

Room temperature gas sensing properties of SnO₂/multiwall-carbon-nanotube composite nanofibers

An Yang, Xiaoming Tao,^{a)} and Rongxing Wang

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Shuncheng Lee

Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Charles Surya

Department of Electronic and Information Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

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Pure SnO₂ and SnO₂ polycrystalline nanofibers doped with multiwall carbon nanotubes (MWCNTs) are synthesized by electrospinning followed by calcination in air at 500 °C. The measurement results by sensors fabricated from these fiber mats at steady state show that the *n*-type SnO₂/MWCNT nanofibers are able to detect carbon monoxide at 50 ppm at room temperature, while the pure SnO₂ nanofibers are insensitive up to 500 ppm. The MWCNT doped SnO₂ nanofibers have demonstrated their potentials for wearable room temperature gas sensors with low cost and power consumption. © 2007 American Institute of Physics. [DOI: 10.1063/1.2783479]

Due to their large surface-to-volume ratio and small grain size, nanostructured materials have been predicted and demonstrated to be excellent candidates for ultrasensitive and highly miniaturized sensors.¹ They are most suitable for intelligent textiles,² which have strict requirements on sensor size and weight, operating temperature, power consumption, and flexibility.

The fundamental mechanism of semiconductor gas sensors relies upon the change in electrical conductivity due to the interaction between semiconducting materials and gas molecules to be detected.³ Tin oxide (SnO₂) has a large band gap and highly achievable carrier concentration that make it suitable for gas sensors,⁴ transparent electrodes,⁵ and other optoelectronic devices.⁶ When a sensor is exposed to air, oxygen is adsorbed on the surface to form negative ions, the adsorbed oxygen has extracted the conduction electrons from the near-surface region of the tin oxide grains leading to an insulating surface layer. Upon exposure to reductive gas species such as CO, the arrested electrons are released by the reactions between the reductive gas and the negatively charged ions: $\text{CO} + \text{O}^- \rightarrow \text{CO}_2 + e^-$, reducing the steady-state surface oxygen concentration and donating a few electrons back to the bulk resulting in an increased conductivity.⁷ Of these negatively charged ions, O⁻ appears on tin oxide surface at a high temperature of about 150 °C.⁸ Most tin oxide gas sensors are effective only at temperatures above 200 °C.⁹

One-dimensional (1D) and quasi-1D metal oxide nanostructures, such as nanowires and nanobelts, have the smallest dimension for effective electron transport and, therefore, may be ideal candidates for translating the gas recognition into an electrical signal.¹⁰ *P*-type TeO₂ nanowires have been investigated for sensing ammonia and nitrogen dioxide at room temperature.¹¹ The complexity and cost of fabrication

as well as power consumption may hinder their applications. Komalkov *et al.*⁷ reported the O₂ and CO sensing properties based on an individual SnO₂ nanowire and a detection limit of a few 100 ppm for CO in dry air at 300 °C was measured. Ultraviolet illumination was used to improve the sensitivity at room temperature.^{12,13} However, this method causes difficulties in portable or miniaturized sensors. Doping with materials in the semiconductors may affect the electron transfer, which is considered in our investigation. Although a host of highly toxic gases (such as CO), water molecules, and biomolecules cannot be detected using intrinsic carbon nanotube devices,¹⁴ external or internal functionalization schemes have recently been proposed to overcome these detection limitations.¹⁴ Through rational chemical or physical modification of MWCNTs, the binding energy between MWCNTs and CO may be increased, which leads to a large electron charge transfer from MWCNTs to CO molecules.

Several methods have been reported for preparing SnO₂ nanowires/nanobelts, including thermal deposition,^{15,16} solution-based crystal growth,^{17,18} laser ablation,¹⁹ electrospinning,²⁰ and template-based approaches.⁷ Among these methods, electrospinning is relatively simple and cost effective to produce nanofibers from a wide variety of polymer solutions. Sb-doped SnO₂ nanofibers were prepared by electrospinning a solution containing poly(vinyl pyrrolidone) (binder), tin and antimony (III) alkoxides, acetic acid and organic solvents.²⁰ A precursor solution containing dimethyldecanoate tin, poly(ethylene oxide)/water, and chloroform was used to electrospin SnO₂ microfibers.²¹ Porous SnO₂ nanobelts have been fabricated by electrospinning and subsequent calcinations in air at various temperatures above 500 °C.²² In this letter, we investigate electrospun SnO₂/MWCNT nanofibers for room temperature detection of carbon monoxide gas. A simple method was developed for dispersing MWCNTs into tin oxide precursor solutions and SnO₂/MWCNT composite nanofibers were obtained via electrospinning process. Based on these fiber mats, gas sen-

^{a)} Author to whom correspondence should be addressed. FAX: 852-27731432. Electronic mail: tctaoxm@polyu.edu.hk

sors were fabricated on flexible substrates. Gas sensing properties were examined for steady state of CO gases.

