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Communications

Heme-Enabled Electrical Detection of Carbon Monoxide at Room Temperature Using Networked Carbon Nanotube Field-Effect Transistors

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The detection of gases using single-walled carbon nanotubes (SWNTs) has been a subject of active research. Kong et al. first demonstrated the sensing of NO_2 and NH_3 with conductivity measurements.[1] Snow et al. used the SWNT random networks to selectively detect various chemicals.[2] Although significant numbers of gases have been successfully detected[1,3–7] by the conductance change of SWNT devices, the electrical detection of carbon monoxide (CO) is still a challenge.[8–10] The sensing of CO is critically important for environmental monitoring and safety control in industries and homes. Solid-state sensors with CO detection capabilities have been reported by using inorganic metal oxides such as SnO_2[11] and In_2O_3,[12] where the combustible gas CO reacts with preadsorbed oxygen species on surfaces of metal oxides; thereby donating electrons and resulting in a conductance change that may be detected via resistometric means. These sensors normally require very high operating temperatures, in the range of 200−400 °C, which is one of the major obstacles toward low-power consumption sensor devices. The reported CO detection limit for these devices was typically around 30−100 ppm. In this communication, we report that the SWNT network field-effect transistors (SNFETs) with Cr-SWNT contact are able to detect the change of drain current (I_d) upon exposure to 4.9 ppm of CO at room temperature. The immobilization of thiolated heme molecules

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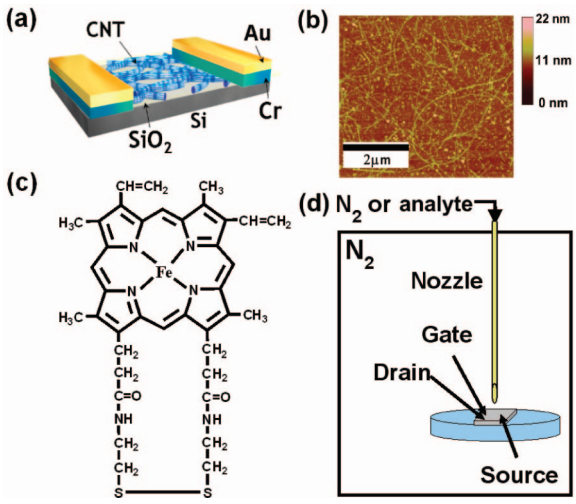

Figure 1. (a) Schematic illustration of the Cr-SWNT contacted SNFET. (b) AFM image of the SWNT networks. (c) Chemical structure of the thiolated heme. (d) Schematic illustration of the setup for gas sensing.

on the device can significantly enhance the detection sensitivity for CO.

CNT networks were synthesized by CVD process[13] using cationized ferritin as catalysts. SNFETs were fabricated in a top contact device geometry (illustrated in Figure 1a), where a highly *p*-doped silicon wafer with an 100-nm-thick SiO_2 layer was used as a back gate and 100 nm of Au electrodes (to form a Au-SWNT contact) or 10 nm Cr/100 nm Au (to form a Cr-SWNT contact) separated by 100 μm were patterned on top of it using standard lithography techniques. Figure 1b shows the typical AFM image of the SWNT networks formed. The thiolated heme (Figure 1c) was prepared by a method described elsewhere[14] (MALDI-TOF mass spectrum shown in Figure S1 in the Supporting Information) and the immobilization of thiolated heme was performed by immersing devices in 1 mM of thiolated heme solution (dichloromethane as a solvent) for 16 h in ambient, followed by intensive rinsing using dichloromethane and air drying. The disulfide is covalently adsorbed on the Au surface and the heme molecules can be securely attached to the Au surface of the SNFETs. All electrical measurements were performed on a standard electrical probe station enclosed in a 200 L glovebox under a nitrogen atmosphere at room temperature. CO (4.9 ppm in pure N_2; National Oxygen Pte Ltd.; certified with gas chromatography) or NO_2 were premixed with pure nitrogen (>99.9995%) to the desired concentration and then introduced through a gas nozzle (1 mm diameter) located 3 mm above the devices (Figure 1d), where the total gas flow flushing onto the device was kept at 500 sccm. Before electrical data were recorded, all devices were purged with high purity N_2 gas until a reasonably constant drain current was achieved.

