

Electrochemically decorated carbon nanotubes for hydrogen sensing

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Received 21 December 2006; accepted 3 April 2007

Available online 8 April 2007

Abstract

Low-density networks of single-wall carbon nanotubes have been modified by palladium nanoparticles using an electrochemical method. A major advantage of this approach is that it allows for selective metal deposition on the electrically contacted nanotubes, whereas the remaining substrate surface and the non-contacted tubes remain essentially unaffected. The Pd-decorated networks function as effective hydrogen sensors enabling the detection of hydrogen concentrations as low as 10 ppm at room temperature. The electrochemical metal deposition scheme is promising for the development of sensor arrays suitable for analysing gas mixtures.

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PACS : 61.46+w; 73.90+f; 82.80.Fk

Keywords: Carbon nanotubes; Hydrogen sensor; Electrochemical modification; Nanoparticles

1. Introduction

Recent research into gas sensors has mainly focussed on device miniaturization as well as the development of sensor arrays capable of selectively detecting a multitude of analytes. For this purpose, single-wall carbon nanotubes (SWCNTs) are promising candidates due to the fact that all carbon atoms are situated on the nanotube surface, and the possibility to implement the tubes into nanoscale devices [1]. Chemiresistors based on both individual semiconducting SWCNTs and networks of SWCNTs have been demonstrated to exhibit good responses towards gases such as ammonia and nitric oxide [2,3]. However, pristine nanotubes are insensitive to gases that lack pronounced electron donor or acceptor capability. Catalytically active noble metals have been widely used to enhance the response of solid-state chemical sensors toward various gases [4]. In this manner, SWCNTs have been rendered sensitive to hydrogen by evaporating palladium on top of them [5]. Hydrogen sensing is essential for the control and monitoring of various industrial processes [6].

While metal evaporation onto SWCNTs is a facile method, it lacks sufficient controllability, since the size of the formed metal islands usually differs significantly from the nominal thickness of the evaporated metal layer. Furthermore, the morphology of the islands depends on the detailed surface properties of the tubes. Optimal sensitivity of the sensors requires efficient control over size and density of the attached metal particles. In fact, a low density of small metal particles would yield only a weak signal, while densely arranged large particles bear a risk to short-circuit the device. Moreover, metal evaporation is not easily viable for large-scale integration into sensor arrays, which is necessary for an analysis of complex gas mixtures. Wet-chemical approaches offer advantages in this respect [7]. In particular, previous investigations have proven electrochemical modification (ECM) to be an efficient tool for modifying individual SWCNTs with organic functional groups [8,9]. Besides enabling effective control over the modification degree, ECM can also be selectively performed on metallic nanotubes [10]. Here we report on the ECM of low-density SWCNT networks by palladium and their use as sensors to detect hydrogen at room temperature. The use of nanotube networks as the active sensor components within the present study helps in overcoming the problem of exclusively obtaining semiconducting SWCNTs, and furthermore ensures the reproducible fabrication of samples with similar electrical characteristics.

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2. Experimental

Purified HiPco SWCNTs (CNI, Houston, TX) were deposited onto aminosilanzed Si/SiO₂ wafers, following a well-established protocol [11]. An AFM image of a network obtained in this manner is displayed in Fig. 1(a). Gold electrodes with a thickness of 100 nm and a separation of ~15 μm were then deposited on top of the nanotube networks using a shadow-mask technique. These electrodes serve both as electrical leads to the nanotubes as well as the working electrode for performing the ECM. Palladium electrodeposition was performed at constant potential within a homemade microcell equipped with Pt counter and pseudo-reference electrodes. Typically a voltage of -1.1 V versus Pt was applied for 15 s in an ethanol solution containing 2 mM Na₂[PdCl₄] and 0.1 M LiClO₄ as supporting electrolyte. These optimized ECM parameters yield well-separated Pd nanoparticles along the contacted nanotubes, as exemplified by Fig. 1(b). The sizes of the Pd particles fall in the range of 25–35 nm. For the hydrogen-sensing experiments, the networks comprising of either pristine or Pd-decorated SWCNTs were placed in a N₂-flushed glass-cell with electrical feed-throughs. A constant current of the order of 10 μA was applied to the samples at room temperature and the voltage drop measured. As sensor signal, the change in resistance with respect to the initial resistance ($\Delta R/R_{\text{ini}}$) was monitored as a function of time. Appropriate hydrogen dilutions in nitrogen were supplied through a mass-flow system (Kalibriersystem MK 5, Umwelt Technik MCZ). Each sensing experiment consisted of four stages: First, the sensor was maintained in pure nitrogen atmosphere until a stable response was obtained (typically 1 min). Subsequently, the sample was exposed to a specified concentration of hydrogen for 3 min. Next, nitrogen was flushed into the cell, under which the sample was kept for 2 min in order to reach a steady state of the sensor response. Finally, the cell was purged with dry air to achieve recovery of the sample.

