Electrochimica Acta 92 (2013) 484–490

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Hybrid tin oxide-SWNT nanostructures based gas sensor

Syed Mubeen[a], Min Lai[b], Ting Zhang[c], Jae-Hong Lim[a], Ashok Mulchandani[a], Marc A. Deshusses[d], Nosang V. Myung[a,*]

[a] Department of Chemical and Environmental Engineering, University of California – Riverside, Riverside, CA 92521, United States
[b] School of Mathematics and Physics, Nanjing University of Information Science & Technology, Nanjing 210044, People's Republic of China
[c] Suzhou Institute of Nano-tech and Nano-bionics (SINANO), Chinese Academy of Science (CAS), Suzhou 215125, People's Republic of China
[d] Department of Civil and Environmental Engineering, Duke University, Durham, NC 27708, United States

ARTICLE INFO

*Article history:*
Received 27 September 2012
Received in revised form 9 November 2012
Accepted 5 January 2013
Available online 11 January 2013

*Keywords:*
Single-walled carbon nanotube
Tin oxide
Gas sensor
Electrochemical deposition
Chemiresistor
Field effect transistor

ABSTRACT

A facile electrochemical functionalization method was utilized to decorate single-walled carbon nanotubes (SWNTs) with tin oxide and their gas sensing performance toward various analytes ($NH_3$, $NO_2$, $H_2$, $H_2S$, acetone, and water vapor) was evaluated at room temperature. Tin oxy-hydroxide was site-specifically precipitated on the surface of SWNTs because of an increase in local pH during electrochemical reduction of nitrate to nitrite ions. By adjusting the amount of charge passed during deposition, the amount of tin oxide deposited on SWNTs was controlled, which altered the electronic and gas sensing properties of the nanostructures. The resulting hybrid nanostructures showed excellent sensitivities upon exposure to trace amounts of both oxidizing gases (limit of detection (LOD) of 25 $ppb_V$ for $NO_2$) and reducing gases (LOD of 10 $ppm_V$ for $H_2$) at room temperature. The enhanced sensing performance was due to the charge transfer between the surface active tin oxide nanoparticles and SWNTs, with the direction of charge transfer depending on the analyte gas. This approach can be applied to fabricate other hybrid metal oxide-SWNTs nanostructures to create highly sensitive gas sensor arrays.



## 1. Introduction

Interaction between metal oxide surface and surrounding gas has been known and extensively studied. Indeed, most of commercial solid-state chemical sensors are based on thick/thin film of doped metal oxides (e.g., $SnO_2$, $In_2O_3$, and ZnO doped with platinum, palladium, etc.) [1,2]. The operating principle of these sensors is based on the surface interaction between metal oxide and analyte. Under ambient conditions, oxygen vacancies are formed on the metal oxide surface due to chemisorption of oxygen, which later exchange electrons with the bulk of material resulting in the formation of an electronic depletion layer close to the surface (i.e., surface charge layer) [3,4]. Thus, when a reducing gas (e.g., CO, $H_2$, and $NH_3$) comes in contact with the metal oxide surface, it reacts with surface oxygen, which then leads to injection of electrons, into nanostructures. It has been observed that when the grain size is comparable to the Debye length, a space charge region is formed in the entire crystallite [4]. Hence significant improvements in gas sensing performance can be achieved by reducing the dimension of nanostructures down to the thickness of Debye length.

Several methods have been employed to synthesize metal oxide nanostructures with different morphologies including nanoparticles [5], nanowires [6], nanobelts [7], nanotubes [8], etc. Most of the initial demonstrations on metal oxide nano-gas sensors have been based on tin oxide ($SnO_2$) nanowires [9–11]. $SnO_2$ is a wide band gap ($E_g$ = 3.6 eV at 300 K) n-type semiconductor, with excellent mechanical stability making it a suitable candidate for gas sensors. Although, a few works report utilizing metal oxide nano-gas sensor for rapid and sensitive detection of analytes, most of these sensors need to be operated at high temperatures due to their poor electrical conductivity at near room temperature which led to high power consumption [12,13]. To provide favorable electronic conduction pathways at room temperature while maintaining its excellent molecular recognition capability, major efforts have been made toward creating hybrid nanostructures [14–18]. Various methods were utilized to synthesize these hybrid nanostructures including sputtering [14], hydrothermal synthesis [15], electrospinning [16], chemical synthesis [17], etc. While the hybrid nanostructures synthesized with these methods demonstrated promising applications toward gas sensing, these methods are expensive, have poor selectivity for the template or lack of control over the amount of deposited materials. In addition, there are some inconsistencies observed over the sensing performance of such hybrid nanostructures, with resistance decreasing for both oxidizing and reducing gas species [14,16,18].