Figure 2a−d show the real-time I_d response upon switching between N_2 and CO (4.9 ppm) for Au-contacted SNFET (Au-SNFET), thiolated heme-modified Au-SNFET (he-Au-SNFET), Cr-contacted SNFET (Cr-SNFET), and thiolated

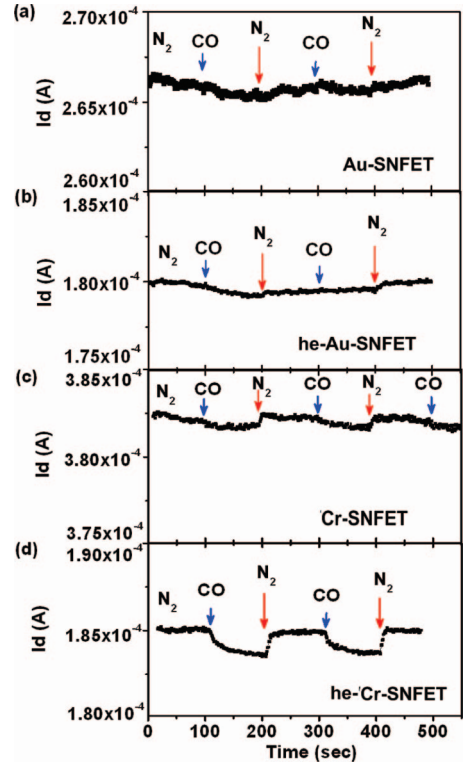

Figure 2. Electronic detection of CO gas using (a) Au-SNFET, (b) he-Au-SNFET, (c) Cr-SNFET, and (d) he-Cr-SNFET. The concentration of CO was 4.9 ppm and the total flow was kept at 500 sccm, $V_g = 10$ V and drain voltage (V_d)= −10 V.

heme-modified Cr-SNFET (he-Cr-SNFET). No significant I_d response was observed for the Au-SNFET after the gas flow was switched from N_2 to CO as shown in Figure 2a, whereas Cr-SNFET had little I_d decrease (<0.5×10^{-6} A; Figure 2c). This implies that the electrode/CNT contact is a factor that can not be ignored in gas detection. This result is consistent with the conclusion drawn from NO or NO_2 detection using pristine SNFETs.[5,6] After modification with thiolated heme the decrease of I_d on switching to CO was significantly enhanced to $\sim 1.5 \times 10^{-6}$ A for Cr-SNFETs (Figure 2d). In this case, the response time is less than 100 s and the I_d was able to recover faster (in a time scale of few seconds) when the gas was switched back to N_2 (Figure 2d). The thiolated heme-modified Cr-SNFET could be reused for up to 40 cycles of N_2-CO testing without any deterioration in the sensing response. However, thiolated heme was not able to enhance the CO detection for the Au-SNFETs, thus further suggesting that the electrical responses to CO may derive mainly from the electrode−SWNT junction. This result is consistent with our recent observation that Au- and Cr-contacted SNFETs behave differently in DNA detection.[15] It may be noted that the thiolated heme is strongly bound to Au (evidenced by XPS analysis in Figure S2 and AFM image in Figure S3, see the Supporting Information) and that the heme molecules sitting close to the metal−SWNT contact may impose short-range interaction to the junction and alter

