated at reduced pressure, and low pressure plasma sources have been already studied for polymer matrix removal by the preparation of inorganic microstructures and layers [4-6]. However, necessity of vacuum equipment enlarges treatment time and increases the cost of method.

Due to the limitations of low pressure plasma processes, there is a tendency to develop the atmospheric pressure sources that could fulfil the requirements for low-cost and fast plasma processes. Among plasma sources applicable for atmospheric pressure plasma assisted calcination Dielectric Barrier Discharges (DBD´s) play an important role. Due to the higher density of reactive oxygen species, e.g. ozone, the speed of the calcination process can be very high [7]. DBD´s plasma is usually characterized by filamentary mode and the diffusiveness of plasma is ensured with flow of appropriate working gas (He, Ar, N_2). However, the oxidation effectivity of polymer template in mentioned gases is reduced.

In our work we used a special type of dielectric barrier discharge - *Diffuse Coplanar Surface Barrier Discharge* (DCSBD) for plasma assisted calcination of fibers containing three types of most commonly used polymers - polyvinylpyrrolidone, polyvinyl alcohol and polyacrylonitrile with suitable precursors. The advantage of DCSBD is generation of diffuse, low temperature, non-equilibrium plasma with very high power density (100W/cm^3) at atmospheric pressure without the need of any special working gas [8,9].

Samples were studied in terms of chemical composition (ATR-FTIR, EDX) and surface morphology (SEM). The method was studied as a separate treatment or pre-treatment procedure before thermal calcination.

1. EXPERIMENTAL

The plasma assisted calcination was performed by DCSBD at atmospheric pressure in ambient air. This type of discharge generates a low temperature, non-equilibrium diffuse plasma in thin layer (0.3 - 0.5 mm) above the ceramics with high surface and volume power density. The plasma consists of a large number of H-shaped microdischarges burning between the strip electrodes prepared by screen printing technology on the bottom side of the ceramic plate (**Figure 1**). The detailed description of DCSBD based technology can be found in [8,9].

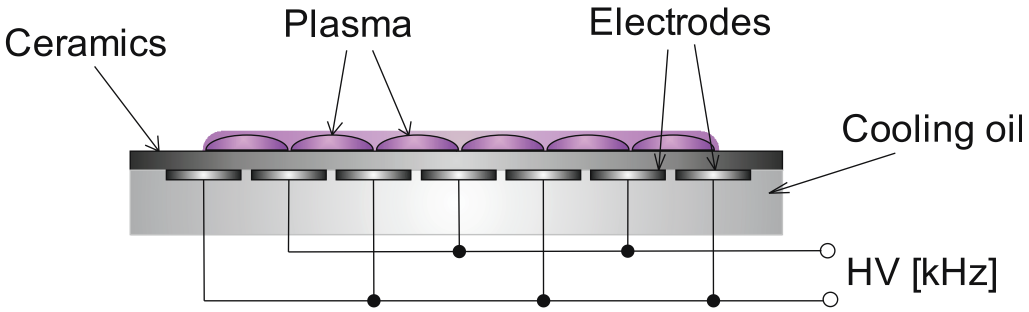

Figure 1 Cross-section of DCSBD electrode system

The samples of composite fibers were prepared by electrospinning (PARDAM Ltd., CZ, IMR SAS, SR) from solution of polyvinyl pyrrolidone + titanium butoxide (*Ti(Bu)/PVP*), polyvinyl alcohol + zinc acetate (*Zn(Ac)/PVA*) and polyacrylonitrile + aluminium trinitrate ($Al(NO_3)_3/PAN$).

DCSBD was powered by sinusoidal HV generator Lifetech VF 700 (Lifetech Ltd., CZ), up to 20 kV peak-to-peak and frequency 14 kHz. The samples were fixed to the movable holder with a distance 0.3 mm above the ceramics and treated during exposure time in the range 1-60 min by moving in the plasma (dynamic regime) at input power 400 W.

To study the influence of the plasma treatment on the fibrous structure and the surface morphology of fibers, SEM Hitachi S-4800 (Hitachi High-Technologies, US) was used. The chemical composition was measured by EDX spectrometer INCA x-sight (Oxford Instruments, UK). ATR-FTIR measurement using Bruker Vector 22 FT-IR Spectrometer (Bruker Optics, US) was carried out for characterization of specific chemical groups in the composite material before and after plasma treatment.

