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Highly sensitive detection of trinitrotoluene in water by chemiresistive sensor based on noncovalently amino functionalized single-walled carbon nanotube

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ABSTRACT

We developed a chemiresistive sensor based on 1-pyrenemethylamine (PMA) functionalized single-walled carbon nanotube (SWCNT) networks for highly sensitive and rapid detection of 2,4,6-trinitrotoluene in water. In this sensor, the SWCNT network was deposited between interdigitated electrodes, and the functional PMA molecule was noncovalently attached to the sidewall of the SWCNTs via π–π interaction. The amino substituent of PMA could selectively interact with 2,4,6-trinitrotoluene to form negative charged complexes on the SWCNT surface. These charged complexes can act as effective molecular gate and strongly change the electrical conductance of the SWCNTs, enabling the sensors easily to detect 2,4,6-trinitrotoluene at 10 parts-per-trillion (ppt) concentration in aqueous solutions, with the response time of less than 1 min, without the need of pre-concentration of the analytes. The functionalized sensors also show excellent selectivity toward 2,4,6-trinitrotoluene over those interfering organic molecules.

1. Introduction

The development of miniaturized smart sensors to detect trace and ultra-trace explosive molecules is crucial for homeland security as well as environment and human health [1]. 2,4,6-Trinitrotoluene (TNT) is one of the best-known explosives, which is not only a security threat, but also has been recognized as important environmental pollutions due to water and soil contamination [2]. TNT is a toxicant as well as a carcinogen for human being [3,4]. It can target the liver, spleen and the circulatory system, leading to severely damage to human health. The maximum allowable concentration in drinking water set by the U.S. Environmental Protection Agency is 2 parts-per-billion (ppb) [2,5]. So far, many laboratory techniques, such as ion mobility spectrometry (IMS), mass spectrometry (MS), high-performance liquid chromatography (HPLC) and surface enhanced Raman spectroscopy (SERS) have been developed to detect TNT and its metabolites. But these methods require expensive and bulk instruments or tedious sample preparation processes. There is a strong demand to develop miniaturized smart sensors for fast and real-time detection of ultra-trace TNT.

The miniaturized smart sensors based on one-dimensional (1D) nanostructures have been received much attention because of their fast and high sensitivity toward molecular adsorption. Some types of one-dimension (1D) nanomaterials, such as silicon nanowires [6], metal oxide nanowires [7] and carbon nanotubes [8–11] have been used to fabricate TNT sensors. Among these materials, single-walled carbon nanotubes (SWCNTs) receive special attention. SWCNTs are nearly ideal quantum wires with every atom on the surface [12], which are expected to exhibit excellent sensitivity toward surrounding chemical species [13]. SWCNTs also possess high aspect ratio, good environmental stability, and excellent mechanical and electronic properties. These features make SWCNTs ideal sensing materials for compact, low cost, low power and potable sensor devices [13–15]. Multiple types of SWCNT devices, such as SWCNT field-effect-transistors (FETs) [16], SWCNT chemiresistors [17] and chemicapacitors [18] have been developed for analyte detection. Among them, the chemiresistors which are based on the simple change in resistance in response to the binding of analytes are very attractive because of their simple structure and the ease of high precise measurement [17,19]. However, the pristine SWCNTs always demonstrate weak response and low selectivity toward specific molecules [20]. So, there is a need to functionalize SWCNTs to improve both the sensitivity and the selectivity of SWCNT sensors [20–23]. Recently, SWCNT-FET sensors functionalized by biomimetic molecules, such as polydiacetylene [2] and peptide [9] have been reported to detect TNT in water and a significant improvement in the sensitivity and selectivity was obtained. When a submonolayer of unbundled SWCNT network

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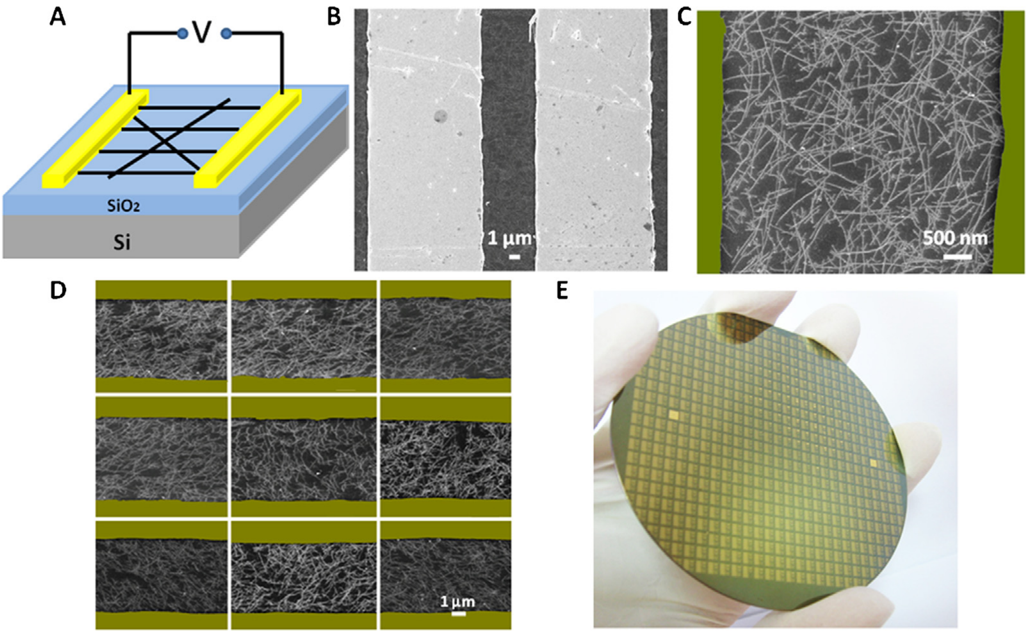

