The manufacture and characteristics analysis of electrospun tungsten trioxide nanofibers

Te-Hua Fang*, Shih-Hong Yang*, Yu-Jen Hsiao* and Deng-Maw Lu*

*Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan, ROC; National Nano Device Laboratories; National Applied Research Laboratories, Tainan, Taiwan, ROC; Department of Mechanical Engineering, Southern Taiwan University of Science and Technology, Tainan, Taiwan, ROC

ABSTRACT
In this study, the effects of calcination temperature on the characteristics of tungsten trioxide (WO3) nanofibers over time were explored. The objective being to observe the effects of calcination temperature and time of exposure on nanofibers when the voltage, work flow rate, and the pinhead used in the process were all fixed. The results showed that when the calcination temperature was increased to 550 °C, fiber structure was damaged. The nanofibers showed the selectivity about 9% at 360 ppm of ethanol gas. The response of ethanol will increase when the concentration increase.

KEYWORDS
electrospinning; calcination; gas sensor; nanofiber; WO3

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1. Introduction
Over the past few years, many studies have been made of the one-dimensional structure of WO3. This structure can be usefully applied in field emission, gas-sensing, electrochromism, and photoelectrochemistry.[1] WO3 also has a wide energy gap, 2.6–3.6 eV, very useful in the photoelectric component field.[2]

Many methods have been used to produce WO3 nanofiber or nanocomposite material, including thermal oxidation,[3] templates,[4] chemical vapor deposition,[5] atomic layer deposition,[6] sol–gel dipcoating,[7] water heating,[8] electrostatic spraying,[9] dielectric-electrical discharge machining,[10] and electrospinning.[11] Of these, the electrospinning technique, which uses an electric field to spin macromolecules from a solution into a fiber, is simple and easy. In this process, macromolecules are used as a thickening agent and play an important support role. An electric field is all that is needed for spinning and a high temperature is not required.

The positive electrode of the electrospinning device is comprised of the pin head and the solution, the negative, or ground side, is the collection plate. As the electric field, which is developed at the pin head and the drop of working fluid, increases in strength, the drop is extended towards the collection plate to form what is known as a Taylor cone [12] which develops when the accumulated electrical charge overcomes the surface tension of the liquid.[13,14] As the cone moves towards the collection plate, its constant whipping causes the formation of a solid fiber. In practice, attention has to be paid to many parameters, which can affect the surface form and diameter, to achieve superior quality fibers. Doshi and Reneker [15] proposed that conductivity, viscosity, and surface tension all affect the fiber spinning process. Control parameters include the work flow rate, working distance, voltage, pin head shape, and diameter. Environmental parameters include temperature and humidity.

In this study, we explored the effect of calcination temperature on the characteristics of electrospin WO3 nanofibers. One-dimensional nanostructure fibers have a very high aspect ratio and can be used as sensory components for gas and humidity. Electrospinning was used to produce all the WO3 nanofibers used as an ethanol gas sensor in this study.

2. Experimental section
Tungstic acid (H2WO4) dissolved in hydrogen peroxide (H2O2) was used as the precursor. The tungstic acid was mixed with the solvent at a concentration of 0.5 M and kept at a constant temperature of 50 °C in a water bath with stirring for 1 h to produce a tungstate hydrogen peroxide solution.[16] The macromolecular thickening agent used was polyvinylpyrrolidone (PVP). The molecular weight of PVP is 2.5 g/mol. The PVP was dissolved in ethanol (EtOH) at an 8 wt ratio, and complete solution...
was achieved without the need for prolonged stirring. The tungstate hydrogen peroxide acid solution was slowly poured into the PVP solution with stirring. Stirring was continued for another 2 h until the mixture was completely uniform.

The glass syringe attachment of the electrospinning machine was then filled with the precursor solution. The device used in this experiment was made by Falco Technologies and has a maximum working voltage of 50 kV (see Figure 1). In this experiment, a working voltage of 16 kV was used and the material input rate was 0.36 ml/h. A stainless steel plate was used as a collector and the receiving distance was fixed at 15 cm. Samples of collected fibers were subjected to four different calcination temperatures (400, 450, 500, and 550 °C). The calcination temperature was increased at a rate of 2.5 °C/min under atmospheric conditions. After calcination, the oven was switched off and the samples were left inside to cool gradually. Samples were calcinated for 1 and 2 h at the four different maximum temperatures.

Square pieces of Indium tin oxide (ITO) conductive substrate (3 × 3 × 0.1 cm) were used to collect and analyze the fibers used in these experiments. To ensure that the cut pieces of substrate were perfectly free of all contaminants a very thorough cleaning process was used:

1. Each substrate square was placed in a glass dish, covered completely with acetone, and sonicated for 10 min.
2. The substrate was then dried in a stream of nitrogen before being placed in pure deionized water and sonicated for another 10 min.
3. The process was repeated using isopropyl alcohol.
4. And then more pure deionized (DI) water.
5. After a final drying with nitrogen the substrate was examined to ensure it was perfectly clean. If necessary the entire cleaning process was repeated.

Figure 1. (a) The electrospinning machine and (b) a simplified schematic.

Figure 2. The TGA curve.

After final cleaning the substrate was dried for 1 h at 95 °C to remove any remaining moisture.

3. Results and discussion

3.1. Structural characterization of electrospun WO₃

There are two steps in the thermogravimetric analysis (TGA) curve as shown in Figure 2. The 7% weight loss seen at the first step was due to water and solvent evaporation between 35 and 250 °C. The second step weight loss of 37% was the result of temperature decomposition of the organic compounds and PVP at 250–300 °C and 300–515 °C, respectively [17].