To prepare a pure SnO₂ precursor solution, 2.4 g poly(vinyl alcohol) (PVA) (molecular weight $M=88 \times 10^3$ g/mol, J&K Chemical, Ltd.) was added slowly to 16 g de-ionized water. The mixture was stirred for 6 h in a water bath at 70 °C until PVA was completely dissolved. Then, this solution was added with 10 g anhydrous tin (IV) chloride (SnCl₄) (IL, USA) followed by magnetic stirring for 6 h. In a typical procedure for SnO₂-MWCNT precursor solution, 120 mg Cetyltrimethylammonium bromide (CTAB) (DuPont) was dissolved in 16 g de-ionized water. 40 mg MWCNTs (NTP, Shenzhen, China) were dispersed in CTAB aqueous solution under sonication for 15 min (800 W, JY92, Ninbo Biotech, Ltd.). 2.3 g PVA was added slowly to the MWCNT dispersion and stirred for 6 h in a water bath at 70 °C. Then, this solution was added with 10 g SnCl₄, followed by magnetic stirring for 6 h. These precursor solutions were loaded into a 20 ml plastic syringe equipped with a 23 gauge, 1.5 in. long stainless steel needle. The needle was connected to a nanofiber electrospinning unit (NEU-010, Kes Kato Tech Co.) which can generate dc voltages up to 40 kV. For the pure SnO₂ nanofibers, the applied voltage was 26 kV and the distance between the needle tip and the collector was 15 cm. The target drum speed and syringe pump speed were set, respectively, to 2 m/min and 0.04 mm/min for the precursor solutions. For the SnO₂-MWCNT nanofibers, the applied voltage was 23 kV and the distance between the needle tip and the collector was 15 cm. The target drum speed and syringe pump speed were set, respectively, to 2 m/min and 0.03 mm/min for the precursor solutions. The as-prepared fiber mats were collected and calcinated (CWF1200, Carbolite Co.) at 500 °C in air to obtain SnO₂ and SnO₂-MWCNT nanofibers. These nanofibers were characterized by field emission scanning electron microscope (FESEM) (JEOL JSM-6335F), x-ray diffraction (XRD) (Philips PW3710, Cu K α radiation), and transmission electron microscope (TEM) (JEOL JEM-2010F).

Polyester substrates [polyethylene terephthalate (PET)], Dupont, $9L \times 6W \times 0.175T$ mm³ with aluminum (Al) electrodes were used in this study. The PET substrates were cleaned in sequence of emerging in nonionic detergent, deionized water, acetone, and isopropyl alcohol for 10 min each with ultrasonic baths, and dried in a vacuum oven for 12 h at 60 °C. The linewidth of the Al electrode was 1 mm. The space between these two electrodes is 3 mm. The Al electrodes were directly pasted into PET substrate using an aluminum conductive adhesive tape (RS Components, Ltd.). To allow the fiber mats directly to contact the electrodes, double sided adhesive carbon tape ($3L \times 0.8W$ mm³) was fixed adjacent to the electrode. Then, the silver conductive paint with Al foil covered the fiber mats directly.