* Corresponding author.
*E-mail address:* myung@engr.ucr.edu (N.V. Myung).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.01.029

Electrochemically assisted deposition has been successfully used to synthesize metal oxide thin films and nanostructures like $SnO_2$ [8], $TiO_2$ [19], and $SiO_2$ [20], etc. by increasing locally the solution pH, which leads to chemical precipitation of metal oxide or oxyhydroxide. Herein, we report a simple, efficient, controllable, electrochemical functionalization of single-walled carbon nanotubes (SWNTs) with tin oxide nanoparticles. Electrochemical quartz crystal microbalance (EQCM) and other electroanalytical techniques were utilized to investigate the effect of various electrochemical parameters including electrolyte composition, applied deposition potential, deposition rate, and morphology. By adjusting the amount of $SnO_2$ deposited on SWNTs, the sensing performance was optimized. Electrochemically functionalized $SnO_2$ on SWNTs surpass the earlier attempted approaches, while still addressing all the requirements typical for a gas sensor including inexpensive synthesis approach, room temperature operation, sensitive detection, etc.

## 2. Experimental

### 2.1. AC dielectrophoretic (DEP) alignment of SWNTs across microfabricated gold electrodes

A single walled carbon nanotubes suspension was prepared by addition of 0.2 mg of commercially available carboxylated SWNTs (Carbon Solutions Inc., Riverside, CA) to 20 mL of N,N-dimethylmethanamide (DMF). The contents were sonicated in a glass vial for 90 min using a VWR model 50D sonicator. All 20 mL of the SWNT suspension were transferred to a 50 mL Teflon centrifuge tube and centrifuged for 90 min at 15,000 × *g* and 23 °C using a Beckman J2-HS centrifuge. Immediately after centrifugation, 10 mL of the supernatant was carefully removed and placed in a glass vial. The supernatant was sonicated for an additional 60 min prior to use. Lithographically patterned Si chips with 16 gold electrode pairs (Ti/Au 20/180 nm thick layers) were utilized as substrates and contacts for sensor assemblages (Fig. S1). The electrodes contained a 3 × 200 μm gap and large contact pads that enabled individual addressability for electrochemical functionalization [21]. SWNTs were aligned across the electrode gaps via AC DEP alignment by adding 1.5 μL drop of SWNT suspension, and applying 1 V (peak to peak) and 4 MHz (Keithley 3390 AC generator, 50 MHz arbitrary waveform generator) frequency. The device resistance was controlled by the alignment time [21]. After nanotube alignment, the nanostructures were annealed for 1 h at 300 °C under a reducing environment (5% $H_2$ + 95% $N_2$) to minimize the contact resistance between the nanotubes and electrode pads.

