Materials Letters 162 (2016) 79–82

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Atmospheric pressure plasma assisted calcination of organometallic fibers

Veronika Medvecká [a,*], Dušan Kováčik [a,b], Anna Zahoranová [a], Monika Stupavská [b], Mirko Černák [a,b]

[a] Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynská dolina F2, 842 48 Bratislava, Slovak Republic

[b] R&D Center for Low-Cost Plasma and Nanotechnology Surface Modifications, Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form
3 September 2015
Accepted 26 September 2015
Available online 30 September 2015

Keywords:
Plasma assisted calcination
CeO_2 inorganic fibers
DCSBD
Dielectric barrier discharge
Atmospheric pressure plasma

ABSTRACT

Plasma assisted calcination of composite submicron fibers ($Ce(NO_3)_3$/polyvinylpyrrolidone) as a novel method for inorganic submicron fibers preparation was studied. Special type of dielectric barrier discharge, so called Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used for the plasma treatment of composite fibers at atmospheric pressure in ambient air for the purpose of oxidation and removing of organic base polymer by the active species produced in plasma. High decrease of C/Ce ratio and formation of porosity on fibers surface were observed after plasma calcination at exposure time in the order of minutes. Due to the low temperature approach and short treatment time, plasma assisted calcination is a suitable and perspective alternative to the conventional high-temperature calcination.

1. Introduction

In recent years, cerium dioxide or ceria (CeO_2) micro- and nanoscale materials have attracted much attention as an electrolyte in the solid oxide fuel cells (SOFCs) [1], for use in catalysis [2], air/water purification [3,4] in water–gas shift reaction [5], gas sensors [6], optical additives or UV absorbent.

In the past few years, many methods have been successfully used for preparation of ceria 1-D nanostructures [7–10]. Ceria fibers such as other inorganic fibers in submicron scale are usually prepared by thermal treatment of composite inorganic/organic fibers [11]. First, a composite fibers consisting of organic base polymer and precursor containing inorganic substance are usually prepared by spinning technique. Subsequently, the composite fibers are exposed to high temperature (500–1000 °C) for several hours to remove the organic template and form inorganic fibers in the process of *thermal calcination* [1,8,10]. Thermal calcination is a long-lasting, economically and energetic demanding process. The high temperature approach brings disadvantages such as high volume losses of material causing degradation of structure, necessity of high temperature resistant substrates and oxidation of substrate causing a low adhesion of fibers.

The low temperature, non-equilibrium plasma generated in working gas with oxidative effect, e.g. oxygen and air, appears to be a suitable tool for the oxidation and removing of organic base polymer at low temperature by active oxygen species in plasma. This type of plasma, generated at low or atmospheric pressure has already been used for plasma calcination by producing nanopowders, inorganic thin layers and inorganic fibers [12–15].

In present work, we used atmospheric pressure plasma generated by Diffuse Coplanar Surface Barrier Discharge [16,17] for plasma assisted calcination of the composite fibers for preparation of CeO_2 fibers.

2. Experimental

2.1. Samples

Composite fibers prepared on microscope slide by forcespinning™ technology [18] from solution of CeO_2 precursor- *cerium (III) nitrate hexahydrate*-$Ce(NO_3)_3$. 6 H_2O, base polymer *polyvinylpyrrolidone* (PVP)–$(C_2H_3–C_4H_6NO)_n$) and organic dissolvents and additives, were provided by Pardam Ltd, Czech Republic.

* Correspondence to: Faculty of Mathematics, Physics and Informatics, Mlynská dolina, 842 48 Bratislava, Slovak Republic

http://dx.doi.org/10.1016/j.matlet.2015.09.109
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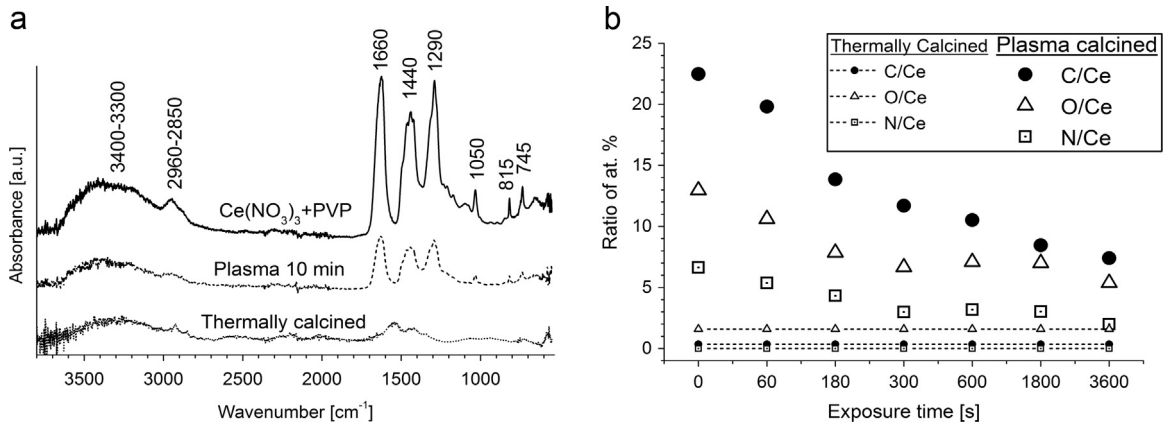

Fig. 1. (a) ATR-FTIR spectra of composite fibers before and after atmospheric pressure plasma treatment with exposure time 10minutes and thermal calcined fibers; (b) Atomic ratio of carbon, oxygen and nitrogen to cerium measured by EDX in dependence on exposure time in plasma.

