Hole doping and surface functionalization of single-walled carbon nanotube chemiresistive sensors for ultrasensitive and highly selective organophosphor vapor detection

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2011 Nanotechnology 22 425501

(http://iopscience.iop.org/0957-4484/22/42/425501)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 202.120.54.135
The article was downloaded on 20/03/2012 at 02:34

Please note that terms and conditions apply.
Hole doping and surface functionalization of single-walled carbon nanotube chemiresistive sensors for ultrasensitive and highly selective organophosphor vapor detection

Liangming Wei¹, Diwen Shi², Peiyi Ye², Zhenqing Dai¹, Haiyan Chen¹, Changxin Chen¹, Jian Wang¹, Liying Zhang¹, Dong Xu¹, Zi Wang¹ and Yafei Zhang¹

¹ Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Institute of Micro/Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China
² School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China

E-mail: lmwei@sjtu.edu.cn and yfzhang@sjtu.edu.cn

Received 14 June 2011, in final form 27 August 2011
Published 21 September 2011
Online at stacks.iop.org/Nano/22/425501

Abstract
We developed a chemiresistive sensor based on doped and functionalized semiconducting single-walled carbon nanotube (SWNT) networks for ultrasensitive and rapid detection of dimethyl methylphosphonate (DMMP) (simulant of nerve agent sarin) vapor. The semiconducting SWNT network was deposited between interdigitated electrodes and modified by solid organic acid tetrafluorohydroquinone (TFQ). The TFQ molecules could not only selectively bind DMMP onto the sidewalls of SWNTs via the strong hydrogen bonding interaction, but also tailor the electronic properties of SWNTs via heavy hole doping. This synergetic effect significantly improved the sensitivity of the devices, and enabled the sensors to easily detect DMMP at 20 parts-per-trillion (ppt) concentration with a response time of less than 2 min, without the need for pre-concentration of the analytes. This sensitivity is about five orders of magnitude higher than that of the unmodified SWNT chemiresistor, and also significantly higher than that of the functionalized SWNT chemiresistors previously reported. Moreover, the SWNT–TFQ sensors could be recovered when DMMP is replaced with referencing gas. The SWNT–TFQ sensors also show excellent selectivity toward DMMP over some interfering organic vapors. The response mechanism, i.e. charge transfer and dedoping was investigated.

Online supplementary data available from stacks.iop.org/Nano/22/425501/mmedia
(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single-walled carbon nanotubes (SWNTs) are nearly ideal one-dimensional (1D) quantum wires with every atom on the surface [1, 2], which exhibit high sensitivity toward gas adsorbates. SWNTs also possess a high aspect ratio, good environmental stability, and excellent mechanical and electronic properties [3]. These features make SWNT ideal sensing materials for compact, low cost, low power, and potable gas-sensing devices [3–9]. Multiple types of
SWNT-based gas-sensing devices, such as chemiresistors [8], chemicapacitors [10], field-effect transistors (FETs) [11, 12], have been developed for sensing applications, but the chemiresistors which are based on the simple change in resistance in response to the binding of gas molecules are very attractive because of their simple structure and the ease of high precise measurement [13–16]. However, the pristine SWNTs always demonstrate weak response and low selectivity toward specific gas molecules due to a weak interaction between SWNTs and gas molecules [17, 18]. So, there is a need to functionalize SWNTs to improve both the sensitivity and the selectivity of SWNT sensors [19–29].

A general approach to functionalize SWNTs for enhancement of the sensor performance is by immobilization of binding ligands, such as organic small molecules [27, 28], polymers [16, 29], metal nanoparticles [21, 22], and biomolecules [30, 31], onto the sidewalls of SWNTs. These binding ligands could selectively bind (or react with) the gas molecules on the sidewalls of SWNTs, and enhance the binding affinity with gas analytes, resulting in an increase in the sensitivity and selectivity. Another effective way to improve the SWNT sensor properties is to dope SWNTs by functional molecules or by impurity atoms [3]. The doping of SWNTs could change the electronic properties of SWNTs, leading to an increase in sensitivity and selectivity toward a certain species of gas analytes [3, 17]. For example, n-type doping of SWNTs by polyethyleneimine rendered SWNTs electron rich, leading to an increase in the sensitivity and selectivity toward electron-withdrawing NO2 [29]. It could be of great interest to synergically combine both these approaches namely immobilization of binding ligands and doping of SWNTs to further enhance the performance of SWNT sensors.

