ELECTROSPUN NANOFIBRE BASED CHEMICAL SENSOR: ELECTRICAL CHARACTERIZATION

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INTRODUCTION

Nanofibre-based gas sensors give the advantage of fast response times and high sensitivity due to the higher surface area to volume ratio compared to thin film sensors. Applications for such biomedical and chemical sensors include the detection of volatile organic compounds, exposure to which can cause serious health effects. In this work, we have investigated both conducting polymer and semiconductor metal oxide nanofibres.

Polyaniline (PANi) is a conductive polymer that is widely used for its simple reversible doping/dedoping chemistry, stable electrical conduction mechanism, and high environmental stability [1]. It has been studied as sensing material for a variety of toxic gases such as CO, NO_2, and NH_3 [1]. However PANi is insoluble in many common organic solvents making it challenging for processing. By adding camphor sulfonic acid (CSA) the polymer is not only doped (i.e., in its conductive state) but it is possible as well to dissolve it in chloroform. PANi behaves like a p-doped semiconductor. In conducting polymer chemiresistors, the electrical resistance of the polymer is modified due to adsorption of chemical species, affecting the mobility of the charge carriers. The presence of electron donating gases reduces the charge carrier concentration, leading to a decrease in conductivity [2]. TiO_2 is a semiconducting metal oxide and is widely used in sensing applications and also recognized as one of the most promising photocatalytic materials [3,4]. Adsorbed oxygen on the surface of the nanofibre will decrease the carrier concentration and mobility and therefore render the nanofibre less conductive. Any species interacting with the adsorbed oxygen will therefore cause a resistance change.

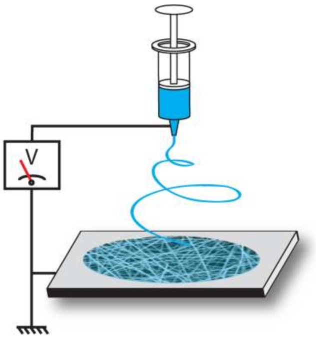

Fig. 1: Electrospinning of a polymer solution. An electric field is applied between a capillary tip and a collection screen. Nanofibres are only formed above a certain voltage threshold.

Electrostatic fabrication or electrospinning is a simple way of fabricating nanofibres from a polymer solution [3]. The stretching forces induced on the jet by the electric field and the rapid evaporation of the solvent causes the formation of solid nanofibres during the passage from the tip to the collection screen (Fig. 1).

MATERIALS AND METHODS

Fabrication of PANi/PEO nanofibres

The PANi/PEO polymer blend solution was prepared as follows: 100 mg PANi (emeraldine base, Sigma Aldrich) was doped with 129 mg of CSA and dissolved in 10 mL $CHCl_3$ for a period of 5h. The resulting deep green solution was then filtered (2 µm filter pore size) and 3.2 g of polyethylene oxide (PEO, MW=2’000’000) was added. After 4h of stirring the solution was filtered again (0.45 µm pore size) and electrospun onto prefabricated interdigitated electrodes (Au, 40 µm spacing) for characterization of nanofibre mats. Isolated fibers were captured on precleaned glass substrates (piranha solution). The electrodes were subsequently patterned using a shadow mask (Au, 150 nm). The distance between the stainless steel tip (20 gauge) and the ground collector (Al foil) was 20 cm and the applied voltage was 12.4 kV.

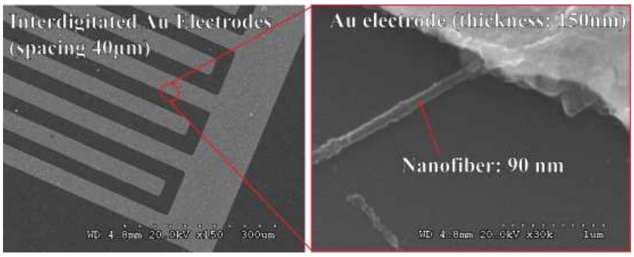

Fig. 2: SEM images of a) Electrospun nanofibre on top of an interdigitated Au electrode with 40 µm spacing b) Single nanofibre under a 150-nm Au layer.

