Fabrication of Ceramic Nanofibers by Electrospinning

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Abstract. Ceramic nanofibers made by electrospinning shows different functions and can be widely used as filtration, biomaterial devices, sensing, catalytic supports and chemical decomposition materials. There are many fabrication methods to obtain ceramic nanofibers. In this paper, ceramic nanofibers with high performance though two main synthesis methods are reviewed.

Keywords: Ceramic, nanofibers, electrospinning, polymer, sol gel

1. Introduction
Electrospinning is a simple and versatile method for generating ultrathin fibers from a rich variety of materials that include polymers, composites and ceramics. A high-voltage electric field to impart a certain amount of charge on the surface of the polymer solution droplets is used in the electrospinning process (Fig. 1). When the electric field force is large enough, the polymer droplets overcome the surface tension to form a jet stream. The stream is generally a helical coil and as the radius of the coil increases, the solvent volatilizes or solidifies during the jet stream, and finally Land on the receiving device. Fibers prepared by electrospinning generally have diameters ranging from tens to thousands of nanometers. There are two main factors influencing the electrospinning process including system parameters and process parameters.

Fig. 1 Chematic diagram to fabricate nanofibers by electrospinning
Ceramic nanofibers, made by electrospinning, could show a suitable new material for the filtration of hot gases in the range of 1200 °C -1800°C. Ceramic nanofibers can operate in ‘aggressive’ environments including high and low pH, high pressures and high temperatures and can also be used for energy feedback. Recent advances in research on ceramic nanofibers were carbonide, nitride and oxide including Al2O3, TiO2, ZrO2, MgO, MnO2, Cu2O, SiC, TiC, AlN, Si3N4, GaN, etc.

2. Fabrication methods
Recently, there are mainly two methods to fabricate ceramic nanofibers. First, nanoceramics based on polymer nanofibers (Fig. 2) due to the stringent requirements on the viscoelastic behavior of a solution (PVP, PVA, PEO, etc are used as the polymer matrices to host inorganic precursors). Second, conventional sol-gel precursor solutions be employed to provide an effective route to ceramic nanofibers.

2.1. Nanoceramics based on polymer nanofibers

2.1.1. Combination of electrospinning with sol-gel methods. This synthesis process is showed in Fig.3 in which the key control elements are precursor preparation, aging time, temperature and polymer matrix. After electrospining, calcium phosphate nanofiber mats are collected. The SEM image (Fig. 4) shows the TCP fibers form a three-dimensional fiber network structure, with the diameter of the fiber scaffold is 5 μm on average. After calcination, the fiber surface is rough, porous and has a large specific surface area.

Fig. 2 Main fabrication of ceramic nanofibers based on polymer nanofibers

Fig. 3 illustrates a flow-chart of the general parameters for the sol-gel process of the present invention with an accompanying viscosity curve [1]
2.1.2. Ceramic nanoparticles be encapsulated into an electrospun nanofiber matrix. Collagen/hydroxyapatite composite nanofibers are obtained by electrospinning through conventional method: conventional composite sol was prepared by mixing the collagen/HFP solution with commercial HA powder and then electrospun. However, a novel method (Fig. 5) is used to prepare homogeneous collagen/hydroxyapatite (HA) composite sols, which then is subsequently electrospun into hybrid nanofibers with the perfect orientation of HA nanoparticles along the collagen matrix.

**Fig. 4** SEM micrographs of (a) TCP fibers and fibers obtained after calcination at (b) low and (c) high magnifications

**Fig. 5** Schematic illustration of the processes for producing the collagen/HA composite fibers [2]

**Fig. 6** Photographs showing the effects of sol volume fraction in the solution on the structure in the electrospun polymer
SEM Photographs (Fig. 6) showing the effects of sol volume fraction, the structures before and after calcination, the range of structures that can be obtained after calcination [3]. Magnetic ceramic nanofibers are mainly prepared with the sol-gel precursor solutions based on polymer nanofibers such as PVP, PVA, PEO, which are used as the polymer matrices to host inorganic precursors, then through a simple way named electrospinning, magnetic ceramic nanofibers can be obtained by controlling the calcination temperature of the precursor fibers. Other ceramic fibers are fabricated by this method, as shown in Table 1.

| Parameters                  | Ceramic fibers | Precursor solutions | Polymer matrices | Solvent                | Calcination temperature |
|-----------------------------|----------------|---------------------|------------------|------------------------|--------------------------|
| TiO$_2$ fibers[4]           | titanium tetraisopropoxide | PVP                | 2-propanol        | 500°C                  |
| Al$_2$O$_3$ fibers[5]       | aluminum acetate        | PVP                | absolute ethanol  | 1200°C                 |
| CeO$_2$–ZrO$_2$ fibers[6]   | Ce(NO$_3$)$_3$·6H$_2$O and ZrOCl$_2$·8H$_2$O | PVP                | alcohol and water | 1000°C                 |
| In$_2$O$_3$ fibers[7]       | In(NO$_3$)$_3$·4 1/2H$_2$O | PVP                | alcohol           | 800°C                  |
| SnO$_2$ fibers              | SnCl$_2$·5H$_2$O        | PVA                | water             | 750°C                  |

2.2. Ceramic nanofibers be fabricated by direct electro-spinning of conventional sol-gel precursor solutions.

The sol–gel precursor can be tetraethyl orthosilicate (TEOS) and titanium (IV) isopropoxide (TiP). Tetraethyl-orthosilicate Si (OC$_2$H$_5$)$_4$ (TEOS), aluminum di-sec-butoxide ethylacetoacetate etc., in order to obtain SiO$_2$/TiO$_2$ composite fibers, SiO$_2$ fibers–Al$_2$O$_3$ fibers, etc. The main process is shown in Fig. 7.

Submicron scale composite fibers of SiO$_2$/TiO$_2$ with various compositions have been prepared by electrospinning a sol–gel precursor of tetraethyl orthosilicate (TEOS) and titanium (IV) isopropoxide (TiP), followed by calcination. Nanostructured SiO$_2$/TiO$_2$ materials have widely been used as anti-reflecting coating, optical-chemical sensors, glasses, supporting materials, and catalysts because of their superior optical and thermal properties as well as chemical durability. Silica fibers can potentially be used as filters and media for catalysts mobilization.
3. Conclusion

In summary, the method of preparing ceramic nanofibers is as shown in Fig. 8 above. Many different methods can be used to prepare this material according to the application field of the material, but several factors should be paid attention to, such as sol viscosity, stabilization of fibrous solution and calcination temperature.

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