Recently, due to the increased threat of terrorist activity and the need for homeland security, SWNT-based chemiresistors for detection of dimethyl methylphosphonate (DMMP) (stimulant of nerve agent sarin) have been extensively investigated [13–16, 27, 28, 31]. To improve SWNT sensor performance, hydrogen-bond acidic substituents, such as hexafluoroisopropanol (HFIP) was usually grafted onto the sidewalls of SWNTs [16, 27, 28]. The acidic substituents could interact with DMMP by the hydrogen bonding interaction. This interaction enhances sorption of the vapors of DMMP onto the surface of SWNTs, leading to an increase in sensitivity and selectivity to DMMP. So far, such a functionalized SWNT sensor can detect DMMP vapor at tens of parts-per-billion (ppb) concentration [16, 27, 28]. However, this sensitivity needs to be further significantly improved since sarin is extremely toxic (according to US National Institute for Occupational Safety and Health, inhalation of only 64 ppb sarin vapor can lead to death within 10 min).

In this paper, we reported a SWNT chemiresistive sensor for rapid detection of DMMP down to 20 parts-per-trillion (ppt) concentration at room temperature. This SWNT chemiresistive sensor was hole doped and surface functionalized by tetrafluorohydroquinone (TFQ). The functional TFQ molecules could not only selectively bind DMMP onto the side walls of SWNTs via the strong hydrogen bonding interaction, but also tailor the electronic properties of SWNTs via heavy hole doping. This synergetic effect significantly improved the sensitivity of the devices, and enabled the devices easy, rapid, and recoverable detection of DMMP at ppt level at room temperature.

2. Experimental details

2.1. SWNT chemiresistor fabrication and functionalization

The SWNT solution (0.01 mg ml−1 in water) with 99% semiconducting nanotubes was purchased from Nano Integris Co. The Si/SiO2 wafer used is a n-doped Si(100) wafer with 300 nm oxide on the top of the Si wafer. The SWNTs were deposited on a Si/SiO2 wafer using a self-assembly method reported previously [32] 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 aminopropytriethoxy silane (APTES) solution (four drop APTES in 20 ml of isopropanol (IPA)) for 15 min, then rinsed with IPA and blown dry with N2. Next, the functionalized wafer was immersed into the 0.01 mg ml−1 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.

A microsyringe (10 μl) was used to drop-cast TFQ on the device. One drop (about 3.3 μl) of TFQ solution (0.3% in acetone) was dropped onto the sensor chips and then the acetone was vaporized at room temperature for about 30 s.

2.2. Characterization

The morphologies of the SWNTs were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55). AFM images of SWNTs were taken on a MultiMode Nanoscope V scanning probe microscopy system (Veeco).

2.3. Sensor testing system

The sensor testing system is shown in figure S1 (available at stacks.iop.org/Nano/22/425501/mmedia). To dilute the DMMP vapors to ppt concentration, three step dilution processes were performed. First, the nitrogen, used as carrier gas, flowed through a porous glass-disk bubbler containing liquid DMMP to form DMMP vapors. The flow ratio of N2 to DMMP vapor was controlled by Beijing Qixing mass flow controllers from 1 to 30 ml min−1. Then this DMMP vapor was mixed with the diluting N2 (1–10 l min−1) in a stainless steel mixer, and the output flow ratio of the diluted DMMP vapor was controlled by Honeywell mass flow controllers (1–1000 ml min−1). The diluted DMMP vapor was further diluted by N2 (1–10 l min−1) to 200 ppt concentration in a glass bottle. To obtain 20 ppt DMMP, the 200 ppt DMMP
was further diluted by N₂ under the control by Honeywell mass flow controllers (20–200 ml min⁻¹). 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. We kept the flow rate of 2 l min⁻¹ that was introduced to the sensing chip, and the surplus gas flow was introduced into the outside environment through the outlet (see the gas testing system in the figure S1 available at stacks.iop.org/Nano/22/425501/mmedia). When the DMMP concentration was varied, the flow rate to the sensing chip was kept constant.

