Solid organic acid tetrafluorohydroquinone functionalized single-walled carbon nanotube chemiresistive sensors for highly sensitive and selective formaldehyde detection

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1. Introduction

Formaldehyde is the most common and best-known indoor air pollutant. It is a Group 1 carcinogen for human being and also irritates the mucosa of the upper respiratory tract by inhalation [1,2]. The maximum allowable concentrations for indoor formaldehyde set by the U.S. Office of Environmental Health Hazard Assessment (OEHHA) are 0.076 and 0.002 ppm for acute exposure and chronic exposure, respectively [2]. To detect formaldehyde, many laboratory techniques, such as differential optical absorption spectroscopy (DOAS), Fourier transform infrared absorption (FTIR) and laser induced fluorescence spectroscopy (LIFS) have been developed, but these methods require expensive and bulky instruments or tedious sample preparation processes. There is a strong demand for fast and real-time indoor formaldehyde detecting methods, which has stimulated researchers to develop miniaturized smart sensors. However, the current sensors still suffer from relatively high detection limit, which makes these sensors mainly suitable for monitoring formaldehyde in workplace environments [2]. Recent advance in nanotechnology has opened up possibilities for novel powerful sensors based on nanomaterials. For example, Zhou et al. [3] describe a cataluminescence-based gas sensor using nanosized V2Ti3O13 as a probe for determination of formaldehyde in air which has a detection limit of 0.06 mg m\(^{-2}\). Peng et al. [4] report a ZnO nanorod based formaldehyde sensor which shows detect limit of 1.78 parts-per-million (ppm) at room temperature. The metal oxide thin film such as NiO [5,6], ZnO/In2O3 [7], CdO/In2O3 [8] and SnO2 [9] are generally used as sensing materials for detect formaldehyde. These sensors can detect formaldehyde at ppb level, but they need to be operated at high temperatures of 90–400 °C.

Among different sensing materials, the single-walled carbon nanotubes (SWNTs) receive special attention. SWNTs are composed almost entirely of surface atoms [10–13], and are expected to exhibit excellent sensitivity toward gas absorbsate. SWNT sensors offer significant advantage over conventional metal oxide based sensor materials in that: room temperature operation, high sensitivity and easy miniaturization for construction of massive sensor arrays [10–13]. SWNTs also possess good environmental stability, excellent electronic properties and ultrahigh ratio of surface to volume [12]. These features make SWNTs ideal sensing materials for compact, low cost, low power and portable gas-sensing devices [13]. Since Kong et al. [14] first made use of SWNT field-effect...
transistors (FETs) to detect NO₂ and NH₃, the SWNT-based gas sensors have been successfully used to detect variety of gas or chemical vapors, such as NO₂ [15], O₂ [16], HCl [17], explosive and organophosphor vapors [18–23]. The detection limits were also significantly improved down to parts per trillion (ppt) concentration levels [24,25]. However, the utilization of SWNT sensors to detect formaldehyde is limited, mainly because of a weak physical adsorption between SWNTs and formaldehyde [26].

A theoretical study indicated that boron-doped SWNTs might be a potential candidate for detecting formaldehyde [26]. An antimony-carbon nanotube-SnO₂ film has been used to detect 500 ppm of formaldehyde [27]. A sensitivity of 30 parts-per-billion (ppb) has been obtained when SnO₂ film was doped by OH-functionalized multi-walled carbon nanotube, but it needs to be performed at high temperature (250 °C) [28]. Very recently, a sensor array consisting of 32 sensor elements with pristine and functionalized SWNTs was used for detecting formaldehyde [29]. It was found that the pristine SWNT array exhibited higher sensitivity, compared with polymer, metal and metaloxide nanoparticles functionalized SWNT sensors. However, the pristine SWNTs scarcely exhibit selectivity toward specific gas molecules [30].

Here, we report a highly sensitive and selective detection of formaldehyde with the use of SWNT chemiresistive sensors which is functionalized by solid acid tetrafluorohydroquinone (TFQ). This functionalized sensor could easily and recoverably detect formaldehyde at the ppb level at room temperature. This functionalized SWNT sensor also exhibited excellent selectivity to formaldehyde over those interfering organic vapors, such as water, methanol, toluene, benzene, acetone, dichloromethane, hexane, and chloroform vapors.

