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Fabrication of alumina ribbons with mixed solvent system in electrospinning

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Alumina ribbons were fabricated facilely via using mixed solvent of ethanol and ethyl ether in electrospinning, and α-alumina ribbons were obtained after the as prepared ribbons were calcinated at 1200 ^{o}C for 1 h. The as prepared ribbons are composed of dense skin and porous inner structure, the thickness and width of which are of 1 μm and 3-5 μm respectively. After calcination, the corresponding sizes of the ribbons shrunk to ~ 200 nm and 2-3 μm separately. If solo solvent (ethanol) was used in the electrospinning experiment, only round alumina fibers were obtained.

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Keywords: Electrospinng, Mixed solvent, Ribbon, Optical fiber

1. Introduction

The ribbon-shaped ceramics have distinctive properties and been received intensive attentions in fundamental research and technological applications [1-6]. Alumina has been widely used as functional materials in the area microelectronics and optics for their high mechanical strength, excellent thermo-stability and low cost [7, 8]. Compared with conventional alumina, the ribbon-shaped alumina has many novel properties because of the unique morphology. For example, the alumina ribbon is an ideal strengthen material because of the high aspect ratio (ratio of length to thickness) [9]. Besides that, the alumina ribbon has proper cross-sectional geometry for a waveguide and is regarded as excellent ultra-low-loss optical fibers [10, 11].

As stimulated by the novel properties of alumina ribbons, several methods have been developed to synthesize alumina ribbons, including vapor-liquid-solid (VLS) deposition method with well defined geometry, control of temperature in a simple chemical route and twinning-mediate growth [9, 12, 13]. However, the fabrication of alumina ribbons with a simple method is still full of challenges.

Electrospinning has been recognized as a simple and versatile method to generate 1-D structures and with potential to be further developed for large scale fabrications [14]. A variety of round-shaped metal oxide fibers has been synthesized by electrospinning [15, 16]. In the current study, the preparation of alumina ribbons using electrospinning method is reported. The mixed solvent is used in the electrospinning process and the evaporation speed of the solvent is considered to play a key role in forming the ribbons. The crystalline phase transformation and morphology of the alumina ribbons after calcinated at 1200 ^{o}C is also investigated.

2. Experimental

In a typical procedure, 0.5 g of polyvinylpyrrolidone (PVP) (Mw = 1,300,000, Sigma-Aldrich) was dissolved in 4 ml solvent (mixed solvent, ethanol/ethyl ether = 1/2 vol. % or solo solvent ethanol). Then 0.18 g of aluminum acetylacetonate [$Al(CH_3COCHCOCH_3)_3$] (AP, purity > 95.0%, Sigma-Aldrich) was added to the polymer solutions and stirred for 1 h. The solutions were transferred into a clinical syringe in vertical configuration. A stainless steel needle attached to the syringe was connected to positive terminal of the high voltage source (SL60, SPELLMAN, USA). A grounded aluminum foil placed 20 cm from the tip of the needle was used as target to collect the as-spun fibers. Alumina fibers were fabricated by applying electric voltage of 20 kV between the collector and the needle tip. All the experiments were conducted at 25 ^{o}C with a relative humidity of 20-30%. The as-spun fibers were dried in a vacuum pump and then calcinated at 1200 °C for 1 h to get α-alumina ribbons.

The morphology of ribbons was characterized by scanning electron microscope (SEM, JSM-6700F, JEOL, Japan). The crystalline phases of the alumina ribbons were characterized using the X-ray diffraction (XRD, DMAX2500, Rigaku, Japan) technique with Cu Kα radiation of wave length λ = 0.154056 nm.

3. Results and discussion

Fig. 1. gives the SEM images of as-prepared fibers spun from mixed solvent ethanol and ethyl ether and solo ethanol solvent. Stable alumina ribbons were obtained when mixed solvent of ethanol/ethyl ether (1/2, vol. %) were used (Fig. 1a, b). If solo ethanol was used only round-shaped dense fibers were obtained (Fig. 1c, d), and if solo ethyl ether was used, the electrospinning can not be processed because of the rapid evaporation of the solvent.

The as-prepared ribbons have dense skin and porous inner structure with 1 μm in thickness and 3-5 μm in width. The diameter of the round fibers spun from the ethanol solution is dense with the diameter of about 1 μm.

