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Selective sensing of hydrogen sulfide using silver nanoparticle decorated carbon nanotubes

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\textbf{Abstract:} This paper reports a selective method of sensing hydrogen sulfide in gaseous state using silver nanoparticle decorated single walled carbon nanotubes (SWCNT) at room temperature. The transduction platform is a simple resistor which was constructed by drop-casting of a random network of silver-nanoparticle decorated carbon nanotubes onto a channel joining two electrodes. This study shows the differential sensing of hydrogen sulfide with respect to interfering analytes such as carbon monoxide and nitric oxide, displaying the different mechanisms involved in the sensing of the gases. These results indicate the possibility of fabricating simple devices with low power consumption based on flexible plastic substrate for selective sensing of gaseous molecules at room temperature by appropriately functionalizing the carbon nanotubes (CNTs).

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Gas sensors and sensor arrays for the detection of gaseous molecules have attracted much attention in recent years. The ultimate goal of gas sensor research is to create ‘electronic noses’ that can detect a wide range of gases that are present in ambient atmosphere at low concentration levels with sufficient reproducibility, selectivity and sensitivity. Such research would ultimately produce technology that would be expected to be useful for many applications such as food processing, environmental remediation, agriculture, medical diagnostics and defense. One of the major challenges of current gas sensor research is the issue of selectivity [1]. However, sensitivity and selectivity is enhanced by the advent of nanotechnology on the gas sensitive layers and also by altering the sensing layer’s chemical moieties to act as receptors for the target molecules.

Carbon nanotubes (CNTs) are a class of advanced functional materials that have many novel applications. There are essentially two different types of carbon nanotubes, namely the metallic nanotubes and the semiconducting nanotubes [2]. In addition, these tubes can be either single-walled or multi-walled [3]. This study focuses on the single-walled nanotubes (SWCNT) that have attracted much attention in a wide range of scientific research fields [4]. This is due to their small dimensions and unique properties. One of its main applications is in the field of gas sensors. SWCNTs-based sensors is the next generation of sensors that has the potential of revolutionizing the sensor industry due to their inherent properties such as their extremely small size, high electrical conductivity [5] and high specific area. It has been proven that carbon nanotubes have a high affinity for a wide range of gases which when physisorbed [6] or chemisorbed [7] onto its surface would produce a change in the electronic structure of the carbon nanotube as the adsorbed molecule would participate in charge transfer with the CNTs either as an electron donor [8] or acceptor [9]. However highly selective sensing is still elusive as false positives prove to be a major problem as the sensing mechanisms involved are generic and are not specific to the target molecules.

In this study, selective sensing of hydrogen sulfide (H₂S) was realized by using a resistive platform with Ag-decorated SWCNTs as the conducting channel. It has been observed that the...
electronic properties of silver decorated SWCNTs gave a strong electrical response upon H$_2$S exposure as compared to common interfering gases like carbon monoxide (CO) and nitric oxide (NO). Ag has a strong affinity to H$_2$S and hence it is hypothesized that H$_2$S will form Ag$_2$S by reacting with the surface of these nanoparticles. This will invariably alter the electrical properties of the nanotube network since the Ag nanoparticles are attached to the carbon nanotubes.

Carboxylic acid functionalized SWCNT (COOH-SWCNT) produced by arc discharge were bought from Carbon Solutions, Inc. To enhance the functionalization with carboxylic acid moieties, these tubes were refluxed at 130 °C with a 2 M solution of HNO$_3$ for 24 h. 1 mg of the prepared tubes was then added to 100 ml of deionized water and sonicated for 20 min to fully suspend the tubes. Ag decoration has traditionally been done by evaporation; however, recently, decoration has also been done by wet chemical routes [10]. In this study, chemical reduction was used for Ag decoration. 15 mg of the prepared functionalized SWCNT, sonicated in 20 ml of deionized water for 20 min, was added to 20 ml of AgNO$_3$. A solution of NaOH was added to the SWCNT-AgNO$_3$ solution till the pH reaches 6.3. Subsequently, the solution was incubated and stirred constantly for 2 h. The tubes were then harvested by filtration, washing with deionized water and dried at 30 °C. 1 mg of the dried tubes was then weighed out and sonicated for 20 min in 100 ml of deionized water. The silver-decorated nanotubes (Ag-SWCNT) were characterized by a High Resolution Transmission Electron Microscope (HRTEM), JEOL 2010 operating at an acceleration voltage of 200 kV and with a LaB6 filament, and with X-Ray Photoelectron Spectroscopy (XPS) using a Kratos AXIS spectrometer (UK) with a monochromatic Al K-alpha X-ray radiation at 1486.71 eV.

Figure 1a shows the schematic of the sensing device, which consists of two Au electrodes of thickness 150 nm spaced 200 µm apart. The Au electrodes were sputtered on to a glass substrate with a 5 nm Cr layer for adhesion. 2 µl of COOH-SWCNT and Ag-SWCNT were drop-cast on to the channel between the electrodes thereby forming a network of nanotubes across the channel. The devices were then exposed to N$_2$ (>99.9995%), CO, NO and H$_2$S gases purchased from National
The concentration of the target gases were maintained at 2 ppm and the total gas flow for all experiments was fixed at 500 sccm. The electrical measurements were then performed using a Keithley 4200 Parametric analyzer enclosed in a 200 L glove box in a N₂ atmosphere with a fixed bias of -0.1 V applied on one of the electrodes. The corresponding drain current (I_d) was then measured with respect to time. The device was held in a constant flow of N₂ for the first 200 s and subsequently, the device was exposed to the target gas of interest for a fixed time interval of 50 s subsequently followed by N₂ exposure of another 50 s.