The electrical signal of the sensor was monitored using a semiconductor parameter analyzer (Agilent 4156C). First, the sensor chip was exposed to the N₂ flow (no DMMP) to get a stable baseline signal. The N₂ flow rate was kept at 2 l min⁻¹, which is equivalent to that of the testing gas. 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 (25 °C). The DMMP was desorbed from the SWNT surface by N₂ blowing together with illumination with a lamp (the wavelength was 710 nm and the power was 200 W). The sensor response was evaluated by the resistance change at a sampling voltage of 1 V.

To measure the I–V curves for each concentration of DMMP, the sensor device was exposed to the DMMM for 2 min. Before the next measurement of the I–V curve, the resistance of the sensor was returned to its initial value by N₂ blowing together with mild illumination with a lamp.

3. Results and discussion

Figure 1 panels (a) and panels (b) show the schematic and optical image of the SWNT chemiresistor structure, respectively. In this chemiresitive sensor, the SWNTs were used as conducting channels in the interdigitated electrodes. This electrode had a total area of 0.7 mm x 0.85 mm and line width of 10 μm. The random network of semiconducting SWNTs was formed between these interdigitated electrodes, as shown in the AFM image of the SWNT network between interdigitated electrodes (figure 1(c)). The functionalization of the SWNT sensors was performed by dropping one drop of TFQ acetone solution onto the sensors and then vaporization of acetone at room temperature. The AFM image shows that many TFQ particles are absorbed on the SWNTs and the average height of the SWNTs increases from 4.5 to 14 nm after functionalization (figure S2, supporting information available at stacks.iop.org/Nano/22/425501/mmedia).

A conductance between two electrodes was measured to investigate the sensory response. The sensor response (R) in conductance is defined as \( R = \Delta G / G_0 = (G - G_0) / G_0 \), where \( G_0 \) and \( G \) are the conductance of nanotubes before and after exposure to the testing gas. Figure 2(a) shows the I–V curves obtained under DMMP concentrations.
Figure 2. (a) I–V curves measured on a TFQ functionalized SWNT sensor showing the response to different concentrations of DMMP. ((b), (c)) Normalized conductance change ($\Delta G/G_0$) versus time of the sensor upon exposure to different concentrations of DMMP. 20 and 60 ppt of DMMP were obtained using a three-steps diluting processes. (d) The conductance change versus DMMP concentration from 20 ppt to 5.4 ppb.

from 20 ppb to 12 ppm (the I–V curves were asymmetric, which might be caused by the asymmetric contact and/or by some pollution absorbed on the electrodes [33–37]). With the increasing DMMP concentration, the conductance of the TFQ functionalized SWNT sensor monotonically decreased from 19 to 8 $\mu$A. Four sensing cycle experiments with lower DMMP concentration from 200 ppt to 5.4 ppb were also carried out (figure 2(b)). The results show that the TFQ functionalized sensor exhibits fast response and is ultrasensitive to the presence of DMMP vapor. For instance, it gave 3.4% conductance change upon exposure to 200 ppt of DMMP with a response time of less than 2 min, without the need for pre-concentration step. Furthermore, a conductance change of 1.7% was clearly observed in response to 20 ppt of DMMP (figure 2(c)). This sensitivity is about five orders of magnitude higher than that of the control unmodified SWNT sensor which has a detection limit of about 1 ppm toward DMMP (figure S3, supporting information available at stacks.iop.org/Nano/22/425501/mmedia), and about three orders of magnitude better than that of the HFIP functionalized SWNT sensors previously reported (detection limit being about 20–50 ppb) [16, 27, 28]. Our sensor also provided a sensitivity that is better than those of state-of-the-art methods such as gas chromatography–mass spectroscopy (GC–MS), ion mobility spectrometry, flame photometric detection, and photoionization detection (detection limit being from ppb to ppm toward DMMP) [3]. Figure 2(d) also shows that the change of the conductance increased with increase in the DMMP concentration from 20 ppt to 5.4 ppb. Importantly, it was found that after four sensing cycle experiments, about 98% of the initial conductance of this device could be recovered by reference gas blowing together with mild illumination using a lamp (figures 2(b) and (c)), which is important for the SWNT sensor practical applications.