2. RESULTS AND DISCUSSION

Figure 2 shows the ATR-FTIR spectra of hybrid fibers before and after plasma treatment. The broad band in the region 3000-4000 cm^{-1} is due to the OH stretching vibrations.

In the FTIR spectra of Ti(Bu)/PVP fibers at about 1650 cm^{-1}, the typical vibration of carbonyl group v(C=O) of PVP can be detected. Symmetric stretching vibration of C-N bond is visible at 1290 cm^{-1} [10,11]. Symmetric and asymmetric stretching and bending vibration of C-H occur in the region 2830-2990 cm^{-1} and 1400-1520 cm^{-1} [12,13], respectively. Peak at about 1370 cm^{-1} belongs to the vibration of C-C bonds in PVP ring [11]. Deformation vibration od (CH$_2$)$_n$ can be observed in the region 720-790 cm^{-1} [14]. Also allowance from stretching and bending vibration of C-C, C-H bonds of titanium butoxide can affect intensity of peaks attributed to organics [15,16]. Vibration of bonds typical for metal alkoxides - butoxy groups (Ti-O-CH$_2$-) and deformation vibration of C-H, C-O and Ti-O-C can be found in the region 1000-1250 cm^{-1} and 400-900 cm^{-1} [17,18], respectively. Peaks attributed to Ti-O bond in the spectra of thermally calcined sample are visible below 800 cm^{-1} [19].

