

Electrospun TiO₂ nanofibers for gas sensing applications

Il-Doo Kim^{*}, Avner Rothschild^{**}, Harry L. Tuller^{***}, Dong Young Kim^{****}, and Seong Mu Jo^{*****}

^{*} Optoelectronic Materials Research Center, KIST, Seoul, Republic of Korea, idkim@kist.re.kr

^{**} Department of Materials Science and Engineering, MIT, Cambridge, MA, USA, avner@mit.edu

^{***} Department of Materials Science and Engineering, MIT, Cambridge, MA, USA, tuller@mit.edu

^{****} Optoelectronic Materials Research Center, KIST, Seoul, Republic of Korea, dykim@kist.re.kr

^{*****} Optoelectronic Materials Research Center, KIST, Seoul, Republic of Korea, smjo@kist.re.kr

ABSTRACT

Nanostructured TiO₂ 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 TiO₂ fiber mats for use in gas sensors demonstrating exceptionally high sensitivity to NO₂, a toxic gas responsible for acid rain and other air pollution effects, and high sensitivity to H₂, a potentially explosive gas.

Keywords: TiO₂, nanofiber, electrospinning, sensor, NO₂, H₂

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 TiO₂, a semiconducting oxide, can be modulated by the chemisorbed species on its surface. Chemisorbed oxygen species (O₂^{-(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 TiO₂ 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 TiO₂ nanofiber sensors.

In this work we report the fabrication of electrospun TiO₂ fibers obtained through the phase separation of TiO₂ gel and poly(vinylacetate) during solidification. We investigate the response of TiO₂ nanofiber gas sensors to a number of gases and demonstrate exceptionally high sensitivity to NO₂, an atmospheric pollutant and H₂, a potentially explosive gas.

2 EXPERIMENTAL

TiO₂ 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. TiO₂ fiber mats (Fig. 1(a)) were directly electrospun on Al₂O₃ substrates prepared with interdigitated Pt electrodes arrays (200 μm Pt fingers spaced 200 μm apart). The as-spun TiO₂ 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 TiO₂ 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 TiO₂ structure with (101) and (200) peaks.

The sensitivity of the TiO₂ nanofibers towards H₂ and NO₂ gases was tested at temperatures between 300 and 350°C. The electrospun TiO₂ nanofibers were mounted on Al₂O₃ sample holders and contacted by Pt wires which were attached to the interdigitated electrode arrays on the Al₂O₃ 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 TiO₂ 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 H₂ in air, 100 ppm NO₂ in air, 1000 ppm CO in air, and 1% CH₄ 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 TiO₂ fiber mats is defined as the ratio R₀/R or R/R₀ for reducing (H₂, CO, CH₄) or oxidizing (NO₂) gases, respectively, where R₀ 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 TiO₂ nanofibers. The as-spun PVAc/TiO₂ composite fibers exhibit a range of diameters from 200 to 600 nm. After calcination in air for 30 min to remove the PVAc, TiO₂ fiber mats were observed as shown in Fig. 2 (a). As previously reported in Ref [9], in the initial stages of electrospinning, the TiO₂ sol precursor converts to a TiO₂ gel when the fibers are exposed to moisture. Liquid-liquid phase separation results in TiO₂-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 TiO₂ nanofibers without fibrillar structure.

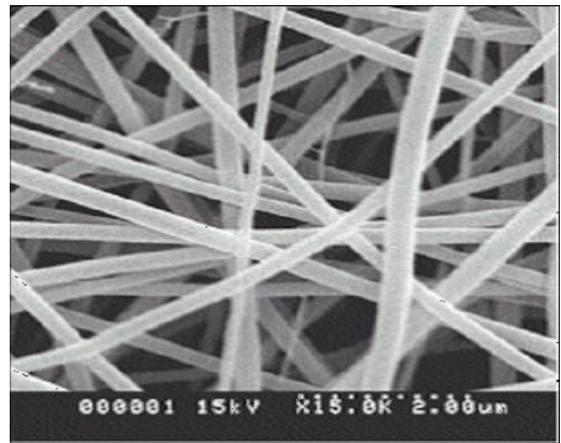


Figure 1. SEM image of as-spun TiO₂/PVAc composite fibers fabricated by electrospinning from a DMF solution.