To explore the sensing mechanism of the DMMP response in our TFQ/SWNT sensors, the transfer characteristics ($I_{sd}$ versus $V_g$) of the sensor were measured using the Si substrate as a back gate. The measurement was operated at a constant source–drain voltage of 1 V and a gate voltage between $-15$ and $+15$ V. As shown in figure 3(a), the SWNT device shows p-type semiconductor behavior with holes as the majority carriers, evidenced by the decreasing electrical conductance when the gate voltage ($V_g$) was swept from negative to positive values. For bare SWNT sensors, the decrease in conductance upon exposure to DMMP was attributed to charge transfer from the electron-donating DMMP molecule to the nanotubes [13, 14]. The nanotubes retained p-type semiconductor behavior after absorption of TFQ onto the nanotubes, but a significant increase in the conductance of nanotubes by 460% (figure 3(b)) and a positive shift of threshold voltage were observed.
Scheme 1. Possible DMMP sensing mechanism of the TFQ functionalized SWNT sensor. TFQ hole doped the SWNTs via addition of $H^+$ onto the nanotubes. When DMMP interacted with the acid hydroxyl groups on the surface of SWNTs, the strong hydrogen-bond interaction between acid hydroxyl groups and DMMP not only promoted sorption of DMMP vapors onto the SWNT films, but also dedoped SWNTs.

Figure 3. (a) The source–drain current ($I_{ds}$) versus gate voltage ($V_g$) of the bare and functionalized SWNT sensors. Source–drain bias voltage = 1 V. The TFQ functionalized SWNT sensor was exposed to 16 ppm of DMMP. (b) $I$–$V$ curves of the bare SWNT and fluorinated molecule functionalized SWNT sensors. (figure 3(a)). These results confirmed that the absorbed TFQ enriched the hole carriers on the nanotubes by p-doping [4, 38].

We also observed no enrichment in the hole carriers when SWNTs were functionalized by electron-deficient 1,2,4,5-tetrafluorobenzene (TFB) (figure 3(b)). Because TFQ has the same electron-deficient property as TFB, the enrichment in the hole carriers by TFQ was not induced by electron transfer from the nanotube to TFQ, but by the acid hydroxyl groups of TFQ which were expected to hole dope the SWNTs via addition of $H^+$ or holes onto the nanotubes. Considering the fact that the fluorinated phenols interact with DMMP by strong hydrogen bonding [39], the acid hydroxyl groups in TFQ played two important roles in enhancing the sensitivity of our devices: improving the binding affinity with DMMP via formation of hydrogen bonding and tuning the Fermi level of the SWNTs via heavy hole doping. This hole doping of SWNTs is a very important element for our sensor performance because the electrical conductance of nanosensing elements can be strongly modulated by doping/dedoping [40–44]. When DMMP interacted with the acid hydroxyl groups on the surface of SWNTs, the strong hydrogen-bond interaction between acid hydroxyl groups and DMMP not only promoted sorption of DMMP vapors onto the SWNT films, but also dedoping of the TFQ functionalized SWNTs (scheme 1). This positive synergetic effect caused significant hole depletion in the p-type SWNTs upon exposure to DMMP, resulting in a sharp decrease in the conductance and a negative shift of the threshold voltage (figure 3(a)). The dedoping of the TFQ functionalized SWNTs upon exposure to DMMP was evidenced in an experiment where a mixture of TFQ and DMMP (the molar ratio of DMMP: hydroxyl groups being 1:1) was dropped onto the SWNT networks and then the solvent was vaporized. As shown in figure 4, the SWNTs retained p-type semiconductor behavior after absorption of DMMP–TFQ onto the nanotubes, but a decrease in the conductance of the nanotubes was observed (as opposed to significant increase for TFQ alone). This result confirmed that the TFQ molecules can no longer hole dope the nanotubes after they interact with DMMP.
We also used 3,5-bis(trifluoromethyl) phenol (BTP-A) to functionalize the SWNT sensor. BTP-A can interact with DMMP by strong hydrogen bonding as TFQ does [39]. The nanotubes retained p-type semiconductor behavior after functionalization by BTP-A (figure 5(a)), but no increase in the conductance was observed after the functionalization (figure 3(b)), suggesting BTP-A cannot hole dope SWNTs. The sensors response to DMMP shows an increase in the sensitivity after being functionalized by BTP-A (figure 5(b)), which could be ascribed to the strong hydrogen bonding between DMMP and BTP-A [39], but the sensitivity was significantly lower than that of a device functionalized by TFQ (figure 5(b)). This result further confirms that the synergetic effect of enhancement of binding affinity and the heavy H+ doping seems essential for the ultrasensitivity of our devices.

