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Functionalization of Single-Walled Carbon Nanotube Sensors for Highly Sensitive and Selective Organophosphor Vapor Detection

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Abstract:
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Introduction

In recent year, the chemical sensors based on single-walled carbon nanotubes (SWNTs) have received much attention due to their unique structure and electrical properties [1]. Multiple types of SWNT-based sensor devices such as field effect transistors [2], chemicapacitors [3], and chemiresistors [4] have been developed for sensing application, but the chemiresistors which are based on the simple change in resistance in response to the binding of analytes are leading ones due to the low power consumption and the ease of high precision resistance measurement [4]. In this paper, we demonstrated an highly sensitive and recoverable detection of dimethyl methylphosphonate (DMMP) via functionalization of semiconducting SWNT (s-SWNT) chemiresistors by 4, 4′-(hexafluoroisopropylidene) diphenol (HFIP-A). The sensitivity to DMMP can reach as low as tens of parts-per-billion (ppb) with the response time of less than 1 min.

Experimental

Single-walled carbon nanotube solution (0.01 mg/ml in water) with 99% semiconducting nanotubes was purhased from Nano Integris Co. The SWNTs were deposited on the Si/SiO_2 wafer using a self-assemble method reported previously [5] with minor modification. The 3 in. Si/SiO_2 wafer was first to be cleaned with H_2SO_4/H_2O_2 (3:1V/V). The cleaned wafer was immersed into the aminopropyltriethoxy silane (APTES) solution (4 drop APTES in 20 ml of isopropanol (IPA) for 15 min, then rinsed with IPA and blown dry with N_2. Next, the functionalized wafer was immersed into the 0.01 mg/ml SWNT solution for 45 min, and then rinsed by water and IPA repeatedly, and blown dry with N_2. Following the SWNT deposition, the chemiresistive sensors were fabricated using a standard microfabrication procedure. Briefly, the passivated interdigitated electrodes were deposited with the use of a patterned photoresist mold. The interdigitated electrodes were made by sputtering 50 nm Ti and 180 nm Au onto this mold, and a lift-off technique was used to remove the photoresist. The schematic view of the device and optical image of our sensors were shown in Fig. 1. The functionalization of the SWNT sensors was performed by dropping one drop of HFIP-A solution (0.3% in acetone) onto the sensors and then vaporization of acetone at room temperature for about 30 seconds.

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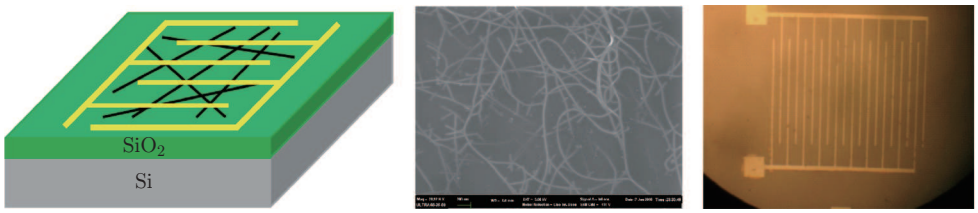

Fig. 1 Schematic view of the device (a), optical image of our sensors (b) and a percolative network of carbon nanotubes between two gold electrodes (c).

The morphologies of the SWNTs were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55). The percolative network of carbon nanotubes between two gold electrodes were shown in Fig. 1(c).

The different concentrations of DMMP were produced by regulating the flow ratio of the dilution gas to that of the flow rate of the carrier gas. The DMMP vapor was delivered into the sensing chip to test the sensor performance. The electrical signal of the sensor was monitored using a precision semiconductor parameter analyzer (Agilent 4156C). After a stable baseline electrical signal was obtained, the DMMP vapor with required concentration was introduced, and all sensing measurements were carried out at room temperature. The sensor was flushed with N_2 and illuminated with an IR lamp to desorb the DMMP from the SWNT surface after each testing cycle. The sensor response was evaluated by the resistance change at a sampling voltage of 100 mV.