2.2. Experimental setup

Plasma assisted calcination of composite fibers was performed by a special type of surface dielectric barrier discharge – *Diffuse Coplanar Surface Barrier Discharge (DCSBD)*. It consists of several silver parallel stripline electrodes prepared on the bottom side of ceramic plate (alumina 96%). DCSBD produces the thin layer of non-equilibrium, low temperature macroscopically diffuse plasma with effective thickness 0.3–0.5 mm, which is suitable for surface modification of various materials [19–22], at atmospheric pressure in any working gas, including electronegative gases, e.g. oxygen. Plasma power density was estimated to 100 W/cm^3, rotational temperature was determined to 350 K and electron 7000 K [22]. The DCSBD is described more detailed in [16,23]. Plasma treatment was realized in ambient air at atmospheric pressure in dynamic regime. Samples were fixed to the holder on rail cart and treated in plasma by moving periodically from one side to the other and back above DCSBD ceramics. The distance between sample and ceramic plate was fixed to 0.3 mm, exposure time was in the range 1–60 min at input power 400 W.

2.3. Characterization of fibers

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed to investigate the removal of organic base polymer by using Bruker Vector 22FT-IR spectrometer, in the range of 4000–500 cm^{-1}, with additional accessories Pike MIRacle™ at parameters 60 scans and resolution 2 cm^{-1}. Morphology of fibers was observed by Scanning Electron Microscope (SEM) Hitachi S-4800 (Hitachi, Japan) at an accelerating voltage of 2 kV and current flow 10 μA. EDX spectrometer INCA x-sight (Oxford Instruments, UK) was used for determination of chemical composition. The EDX spectra were acquired at a magnification of 1000 at acceleration voltage of the electron beam of 10 kV and emission current of 10 μA. The XPS measurements were performed using ESCALAB 250Xi (ThermoFisher Scientific). System is equipped with 500 mm Rowland circle monochromator with microfocused Al Kα X-Ray source. An X-ray beam with 200 W power (650 μm spot size) was used. The survey spectra were acquired with pass energy of 50 eV and resolution of 1 eV. The pass energy and resolution for high resolution scans were 20 eV and 0.1 eV, respectively. In order to compensate the charges on the surface electron flood gun was used. Spectra were referenced to the hydrocarbon type C 1 s component set at a binding energy of 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software.

3. Results and discussion

3.1. ATR-FTIR measurements

In the measured infrared spectra (Fig. 1a), the significant peaks characteristic for PVP are identified at about 1660 cm^{-1}, 1440 cm^{-1} and 1290 cm^{-1} attributed to the stretching vibrations of carbonyl (C=O) group, C–H scissoring vibrations and C–N symmetric stretching, respectively [1,24–27]. It is possible to observe the decrease of the peaks corresponding to organic material of base polymer after plasma treatment including also asymmetric and

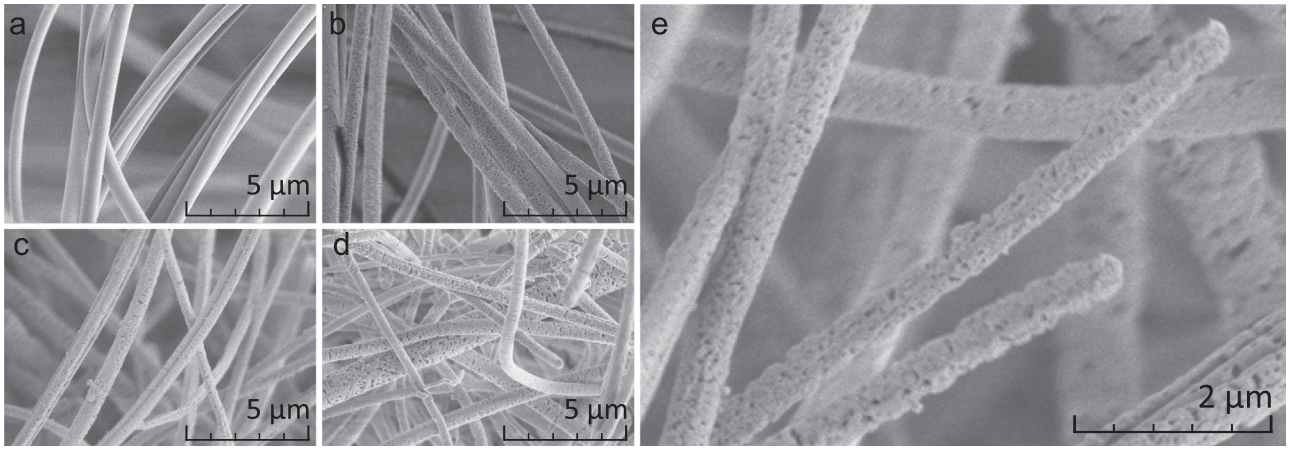

Fig. 2. SEM micrographs of composite fibers before (a) and after plasma calcination at exposure time 10 min (b), 30 min (c, e) and 60 min (d).