The use of sorted, 99% semiconducting SWNTs is another important factor for the high sensitivity of our sensors. Our previous study has shown that the unsorted SWNT network sensors exhibited a detection limit of about 5 ppm toward DMMP [14], whereas the sorted, 99% semiconducting SWNTs exhibited a detection limit of about 400 ppb (figure S3 available at stacks.iop.org/Nano/22/425501/mmedia). The detection limit decreased to 50 ppb when the unsorted SWNT sensors were functionalized by TFQ (figure S4 available at stacks.iop.org/Nano/22/425501/mmedia), but it was significantly higher than that of the TFQ functionalized sorted SWNT sensors (about 20 ppb). The explanation for this different sensing behavior is that, for unsorted SWNTs, the electrical properties of the SWNT network are dominated by the metallic SWNTs in which small shifts of the Fermi level do not result in a substantial change in the density of state at the Fermi level and thus in the charge carried in the nanotube [4, 11].

The sensitivity and selectivity of the sensors to some interfering organic vapors including water, methanol, toluene, benzene, acetone, dichloromethane, hexane, and chloroform were also investigated. Figure 6 shows that the TFQ functionalized sensor exhibits excellent selectivity to DMMP when exposed to those interfering vapors. For example, the conductance change of the sensors upon exposure to 16 ppm of DMMP was 61%, whereas that change was only 6% upon exposure to 3020 ppm of acetone. At a concentration of 400 ppb, the interfering organic vapors did not give appreciable signals, whereas DMMP gave rise to 42% conductance changes (figure S5, supporting information available at stacks.iop.org/Nano/22/425501/mmedia). This makes our sensor an ideal candidate for the ultra-trace detection of DMMP. Several reasons might account for the excellent selectivity toward DMMP: first, DMMP is a hydrogen-bond basic molecule, and it can interact with hydrogen-bond acidic TFQ by strong hydrogen bonding [39]. This hydrogen-bond interaction significantly promotes sorption of DMMP vapor onto the nanotubes, leading to high sensitivity to DMMP; second, DMMP is a strong electron donor [13], and the electrons could be transferred from DMMP to the p-type nanotubes upon adsorption of DMMP onto the nanotubes, resulting in a significant change in the conductance of SWNTs; last, TFQ could highly hole dope the SWNTs. These hole-doped SWNTs might have higher binding affinity for the electron-donating DMMP.
4. Conclusions

In conclusion, we have successfully developed a chemiresistive sensor for ultrasensitive, rapid and recoverable detection of DMMP with the use of TFQ functionalized SWNT networks. This device was capable of detecting DMMP at 20 ppt concentration with a response time of less than 2 min, without the need of pre-concentration of the analytes. Moreover, this functionalized SWNT sensor exhibited excellent selectivity to DMMP when exposed to those interfering organic vapors. The reason for the ultrasensitivity of our device could be ascribed to the positive synergetic effect of enhancement of binding affinity between DMMP and nanotubes, the heavy hole doping of SWNTs by TFQ and the sorted semiconducting SWNTs. This positive synergetic effect caused significant hole depletion in the p-type SWNTs upon exposure to DMMP. We propose that a positive synergetic combination of doping of SWNTs and enhancement of binding affinity between sensitive elements and analytes is an efficient approach to produce highly sensitive SWNT devices, which might be applicable for ultrasensitive detection of other types of analytes.

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (Nos. 20504021, 50730008, 60871008, 61177052), The Fund of Defence Key Laboratory of Nano/Micro Fabrication Technology, the Natural Science Foundation of Shanghai (No. 10ZK1416300), a Shanghai Science and Technology Grant (No. 1052nm05500), the Shanghai Rising-Star Program (Grant No. 10QA1403500) and the SMC Excellent Young Faculty Project of ‘ChenXing Scholar’.

References

[22] Wongwiriyapan W et al 2011 Nanotechnology 22 055501
[31] Staii C and Johnson A T 2005 Nano Lett. 5 1774–8