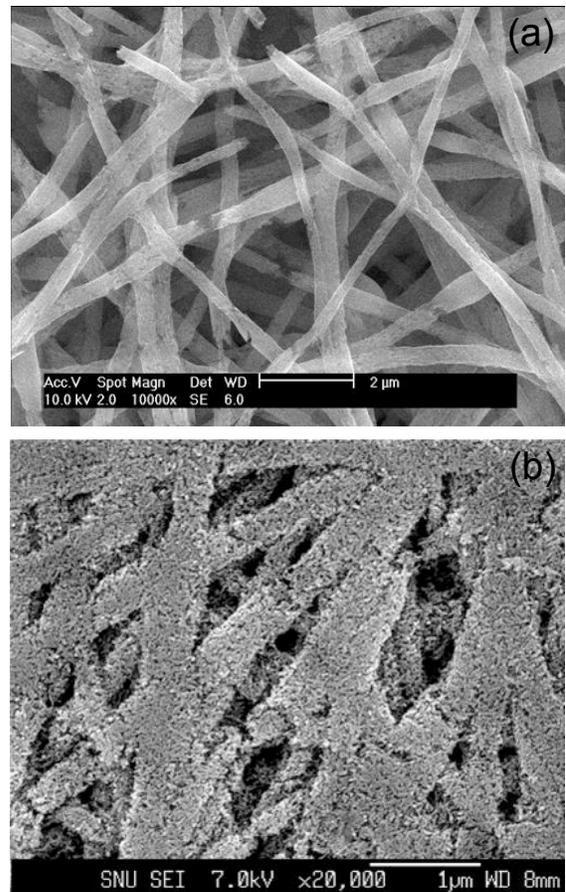


Figure 2. (a) SEM image of TiO₂ fiber mats after 450°C calcination. (b) High resolution SEM image of TiO₂ nanorod structure which was pretreated with mechanical press at 120°C for 10 min before calcination.

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 m²/g.

In order to investigate the potential advantages of the enhanced surface activity of the TiO₂ 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 (H₂) and oxidizing (NO₂) 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 NO₂, with response magnitudes, R/R₀, as high as ~100 upon exposure to some tens of ppm of NO₂ in air and response to levels as low as 500 ppb (Fig. 3).

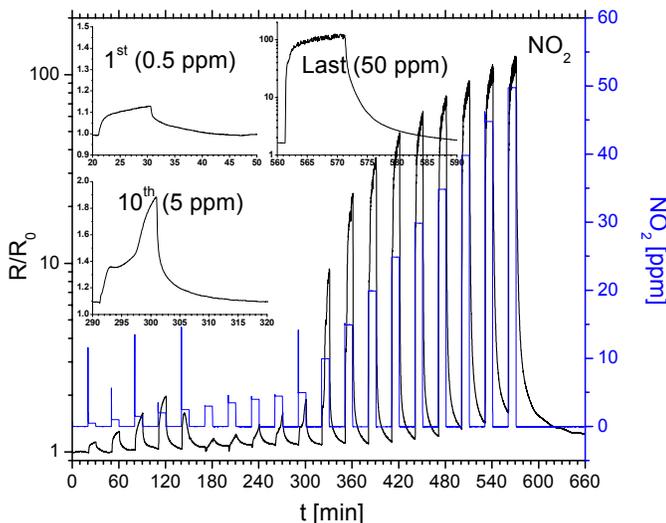


Figure 3. The resistance response during exposure to successive pulses with increasing concentrations of NO₂ in air at an operating temperature of 350°C.

These results point to TiO₂ nanofibers as promising candidates for gas sensors in environmental and medical applications in which low ppm levels of NO₂ need be detected. As shown in inset of Fig. 3, such ultra-sensitive levels of detection can be obtained by use of nanofiber TiO₂ sensor prototypes.

The response to reducing gases, while not as high as for NO₂, was still significant. Amongst the gases tested in this study, the sensitivities to H₂ were significantly higher than for CO and CH₄.

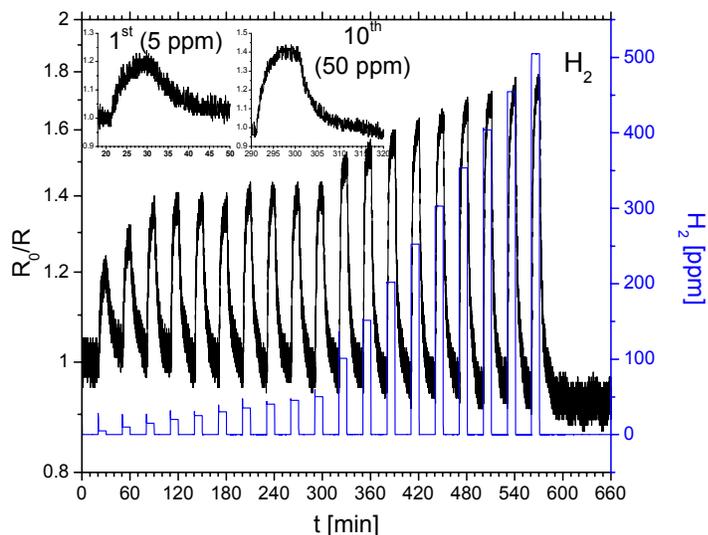


Figure 4. The resistance response during exposure to successive pulses with increasing concentrations of H₂ in air, operating at a temperature of 300°C.

Thus, these sensors demonstrated preferential selectivity towards H₂ amongst the reducing gases tested. We demonstrate detection of H₂ down to 5 ppm level using TiO₂ fiber mats as shown in inset of Fig. 4. Note that the response magnitude (y-axis) in Figs. 3 and 4 is opposite, R/R₀ and R₀/R, respectively.

4 SUMMARY AND CONCLUSIONS

In summary, TiO₂ fiber mats were prepared for use in gas sensors by the electrospinning method. These demonstrated high sensitivity to NO₂ (oxidizing gas) and H₂ (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 exposure to 50 ppm NO₂ in air. This work demonstrates that TiO₂ fibers are promising candidates for ultra-sensitive gas sensors capable of detection of various gases down to sub ppm levels.

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