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Morphology variation of nanofibers from controlling matter diffusion in calcination processes

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HIGHLIGHTS

- Metal oxides with verious morphologies were fabricated via controlling calcination process.
- Heating rate plays important role for the morphologies.
- Hollow fibers were created via a two-step calcination which controlling matter diffusion.

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ABSTRACT

One dimensional metal oxide materials with verious morphologies were successfully fabricated via a single nozzle electrospinning method and subsequent calcination process. The matter diffusion in calcination process plays an important role for the morphology. With low heating rate of 1 or 5 °C/min, SnO_2 samples tended to form solid nanofibers consisted of small nanoparticles with uniform size. Using same conditions, CeO_2 samples preferred to form belt morphology while Co_3O_4 tended to form a chain. This is ascribed to the difference of diffusion of these metal oxides during calcination. To fabricate hollow fibers, a two-step calcination route was used. A heating rate of 1 °C/min was used at less than 300 °C to create dense solid fiber. Low heating rate at low temperature could be beneficial to enhancing Kirkendall effect remarkably. A heating rate of 15 °C/min was used during temperature rising from 300 to 550 °C, in which the quick decomposition of poly(vinylpyrrolidone) occurred. Such quick decomposition resulted in the fast diffusion of metal oxides to the surface layer of fibers. SnO_2, CeO_2, and SnO_2/CeO_2 hollow fibers were successfully fabricated through the two-step calcination. In addition, SnO_2 and Co_3O_4 tended to form on SnO_2/CeO_2 and Co_3O_4/CeO_2 composite structure during calcination process.

1. Introduction

In recent years, one dimensional (1D) nanostructures, including nanofibers [1], nanowires [2], nanobelts [3], and nanotubes [4], have attracted intensive interest in both fundamental and industrial research due to their amazing properties, such as low density, high surface-to-volume ratios, good structural stability, and the directional mobility of charge carriers, resulting their wide applications in catalyst [5], gas sensors [6], energy storage [7], drug carriers [8], and energy conversion [9]. Numbers of synthetic approaches for 1D nanostructures have involved template-assisted electrodeposition [10], solvothermal synthesis [11], anodic oxidation [12], and self-assembly [13]. However, these methods often suffer from sacrificial templates, surfactant, and tedious procedures. Recently, electrospinning has been extensively regarded as a flexible platform for 1D nanostructure preparation due to its noticeable advantages over these methods, including cost-effectiveness, high-throughput, and easy fabrication in previous research [14].

Recent works have been illustrated that not only solid but also hollow fibers can be prepared by electrospinning. In a conventional concept, the strategy for the hollow structural materials prepared by electrospinning are classified into three major methods, coaxial electrospinning [15–17], fiber templates [18–21], and single nozzle co-electrospinning [22,23]. However, these methods exist many difficulties in their preparation process. Coaxial electrospinning process needs two different spinning solutions to prepare core/shell composite fibers by a special spinneret with two coaxial

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capillaries. After the removal of core section by calcination, hollow structure could be obtained. However, many electrospinning parameters including the rate of core and shell solution and viscosity must be strictly controlled. In addition, the hollow fibers prepared by coaxial electrospinning usually have large diameter and irregular morphologies. Fiber template method involves multiple sections, like preparation of fiber templates, coating on the fiber with special precursors, and etching steps, resulting in a rather complex process. The mechanism of single nozzle co-electrospinning method is phase separation. Thus, it is necessary to choose two different polymers with specific properties, including interfacial tension, viscosity, and elasticity. Apart from these, R. Jose et al. showed the fabrication of solid and hollow SnO_2 fibers via controlling the concentration of the precursor spinning solution [24,25]. Moreover, the strategies mentioned above were focused on the design of the as-spun fibers rather than calcination process.

To the best our knowledge, no one has reported a detailed study on the effect of heating rate in calcination process during single-spinneret electrospinning as well as the possible mechanism. Motivated by the above concerns, we proposed a two-step calcination route, a method of two temperature rising processes with different heating rates during calcination, to prepare hollow nanostructures. The heating rate-dependent experiments were carried out to monitor the morphology evolution process of the various metal oxides, including SnO_2, CeO_2, and Co_3O_4. A possible formation mechanism of hollow fibers prepared by two-step calcination is proposed.

2. Experimental

2.1. Materials

N,*N*-dimethylformamide (DMF) was taken from Tianjin Chemical Reagent Institute. Poly(vinylpyrrolidone) (PVP; Mw ≈ 1,300,000) was purchased from Aladdin Reagent Company. $SnCl_2 \cdot 2H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Company. All chemicals were analytical grade reagents and they were used directly without any further purification.