The detailed gas sensing experimental setup was described elsewhere.^{23,24} The sensitivity (S) is defined as $S = R_a/R_g$, where R_a is the electrical resistance in atmospheric air (~22% relative humidity) and R_g the resistance of the fiber mats in CO-air mixed gas. The sensitivity was evaluated according to the resistance variation under a dc voltage of 3 V. Air mixed with a given concentration of CO gas was flowed at 3000 ml/min through the gas chamber at 23.5 °C and ambient pressure. The electrical measurements were made using a Solartron 1287 Electrochemical Interface along with Solartron 1252A frequency response analyzer. The con-

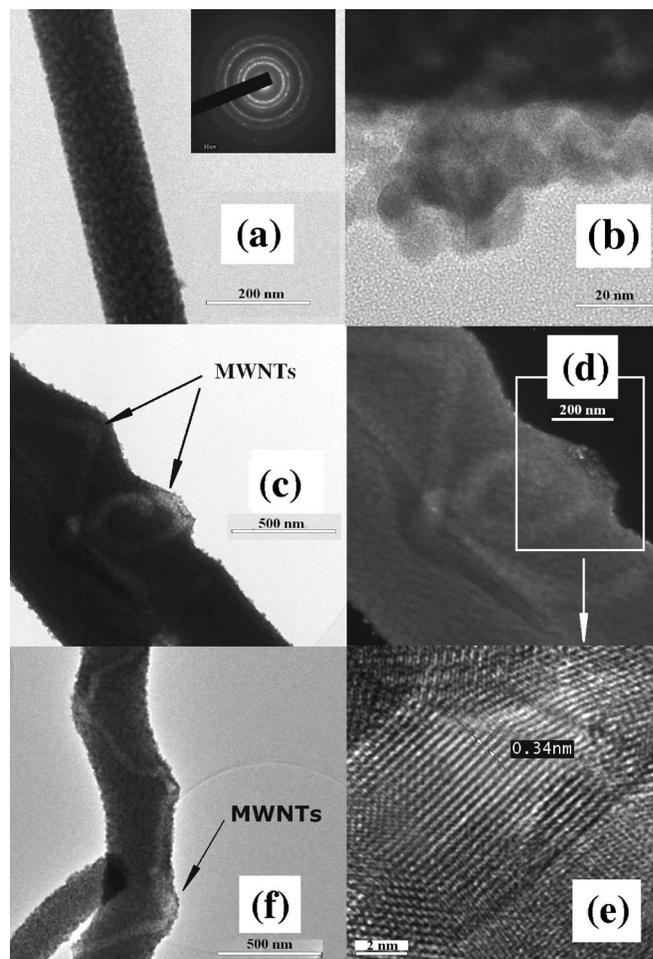


FIG. 1. [(a) and (b)] TEM images of SnO₂ nanofibers calcinated at 500 °C. [(c) and (f)] Bright field TEM images of SnO₂-MWCNT nanofibers calcinated at 500 °C. (d) Dark field TEM images of SnO₂-MWCNT nanofibers calcinated at 500 °C. (e) HRTEM image of a small section of MWCNTs.

centration of CO was continuously measured by a chemiluminescence CO analyzer.²⁴ After the inlet and outlet concentration achieved equilibrium (1 h), the electrochemical interface was turned on and recorded the data.

FESEM micrographs show that the electrospun SnO₂ and SnO₂-MWCNT nanofibers are randomly oriented on the substrate and the diameters of the fibers lie between 300 and 800 nm. The curved nanofibers have a typical length of several tens of millimeters. Figure 1(a) is a low-magnification TEM image of pure SnO₂ nanofibers and the corresponding ringlike electron diffraction pattern indicates that the nanofibers are polycrystalline. High resolution TEM micrograph [Fig. 1(b)] reveals that samples calcinated at 500 °C consist of randomly orientated nanocrystallites of SnO₂ with approximate 15 nm in diameter. The in-plane bright field TEM micrograph of SnO₂-MWCNT composite nanofibers and its corresponding dark field one are indicated in Figs. 1(c),(d), respectively. One nanotube is found to orient along the fiber axis, while another exhibits some degree of tortuosity. Figure 1(e) is a HRTEM image of the MWCNT wall showing the 0.34 nm separations between adjacent graphene sheets which coincides with the plane spacing of multiwall carbon nanotubes. The XRD patterns of the nanofibers calcinated at 500 °C show that the SnO₂-MWCNT nanofibers have diffractive peaks associated with rutile SnO₂.²⁵ It is difficult to elicit the characteristic peaks of the MWCNTs (002), mainly

