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 semiconductor 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$_2$O$_3$ 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$_2$O$_3$ sample holders and contacted by Pt wires which were attached to the interdigitated electrode arrays on the Al$_2$O$_3$ 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 450ºC calcination. (b) High resolution SEM image of TiO$_2$ nanorod structure which was pretreated with mechanical press at 120ºC 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).

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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