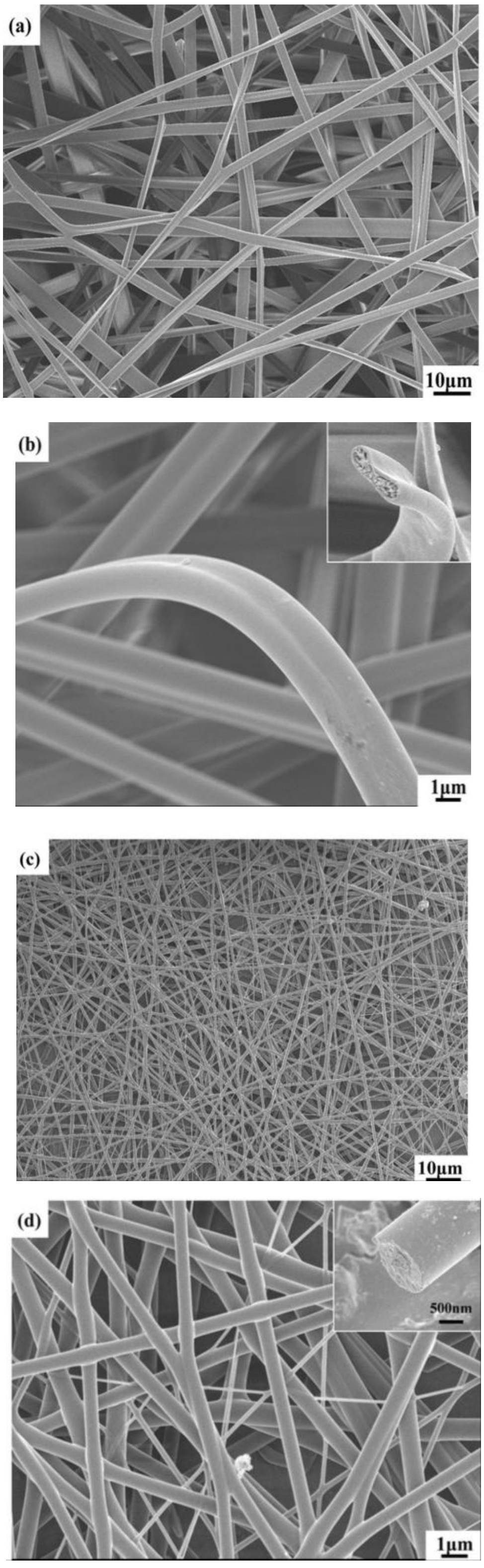

Fig. 1. SEM images of as-prepared fibers using mixed solvent (a), (b) and using ethanol only (c), (d). (a) in small magnification; (b) in high magnification and the cross section on the upright; (c) in small magnification; (d) in high magnification and the cross section on the upright.

The formation of the alumina ribbons is related with the solvent evaporation. At room temperature, ethyl ether has much higher vapor pressure, which is about 10 times higher than that of ethanol [17]. When the fibers are spun out, ethyl ether rapidly evaporates from the surface of the fibers and a skin formed on the fiber. The skin will collapse to form the ribbon shaped fibers under the air pressure when the inner solvents gradually escaped [18]. The rapid evaporation of the ethyl ether leaves space inner the ribbon, which can't be filled completely during the collapse process. As a result the ribbons have the porous inner structure and the diameter is larger than that of the round fibers. When the sole solvent ethanol is used during the electrospinning, the ethanol was evaporated from the fibers comparatively slow and uniformly, so the fibers are round-shaped and have the dense structure. Therefore the presence of the solvent with low boiling point leads to the formation of the alumina ribbons in electrospinning experiment. The shape and inner structure of the as-spun fibers is controlled by the composition of the solvent.

The XRD results of the as-prepared ribbons and the ribbons calcinated at 1200 ^{o}C are shown in the Fig. 2. No peaks are confirmed in the as-prepared ribbons indicating they are amorphous. After calcinated at 1200 ^{o}C, the XRD pattern of the ribbons is identical with the typical pattern of α-alumina phase (JCPDS card no. 81-1667), indicating the formation of crystallized α-alumina ribbons.