Results and Discussion

A conductance between the two electrodes was measured to investigate the sensory response under no bias voltage. The sensor response (R) in conductance is defined as $R = G/G_0 = (G\text{-}G_0)/G_0$, where G and G_0 are the conductance of nanotubes before and after exposure to the test gas. Figure 2 shows that HFIP-A functionalized s-SWCNT sensor is highly sensitive for DMMP. For instance, it gives 5% conductance change upon exposure to 20ppb of DMMP, whereas no visible sign was observed for bare SWNT sensors under such concentration. This sensitivity is very higher than that of the control unmodified SWNT sensor (sensitivity limit being 500 ppb). Additionally, three sensing cycle experiments with lower DMMP concentration from 20 ppb to 80 ppb were also carried out (Fig. 2). The results show that this sensor was almost 100% recovered by reference gas blowing together with mild illumination using an IR lamp.

It is known that the fluorinated phenol with hydrogen-bond acidity interacted with the strongly hydrogen-bond basic organophosphorus compounds by hydrogen bonding. These hydrogen bonding interactions promoted sorption of DMMP vapors onto the SWNT film, which increased the sensor response. Every HFIP-A molecule owns two acid hydroxyl groups, which make the absorbed HFIP-A easy to bind DMMP on the side walls of SWNTs.

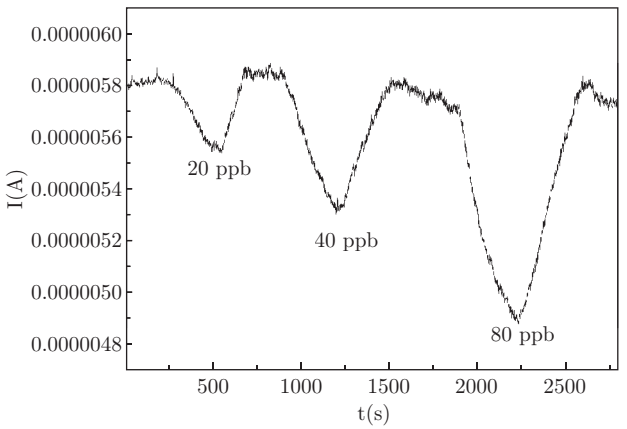

Fig. 2 Change in the conductance normalized by initial conductance (G_0) for HFIP-A functionalized SWNT sensors exposed to various concentration of DMMP.

To explore the sensing mechanism of HFIP-A /SWNT as sensor for DMMP detection, we fabricate a FET architecture to perform sensory studies. As shown in Fig. 3, the SWNT device shows p-type semiconductor behavior with holes as the majority carries,

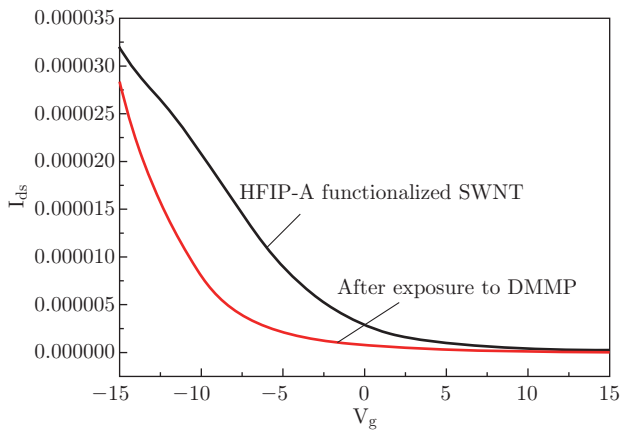

Fig. 3 Ids-Vg curves for a sensor before (a) and after exposure to DMMP (b).

evidenced by the decreasing electrical conductance when gate voltage (V_g) was swept from negative to positive values. For SWNT sensors, the decrease in conductance and shift of threshold voltage to negative value upon exposure to DMMP was attributed to a charge transfer from the electron-donating DMMP molecule to the nanotube. This charge transfer reduced the majority hole carries in the nanotubes and decreased the conductance.

Conclusions

In conclusion, we have successfully developed a chemiresistive sensor for highly sensitive and rapid detection of DMMP with the use of HFIP-A functionalized SWNT networks. This device was capable of detecting DMMP at tens of ppb level with the response time of less than 2 min. The reason for the high sensitivity of our device could be ascribed to the enhancement of binding affinity between DMMP and HFIP-A

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