2. Experimental details

2.1. Fabrication and functionalization of SWNT chemiresistor

For the fabrication of SWNT chemiresistive sensor, the sorted, 99% semiconducting SWNTs (purchased from Nano Integris Co.) were first deposited on a Si/SiO₂ wafer using a self-assembly method reported previously [25,31] with minor modification. The 3 in. Si/SiO₂ wafer was first to be cleaned with H₂SO₄/H₂O₂ (3:1, v/v). The cleaned wafer was immersed into the aminopropyltriethoxy silane (APTES) solution (4 drop APTES in 20 ml of isopropanol (IPA), i.e. about 1% (ml/ml)) for 15 min, then rinsed with IPA and blown dry with N₂. 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 N₂. 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 of Ti and 180 nm of Au onto this mold, and a lift-off technique was used to remove the photoresist. It should be mentioned that direct deposition of SWNTs on the surface of Si/SiO₂ will result in low density and un-uniform deposition of SWNTs on the surface [25,31]. Here, APTES was used to functionalize the Si/SiO₂ surface to form amino-terminated monolayer, and then enhance the affinity between SWNTs and Si/SiO₂ wafer [32].

The functionalization of the SWNT sensors was performed by dropping one drop of TFQ solution (0.3% in acetone) onto the sensors and then vaporizing acetone at room temperature.

2.2. Characterization

The morphologies of the SWNTs were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55).

2.3. Sensor testing system

The desired formaldehyde concentration was obtained by dilution of the 100 ppm of formaldehyde (Weichuang Standard Gas Co.) with air. The formaldehyde vapor was delivered into the sensing chip (air used as carrier gas) to test the sensor performance. The electrical signal of the sensor was monitored by using a semiconductor parameter analyzer (Agilent 4156C, DC power was used). After a stable baseline electrical signal was obtained, the formaldehyde vapor with required concentration was introduced. All sensing measurements were carried out at room temperature (20 °C). The sensor response was evaluated by the resistance change at a sampling voltage of 1 V. Both formaldehyde and air gas used were dried, and the concentration of water vapor in these samples was less than 50 ppm. To prepare formaldehyde gas with different relative humidity, the formaldehyde gas was mixed with saturated water at calculated ratio.

3. Results and discussion

The schematic and SEM images of the SWNT chemiresistor structures were shown in Fig. 1 panels (a) and panels (b), respectively. The interdigitated electrodes with a total area of 0.5 mm x 0.85 mm and line width of 10 μm were fabricated by using a standard microfabrication method. In this chemiresistive sensor, the semiconducting SWNTs bridged the interdigitated electrodes and acted as conducting channels (Fig. 1c). The functionalization of the SWNT sensors was performed by dropping one drop of TFQ acetone solution onto the sensors and then vaporizing acetone at room temperature. The SEM images show that the SWNTs network was fully covered by a thin film of TFQ after TFQ was dropped onto the SWNT network (Fig. 1d).

The sensing experiments were carried out using a home-made sensing setup as reported in our previous work [25]. Briefly, the sensor chip was placed in a sealed cell with gas inlet/outlet. The formaldehyde vapor diluted by air was delivered into the sensing chip to test the sensor performance. A conductance between two electrodes was measured to investigate the sensor response, and the sensor response (R) in conductance is defined as R = ΔG/G₀ = (G – G₀)/G₀, where G₀ and G are the conductance of nanotubes before and after exposure to the testing gas. Five sensing cycle experiments with formaldehyde concentration from 150 ppb to 5 ppm were carried out. The results show that the TFQ functionalized sensor exhibits fast response and high sensitivity to the presence of formaldehyde vapor (Fig. 2a). For instance, the response time (defined as time duration for conductance change by 10%) of the sensor to 150 ppb of formaldehyde was about 39 s, without the need for pre-concentration step. With the increasing formaldehyde concentration, the conductance of TFQ functionalized SWNT sensor increased (Fig. 2b). A nearly linear dependency between the response and the concentration of formaldehyde at low concentration from 150 ppb to 600 ppb was observed. At higher concentration, the response tends to saturate, which might be ascribed to the saturated adsorption of formaldehyde on the surface of SWNTs and hence leading to the saturation response. Importantly, our sensor could be fully recovered by reference gas blowing (Fig. 2a), which is important for the practical application. It should be mentioned that the control “unfunctionalized” SWNT sensors gave no observable signal upon exposure to high concentration of formaldehyde (1 ppm) (Fig. 2c). This result confirms that the functional molecule TFQ plays a key role in enhancing the sensitivity of our sensors. The reproducibility of our sensor was also studied. Fig. 3 shows the conductance changes after the functionalized sensors were exposed to five cycles of 150 ppb formaldehyde. It was found that our sensors still show large response after repeating exposure to formaldehyde, suggesting a good reproducibility for our sensors.
Kauffman [10] and Bondavalli et al. [13] have discussed the sensing mechanism in SWNTs for various gases and vapors in review articles. It is generally believed that the charge transfer from the analyte molecules to the nanotubes and/or the scattering effect induced by the target analyte across the nanotubes may account for the conductance change of SWNTs. The adsorption of electron-withdrawing analyte molecules (such as NO$_2$) on the p-type SWNTs enriches hole carriers in the nanotubes and enhances the SWNT conductance, whereas the adsorption of electron-denoting analyte molecules (such as NH$_3$) causes reduced conductance due to hole depletion. To explore the sensing mechanism of the formaldehyde response in our TFQ/SWNT sensors, we fabricated a SWNT field effect transistor using the Si substrate as a back gate [23–25,33]. The measurement was operated at a constant source–drain voltage of 1 V and gate voltage between −15 and +15 V, and the transfer characteristics ($I_{ds}$ vs. $V_{g}$) of the transistor were measured. As shown in Fig. 4, the source–drain current $I_{ds}$ decreased with more positive gate voltages ($V_{g}$), indicating that the TFQ/SWNT device shows p-type semiconductor behavior with holes as the majority carriers. The nanotube sensors retained p-type semiconductor behavior after absorption of formaldehyde onto the nanotubes, but an increase in the conductance was observed (Fig. 4). The density functional theory has shown that adsorption of formaldehyde on the nanotubes resulted in a donation of 0.021−0.039 electrons from formaldehyde to nanotubes [26]. Since the TFQ/SWNT sensor is p-type in air, the donation of electrons to nanotubes should have caused decrease in the conductance. Our and other group’s experimental results (an increase in the conductance upon exposure to formaldehyde) [26] are opposite to the theory calculation. If the theory calculation is correct, the increase in the conductance upon formaldehyde exposure is not consistent with the charge transfer process. We first assumed that some formaldehyde might be oxidized to formic acid in the air, and the formic acid might hole dope the SWNTs via addition of $^+$H$^+$ onto the nanotubes. However, when the air was replaced by pure N$_2$, the increase in the conductance was still observed. So, the oxidation mechanism did not accounted for the responsive behavior.

To explain the mechanism for the formaldehyde response in our TFQ/SWNT sensors, several facts should be considered: the interaction between the functional molecule TFQ and formaldehyde played a key role in the response to formaldehyde, and formaldehyde alone cannot increase the hole carriers and enhance the conductance; Aldol interaction might exist between TFQ and formaldehyde [34]. Here, a possible mechanism for the formaldehyde response in our TFQ/SWNT sensors might be that: the acid hydroxyl groups of TFQ could interact with the formaldehyde to form weak and reversible cation intermediate complexes (Fig. 5). Since these charged intermediate complexes are close to the surface of the nanotube sensing elements, the formation of charged species is equivalent to applying a negative chemical gate voltage, which could significantly enhance the conductance of the nanotubes via enrich the hole carrier in the p-type semiconducting SWNTs. Since no $\alpha$-H exists in formaldehyde and TFQ molecules, the reversible charged intermediate complexes could not further form irreversible aldon compound via Aldol condensation. So, the sensors can be recovered by reference gas blowing. However, we emphasize that we cannot here give direct evidence for this possible mechanism due to the limitation of our present experimental setups. Further studies, including modeling of formaldehyde adsorption, comprehension of the interaction of formaldehyde and the functional groups, are needed to understand the sensor response mechanisms.

The sensitivity and selectivity of the sensors to some interfering organic vapors including water, methanol, toluene, acetone, dichloromethane, hexane and chloroform were also investigated (Fig. 6). The results clearly show that all the interfering organic vapors cause a decrease in conductivity, whereas formaldehyde brings about a pronounced increase in the conductance. The opposite sign caused by the interaction of formaldehyde with the TFQ functionalized nanotubes shows that the TFQ functionalized sensor...
Fig. 2. (a) Normalized conductance change ($\Delta G/G_0$) versus time of the TFQ functionalized sensor upon exposure to different concentrations of formaldehyde, (b) plot of conductance change versus formaldehyde concentration (the conductance changes calculated based on exposure of the sensor to formaldehyde for 3 min) and (c) $\Delta G/G_0$ versus time of the unfunctionalized SWNT sensor upon exposure to 1 ppm of formaldehyde.

Fig. 3. The conductance changes after the TFQ functionalized sensors were exposed to five cycles of 150 ppb formaldehyde.

Fig. 4. $I_d-V_g$ of the TFQ functionalized SWNT sensors (a) and the sensors after exposure to 30 ppm of formaldehyde (b). The source-drain bias voltage was 1 V.

Fig. 5. A possible mechanism for formaldehyde interaction with the functional molecule TFQ on the surface of SWNTs. The acid hydroxyl groups of TFQ could interact with the formaldehyde to form weak and reversible charged intermediate complexes. These charged intermediate complexes are close to the surface of the nanotube sensing elements, and it could significantly increase the conductance of the nanotubes via enrich hole carries in the semiconducting SWNTs.
The use of sorted, 99% semiconducting SWNTs in our study is another important factor for the high sensitivity of the sensors. Many studies have confirmed that the metallic SWNTs show lower sensitivity toward analytes due to reduced density of states near the Fermi level in metallic SWNTs as compared with the valence band edge of semiconducting SWNTs [14,35]. When we used the pristine unsorted SWNT network sensors to detect formaldehyde, it was found that this sensor did not produce any observable signal upon exposure to 5 ppm of formaldehyde (Fig. 7a), whereas the pristine sorted, 99% semiconducting SWNTs (not functionalized by TFQ) gave a distinct response signal at the same concentration (Fig. 7b). The explanation for this different sensing behavior is that, for unsorted SWNTs, the electrical properties of the SWNT network is dominated by the metallic SWNTs in which the conductance band density of state is quite flat, and a shift in position of Fermi level results in little change in the conductivity, whereas the Fermi level of semiconducting SWNTs shifts close to (or away from) valence band could results in a substantial change in the conductance [14,35].

Last, the humidity of the testing gas has a very important effect on the response properties. We introduced different concentration of water into the testing gas, and found that increase in the water concentration significantly decrease the response properties (Fig. 8). The water might play two roles in decreasing the sensitivity of our devices: donating electrons into the nanotubes or introduction of charge trapping sites on the nanotubes, resulting in decreasing the conductance [10], which could offset the increase in the conductance causing by absorption of formaldehyde; preferential interaction with the acid hydroxyl groups of TFQ via hydrogen-bond interaction, which would block the formation of charged intermediate complexes between formaldehyde and TFQ.

4. Conclusions

In conclusion, we have successfully developed a TFQ functionalized SWNT chemiresistive sensor for highly sensitive, rapid and recoverable detection of formaldehyde. The interaction of formaldehyde with TFQ on the surface of SWNTs caused significant increase in the conductance of the SWNT sensors, which made the sensors easily detect formaldehyde at ppb concentration level with the response time of less than 1 min, without the need of pre-concentration of the analytes. Additionally, the functionalized sensors show excellent selectivity toward formaldehyde over those interfering organic vapors. A possible mechanism for the formaldehyde response in our TFQ/SWNT sensors was also discussed. It was assumed that the acid hydroxyl groups of TFQ might interact with the formaldehyde to form week and reversible charged intermediate complexes which could significantly change the conductance of the nanotubes via tuning the carrier mobility and density in the semiconducting SWNTs. Although more work is required to fully understand the sensing mechanism, our study opens the way to design new chemical sensors for detection of formaldehyde with high sensitivity.
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References


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