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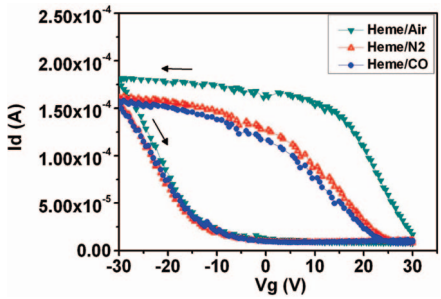

Figure 3. Transfer characteristics for a he-Cr-SNFET measured, respectively, in air, N_2, and CO. The concentration of CO was 4.9 ppm and the total flow was kept at 500 sccm, $V_d = 5$ V.

the contact property.[16–18] However, we still can not exclude the possibility that there may be some heme molecules that may attach to the SWNTs near the junction area and contribute to the contact modification although the heme molecules are not detectable (below XPS detection limit).

To address the sensing mechanism for the electrical detection of CO, particularly the electrical response upon the standard gas switching cycles between N_2 and CO, we show in Figure 3 the typical transfer characteristics for he-Cr-SNFET measured, respectively, in air, N_2, and CO. In general, the SNFET behaves as a very hysteretic *p*-type transistor. We note that for he-Cr-SNFET, the I_d is decreased and there is a small negative shift in threshold voltage (V_{th}) while switching from N_2 to 4.9 ppm of CO. However, these phenomena are not observed for the he-Au-SNFET (the transfer curves in N_2 and in CO are overlapped; data not shown here) although the difference between two devices is only with or without the thin layer of Cr. This implies that the CO gas detection is dominated by the change in electrode−SWNT contact rather than the change in channel conductance or the direct doping to SWNTs induced by CO exposure. It has been reported that Cr atom at 298K is able to form association complexes with O_2 but shows no tendency for the formation of adducts with CO.[19] This could suggest that the Cr atoms adjacent to the physical Cr-SWNT contact were oxidized by O_2 initially as the device was exposed to the ambient. The immobilization of heme molecules in ambient further bring another component (heme-O_2) to the junction, taking in to consideration that O_2 is known to have a strong interaction with heme and is likely to be brought to the Cr-SWNT contact by heme molecules. While switching from N_2 to CO, the dynamic-equilibration between Cr, O_2, and heme is likely to be affected because of the larger affinity of heme molecules toward CO, which may result in the modification of the Cr-SWNT contact and therefore lead to a change in I_d.

A sensing mechanism in CNT devices has been an area of intense research and debate; the possible contributors are thought to include channel doping, scattering centers due to CNT-analyte interactions, and contact modulation. Several recent publications have highlighted the contribution of the contacts toward sensing behavior for biomolecule detection[15,20] as well as exposure to NO/NO_2,[5,6] and O_2.[21] Junction-blocking studies have attributed sensing behavior to contact modulation,[5,6] and theoretical and experimental studies have provided strong evidence that exposure to O_2, NH_3, and other gases can modify the work function and significantly affect the Schottky barrier and hence the device characteristics. This study further corroborates the substantial contribution of gaseous analyte induced contact modulation and suggests that receptor molecules such as heme can help differentiate and accentuate the sensing capabilities of CNT-based field-effect transistors.

In summary, we demonstrate that the electrical detection of 4.9 ppm CO at room temperature is achieved by using Cr-SWNT-contacted SNFETs and the heme molecules significantly enhance the detection sensitivity for CO. It is proposed that the CO sensing is mainly from the change in Cr-SWNT interface, not dominated by the change in channel conductance or direct electronic doping. We note that Cui et al. have suggested that O_2 can interact directly with the metal−SWNT junction and likely change the electronic state at the interface, [18] which is another supporting evidence for the mechanism proposed here. Separate from the CO detection reporting in this communication, we have also observed that using the Au- and Cr-contacted SNFETs can improve the detection limit of an oxidative gas NO_2 from 1 ppm to around 100 ppb after modification with thiolated heme molecules. The role of receptor molecules on the detection selectivity and sensitivity is crucial for the future applications and warrants further studies.

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Supporting Information Available: Figures S1−S3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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