Fig. 1. (A) The illustrative schematic of the SWCNT chemiresistive sensors. The straight black and yellow lines indicating SWCNTs and metal electrodes, respectively; (B) FE-SEM image of the electrode structure of SWCNT chemiresistors; (C) FE-SEM image of SWCNTs bridging the conducting channels; (D) FE-SEM images showing SWCNTs deposited at different position on the electrode patterning wafer (E).

was used to fabricate SWCNT-FET sensors, a rapid response to TNT solution (less than 2 s) was also observed [8]. However, the current SWCNT sensors for practical detection of TNT molecules still cannot satisfy the requirement in terms of sensitivity, selectivity, simple structure and easy operation. Herein, we demonstrate highly sensitive (down to ppt level) and rapid detection of TNT (response time < 30 s when exposure to 10 ppt TNT) in water using SWCNT chemiresistive sensors, which was noncovalently functionalized by 1-pyrenemethylamine (PMA). The functional PMA molecules strongly bond onto the surface of SWCNTs via π–π interaction. The amino substituent of PMA could selectively interact with TNT to form negative charged complexes on the SWCNT surface (Scheme 1). These charged complexes can act as effective molecular gate and strongly change the electrical conductance of SWCNTs, enabling the sensors easily to detect trinitrotoluene at parts-per-trillion (ppt) level. Our functionalized SWCNT chemiresistive sensor also exhibited excellent selectivity to TNT over those interfering molecules, such as 2,6-dinitrotoluene (DNT) and 2,4-dinitrotoluene (2,4-DNT).

2. Experimental details

2.1. SWCNT network deposition and sensor fabrication

To fabricate our gas sensors, the Si/SiO_2 wafer substrate was first ultrasonically rinsed with toluene, acetone, ethanol, deionized (DI) water and Piranha solution (98% H_2SO_4:30% H_2O_2 = 3:1(v/v)) to clean the wafer. This clean wafer was immersed in aminopropyltriethoxysilane (APS) aqueous solution (1.5 mM) for 2 h, subsequently washed by DI water and kept in a vacuum evaporator at 120 °C for 1 h to form the amino-terminated monolayer on the surface of the Si/SiO_2 substrate. The purified carboxyl-functionalized SWCNTs (Carbon Solutions Inc) were ultrasonically dispersed in DI water for 2 h. The pretreated Si/SiO_2 substrate modified with an APS monolayer was immersed in the SWCNT suspension, followed by rinsing with ethanol and DI water and drying with the aid of nitrogen flow.

The SWCNT sensors were fabricated using standard microfabrication procedures as our previous report [19]. The interdigitated electrode fingers were made by sputtering 10 nm Cr and 180 nm Au onto the patterned photoresist mold. We introduced lift-off process to remove the photoresist. Finally the electrodes were ultrasonically rinsed in acetone and ethanol repeatedly, washed with DI water thoroughly and then dried by nitrogen flow before they were used.

The functionalization of the SWCNT sensors was performed by immersing the SWCNT sensor chip in 1-pyrenemethylamine hydrochloride (PMA·HCl) solution (0.036% in water) for 24 h, and then rinsing the sensor chip by DI water and ethanol to remove excessive PMA·HCl. The resulting PMA·HCl functionalized sensor chip was further immersed in triethylamine for 24 h to transform PMA·HCl to PMA. Last, the functionalized sensor chip was washed thoroughly by ethanol and dried at 60 °C.

2.2. Sensor testing system

The electrical signal of the sensor was monitored by using a semiconductor parameter analyzer (Agilent 4156C). First, a drop of DI water (10 µL, containing 0.05% DMSO) was dropped onto the sensor chip such that entire channel of electrodes was covered. Sensor measurements were performed by measuring current versus time at a constant voltage (0.5 V). After a stable baseline electrical signal was obtained, a drop of TNT solution (2 µL, containing 0.05% DMSO) was added to the droplet of water (10 µL). A solution with higher concentration of TNT was added to the existing droplet after the current stabilized. This was repeated with multiple concentrations. All sensing measurements were carried out at room temperature (25 °C).

2.3. Characterization

The morphologies of the SWCNTs and the sensors were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss