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A vapor response mechanism study of surface-modified single-walled carbon nanotubes coated chemiresistors and quartz crystal microbalance sensor arrays

Hung-Ling Lu [a], Chia-Jung Lu [a,*], Wei-Cheng Tian [b], Horn-Jiunn Sheen [c]

[a] Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan
[b] Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan
[c] Institute of Applied Mechanics, National Taiwan University, Taipei, Taiwan

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ABSTRACT

This paper compares the selectivity and discusses the response mechanisms of various surface-modified, single-walled carbon nanotube (SWCNT)-coated sensor arrays for the detection of volatile organic compounds (VOCs). Two types of sensor platforms, chemiresistor and quartz crystal microbalance (QCM), were used to probe the resistance changes and absorption masses during vapor sensing. Four sensing materials were used in this comparison study: pristine, acidified, esterified, and surfactant (sodium dodecyl sulfate, SDS)-coated SWCNTs. SWCNT-coated QCMs reached the response equilibrium faster than the chemiresistors did, which revealed a delay diffusion behavior at the inter-tube junction. In addition, the calibration lines for QCMs were all linear, but the chemiresistors showed curvature calibration lines which indicated less effectiveness of swelling at high concentrations. While the sorption of vapor molecules caused an increase in the resistance for most SWCNTs due to the swelling, the acidified SWCNTs showed no responses to nonpolar vapors and a negative response to hydrogen bond acceptors. This discovery provided insight into the inter-tube interlocks and conductivity modulation of acidified SWCNTs via a hydrogen bond. The results in this study provide a stepping-stone for further understanding of the mechanisms behind the vapor selectivity of surface-modified SWCNT sensor arrays.

1. Introduction

Volatile organic compounds (VOCs) represent a special category of hazardous substances that pose adverse effects to both the environment and human health [1]. Due to the diversity in chemical structures, the analyses of VOCs are usually performed using field sampling methods (i.e., canisters or adsorbent tubes) followed by in-lab analysis using a gas chromatograph–mass spectrometer (GC–MS) [2]. Although these analytical methods provide accurate assessments of VOC concentrations, they are often too expensive for continuous use and/or real-time analyses. On the other hand, chemical sensor arrays with cross sensitivity to VOCs can provide sufficient selectivity and detection limits for applications where immediate attention or continuous monitoring is called for [3].

Over the past few decades, several types of chemical sensors have been developed for the purpose of volatile compound or scent detection [4]. These sensor applications include metal oxide sensors [4], acoustic wave sensors (i.e., QCM and SAW) [5,6], optical sensors [7–9], and chemiresistors [10–12]. Recent research effort has been focused on improving the performance of these sensors by either employing nano structures to conventional materials such as metal oxide [13], or by applying newly developed nano materials such as metal nanoparticles [8–12] and nano carbon materials [14–16].

Among these newly developed nano materials for chemical sensing applications, carbon nanotubes have drawn much attention due to their highly adsorptive surfaces and their susceptible conductivity to environmental changes. Both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have been demonstrated as highly sensitive materials for gas and vapor detection [14,17]. The earliest gas sensor employing SWCNTs was a field effect transistor device that measured the conductivity changes of a single carbon nano-tube [18]. Several recent studies have shown that measuring the film of randomly stacked CNTs on an interdigit electrode can also achieve a highly sensitive chemiresistor

* Correspondence to: No. 88, Sec. 4, Ting-Chou Rd.,Taipei City, ROC, 11677, Taiwan. Tel.: +886 2 77346132; fax: +886 2 29324249.
E-mail address: cjlu@ntnu.edu.tw (C.-J. Lu).

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[17,19]. Aside from measuring the conductivity changes, CNTs have also been tested on QCM, SAW and optical fiber sensor platforms [20–24]. The efficacy of using CNT-based sensors for VOCs in the environment, for detecting explosives, and for breath analysis has been recently reviewed [25–27].

In addition to the application of pristine CNTs as a sensing material, both covalent and non-covalent surface modifications of CNTs have been attempted in order to create a diversified selectivity for CNT-based sensors [28]. Non-covalent modifications can be achieved via either a polymer composite [24,28–31] or surface adsorption with π–π stacking attractions [32]. The swelling mechanism that is particularly important for polymer-coated CNT sensors was explored by Feller et al. [33]. Covalent modification requires a few more steps in the chemical synthesis. Functional groups that provide specific chemical forces can be grown on the surface of CNTs [34]. Several recent studies have demonstrated surface modifications using porphyrin or other metal complexes on CNTs for highly selective detection [21,35–38].

In the present study, we investigated a series of surface-modified SWCNTs coated on both chemiresistors and QCMs. Both covalent and non-covalent modified SWCNTs were tested. By simultaneously observing both sorption mass and conductivity changes, we were able to investigate the mechanism behind selectivity changes as well as the progression of surface modifications. Different response behaviors for both sensor platforms were used to interpret how surface-modified SWCNTs react to incoming vapors as well as the role of the interactions among nanotubes in a film. The experiment design in this work enabled the observation of different aspects of surface-modified SWCNTs during vapor sensing.