The SEM images (Hitachi SU8000) in Figure 3 show the shape of fibers that have been calcined for 1 h at temperatures from 400 to 550 °C. As the temperature is increased, the fiber structure begins to show damage. At 400, 450, and 500 °C the fibers maintain their shape. However, at 550 °C a considerable number of broken fibers are evident. This is probably because the macromolecules are
completely removed at the higher calcination temperature. A 2.5 °C/min increase in temperature is also clearly too high, the macromolecules are pulled out too fast [18] and in Figure 3(d) numerous broken structures are evident. It was also shown that PVP is evaporated at more than 515 °C.[17]

The fibers shown in Figure 4 were calcined at 500 °C for one and 2 h. It can be seen that the fiber surface is granular and rough. Image J software was used to measure the diameter of six randomly selected fibers on each image. The average diameter of the fibers shown in Figure 4(a) was 130 nm and those in Figure 4(b) were 100 nm. There is a clear decrease in average diameter with an increase in temperature.

X-ray diffraction (XRD) analysis was used to determine the effects of different calcination temperature and time on the crystallization state of the WO₃ nanofibers. Three main peaks were observed at 23.1°, 23.6°, and 24.4° at 2θ (JCPDS Card No. 83-0950) as shown in Figure 5(a) and (b). In the figure it can be seen that as the calcination temperature increases, the three main WO₃ peaks become more obvious. A comparison of the figures also shows that the other WO₃ peaks in the sample with longer calcination time are also stronger. The data do not show the enhancement of a particular lattice direction but an increase of the crystallization volume fraction.

The absorption and transmission spectra were measured at room temperature using a Hitachi U-4100 UV–vis–NIR spectrophotometer. The UV/visible absorption spectra (250–800 nm) of specimens subjected to 1 h of calcination, using air as a baseline, are shown in Figure 6(a). According to the TGA curve, PVP is not completely

Figure 3. SEM images of fibers: (a) 400 °C, (b) 450 °C, (c) 500 °C, and (d) 550 °C.

Figure 4. SEM images of fibers: (a) 500 °C for 1 h and (b) 500 °C for 2 h.
removed below 550 °C so that sample absorption wavelength starts at about 330 nm. Figure 6(b) shows the calculated optical energy gap values of WO₃ nanofibers at temperatures of 400, 450, 500, and 550 °C were 3.80, 3.70, 3.77, and 3.65 eV, respectively. However, this is still some distance away from the wide energy gap proposed in some other investigations. This discrepancy may be the result of using PVP to facilitate the electrospinning process. The energy gap is given by [19]

\[
\alpha = \frac{C(\hbar \nu - E_g)^{1/2}}{\hbar \nu}
\]

where \(\alpha\) is the absorption coefficient, \(C\) is a constant, \(\hbar \nu\) is the photon energy and \(E_g\) is the band gap.

### 3.2. Transmission spectra and I–V curve analysis

Figure 7 shows the transmission spectra (250–800 nm) for samples calcinated at different temperatures for 1 h. Air was used as the baseline. Comparison of absorption spectra shows that the absorption was at 400 nm, and as transmission approached a similar wavelength it began to decrease, showing that absorption and transmission were in correspondence.
Figure 8 show that the measured $I$–$V$ curves where the fibers were in ohm contact. In this study silver was used as the anode and the ITO substrate was used as the cathode. The input voltage was from $-5$ to $5$ V. Measurements were made at $0.2$ V intervals and the clamp down current was $1.05$ A. Note that the Ohmic resistance rose with temperature, indicating that the conductivity of WO$_3$ decreases with an increase of calcination temperature. This linear behavior revealed good Ohmic contact between the nanofibers and the electrodes. This is very important and ensures that observed sensing is a reflection of the behavior of the fibers and is not affected by the contact between the fibers and the electrodes.[20]

### 3.3. Sensing characteristics analysis

A sample calcinated at $500$ °C was used as an ethanol gas sensor. The response of a gas sensor is calculated by

$$R = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{air}}} \times 100\%$$  \hspace{1cm} (2)

where $R_{\text{air}}$ is the resistance in air and $R_{\text{gas}}$ is the resistance in an alcohol atmosphere, and $R$ is the gas response. [21] Figure 9(a) shows the variation of sensitivity of WO$_3$ nanofibers for different gas concentrations at operation temperature $250$ °C. The nanofibers showed the selectivity about $9\%$ at $360$ ppm of ethanol gas. The response/recovery time is an important parameter used for characterizing sensor as shown in Figure 9(b). It is defined as the time required to reach $90\%$ of the final change in voltage or resistance, when the gas is turned on or off. Figure 9(b) shows the response and recovery time was $\sim 5$ and $\sim 20$ s, respectively.
4. Conclusions

The results of this study showed that an increase in temperature and time reduces the diameter of the fibers. However, a rapid rise to high temperature can damage the structure and cause it to fragment. The XRD analysis also shows that different time and temperatures make the WO$_3$ peaks more obvious. This is because WO$_3$ changes phase with a change of temperature. The UV and visible spectra showed that the WO$_3$ fibers produced in this study absorbed at a wavelength of 400 nm, making them useful for UV detection. Finally, electrical property measurements show that the fibers are n-type semiconductors. This means that the use of electrospinning to apply a layer of p-type semiconductor makes them into PN junctions, which broadens their scope of application.

Author contributions

TH and SH carried out the synthesis and characterization of the samples, analyzed the results, and wrote the first draft of the manuscript. YJ participated in the design, preparation, and discussion of this study. DM contributed ideas for the growth of the samples and revised the manuscript. All authors read and approved the final manuscript.

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Disclosure statement

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ORCID

Te-Hua Fang http://orcid.org/0000-0002-7032-3193

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