

Preparation of Ceria Fibers Via Electrospinning Process

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Abstract

Electrospinning is an interesting technique with various potential applications. CeO₂ fibers production was achieved via this technique. In this work, the prepared condition and the fiber morphology were investigated and described. The optimum condition was 15 kV, 7 cm in distance between needle tip and ground collector, 50 wt% of i-propanol in the co-solvent. The obtained fibers were continuous with a diameter of 900 nm. The smooth electrospun fibers produced were dried for one hour, and then calcined at 450 °C for 3 hours. The calcined fibers were reduced to 600 nm and cracked on the fibers. They were ceria fibers, what verified by EDX, and XRD pattern. They had high specific surface area to volume ratio, and monolith fibers, which is applied for catalytic applications.

Key words: CeO₂, co-solvent, surface tension, viscosity, electrospinning

1. Introduction

Electrospinning technology is a simple and low cost method for making ultra fine polymer [1,2,3], cellulose [4] and metal oxide fibers [5,6,7]. Ultra fine fibers have diameters ranging from 10 μm down to 10 nm by forcing a polymer melt or solution through a spinnerette with an electric field. A polymer fiber is formed during the process of electrospinning from the charged jet of a polymer solution with a suitable viscosity. It is stretched because of the electrostatic repulsion between the charges on the surface. The small diameter of the fibers allows fast mass exchange and the solvent usually evaporates before deposition on the fiber collector. The diameter and the morphology of the fibers are influenced by the solution concentration, viscosity, conductivity, the solvent surface tension, and the strength of the applied electric field. These fibers had great surface area per unit mass so that non-woven fabrics of these nanofibers can be used in various applications. The superfine fibers produced by electrospinning are randomly collected onto thin non-woven fiber mats that behave like micro-porous membranes [8]. The great benefit of this process, what ceria fibers may employed to utilize as catalytic system.

2. Experimental

2.1 Materials

Cerium (III) nitrate hexahydrate ($\text{CeNO}_3 \cdot 6\text{H}_2\text{O}$, 99 %) and Polyvinyl alcohol ($(\text{CH}_2\text{CHOH})_n$, 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. Subsequently, 30 % w/w of PVA was slowly added into the precursor solution, stirring vigorously until a viscous and clear solution was obtained.

The solution was placed into a glass syringe with a 2 mm diameter metal needle. The tip was connected to a DC high voltage generator (15 kV). A grounded aluminum sheet was used as a collector. The electrospun fibers were ejected in a web form onto the collector, then dried at 80 °C for 1 hour and Ceria/PVA fibers were transform to ceria fibers via calcination process at 450 °C for 3 hours [8].

2.3 Characterization

The viscosity of the solution was measured using a viscometer. The fiber morphology was determined using a scanning electron microscope with energy dispersive X-ray spectroscopy mode (JSM-5600 LV, JEOL). The element identification of the ceria fiber was confirmed by using an X-ray diffractometer (PW1830/40, Phillips) with 20 kV (CuK α radiation, $\lambda=1.54060$ Å).

3. Results and discussion

3.1 Fiber morphology

Firstly, the solution was prepared by pure water. The factors were distance between needle tip; 5 cm to 10 cm, and fiber morphology. There found the jammed fibers on the ground collector at the whole distance. The fiber characterizations displayed in figure 1.

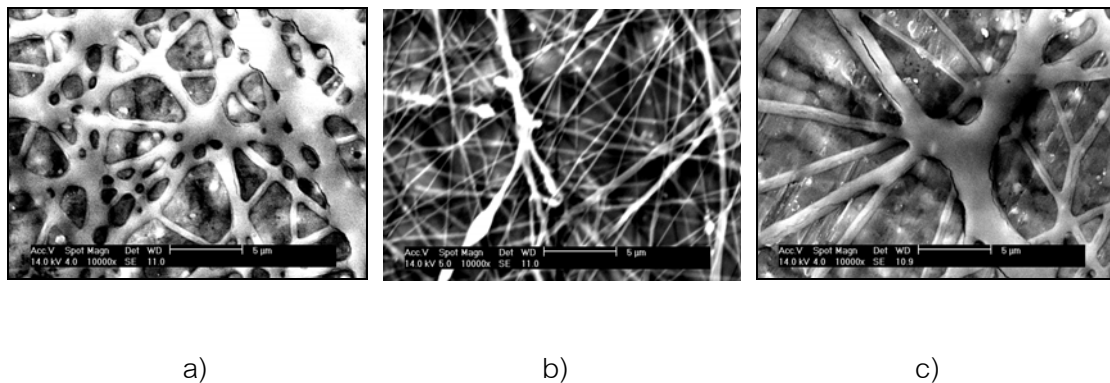


Fig. 1 the fiber characterization by effect of distance

a) 5 cm b) 7 cm c) 10 cm

In figure 1, the jammed electrospun fibers were obtained, which water had slowly vaporization effect. The water vaporization had an effluent to draw fibers. Moreover, the distance was a significant key for controlling the fibers shape. At 7 cm distance was sufficient distance to draw fibers and good quality in shape for extended study.