The HRTEM image of Ag-SWCNT is shown in Figure 1b. It can be seen from Figure 1b that Ag nanoparticles of ~ 4 nm in size were tethered on to the bundles of SWCNT network, which could be due to the reduction of Ag⁺ by the COO⁻ moieties on the SWCNT. The presence of Ag nanoparticles along the SWCNT network was further confirmed by the XPS spectrum. Figure 1c shows the XPS scan of Ag decorated SWCNT with 3d₅/₂ and 3d₃/₂ peaks at 368.3 and 374.3 eV, respectively and corresponding to binding energies of Ag. The device response to H₂S and other common interfering gases was then tested as explained before. Figure 2a shows that for the Ag decorated SWCNT device, the I_d decreases upon H₂S exposure as compared to an increase in I_d for the undecorated SWCNT device. This decrease in I_d is attributed to the increase in the electronic charge density around the Ag nanoparticle as sulphur (S) contributes additional electrons when it interacts with the Ag nanoparticle. This would in turn lead to electron-hole recombination at the nanoparticle-SWCNT interface, which would decrease the hole density and hence decreasing the I_d. The change in I_d was not recoverable due to the permanent formation of silver sulphide (Ag₂S) as Ag has a good affinity to S. XPS scan of Ag-SWCNT device that has been exposed to H₂S confirms the formation of Ag₂S. Figure 2b shows the 2p₃/₂ sulphur peak has shifted to 161.5 eV upon exposure to H₂S, from a value of 162.5 eV, which corresponds to the binding energy of pure S. Furthermore, it has been reported that the binding energy of S in Ag₂S compound is 161.4 eV [11] which is in accordance with our observations.
Figure 3a and b shows the responses of the devices with Ag-SWCNT and COOH-SWCNT to NO and CO, respectively. It can be seen that $I_d$ decreased for the Ag-SWCNT devices which is in agreement with the previous observations [12]. The decrease in $I_d$ could be due to the charge transfer between the SWCNT and NO molecules. It can also be seen that the NO response for the Ag-SWCNT device was much larger than that of the functionalized SWCNT, which might be due to the higher affinity between NO molecules with single unpaired electron and Ag with a lone electron. The increase in $I_d$ upon CO exposure as shown in Figure 2c could be due to the presence of charge species around the SWCNT network. The gas molecules (CO, NO and $H_2S$) may be physisorbed on to the SWCNT network, which induced additional charge carriers in the SWCNT network. Hence, hole doping occurs when the gas molecules are physisorbed on to the SWCNT network and subsequently increasing the $I_d$. As shown in Figure 3a and b, when exposed to $N_2$, the adsorbed molecules were desorbed from the device resulting in $I_d$ tracing back to the original values. It also shows that the bonding between CO/NO molecules and the undecorated SWCNT network is weak, i.e., the gas molecules were attached to the carboxylic acid moieties via weak hydrogen bonding as reported by Fu et al. [6].

In summary, a simple resistive gas sensor based on Ag-nanoparticle decorated SWCNTs (Ag-SWCNT), which is selective to $H_2S$ at room temperature, has been fabricated. Although a glass substrate was used in this study, a similar device can be fabricated on a flexible plastic substrate achieving a light-weight and selective $H_2S$ sensor with low power consumption. Of all the devices fabricated, upon $H_2S$ exposure, only the device deposited with Ag-SWCNT showed a significant reduction in $I_d$ due to the establishment of permanent bonding between Ag and S molecules. Moreover, the change in $I_d$ values was very much larger for $H_2S$ as compared to that of CO and NO molecules. This gave an indication that the interaction between the $H_2S$ with the Ag nanoparticle decorated SWCNT is very much stronger than NO and CO molecules. A simple methodology to fabricate selective $H_2S$ gas sensors has been reported in this paper. The experiment results confirmed
that simple resistive devices based on SWCNTs, driven by low power, could be used for selective sensing of gaseous molecules when they are appropriately functionalized. Further studies will focus on the influence of Ag nanoparticle size and concentration on the sensor response in order to optimize the sensitivity and selectivity of the Ag-nanoparticle based, resistive H$_2$S sensor.

**References**


**List of Figures**

**Figure 1** (a) Resistive device structure with Au/Cr pads as electrodes and Ag decorated SWCNT as conducting channel. Target gases were introduced via flexible hose 2 mm away from the nanotube channel. (b) HRTEM image of bundles of Ag decorated SWCNT and corresponding X-ray photo-spectroscopy spectrum (c) with peaks at 368.3 and 374.3eV confirming successful decoration of Ag nanoparticles.

**Figure 2** Device response upon gas exposures: (a) H\(_2\)S response showing irrecoverable decrease (of 20 µA) in the current of the Ag decorated SWCNT device as due to Ag\(_2\)S formation compared to the undecorated SWCNT device. (b) XPS sulphur peak shift from 162.5 to 161.5eV which correlates to the sulphur binding energy of 161.4eV in Ag\(_2\)S compound.

**Figure 3** Drain current – time plot of interfering analytes: NO (a) and CO (b) indicating H\(_2\)S selectivity of Ag decorated SWCNT due to negligible I\(_d\) shift upon NO and CO exposure when compared to H\(_2\)S exposure (Figure 2a).
Biography

DWH Fam has received his B. Eng (Hons) from Nanyang Technological University in 2006 and is currently pursuing a PhD in the said college. His research interests include functionalization and nanoparticle decoration of carbon nanotubes for purpose of field effect transistors and gas sensing devices.

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