3. Results and discussion

The unmodified SWCNT networks did not display any measurable signal even at the highest concentration of hydrogen used in this study (150 ppm). This behaviour was profoundly changed after Pd electrodeposition onto the nanotubes. One representative example is provided by Fig. 2, which displays the response of a Pd-decorated network to various hydrogen concentrations. As apparent from Fig. 2(a), this sample exhibits a relative resistance increase of ~3% within 3 min after exposure to a low hydrogen concentration of 10 ppm. For higher hydrogen concentrations (≥ 100 ppm), the resistance increase tends to saturate within this 3 min period (Fig. 2(b)). Extrapolating the sensor response over a longer time interval, the maximum response at which complete saturation is achieved is estimated to be ~85% for all concentrations (dotted lines in Fig. 2(b)). The plot in Fig. 2(c) depicts the 3 min sensor signal as a function of hydrogen concentration.

The sensitivity enhancement imparted by the Pd nanoparticles can be attributed to the well-documented capability of palladium to dissolve and dissociate hydrogen at room temperature [12,13], accompanied by electron transfer to the underlying SWCNTs. The resulting reduction in the concentration of hole carriers within the p-type semiconducting SWCNTs contained in the network then accounts for the observed resistance increase [5,14]. In this connection, it has previously been put forward that hydrogen adsorption reduces the work function of the palladium [15]. However, it is pertinent to consider that initial work on Pd-gate silicon-based FETs [16] as well as recent theoretical [17,18] and experimental [19] studies has demonstrated that the work function of a Pd surface increases by up to 0.3 eV when saturated with hydrogen within an inert atmosphere. Accordingly, the correct description of the effect of hydrogen would involve the formation of a dipole layer on the Pd particle surface, whereupon electrons are donated towards the underlying nanotube and the particle's

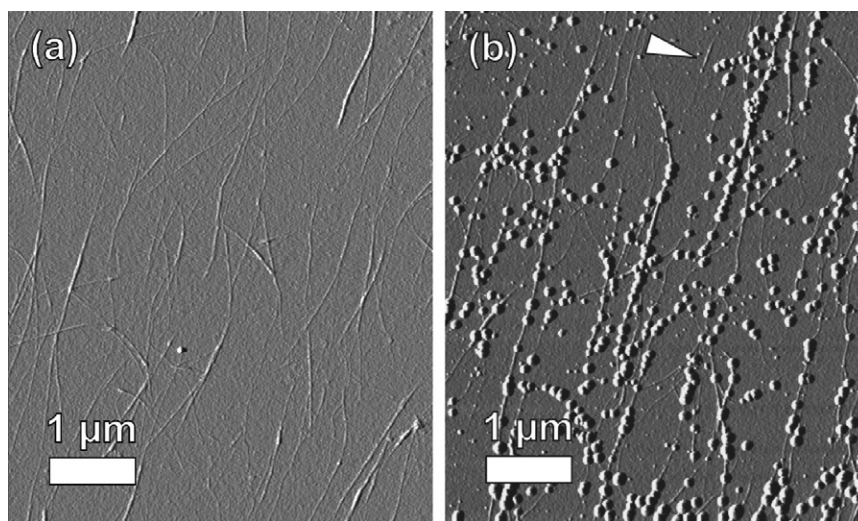


Fig. 1. Atomic force microscope (AFM) image of (a) an unmodified single-wall carbon nanotube (SWCNT) network and (b) a SWCNT network electrochemically modified with Pd nanoparticles. It is noteworthy that tubes that do not form part of the network (marked by an arrow in (b)) and the substrate remain unaffected by the ECM.