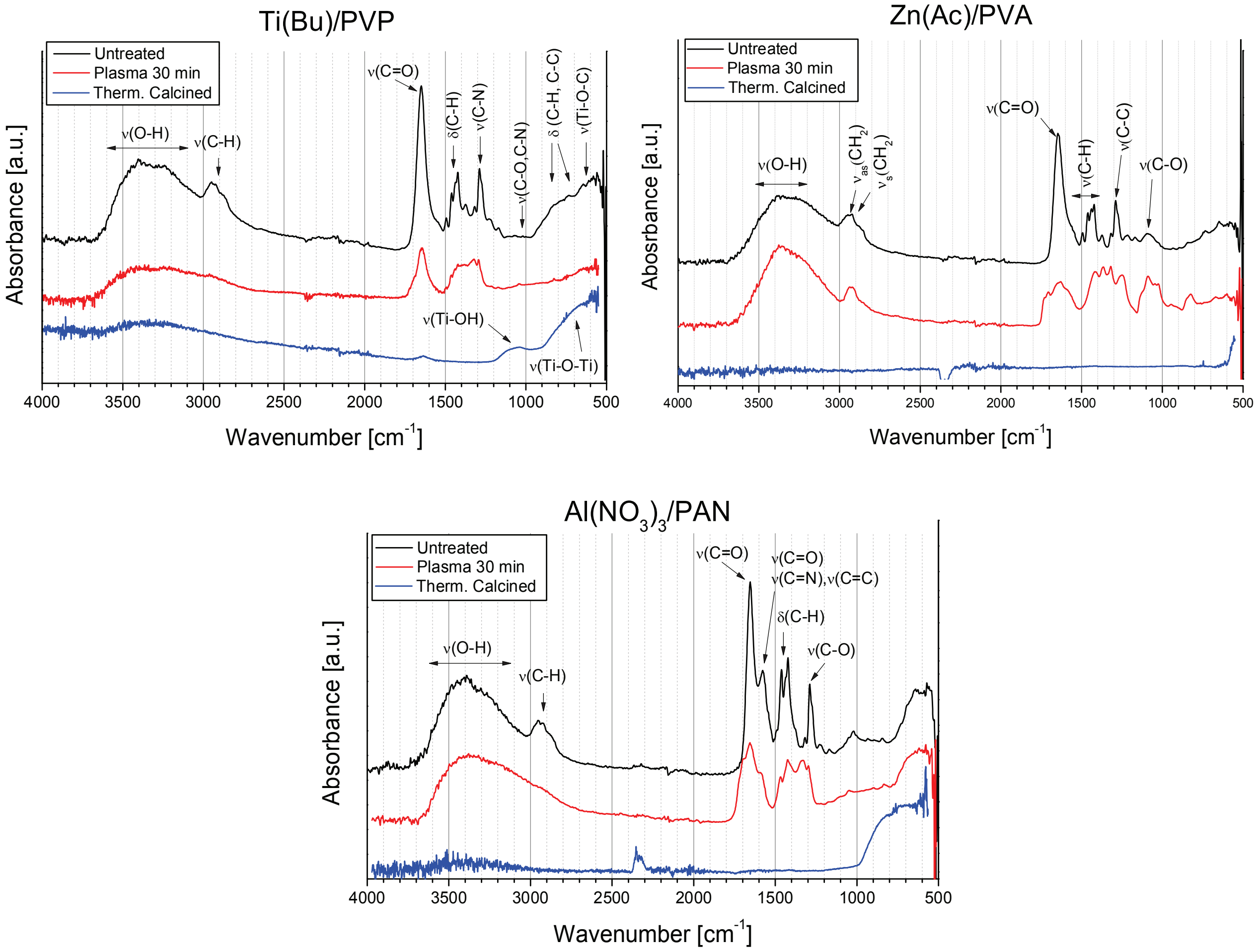

Figure 2 ATR-FTIR spectra of hybrid nanofibers - untreated, treated by plasma for 30 minutes and thermally calcined inorganic fibers

The ATR-FTIR spectra of Zn(Ac)/PVA fibers show all major peaks belonging to polyvinyl alcohol and zinc acetate. The broad bands in the region 3100-3500 cm^{-1} are linked to O-H stretching vibrations in PVA base polymer and water bonded on zinc acetate as dihydrate. At 2940-2950 cm^{-1} was observed peak assigned as symmetric and asymmetric stretching of CH$_2$ group [20,21], which is decreasing after plasma treatment. In the range 600-1500 cm^{-1} characteristic peaks of PVA can be overlapped with peaks of zinc acetate. At 1715 cm^{-1} (1700-1750 cm^{-1}) and 1570 cm^{-1} were assigned peaks attributed to stretching of C=O bond [22,23]. Bands attributed to carbonyl group are influenced except zinc acetate also by the presence of acetate groups remaining from PVA during the hydrolysis of polyvinyl acetate. Decrease and shift of these peaks indicate decomposition of the organic part of composite fibers. Two bands at 1420 cm^{-1} and 1432 cm^{-1} were attributed to asymmetric and symmetric bending of CH_2. At 1326 cm^{-1} and 1232 cm^{-1}, peaks were assigned as wagging vibration of CH_2. C-O stretching vibrations can be observed at 1093 cm^{-1}. At 917-919 cm^{-1}, bands of C-C bond and CH_2 rocking vibrations are observed [24], which disappear after plasma calcination due to decomposition of polymer chain.

In the measured infrared spectra of $Al(NO_3)_3$/PAN fibers, the peaks characteristic for PAN are identified at about 1660 cm^{-1} (stretching vibrations of carbonyl (C=O) group), 1590 cm^{-1}(combination of C=N, C=C and C=O stretching), 1450 cm^{-1}(C-H bending) and 1290 cm^{-1}(C-O stretching). It is possible to observe the decrease of the peaks corresponding to organic material of base polymer after plasma treatment, including also asymmetric and symmetric stretching vibration of methylene (CH_2) groups at 2960-2920 cm^{-1} and 2890-2850 cm^{-1}, respectively [25,26]. We can observe the contribution of peaks attributed to nitrate ion (NO_3^-) in precursor visible at about 1490, 1370, 1275 and below 800 cm^{-1} [27]. Peaks attributed to Al-O and Al-O-Al bonds might be visible below 700 cm^{-1}.

