



Ceria Fibers Via Electrospinning Process: The Effect of Co-Solvent

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ABSTRACT

Electrospinning is an interesting technique with various potential applications. In this work, CeO_2 fiber production was achieved via this technique. The effect of co-solvent (i-propanol and water) was investigated and described. It was found that the surface tension was reduced when the amount of i-propanol was increased and the viscosity was greater when the amount of i-propanol in the co-solvent was higher. The smooth electrospun fibers produced at 50 wt% of i-propanol were dried for one hour then calcined at 450 °C for 3 hours. The obtained fibers were continuous with a diameter of 600 nm. They had high specific surface area to volume ratio which is suitable for catalytic applications.

Keywords: CeO_2 , co-solvent, surface tension, viscosity, electrospinning.

1. INTRODUCTION

Electrospinning is a process in which a high voltage extrudes a jet of viscous solution through a capillary to a collector. It is a simple process and cost effective. The fibers obtained are continuous and randomly packed over a supporter. This technique creates a high specific surface area to volume ratio, high porosity, and continuous fibers. It has potential in many applications including textile devices [1,2], catalysts [3,4], membranes [5], sensors [6], biomedical applications [2,7], filtration, and template [6-9]. The fiber morphology and diameter of the polymeric systems are controlled by processing variables and the properties of the solution.

Cerium oxide (CeO_2 , ceria) is a pale yellow to white powder. It is a promising material

with rapidly increasing uses in numerous fields. It is important in the chemical makeup of an excellent catalyst in fuel cells, gas sensors and mechanical polishing. Ceria powder can be synthesized via many process including hydrothermal [10-12], combustion system [13,14], sol-gel technique [15,16], mechano-chemical technique [17], deposition-precipitation [18], and co-precipitation [19]. However, there is no report on the preparation of CeO_2 fibers via the electrospinning.

This study aimed to prepare ceria fibers by an electrospinning process. The effect of the co-solvent was investigated and described. The synthesized fiber will be used as a catalytic membrane in a water-gas-shift reaction in the further work.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99 %) and polyvinyl alcohol (PVA, $(\text{CH}_2\text{CHOH})_n$, Mw 30,000-70,000, 95 %) from Aldrich Chemicals and iso-propanol ($(\text{CH}_3)_2\text{CHOH}$, 99%) from Fisher Chemicals were used without further purification.

2.2 Preparation of Ceria Fibers

Cerium nitrate (1.0 M) was dissolved and stirred continuously in a co-solvent of water and i-propanol. The varied factor was weight percent of i-propanol. Initially, 0 wt. of i-propanol was observed then step up to 10, 30, and 50 wt%, respectively. Subsequently, 20 % w/w of PVA was slowly added into the precursor solution, stirring vigorously until a viscous and clear solution was obtained.

The solution was poured into a glass syringe equipped with a 2 mm diameter metal needle. The 15 KV of electrical field between the needle tip and the aluminum sheet collector (7 cm apart from the tip) was created. The electrospun fibers were ejected in a web form onto the aluminum ground collector, then dried at 80°C for 1 hour and calcined under air at 450°C for 3 hours.

2.3 Characterization

The viscosity of the solution was measured using a viscometer (DV-II⁺, Brookfield). The morphology of obtained fiber was determined by a scanning electron microscope with energy dispersive X-ray spectroscopy mode (Model S-510, Hitachi). The mixture solution behavior on temperature function with Simultaneous DSC-TGA Analyzer (SDT 2960, TA Instruments), The crystal structure of the ceria fiber was confirmed by using an X-ray diffractometer (Model PW1830/40, Phillips) with 20 kV, using Cu K α irradiation ($\lambda=1.54060 \text{ \AA}$).