The second, the jammed effect were reduced, what co-solvent was preferred to answer this trouble. The co-solvent was mixture solution between water and i-propanol. I-proanal was an alternative choice due to great vaporized than water. The improvement fibers found in figure 2.

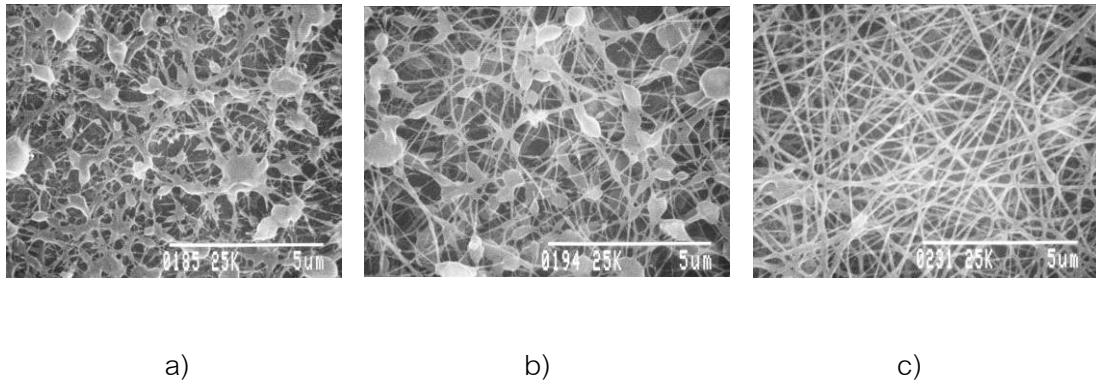


Fig. 2 SEM micrographs of obtained fibers

a) 10 wt. i-propanol b) 30 wt. i-propanol c) 50 wt. i-propanol

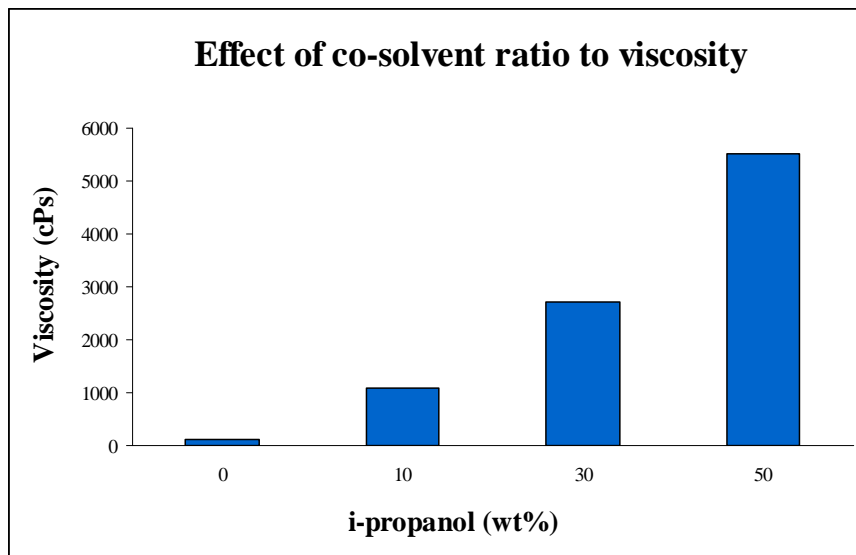


Fig.3 Effect of co-solvent ratio to viscosity

The transformation of electrospinning fibers was conducted by surface tension and viscosity. Namely, these parameters can influence to the characteristic of bead on the fibers. The surface tension of water and i-propanol are 72.3 mN/m and 22.3 mN/m, respectively [10]. The co-solvent had lower surface tension than water due to the mixing effect. The generated fibers were smooth and continuous when reduce the surface tension showed in SEM picture as Fig.2. SEM is primarily used to study the surface, or near face, structure of bulk specimens. The solvent was modified by varying the weight percent of i-propanol from 10 to 50, when the consequence showed in Fig. 2 a), b), and c). The first, 10 % weight of i-propanol appeared as enlarged droplets on the aluminum collector, some polymer solution could stretch to fiber form. When co-solvent solution percentage increased, the droplets were

transformed. The beads gradually disappeared till the smooth fiber occurred at 50 percentage co-solvent.

Therefore, 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 particles were formed as shown in Figure 2 (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 [11]. This implies that PVA can dissolve 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.

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 particles were formed as shown in Figure 2 a. This is confirmed by the result presented in figure 3.

3.2 SEM/EDX

The SEM images in Figures 4a) and 4b) show the morphology of the cerium oxide fibers before and after calcination at 450°C for 3 hours. The generated fibers had a diameter of 900 nm before and a diameter of 600 nm after calcination.