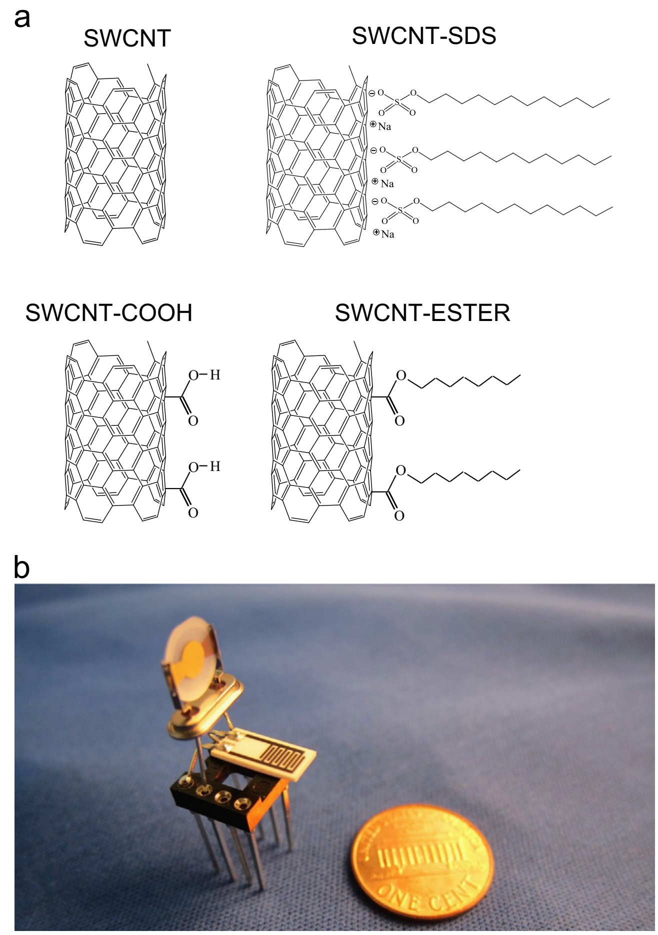

Fig. 1. (a) Chemical structures of surface modified SWCNTs (b) Photo of QCM and chemiresistor sensor platforms.

2. Experimental

2.1. Materials

High purity (> 90%) single walled carbon nanotubes were purchased from Sigma-Aldrich and used as obtained. Chemicals for surface modification synthesis such as nitric acid, thionyl chloride, octanol and sodium dodecyl sulfate (SDS) were purchased from J. T. Baker. Organic solvents for both the synthesis process and test vapor generation were obtained from either Fluka (Japan) or Alfa Aesar (UK) with a purity of 98% or higher.

2.2. Surface modification of SWCNTs

Four different SWCNTs were tested in this study: pristine, acidic surface, ether surface, and SDS-coated (Fig. 1a). The non-covalent modification of SDS surface adsorption was prepared by suspending SWCNTs in a SDS/toluene solution. The molar ratio of SDS to the carbon atoms of SWCNTs was 1:10. The mixture solution was stirred and then ultrasonically resonated for 30 min. The SWCNT in the SDS solution was then filtered, rinsed with excess amount of toluene and dried in an oven for later use. The covalent modification of SWCNTs started with acidification to form a carboxylic acid group at the surface. SWCNTs were suspended in a mixed-acid solution containing H_2SO_4:HNO_3 = 3:1. The suspended solution was stirred and ultrasonically resonated and then refluxed for 3 h. The acidified SWCNTs (i.e., SWCNT-COOH) were filtered, washed with an excess amount of deionized water and then dried in an oven.

Esterification was carried out by mixing 0.2 g of dried SWCNT-COOH with excess thionyl chloride ($SOCl_2$) in dimethylformamide (DMF) with refluxing under nitrogen at 70 °C for 24 h. The SWCNT-COOHs were converted to SWCNT-COCls in this step. After allowed to cool to room temperature, the SWCNT-COCls were rinsed with a large amount of dehydrated tetrahydrofuran (THF) and dried in a vacuum oven. Dried SWCNT-COCl was then mixed with 1 mL pyridine and 80 mL octanol and then refluxed at 117 °C for 4 days. After reflux, the solution was cooled to room temperature. The excess octanol was removed by a filtering of the solid SWCNT-$COOC_8H_{17}$ (i.e., labeled as SWCNT-ESTER for later discussions) and the final product was washed repeatedly with ethanol and THF. In terms of interacting with analytes, the polar attraction was more important than the weak dispersion from the interaction with an aliphatic chain in this SWCNT-ESTER structure.

2.3. Sensor devices

10-MHz, AT-cut, gold-electrode QCM devices were purchased from Taitein electronics, CO., Taiwan. The 10-MHz driving circuitry was constructed in-house. A screen-printed interdigit electrode (IDE) was obtained from Ghitron Technology Co., Ltd (Taiwan). There were 5 pairs of carbon electrodes with lengths of 4 mm and widths of 0.25 mm that were spaced 0.15 mm apart. The SWCNTs were dissolved in THF and spray-coated on both QCM and IDE. The spray-coat procedure was performed using a small airbrush with regulated-pressure nitrogen gas from a cylinder. The electrodes were buried under the SWCNT film. The resistance of the chemiresistor was measured through a bridge circuit. The thickness of the films was examined by cross-section SEM images (i.e., see Supporting information). The thickness of the SWCNTs on IDE was ~17 μm. The thickness of the SWCNTs on QCM was ~33 μm. We intentionally added more mass to the QCM to enhance the sensitivity for this device. Fig. 1b shows the photos of both sensors as one unit. The