3. RESULTS AND DISCUSSION

3.1 Solution Properties

In the electrospinning process, the property

of the solution plays a significant role in the fiber morphology. The key properties are surface tension, polymer solubility, and viscosity [20]. When the constant electrical field is applied to the polymer solution reservoir, the surface of polymer is charged incidentally. When the charge overcomes the surface tension of the solution, the solution jet is accelerated from the needle tip to stretch onto the collector. In an aqueous mixture system, the apparent surface tension can be estimated from the surface tension of each component by mole fraction average. The surface tension was a cohesion force resulting from the intermolecular forces, in fact the surface tensions of water and i-propanol are 72.3 mN/m and 22.3 mN/m, respectively [20].

Figure 1 shows the morphology of the obtained electrospun fibers prepared with co-solvent solution having different amount of i-propanol. It is found that when the amount of i-propanol was increased, the shape of the collected product was transformed from connected spheres to smooth fibers having average diameter of $900 \pm 250 \text{ nm}$ (S.D.=90). This transformation can be attributed to the reduction of surface tension of the solution resulting from adding i-propanol. Because i-propanol has much lower surface tension than water as mentioned earlier, the more i-propanol was added into water, the lower surface tension of the mixture was achieved.

Moreover, the viscosity of the solution also has an effect on the electrospinning and the fiber morphology. When the viscosity of the solution was too low, electrospinning occurred and connected dots were formed as shown in Figure 1 (a). The viscosity of the mixture depends on the PVA solubility which can be explained by the dielectric constant of a solvent. The dielectric constant is a relative measure of polarity. Water has a dielectric constant of 80 (high polarity), while i-propanol

has a dielectric constant of 20 (semi-polar), and PVA has a dielectric constant of 2 (low polarity) at 20°C [21]. This implies that PVA can be dissolved in i-propanol better than in water. Thus, the addition of i-propanol into the co-solvent will enhance the solubility of

the PVA and increase the viscosity of the solution. This is confirmed by the result presented in Table 1. However, if the viscosity is too high, it will be very difficult to draw a fiber from the tip of the syringe.

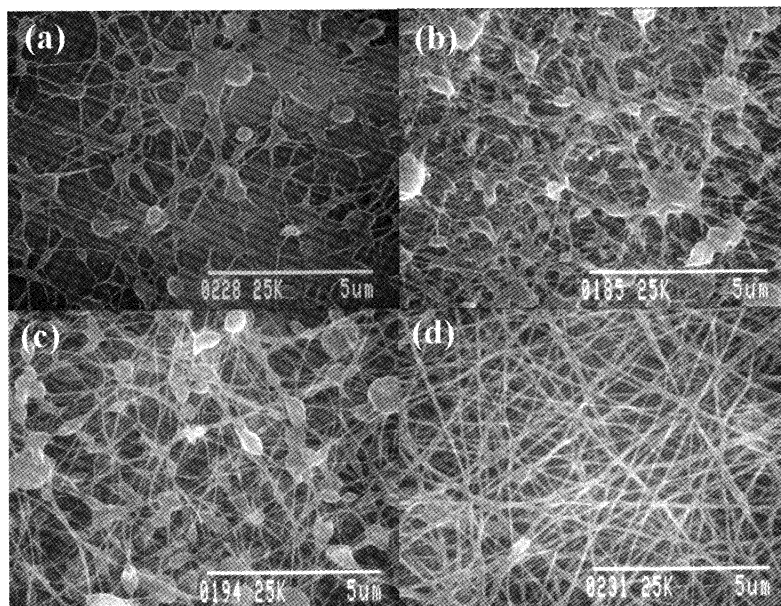


Figure 1. SEM micrographs of obtained fibers (a) 0 wt.% i-propanol, (b) 10 wt.% i-propanol, (c) 30 wt.% i-propanol, (d) 50 wt.% i-propanol.

Table 1. Viscosity of mixed solution with varied amount of i-propanol.

i-propanol (wt.%)	Viscosity (Pa.s)
0	1
10	10.8
30	20.7
50	50.5

3.2 Fiber Morphology

Thermal gravimetric analysis was used to measure the weight loss of PVA solution prepared in co-solvent of 50 wt% i-propanol and water compared with the mixed solution of cerium nitrate and PVA using i-propanol

as co-solvent. The heating rate was set up at 20°C/min under flowing air. The result is shown in Figure 2. The dashed line represents PVA thermal behavior and the solid line represents mixture of cerium nitrate and PVA.

