Tin Oxide Nanofiber and 3D Sponge Structure by Blow Spinning

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Abstract. \textit{SnO}_2 nanofibers show wide applications in many advancing areas, such as gas sensors and semiconductors. The traditional methods of fabricating \textit{SnO}_2 nanofibers include electrospinning, hydrothermal synthesis etc. In this work, \textit{SnO}_2 nanofibers were prepared by blow spinning, which is a convenient and high-efficiency method. Meanwhile, a 3D sponge nanofiber network can be produced by accumulating fibers in a novel collector. While traditional \textit{SnO}_2 nanofibers obtained from previous work show high brittleness, the \textit{SnO}_2 nanofiber sponge has good resilience against external compression and can recover to its original shape.

1. Introduction

One-dimensional (1D) materials have been synthesized and applied to various applications, such as biomaterials, energy storage devices, environment filters, sensors and catalysis [1-4]. Tin Oxide (\textit{SnO}_2) nanofiber is an important semiconductive material which attracted the interest of many research areas. \textit{SnO}_2 nanofibers and its composite structures exhibit excellent properties such as gas sensors since the electrical conductivity change dramatically upon contacting corresponding reactive gas [5]. And \textit{SnO}_2 nanofiber can also be applied in UV detection, biomedical devices and electrodes [6-8]. Recently, there are some methods to fabricate \textit{SnO}_2 nanofibers. Hydrothermal synthesis is a typical method to produce \textit{SnO}_2 nanowire, as well as self-catalysis growth method which can get \textit{SnO}_2 nanowire with high purity through evaporation of \textit{SnO} and \textit{Sn} powders [9,10]. Electrospinning is a widely studied method to fabricate nanofibers, due to its convenient preparation process and high aspect ratio. Moreover, electrospinning can fabricate various kinds of materials by different sol-gel hybrid, such as polymer, ceramic and metal [11]. So, the research of \textit{SnO}_2 nanofiber in different area has been obtaining huge advantages by electrospinning. However, the high voltage requirement and low efficiency are two key problems to introduce electrospinning into industry [12]. Blow spinning is an excellent method to prepare nanofibers [13]. It has the advantage of electrospinning, such as can get large aspect ratio, uniform nanofibers and can operat under room temperature. In addition, it’s safer than electrospinning due to the absence of high voltage. Blowspinning has a much higher efficiency compared with electrospinning. It’s also feasible to prepare 3D nanofiber sponge. Recently, blow spinning got wide attention of many research groups. Titanium oxide, zirconium oxide and barium titanate nanofiber sponges with high resilience have been fabricated by blowspinning [14].
Polyacrylonitrile (PAN) nanofiber window screen were fabricated to filter particle matters [15]. Blowspun Ag and ITO nanofiber films show low sheet resistance yet high transparency [16,17]. In this study, SnO$_2$ nanofiber was prepared via blow spinning. Meanwhile, and resilient 3D SnO$_2$ nanofiber sponge can be collected by a porous cage. The 3D porous structures expressed promising potential applications in different areas, such as SiO$_2$ aerogel in thermal insulation application, carbon cellular aerogel for oil absorption, biological materials sponge for wound healing, ceramic porous filter in PM$_{2.5}$ filtration and nitrogen oxide gas catalysis [18-20]. The wide applications of the 3D sponge resulting from their ultralight density, highly porous and large surface area. However, brittleness and poor mechanical properties usually limit the application and service life of these 3D structure. Hence, many researches focus on increasing the mechanical property, realizing the resilience both at room temperature and high temperature of these foams [21,22]. Ceramic 3D structures have good chemical stability over a large temperature range, but they are usually limited by their brittle property. Some new generations of ceramic forms, like double-negative-index ceramic and fire-resistant ceramic nanofibrous aerogels, realized the elastic property [23, 24]. Here, the SnO$_2$ nanofiber sponge fabricated by blow spinning also exhibited excellent resilience. We think that blow spinning, as a convenient and efficient method, will greatly promote the productivity of SnO$_2$ nanofibers and the resilient SnO$_2$ nanofiber 3D structure which has potential applications in wearable devices.

2. Experiment and Characterization

The preparation of SnO$_2$ nanofiber is a typical blow spinning progress. The precursor solution is similar with the one using in electrospinning. 1.4 g SnCl$_2$·5H$_2$O and 0.6 g PVB were added in the 8 g ethanol. After mixing about 6 h at room temperature, the solution was transferred into a 1 mL injector. During the blow spinning progress, the speed of injection rate was 3 mL/h, the size of the needle was 30 G (0.16 mm inside dimension), the rate of airflow was ~10 m/s, and the distance of the collector was 10 cm. After 10 min, we can get the SnCl$_2$/PVB nanofiber sponge as shown in Figure 1b. The SnCl$_2$/PVB nanofiber sponge was transferred into the muffle immediately. It was heating at 500 °C in air for 100 min with 2 °C/min heating rate. Finally, the SnO$_2$ nanofiber sponge was prepared.

The SEM image of PAN, PEO and SnO$_2$ nanofibers were obtained from LEO-1530, Zeiss. TEM images of SnO$_2$ nanofiber were measured by JEOL-2010 with the voltage of 120 kV. The XRD pattern was recorded by D/max-2500 Rigaku with Cu Kα radiation, and the 2θ ranging from 20° to 80°. The nitrogen physisorption isotherms and different pore volume as a function of pore width of the nanofiber sponge was tested by Tristar II 3020 Micromeritics at a temperature of 77 K.