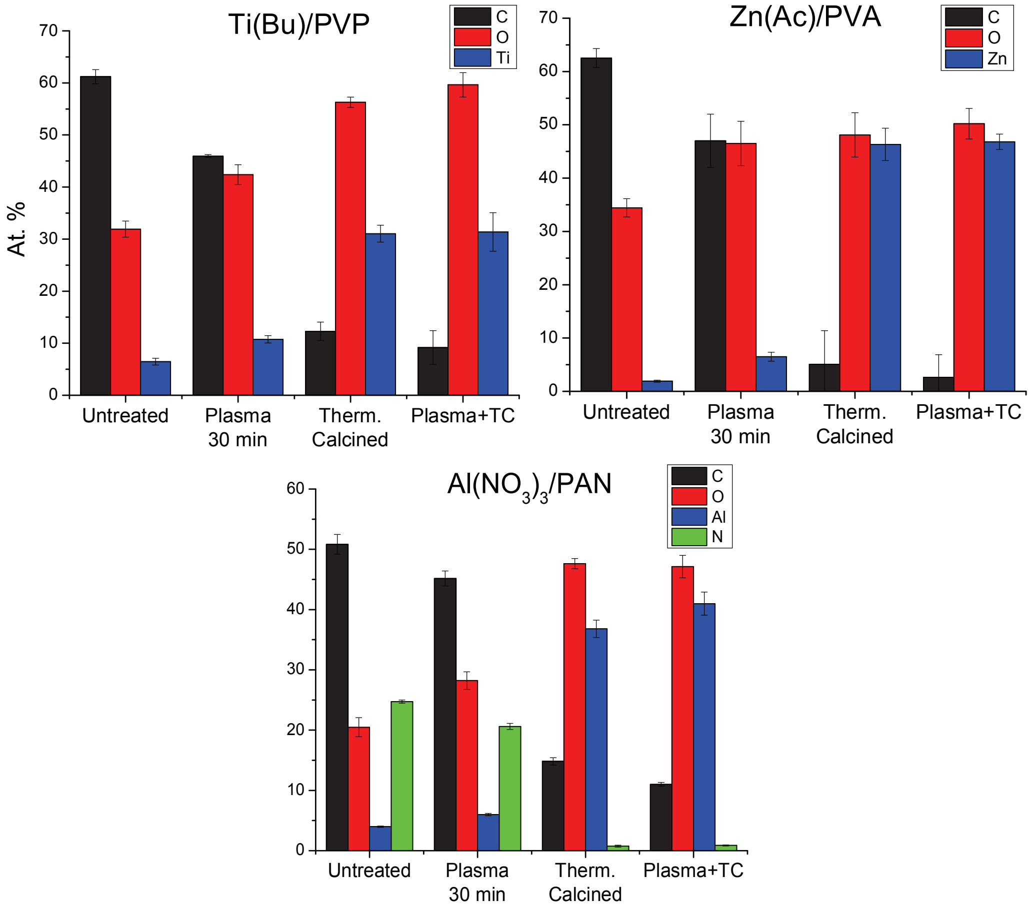

Figure 3 Chemical compositions of hybrid nanofibers - untreated, treated by DCSBD plasma for 30 minutes and inorganic fibers prepared by conventional thermal calcination and combination of plasma pretreatment for 30 minutes and thermal treatment

Figure 3 shows the chemical compositions of samples - untreated precursor/polymer fibers, fibers treated by DCSBD plasma for 30 minutes, inorganic fibers prepared by conventional thermal calcination at 700-1000°C for 6-10 hrs with controlled heating rate and inorganic fibers prepared by combination of plasma pre-treatment and 2-4 hrs sintering at around 700°C without the control of heating rate.

The strong decrease of carbon and simultaneous increase of oxygen and metal contents was observed on the samples treated by plasma. Oxidation during PAC produces easy removable volatile products from base polymer and organic parts of precursors (C,N,O,H). Plasma treatment oxidation of organics was most effective on Zn(Ac)/PVA fibers due to the low chemical stability of this type of base polymer. PAN was considered as the most resistant. Comparing the results obtained on inorganic fibers prepared by thermal calcination and combination of plasma and shorter exposition to the high temperature, we can see, that plasma pre-treatment allows shortening of sintering process and decrease of required temperature to reach comparable chemical composition.