In figure 2, the weight change can be

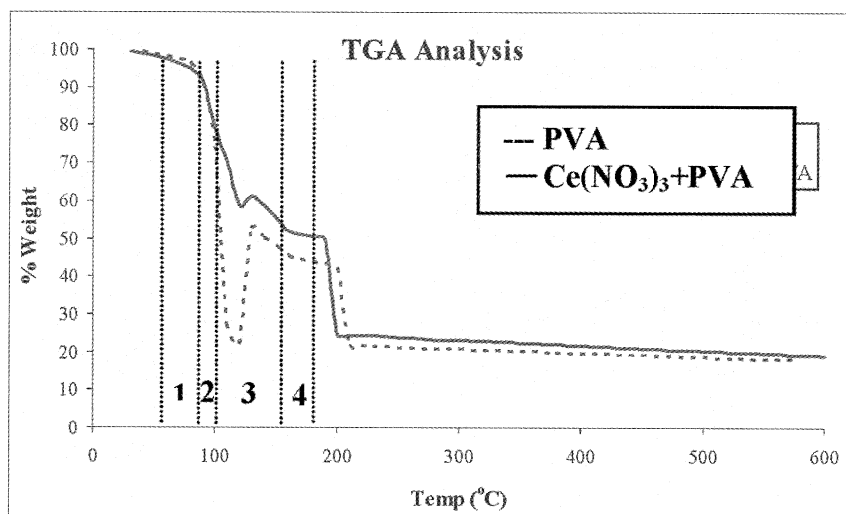


Figure 2. TGA curves of PVA and PVA+Ce(NO₃)₃.

classified into 4 regions representing vaporization of solvent, partial oxidation of PVA, degradation of PVA, and PVA and Ce(NO₃)₃ decomposition, respectively. In the region 1, the co-solvent was vaporized at its boiling point [22]. In the region 2, the parts of PVA structure were cracked and subsequently reacted with oxygen forming intermediate substances resulting in weight gain [23]. Then, at temperature above 130°C, PVA started to be degraded gradually until reaching 200°C. Finally at 190°C, Ce(NO₃)₃ and PVA were decomposed abruptly to be CeO₂ (ceria) and ash, respectively. It should be noted that pure PVA was decomposed at

temperature slightly higher than Ce(NO₃)₃+PVA (solid line) [24].

The morphology of the ceria fibers were examined using a SEM as shown in Figure 3. The fiber diameter was measured from the SEM image using an image analyzer software (Image J 1.42). Before calcination process, the obtained fibers had smooth surface having average diameter of 900 ± 250 nm (S.D. = 90). After calcination at 450°C for 3 hours, their surface were cracked resulting from the gases evolution during the PVA and Ce(NO₃)₃ decomposition and their sizes were shrunk to 630 ± 80 nm with narrower distribution (S.D.=29).

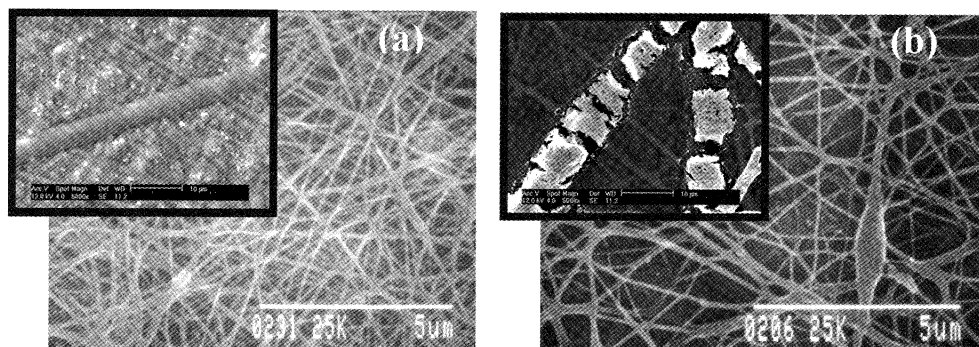


Figure 3. SEM images of electrospun fibers (50 wt.% i-propanol)
(a) before calcination (b) after calcination.

