Electrospun TiO_2 nanofibers for gas sensing applications

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ABSTRACT

Nanostructured TiO_2 has attracted much attention for a variety of applications including photocatalysts, electrodes for water photolysis, dye-sensitized solar cells, and gas sensors. In this work we report on TiO_2 fiber mats for use in gas sensors demonstrating exceptionally high sensitivity to NO_2, a toxic gas responsible for acid rain and other air pollution effects, and high sensitivity to H_2, a potentially explosive gas.

Keywords: TiO_2, nanofiber, electrospinning, sensor, NO_2, H_2

1 INTRODUCTION

Recently, significant progress had been made in developing chemical sensing architectures based on various one-dimensional nanostructures by using semiconducting oxides [1-3]. The use of nanofibers in gas sensing provides unique structural features and high surface areas that are expected to promote the sensitivity of the oxide materials to the gaseous components as well as affecting the temperature dependence on sensing [4]. One-dimensional (1D) structures can also provide the lowest dimensionality for effective transport. Therefore they can be useful as building blocks in bottom-up assembly in many areas including nano-electronics and photonics [5]. In particular, increasing worldwide concerns regarding environmental degradation and health hazards have stimulated growing interest in means for detecting and monitoring potentially toxic chemicals.

A commonly applied gas sensing mechanism involves chemically induced resistivity changes in semiconducting materials. For example, the conductivity of TiO_2, a semiconducting oxide, can be modulated by the chemisorbed species on its surface. Chemisorbed oxygen species ($O_2^-{}_{(ads)}$ or $O^-{}_{(ads)}$), accept electrons from the conduction band, thereby inducing an electron depletion layer which in turn results in increased band bending. In polycrystalline semiconductors and, as discussed in this work, in fiber mats, this results in the development of potential barriers between the grains or fibers. As a result, the conductivity of TiO_2 specimens is expected to decrease when exposed to an oxidizing gas and inversely decrease when exposed to a reducing gas. Although the use of one-dimensional nanostructures provides the prospect of high sensitivity and fast detection due to high surface-to-volume ratios, the incorporation of nanowires or nanofibers into sensing device systems is complicated by difficulties associated with selection of appropriate processes and achieving reproducibility. A variety of methods have been suggested for the preparation of nanofiber or nanowire, macroporous structures [6-8]. Among them, electrospinning is one of the most simple, versatile and cost-effective approaches. In a typical process for inorganic fibers, a sol-gel precursor solution with polymeric binder is extruded from the orifice of a needle under a high electric field. The polymeric binders are subsequently easily removed during calcination of the electrospun fibers. Indeed, there are many reports related to the preparation of semiconducting oxide nanofibers by electrospinning. However, to date, there are no reports about electrospun TiO_2 nanofiber sensors.

In this work we report the fabrication of electrospun TiO_2 fibers obtained through the phase separation of TiO_2 gel and poly(vinylacetate) during solidification. We investigate the response of TiO_2 nanofiber gas sensors to a number of gases and demonstrate exceptionally high sensitivity to NO_2, an atmospheric pollutant and H_2, a potentially explosive gas.

2 EXPERIMENTAL

TiO_2 fibers were electrospun from a solution of dimethyl formamide (DMF) (37.5 ml) of 3 g of poly(vinyl acetate) (PVAc, Mw=850000 g/mol), which was synthesized using bulk radical polymerization, 6 g of titanium(IV) propoxide (Aldrich), and 2.4 g of acetic acid as a catalyst. As in typical electrospinning procedures, the precursor solution was loaded into a syringe and connected to a high-voltage power supply. An electric field of 15 kV was applied between the orifice and the ground at a distance of 10 cm. TiO_2 fiber mats (Fig. 1(a)) were directly electrospun on Al_2O_3 substrates prepared with interdigitated Pt electrodes arrays (200 μm Pt fingers spaced 200 μm apart). The as-spun TiO_2 fiber mats were then pressed using preheated plates at 120°C for 10 min. Subsequently, the samples were calcined at 450°C for 30 min in air to remove

the organic constituents and crystallized the TiO_2 fiber mats into the anatase phase. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to examine the phase composition and microstructure of the films, respectively. X-ray diffraction patterns showed anatase phase of TiO_2 structure with (101) and (200) peaks.