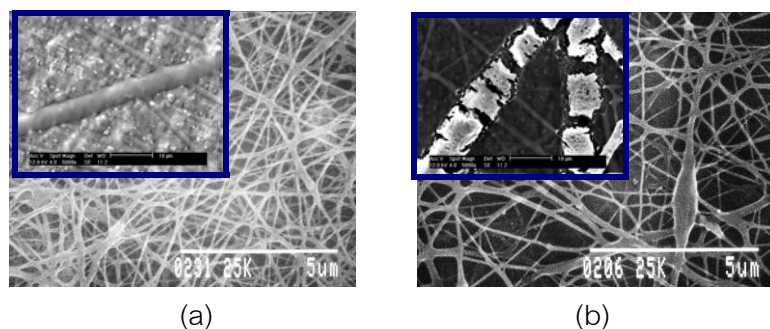


Fig.4 SEM images of electrospun fibers (50 wt. i-propanol)

(a) before calcination b) after calcination

Energy Dispersive Spectrometer (EDS) has been a great advance in the suite of analytical techniques available for rapid qualitative analysis. However, there are some serious limitations to be considered as it is impossible to detect elements lighter than sodium with a standard detector.

The composition of elements (pretreatment and after calcination at 450°C) are displayed in Table 1. The totals refer to atom percentage (% atom) of the elements in the system. The pretreatment comprised of $(\text{CH}_2\text{CHOH})_n$, CeNO_3 , H_2O and $\text{CH}_3\text{CH}_2\text{CHOH}$. The percentages of C, N, O and Ce are shown, but hydrogen was smaller than sodium so it could not be detected.

Table 1 Elemental composition of the fibers (before and after calcination)

| Element | C (%) | N (%) | O (%) | Ce (%) |
|---------|-------|-------|-------|--------|
| Before | 18.44 | 19.48 | 55.29 | 6.79 |
| After | 1.50 | 12.25 | 57.92 | 28.31 |

Moreover, the low percentage of carbon in the calcinated fibers implies that it went into the ash of the residual polyvinyl alcohol. Some nitrate compound still remained in the process, however, oxygen and cerium had the highest percentages. The calcination process was a heat treatment to effect phase transformations. It induced the calcination process that transformed the polyvinyl alcohol/cerium nitrate composite fibers to CeO_2 fibers. The percentages of cerium and oxygen were 28.31 and 57.92, respectively. The yield proportion was approximately 1:2 and there was a strong possibility that it was CeO_2 .

3.3 X-ray diffraction (XRD)

The crystalline structure of ceria had been investigated by many researchers. X-ray diffractometry (XRD) is mainly used for the identification of compounds by their diffraction patterns. It has been shown that a single crystal with a particular set of atomic planes oriented toward the X-ray beam diffracts X-rays at an angle θ determined by the distance between the planes.

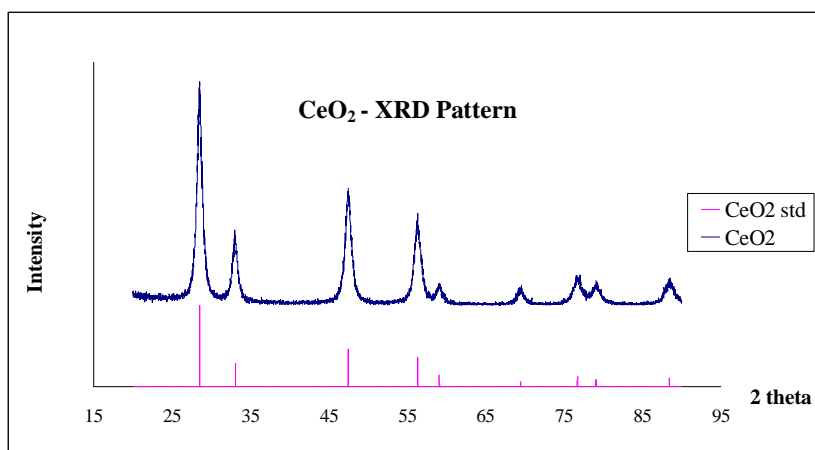


Fig.5 XRD pattern of ceria synthesizer

Figure 5 shows the crystalline phase present after calcination treatment. The diffraction method is ideally suited for characterization and identification of polycrystalline phases. The same substance always gives the same pattern. The results here displayed sharp and intense peaks corresponding to CeO₂ as matched with the database in JCPDS (file number: 81-0792). Thus, it was almost certain that the product was CeO₂ confirming the earlier EDS verification.

4. Conclusions

Ceria (CeO₂) fiber was successfully prepared by an electrospinning technique. The factors relevant were the solution properties of the solvent as vaporization, viscosity, polarity, and distance between tip and ground collector 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 solubility. Smooth fibers were produced with 50 wt% i-propanol. The CeO₂ fibers obtained after the calcination at 450°C for 3 hours had an average diameter of 600 nm. The EDS and XRD results verified the formation of CeO₂.

5. Acknowledgements

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