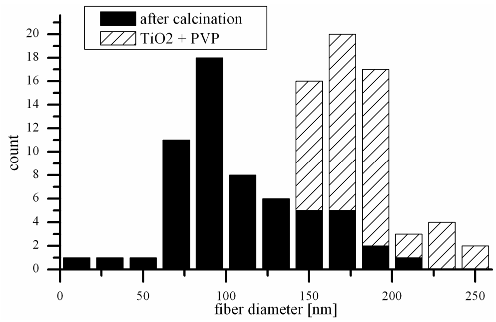

Fig. 3: Diameter of nanofibres decreases from 160 nm to 90 nm after calcination.

Fabrication of TiO_2 nanofibres

The fabrication of TiO_2 nanofibres includes the electrospinning of a polymer solution mixed with a sol-gel precursor. 0.7 g of polyvinyl pyrrolidone (PVP) was mixed with 7.5 mL of ethanol. In a separate beaker 1.5 g of tetrabutyl titanate ($Ti(OC_4H_9)_4$, >95%) was mixed with 3 mL of anhydrous ethanol and 3 mL acetic acid (>95%) to stabilize the solution and control the hydrolysis reaction. Both solutions were stirred for 10 min before mixed together and stirred for another 30 min after the mixing. The solution was then loaded into the eletrospinning apparatus. The distance between the stainless steel tip (gauge 20) and the ground collector (Al foil) was 10 cm and the applied voltage was 8.2 kV. The gel fibers were then calcinated at 500 °C for 2h to produce TiO_2 fibres.

The crystalline structure of the TiO_2 fibres was characterized by using an X-ray diffractometer (XRD). A scanning electron microscope (Hitachi, Japan, S-3000N SEM) was used to observe the morphology as well as measure the fibre diameter. For electrical characterization a Solartron Impedance Analyzer (1260) and sourcemeter from Keithley Instruments (6430) were used.

RESULTS

Fig. 2a shows an SEM image of nanofibres on interdigitated electrodes. Fig. 2b shows one single TiO_2 nanofibre embedded in an Au layer. The nanofibres have a length of several mm and an average diameter of 90 nm after calcination. Figure 3 shows the change in diameter of TiO_2 fibres. PANi/PEO fibres do not undergo calcination. Their average diameter is 540 nm.

The X-ray diffraction pattern of the TiO_2 nanofibres is shown in Fig. 4. The bragg peak near 25.28° is usually taken as the diffraction of the (101) plane of the anatase phase. The other two phases (rutile and brookite) are not or only very little present.

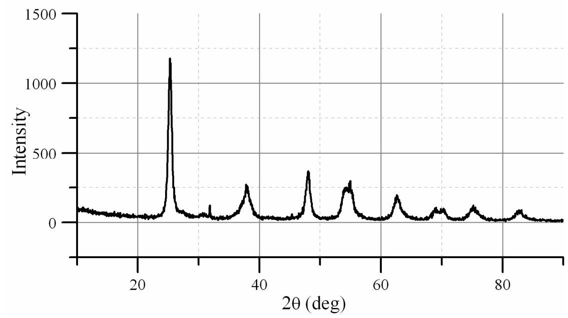

Fig. 4: XRD pattern of TiO_2 nanofibres. The peak at $2\theta = 25.28°$ is often taken as the characteristic peak of anatase.

The fabricated sensor shows extremely high sensitivity. Figure 5 shows two different I-V curves, one in air and one with ~30000 ppm Ethanol in air at room temperature. For a voltage sweep between 5 and 40 V, the resistance is almost a thousand fold higher without ethanol, because of the increased grain boundary resistance due to oxygen adsorption at the surface. The measurement is shown for 10 nanofibres in parallel.

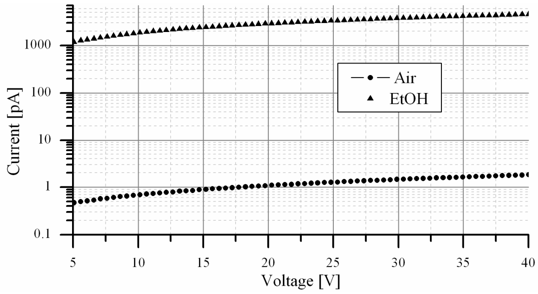

Fig. 5: I-V curve for 10 TiO_2 nanofibres in parallel when exposed to air and ethanol vapour (30000 ppm).