The sensitivity of the TiO_2 nanofibers towards H_2 and NO_2 gases was tested at temperatures between 300 and 350ºC. The electrospun TiO_2 nanofibers were mounted on Al_2O_3 sample holders and contacted by Pt wires which were attached to the interdigitated electrode arrays on the Al_2O_3 substrates using silver paste (SPI Silver Paste Plus, SPI Supplies, Chester, PA, USA). The sample holders were then inserted inside a quartz tube placed within a tube furnace (Lindberg/Blue Model M 0.8 KW Tube Furnace). Pt/Pt-Rh (type *S*) thermocouples were used to measure temperature *in-situ*. The resistance was measured under a DC bias voltage of 0.1 V using a 4-channel DC power supply and ammeter (HP 6626A and 4349B, respectively). The TiO_2 nanofiber resistances were measured during exposure to different gas compositions using dry air as a carrier gas and pre-mixed bottled gases of 1000 ppm H_2 in air, 100 ppm NO_2 in air, 1000 ppm CO in air, and 1% CH_4 in air (BOC Gases, Riverton, New Jersey), together with mass flow controllers (MKS 1359C mass flow controllers and an MKS 647A controller). To eliminate interfering effects due to changes in gas flow rate, the gas sensing tests were carried out at a constant flow rate of 200 sccm. The flow rates of the carrier and test gases were varied between 200:0 sccm to 100:100 sccm in order to modulate the concentration of the test gas between 0 to 50% of the gas concentration in the pre-mixed gas bottle. The gas sensitivity of the TiO_2 fiber mats is defined as the ratio R_0/R or R/R_0 for reducing (H_2, CO, CH_4) or oxidizing (NO_2) gases, respectively, where R_0 is the baseline resistance in air and R is the resistance during the test under the presence of the test gas.

3 RESULTS

Figure 1 shows SEM images of electrospun TiO_2 nanofibers. The as-spun PVAc/TiO_2 composite fibers exhibit a range of diameters from 200 to 600 nm. After calcination in air for 30 min to remove the PVAc, TiO_2 fiber mats were observed as shown in Fig. 2 (a). As previously reported in Ref [9], in the initial stages of electrospinning, the TiO_2 sol precursor converts to a TiO_2 gel when the fibers are exposed to moisture. Liquid-liquid phase separation results in TiO_2-rich and PVAc-rich phases due to the concentration instability that arises after solvent evaporation. The separated phases are elongated during the spinning step, resulting in an aligned fibrillar structure in the fiber-axis direction. This unique structure could further enhance surface activity compared to normal TiO_2 nanofibers without fibrillar structure.

Figure 1. SEM image of as-spun TiO_2/PVAc composite fibers fabricated by electrospinning from a DMF solution.

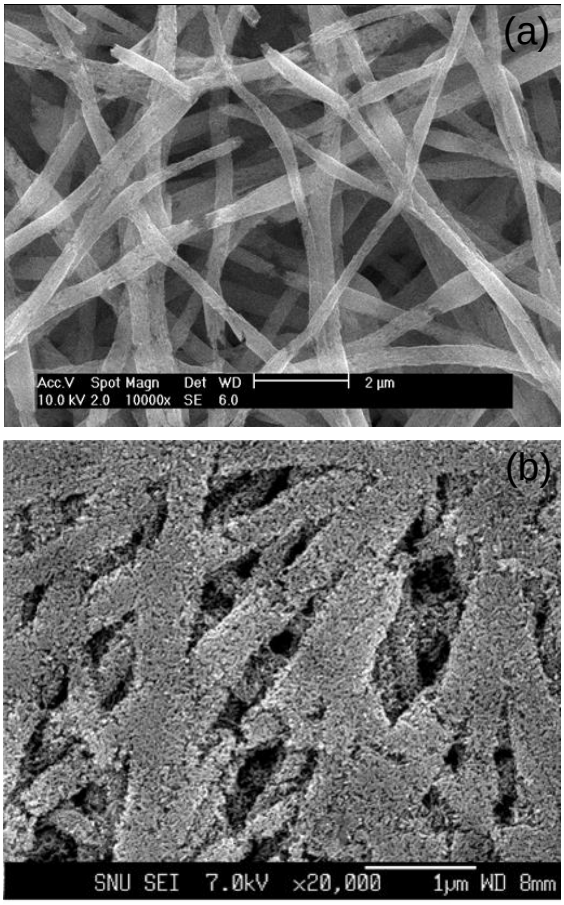

Figure 2. (a) SEM image of TiO_2 fiber mats after 450°C calcination. (b) High resolution SEM image of TiO_2 nanorod structure which was pretreated with mechanical press at 120°C for 10 min before calcination.

The resultant fibers exhibited a bundle structure consisting of ~ 20 nm thick fibrils as shown in Fig. 2 (b). This unique morphology results in an exceptionally high

surface-to-volume ratio, highly advantageous for gas sensors. The specific area measured by BET was 90 m^2/g.