Hybrid precursor/polymer fibers have a smooth surface. After plasma calcination, the surface of Ti(Bu)/PVP and Zn(Ac)/PVA fibers turned rough. DCSBD PAC causes the increase of porosity of fibers which is very beneficial for a wide range of applications. The fibers diameter ranges from 0.5-1 µm and it can be visible the shrinking of fibers after plasma treatment. It was observed, that plasma has also positive effect to remain fibrous structure and avoid breaking of fibers when the heating rate is not controlled [28] and allows also preparation of composite fibers consisting of polymer core with ceramic shell, where the desired surface with additional mechanical properties were obtained [29].

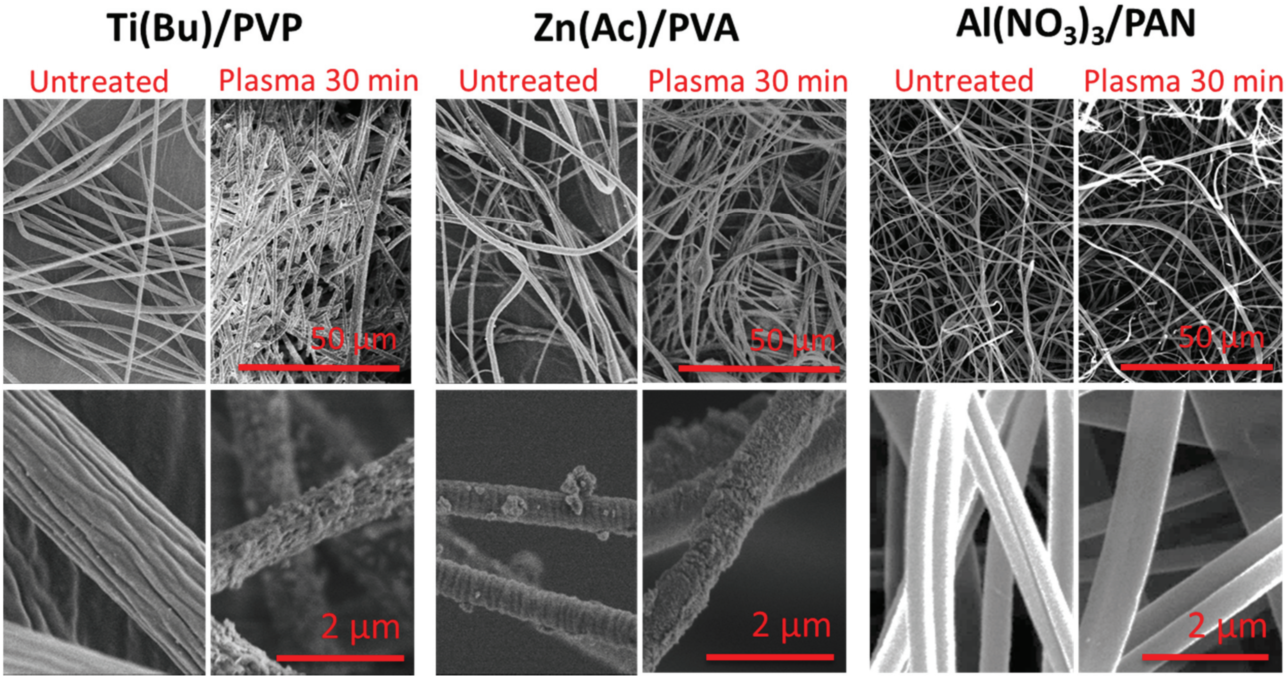

Figure 4 SEM micrographs of precursor/polymer fibers before and after plasma treatment

3. CONCLUSION

The observed fast removal of organics within short exposure times (less than 1 hour) and low-temperature approach (approx. 50-60°C) makes the plasma assisted calcination using DCSBD an advantageous alternative to conventional thermal calcination for preparation of inorganic fibers and allows the use of wider range of materials and substrates sensitive to high temperature. As a pre-treatment method it can be used for significant shortening of the conventional calcination process duration and can significantly decrease the energetic requirements of the whole process. Diffuse character and macroscopically homogeneous plasma even without the need of any expensive noble working gas, generated by DCSBD, is applicable for the production of inorganic fibers in the submicron range without damage of their fibrous structure. In addition, the increase in porosity of fibers was observed, which is very beneficial in applications requiring large surface-to-volume ratio.

ACKNOWLEDGEMENTS

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