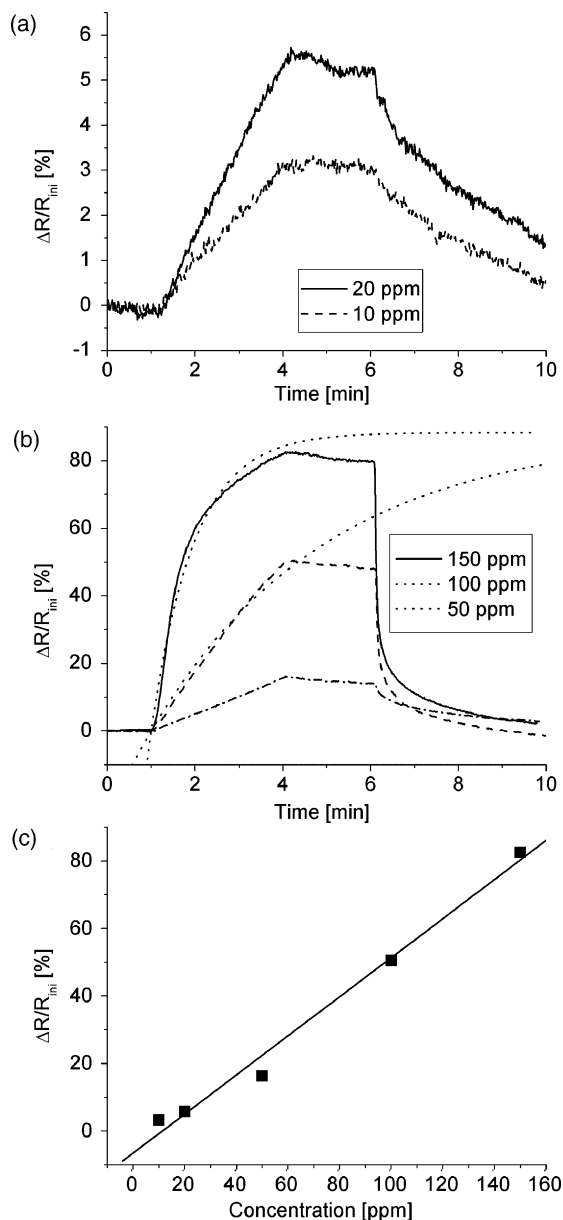


Fig. 2. (a and b) Sensor response (relative change of resistance) of Pd nanoparticle-modified carbon nanotubes when exposed to low concentrations of hydrogen (1–4 min). The sample was then left in pure nitrogen (4–6 min), followed by purging the cell with dry air (6–10 min). The dotted lines in (b) extrapolate the sensor response for the case of an extended exposure to hydrogen. (c) Three-minute response as a function of hydrogen concentration.

work function is increased. The hydrogen atoms inside the Pd particles are stable under nitrogen atmosphere, whereas upon exposure to air they readily react with oxygen under formation of water [6] with concomitant recovery of the original resistance (Fig. 2(a) and (b)).

A saturation signal of 85% is reached after prolonged exposure to hydrogen as is best discernible for the case of 150 ppm in Fig. 2(b). This compares favourably with the saturation value of $\sim 38\%$ reported for Pd-modified SWCNT-network sensors obtained through metal evaporation upon 400 ppm hydrogen exposure [5]. One possible factor contributing to the stronger response of the present sensors could be

the improved contact between the nanoparticles and the nanotube achieved through the electrochemical deposition procedure. On the other hand, the saturation response of the Pd-SWCNT network is lower than that of individual semiconducting SWCNTs with evaporated palladium, which amounts to 100% at only 40 ppm hydrogen exposure [5]. However, it should be kept in mind that the small number of adsorption sites available on individual SWCNTs renders the tubes sensitive only within a limited range of hydrogen concentrations, which restricts their applicability.

The quasi-linear calibration curve in Fig. 2(c) signifying a non-Langmuirian response can be understood by the limited desorption of the hydrogen atoms from the Pd surface due to the absence of oxygen. Of further relevance is the fact that Fig. 2(c) shows the response after 3 min exposure rather than at equilibrium. Only in the presence of oxygen, an equilibrium between hydrogen adsorption and desorption can be established on the Pd surface. Under this condition, the adsorption process is determined by the hydrogen concentration itself, while the desorption process is governed by the concentration of chemisorbed oxygen species, which combine with hydrogen atoms to water [20]. This leads to a Langmuir-like dependence of the hydrogen coverage of a Pd surface [21], as has been documented for Pd-gated Si-based FETs [22].

4. Conclusion

In conclusion, we have demonstrated that electrodeposition of palladium is a prospective method to obtain gas sensors from SWCNT networks. It offers the advantage of selective functionalization of the contacted tubes combined with intimate metal nanoparticle/nanotube contacts. The Pd-decorated networks show good room temperature responses against hydrogen down to a concentration as low as 10 ppm. The ability to modify SWCNTs with a range of metal particles through controlled ECM [23] paves way for the fabrication of sensor arrays with the ability to selectively sense various gases.

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