### 2.2. Electrochemical assisted deposition of tin oxide

Two different electrolytes were utilized for $SnO_2$ deposition on SWNTs. Solution A consisted of 100 mM $NaNO_3$ (≥99.0%, Sigma–Aldrich, MO), 75 mM of $HNO_3$ (70%, Sigma–Aldrich, MO), and 20 mM of $SnCl_2{\cdot}5H_2O$ (≥98%, Sigma–Aldrich, MO) [8]. Solution B consisted of 20 mM of $SnCl_2{\cdot}5H_2O$ in the absence of nitrate. The pH of both the solutions was adjusted to 1.3 by adding concentrated HCl (37%, Sigma–Aldrich, MO), and the solutions were aged for 12 h. Two different working electrodes were used throughout the experiment. For electrochemical quartz crystal microbalance (EQCM) studies, spray-printed SWNTs on gold coated quartz-crystal resonators (type 1) were used as the working electrode which was immersed in 10 mL of electrolyte with the Pt counter (99.99%, Sigma–Aldrich, MO) and the Ag/AgCl reference electrodes fabricated in our laboratory to form electrochemical cell. For electrical characterization and sensing experiments, AC DEP aligned SWNTs between two gold electrodes (type 2) were used as the working electrode. The electrochemical cell was formed by dispensing a 3 μL drop of electrolyte on top of the aligned SWNTs network and positioning platinum and Ag/AgCl wires inside the droplet using micropositioners. Linear sweep voltammetry (LSV) and chronoamperometry (CA) were carried out at room temperature using a potentiostat/galvanostat (EG&G, Princeton Applied Research 263A Potentiostat/Galvanostat, NY). During LSV experiment, the potentials were scanned from +100 mV of open circuit potential to −1.0 V vs. Ag/AgCl at a scan rate of 10 mV $s^{-1}$. In situ monitoring of the deposition process during potential sweep was done using EQCM (Maxtek RQCM quartz microbalance instrument (INFICON, NY)). For CA experiments, a fixed cathodic potential (−0.4 V for solution A and −0.6 V for solution B vs. reference electrode) was applied for a defined period of time. After electrochemical assisted deposition, the working electrodes were immediately rinsed with deionized water to prevent any undesirable chemical precipitation. For materials characterization including XRD and FT-IR, tin oxide coated spray-printed SWNTs were used. For composition and morphology analysis (i.e., SEM, TEM, and EDX), tin oxide coated on AC DEP aligned SWNTs were used. Selected area electron diffraction (SAED) and EDX spectra were taken at random points.

### 2.3. Electrical characterization and gas sensing measurements

Electrical characterizations were performed in a three point probe configuration using Keithley 2636 System. The FET transfer characteristics were measured by applying a constant bias ($V_{SD}$) of 1 V between source and drain electrodes while sweeping gate voltages ($V_G$) between ±20 V. For gas sensing studies, the functionalized chip was assembled onto a pin chip holder by wire bonding (West Bond Inc., Model 7443A) and was subsequently loaded on a custom made bread board designed for the sensing system [22]. Each sensor was subjected to 1.0 V DC potential and the current was continuously monitored, the electrical resistance was then determined by applying Ohm's Law. A baseline was achieved with exposure to dry air as the carrier gas (99.99% purity) and various analytes were tested by placing analyte cylinders in series to the dry air. Different analyte concentrations were attained by dilutions with the carrier gas. The exposure and recovery time was fixed at 15 and 20 min, respectively, while the gas flow rate was kept constant at 200 sccm by mass flow controllers (Alicat Scientific Incorporated) [21,22]. All experiments were performed at room temperature. All results shown in Figs. 5 and S2 are from 5 sensors or more, with resistance values selected in the range of 10–100 kΩ for consistency.

## 3. Results and discussion

### 3.1. Electroanalytical studies of $SnO_2$ on SWNTs

Scheme 1 illustrates the electrochemical functionalization of SWNTs with tin oxides. Unlike other methods, electrochemical functionalization with $SnO_2$ is simple, rapid and requires no pretreatment of the substrate. It involves electrochemical reduction of nitrate ions by applying suitable cathodic potential to electrode (SWNTs in this case) resulting in the generation of hydroxyl ions. The generated hydroxyl ions then locally increase the pH near the electrode surface, resulting in the chemical precipitation of tin oxyhydroxide, which is later converted to tin oxide by annealing in nitrogen environment [8,19].

Various electroanalytical techniques including linear sweep voltammogram (LSV) and electrochemical quartz crystal microbalance (EQCM) were carried out at room temperature using a three electrode electrochemical cell configuration to determine the deposition mechanism and optimum deposition potential (see Section 2 for further details). Fig. 1 shows plots of LSVs and in situ