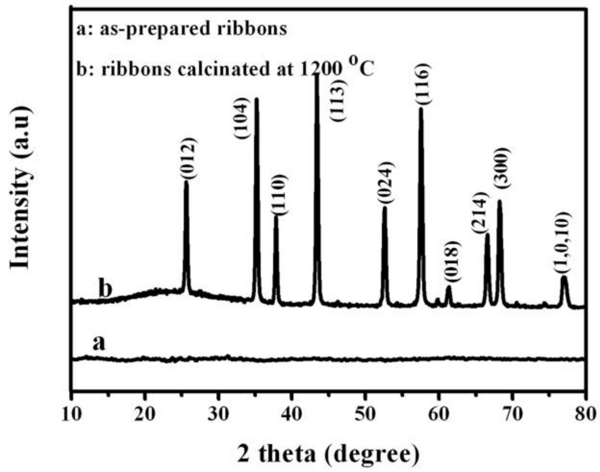

Fig. 2. XRD patterns of as-prepared ribbons and the ribbons after calcinated at 1200 ^{o}C.

Fig. 3. shows the SEM images of the ribbon-shaped and round-shaped fibers after calcinated at 1200 ^{o}C. The calcinated ribbons shrink to 2-3 μm in width and 200 nm in thickness. After calcination, the inner structure of the ribbons becomes denser than the as-prepared ribbons, which is caused by the further collapse during the calcination process. The round-shaped fibers also shrink, the diameter of which is about 100 nm. The shrinkage of the calcinated ribbons is attributed to the loss of the solvent, degradation of PVP, decomposition of the aluminum acetylacetonate and the succeeding sintering [19,

20]. Nevertheless, the calcinated fibers became very brittle and the length/width ratio is greatly decreased. Research to the preparation of the fibers with high length/width is undergoing.

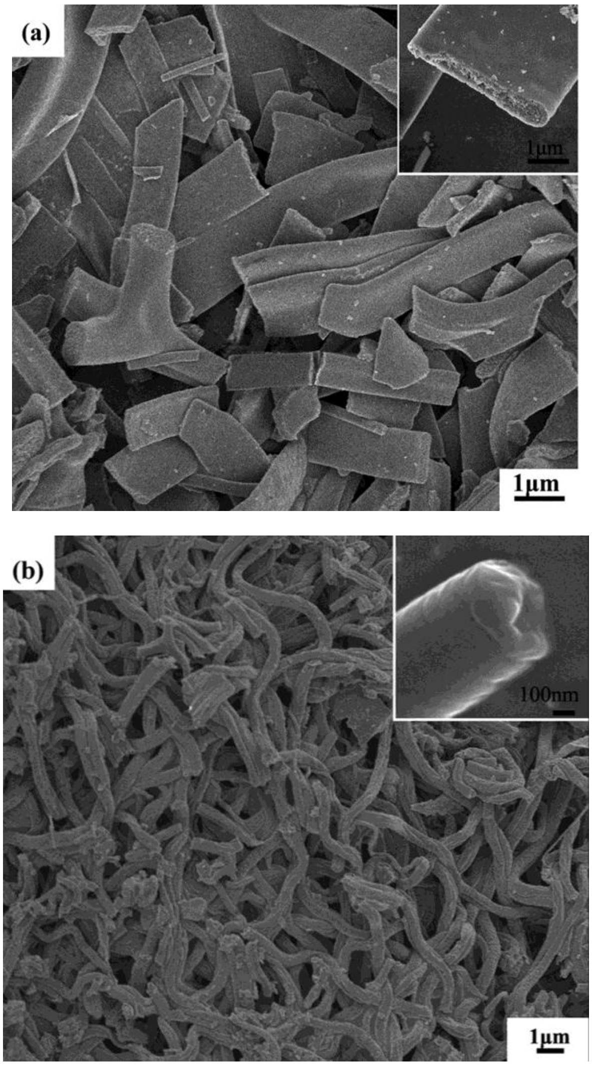

Fig. 3. SEM images of the fibers after calcinated at 1200 ^{o}C using mixed solvent (a) and using ethanol only (b).

4. Conclusions

Alumina ribbons were prepared by electrospinning using ethanol and ethyl ether as mixed solvent. This is a facile method to synthesize alumina ribbons. After calcinated at 1200 ^{o}C, α-alumina ribbons were fabricated successfully. The size of the ribbons is about 200 nm in thick and 2-3 μm in width. Comparison of solvent effect in the electrospinning process shows that the shape of the fiber can be conveniently controlled by choosing different solvent system. This method could potentially be further developed for fabrication of alumina ribbons at large scale and can be broadened to prepare other ribbon-shaped materials.

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