2.2. Preparation of 1D metal oxide nanostructures via electrospinning and subsequent calcination

The preparation of spinning precursor solutions was carried out by a typical single-spinneret electrospinning method, as shown in Fig. 1(a). A certain quantity of inorganic salts (e.g. $SnCl_2 \cdot 2H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$) and 6 mL of DMF were mixed together and stirred vigorously for 3 h at room temperature. Then 1 g of PVP was added to the mixture and the mixture was allowed to stir for 12 h. After that, a viscous mixture of inorganic salts and PVP was obtained. This solution was used to prepare 1D nanostructures.

Each solution was filled into a 5 mL syringe equipped with a stainless steel needle having an inner diameter of 0.8 mm. The precursor fibers were prepared by electrospinning with a direct current (DC) voltage of 15 kV applied on the needle. A flat aluminum foil was used as the collector, which was placed 15 cm below the needle. The optimal feed rate was chosen at 7 μL/min. During electrospinning process, the as-spun fibers were obtained on the collector continuously. Then the as-spun $SnCl_2$/PVP fibers were calcined at 550 °C for 3 h in air with heating rates of 1 °C/min and 5 °C/min, named as samples "Sn-1" and "Sn-5", respectively. In addition, some of the as-spun fibers were calcined by a two-step calcination method. For example, as-spun $SnCl_2$/PVP, $Ce(NO_3)_3$/PVP and $SnCl_2/Ce(NO_3)_3$/PVP fibers were firstly calcined at 300 °C with a heating rate of 1 °C/min from room temperature. Then the samples continued to be calcined at 550 °C for 3 h with a heating rate of 15 °C/min. Finally, SnO_2 nanotubes, CeO_2 nanotubes and SnO_2/CeO_2 composite nanostructures were obtained, named as sample "Sn-two", "Ce-two" and "Sn–Ce-two", respectively. After the fibers were naturally cooled down to room temperature, 1D metal oxide nanostructures were obtained. Table 1 illustrates the preparation conditions and properties of the samples.

2.3. Characterization

The morphology observation of samples was carried out using a field emission scanning electron microscope (FESEM, QUANTA 250 FEG, FEI, America). The transmission electron microscopy (TEM) observation and selected area electron diffraction (SAED) pattern of samples were taken using a JEM-2010 electron microscope. The absorption spectra of samples were recorded using a conventional spectrometer (Hitachi U-4100) at room temperature with a quartz cell. The crystal structures and phase composition of samples were identified using an X-Ray Diffraction (XRD) meter (Bruker D8-Advance, Germany).

3. Results and discussion

Fig. 1(a) shows the schematic diagram of electrospinning apparatus for preparing as-spun fibers. There are a variety of parameters that influence the morphology and diameter of the electrospun fibers, including the operational conditions, intrinsic properties of the solution, and environmental parameters. As shown in Fig. 1(b), $SnCl_2$/PVP fibers were obtained on the collector by this single-spinneret electrospinning method with appropriate parameters. The as-spun fibers were rather smooth on the surface due to the amorphous nature with a diameter ranging from 500 to 600 nm. And the fibers were distributed randomly but uniformly resulting from the bending instability of the spinning jet [26]. It is not hard to find that the general feature of the as-spun fibers was identical regardless of the different precursors in the spinning

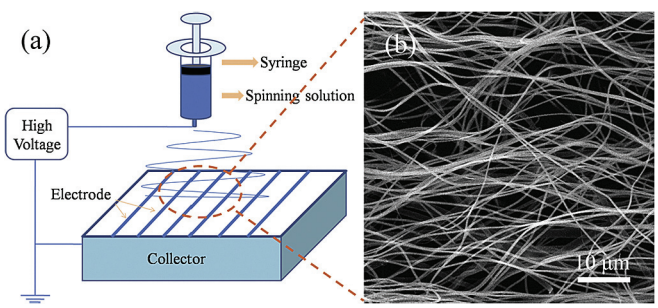

Fig. 1. (a) Schematic diagram of electrospinning apparatus. (b) SEM image of $SnCl_2$/PVP as-spun fibers.

Table 1
Preparation conditions of samples.

Sample	Heating rate (°C/min)	Morphology	Diameter/width (nm)
Sn-1	1	solid fibers	220
Sn-5	5	hollow fibers	550
Sn-two	two-step calcination	hollow fibers	480
Ce-1	1	belts	1000
Ce-5	5	belts	450
Ce-two	two-step calcination	hollow fibers	370
Co-5	5	chains	190
Co-two	two-step calcination	chains	150
Sn–Ce-two	two-step calcination	hollow fibers	320
Co–Ce-two	two-step calcination	solid fibers	470

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