3. Result and Discussion

Similar with the process of electrospinning, the basic precursor solution of blow spinning is mixed with polymer and solvent. The schematic of blow spinning is shown in Figure 1a. The device of blow spinning includes a concentric needle that consists of two parts: the inner and the outer nozzle. The precursor solution was pumped through the inner nozzle, while compressed gas was blown through the outer nozzle. At the exit of concentric needles, the airflow stretches the precursor solution into fibers. With the stretch distance increasing and solvent evaporating, the nanofiber was collected by the porous cage collector. Figure 1b 1c and 1d show the SEM images of different kinds of blowspun nanofibers. The diameter of these nanofibers can be controlled by the polymer concentration of precursor solution, collection distance, the speed of airflow and the size of needles. As shown in Figure 1b-d, the diameter of PAN nanofiber, PEO nanofiber, and ceramic nanofiber were around 800 nm, 90 nm and 100 nm respectively. PAN was dissolved by the organic solvent dimethyl formamide (DMF), polyethylene oxide (PEO) was dissolved in water, and the precursor solution of ceramic nanofiber contains different ionic salt, which reflect blow spinning can prepare lots of different systems’ nanofiber. Moreover, the solvent of precursor solution is easier to evaporate in the process of blow spinning than electrospinning because of the high-speed airflow increases the speed of evaporation. And blow spinning is also feasible for high-concentration ionic salt solution without the requirement of high voltage.
Figure 1. (a) The schematic of blow spinning. (b-d) The SEM images of PAN nanofiber, PEO nanofiber and ceramic nanofiber which were fabricated by blow spinning.

Figure 2. (a-b) The photograph of precursor nanofiber sponge and SnO₂ nanofiber sponge. (c) The SEM image of precursor nanofiber. (d) The XRD result of SnO₂ nanofiber.

Figure 2a shows the original precursor SnO₂ nanofiber sponge that was fabricated by blow spinning within 20 minutes. The diameter of the SnCl₄/PVB nanofiber was about 2 um. From the SEM in Figure 2c, the diameter of the fibers was uniform. After high temperature sintering in air, the SnCl₄/PVB nanofiber became SnO₂ nanofiber. The sponge volume and diameter of the fiber underwent a shrinkage. As shown in Figure 2b, the volume of SnO₂ nanofiber sponge is around 1 cm³ and the average diameter of SnO₂ nanofiber is 500 nm (Figure 3b). The X-ray diffraction (XRD) pattern of SnO₂ was displayed in Figure 2d. From the diffraction peaks of XRD, the SnO₂ was rutile tetragonal crystalline phase. We cut a small piece of SnO₂ nanofiber sponge and observed it in the scanning electron microscope (SEM). The SEM image exhibited that the distribution of SnO₂ nanofibers and pores were uniform (Figure 3a). As shown in Figure 3c, the surface of the SnO₂ nanofiber was rough and porous which means it had large specific surface area. Figure 4a-c are the transmission electron microscope (TEM) images. From Figure 4b, it also exhibited that the surface of
the nanofiber was rough. The grain size of the SnO\textsubscript{2} nanofiber was \(\sim 10\) nm and the interplanar spacing of (110) is 0.335 nm. The high-resolution TEM (HRTEM) image is displayed in Figure 4c, and the upper inset is the selected area electron diffraction (SAED) pattern, which exhibited the SnO\textsubscript{2} nanofiber is polycrystalline.

![Figure 3](image1.png)

Figure 3. (a) The SEM image of SnO\textsubscript{2} nanofiber sponge. (b) The SEM image of SnO\textsubscript{2} nanofiber. (c) The SEM image of the surface of SnO\textsubscript{2} nanofiber.

![Figure 4](image2.png)

Figure 4. (a-c) The different magnification TEM images of SnO\textsubscript{2} nanofiber (upper inset of figure c is SAED pattern of SnO\textsubscript{2} nanofiber)

To further study the pore width of SnO\textsubscript{2} nanofiber sponge, \(\text{N}_2\) adsorption-desorption isothermal was tested at 77 K. As shown in Figure 5a, the relevant curve could be categorized as type IV with the H1 hysteresis loop [25]. The different pore volume with pore size of SnO\textsubscript{2} nanofiber sponge curve was displayed in Figure 5b. The pore size mainly distributed around 10 \(\mu\)m. The SnO\textsubscript{2} nanofiber sponge had great resilience as other ceramic nanofiber sponge that we reported before. The force-displacement curve of Figure 5c exhibited the resilient of SnO\textsubscript{2} nanofiber sponge. After compressing for 5 cycles and 10 cycles, it can also mainly recover to the original height.

![Figure 5](image3.png)

Figure 5. (a) Nitrogen physisorption isotherms of SnO\textsubscript{2} nanofiber. (b) The different pore volume as a function of pore width. (c) The force-displacement curve of SnO\textsubscript{2} nanofiber sponge.

4. **Summary**

In this study, SnO\textsubscript{2} nanofiber with the average diameter of 500 nm was fabricated by blow spinning. In the mean time, the novel, porous and resilient 3D SnO\textsubscript{2} nanofiber sponge was formed, with pore size around 10 \(\mu\)m. Blow spinning is a low-cost and highly efficient method to fabricate SnO\textsubscript{2} nanofibers that could promote the development of SnO\textsubscript{2} nanofiber industry. The SnO\textsubscript{2} nanofiber sponge structure could take more potential applications in various areas.
Acknowledgement
This work was supported by the National Basic Research of China (Grant Nos. 2015CB932500), the National Natural Science Foundation of China (NSFC) (Grant No. 51661135025, 51522207).

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