In order to investigate the potential advantages of the enhanced surface activity of the TiO_2 fiber mats and short diffusion lengths associated with the 20nm fibrils, prototype gas sensors, using Pt interdigital electrode structures, were fabricated. The electrical response of several gas sensor prototypes was measured during exposure to traces of reducing (H_2) and oxidizing (NO_2) gases mixed in air, at operating temperatures of 300°C and 350°C. The response was reversible and reasonably fast as shown in Figs. 3 and 4, with response times of the order of min. The resistance decreased upon exposure to reducing gases and increased during exposure to oxidizing gases, typical of n-type semiconductor gas sensors.

These sensor prototypes demonstrated exceptional sensitivity to NO_2, with response magnitudes, R/R_0, as high as ~100 upon exposure to some tens of ppm of NO_2 in air and response to levels as low as 500 ppb (Fig. 3).

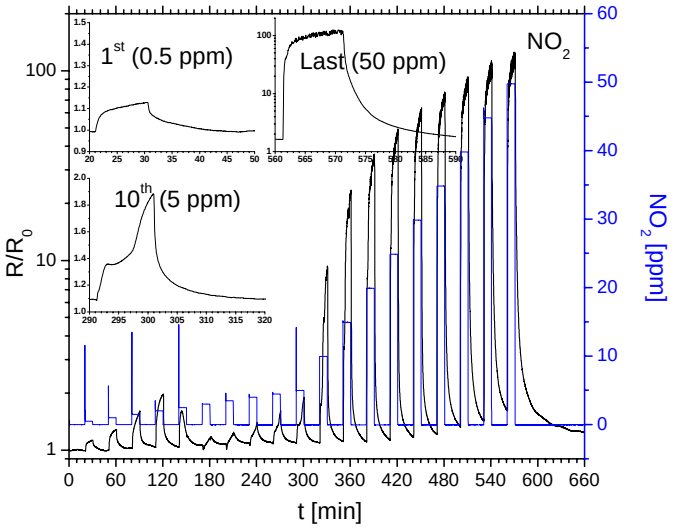

Figure 3. The resistance response during exposure to successive pulses with increasing concentrations of NO_2 in air at an operating temperature of 350°C.

These results point to TiO_2 nanofibers as promising candidates for gas sensors in environmental and medical applications in which low ppm levels of NO_2 need be detected. As shown in inset of Fig. 3, such ultra-sensitive levels of detection can be obtained by use of nanofiber TiO_2 sensor protoypes.

The response to reducing gases, while not as high as for NO_2, was still significant. Amongst the gases tested in this study, the sensitivities to H_2 where significantly higher than for CO and CH_4.

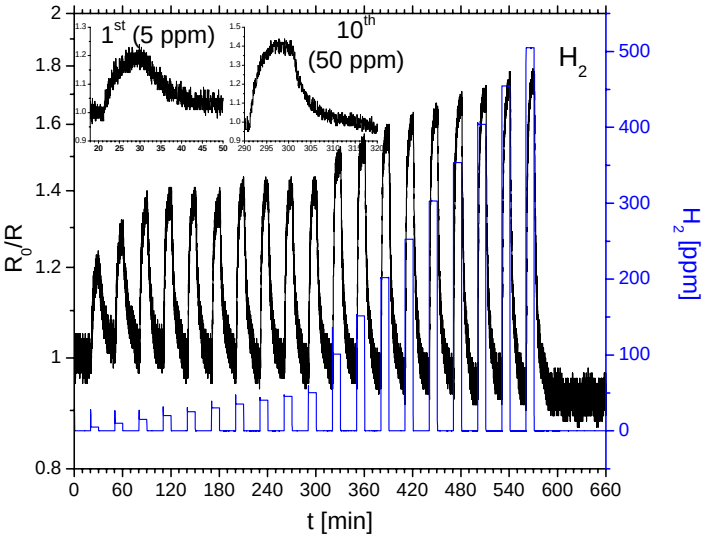

Figure 4. The resistance response during exposure to successive pulses with increasing concentrations of H_2 in air, operating at a temperature of 300°C.

Thus, these sensors demonstrated preferential selectivity towards H_2 amongst the reducing gases tested. We demonstrate detection of H_2 down to 5 ppm level using TiO_2 fiber mats as shown in inset of Fig. 4. Note that the response magnitude (y-axis) in Figs. 3 and 4 is opposite, R/R_o and R_o/R, respectively.

4 SUMMARY AND CONCLUSIONS

In summary, TiO_2 fiber mats were prepared for use in gas sensors by the electrospinning method. These demonstrated high sensitivity to NO_2 (oxidizing gas) and H_2 (reducing gas). The response was reversible and reasonably fast with response times of the order of 1 min. Sensitivities as high as ~100 were measured upon expose to 50 ppm NO_2 in air. This work demonstrates that TiO_2 fibers are promising candidates for ultra-sensitive gas sensors capable of detection of various gases down to sub ppm levels.

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