The elemental compositions of the fibers (before and after calcination) were analyzed by an energy dispersive X-ray spectroscopy. The result is presented in Table 2. It reveals that before calcinations the fiber comprised of $\text{Ce}(\text{NO}_3)_3$, PVA, and residual i-propanol. After calcination, the composition corresponds

to CeO_2 , fixed carbon (ash) and unconverted cerium nitrate, which is in agreement with the TGA analysis. The obtained XRD pattern shown in figure 4 is matched well with the standard pattern of CeO_2 (JCPDS; file number: 81-0792). That means the calcined fibers are in the form of CeO_2 crystal

Table 2. Elemental composition of the fibers.

State \ Element	C (%)	N (%)	O (%)	Ce (%)
Before calcination	18.44	19.48	55.29	6.79
After calcination	1.50	12.25	57.92	28.31

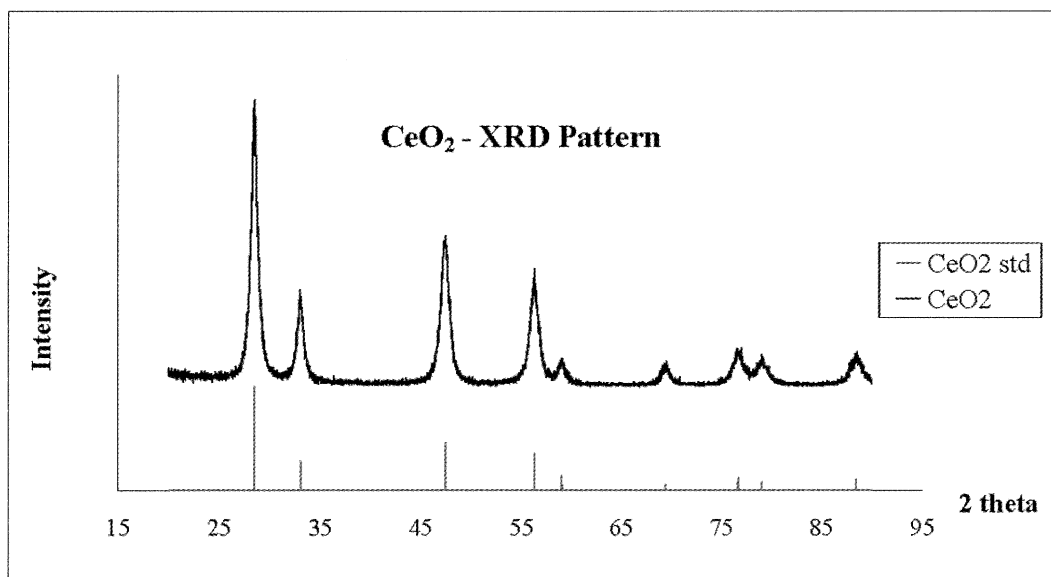


Figure 4. XRD pattern of obtained ceria fibers.

4. CONCLUSIONS

Ceria (CeO_2) fiber was successfully prepared by an electrospinning technique. The solution property of the solvent had a prominent influence on the electrospinning process. The addition of the co-solvent, i-propanol, reduced the surface tension of the feed solution and thereby promoted the

polyvinyl alcohol (PVA) solubility. Smooth fibers were produced with 50 wt% i-propanol. The CeO_2 fibers were obtained after the calcination at 450°C for 3 hours having an average diameter of 600 ± 80 nm. The EDS and XRD results verified the formation of CeO_2 .

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