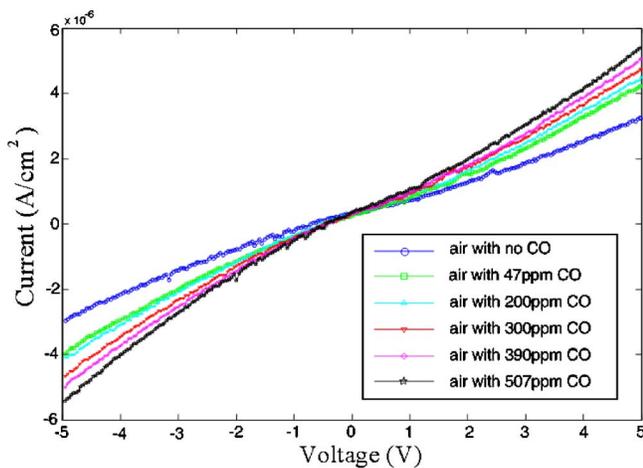
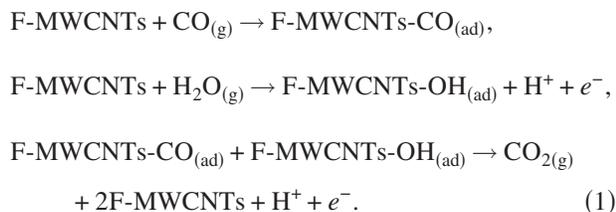


FIG. 2. (a) I - V curves of pure SnO_2 fiber sensor measured in air and 500 ppm CO. (b) I - V curves of SnO_2 -MWCNT fiber sensor measured in air and with concentrations of CO. (c) The sensitivity of SnO_2 -MWCNT fiber sensor vs CO concentration. The applied voltage was 3 V.

because of the overlap of the broad rutile SnO_2 (110) peak and that of MWCNTs. Raman spectrum of SnO_2 -MWCNT composite nanofibers, indicates that the D and G modes of doped MWCNTs at about 1362 and 1578 cm^{-1} , respectively. For the pure SnO_2 nanofibers, the fundamental Raman active mode A_{1g} , which usually appears in polycrystalline SnO_2 materials, is observed at 617 cm^{-1} .

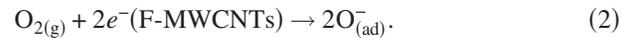
For pure SnO_2 sensors current-voltage (I - V) curves obtained under air and air/507 ppm CO, show no change in resistance. On the contrary, the doped MWCNT fiber sensors are sensitive to the gases, as shown in Fig. 2(b). The resistance decreases upon the introduction of CO gas. The mean sensitivity is 1.29 for 50 ppm CO at 23.5 °C at a bias voltage of $3v$. A linear equation $S = 0.0011c(\text{concentration, ppm}) + 1.1207$ with a correlation coefficient of 0.9502 was obtained over the range of 200–507 ppm.

When pure tin oxide is placed in carbon monoxide at room temperature, few active chemisorbed oxygen ions react with CO, so that no change of resistance was observed. After being pretreated in concentrated CTAB under sonication and possibly calcinations in air, abundant active sites are created on the surface of MWCNT walls which have strong binding energies to CO. As a result, the functionalized MWCNTs have strong tendency to adsorb CO and H_2O molecules, and experience a drastic change in electrical properties when exposed to carbon monoxide. The resistance of the SnO_2 -MWCNT sensor decreases upon the exposure of the reducing gas molecules, suggesting that the functionalized MWCNTs (F-MWCNTs) have a n -type semiconductor behavior. A proposed interaction mechanism of CO molecules with F-MWCNTs can be described as

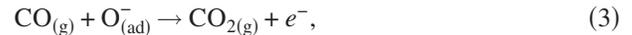


Hence, the concentration of the conduction band electrons increases and the conductance increases. On the other hand,

ion O^- is easily adsorbed on MWCNT surface in air,²⁶



Introduced of CO may cause the desorption of O_2 :



which also attributes to an improvement in the sensitivity. In addition, the work function of the MWCNTs is approximately equal to that of tin oxide; the Schottky barrier between them is very low.²⁷

In summary, the polycrystalline SnO_2 and MWCNT doped SnO_2 nanofibers were synthesized in a large quantity. Gas sensors made from the calcinated SnO_2 -MWCNT nanofibers show a sensitivity to CO gas at room temperature at a low bias voltage of 3 V in steady state. Indicating that the SnO_2 -MWCNT nanofibers are very promising materials for the development of miniaturized gas sensors. Further investigation is being conducted on the sensing behavior of the sensors in transient state. The results will be reported separately in the near future.

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