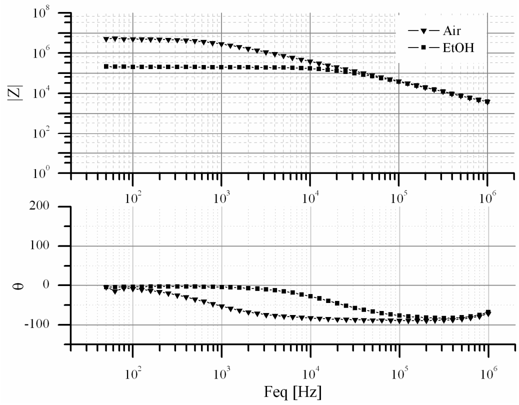

Fig. 6: Impedance spectroscopy curves of TiO_2 nanofibre mats, exposed to air and ethanol (30000 ppm).

The impedance spectroscopy curve in Fig. 6 shows that for low frequencies (< 1kHz) the impedance of TiO_2 fibres is significantly affected by the difference in chemical environment and that for high frequencies the system becomes insensitive. This corresponds to the model where the grain boundary resistance is assumed to be in parallel to the capacitance across the boundary. This resistance is the main parameter affected by the difference in degree of adsorped oxygen (change in interparticle potential barriers)

Figure 7 shows the impedance in a PANi/PEO nanofibre mat as a function of frequency. In many disordered solids including polymers the conductivity increases with frequency [2]. The charge carriers have to hop between two different polymer chains. The higher the PANi concentration relative to PEO the more densely packed the PANi chains are; hence the conductivity increases with higher PANI/PEO ratios [5]. According to hopping models such as the Random Free Energy Barrier (RFEB) [6] model developed by J.C. Dyre the hopping efficiency is enhanced with higher frequencies explaining the decrease in impedance in Fig. 5. This result is an indication that the charge transport is governed by hopping.

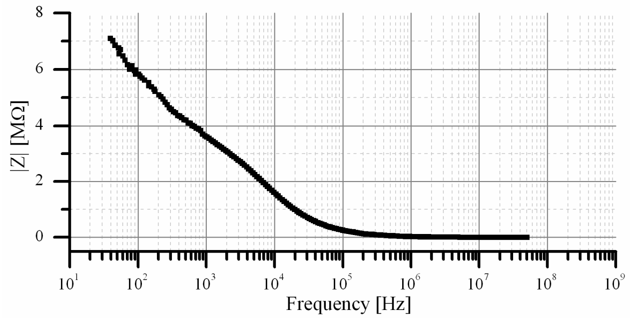

Fig. 7: Impedance spectroscopy curve of PANi/PEO nanofibre mats.

The nanostructured sensor shows a quick response/recovery as shown in Fig. 8. The response becomes stable in less than 5 s when exposed to NH_3 and recovers in less than 15 s. The quick response can be explained by the high surface to volume ratio which facilitates fast mass transfer to and from the region of interaction.

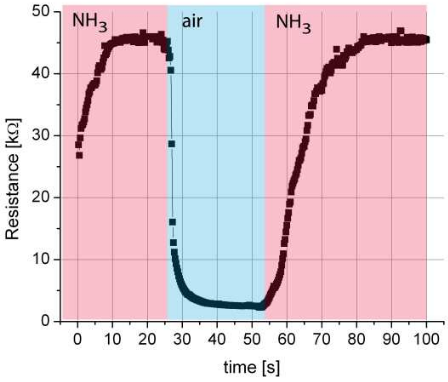

Fig. 8: Resistance change in a nanofibre mat when exposed to NH_3, an electron donating gas. The charge carrier concentration is reduced leading to a decrease in conductivity. The response time is < 5 s.

CONCLUSION

PANi/PEO and TiO_2 nanofibres were successfully fabricated by electrostatic spinning. Impedance measurements were performed on a discrete number of nanofibres as well as on fibre mats. The results show high sensitivity and fast response times.

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