Sensors and Actuators B 147 (2010) 316–321

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Improving the sensitivity of carbon nanotube sensors by benzene functionalization

Hosung Kang[a], Seokho Lim[b], Noejung Park[b], Kyoung-Yong Chun[c], Seunghyun Baik[a,c,d,*]

[a] SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea
[b] Department of Applied Physics, Dankook University, 44-1, Jukjeon-dong, Yongin-si 448-701, Republic of Korea
[c] School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea
[d] Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea

ARTICLE INFO

Article history:
Received 23 December 2009
Received in revised form 23 February 2010
Accepted 10 March 2010
Available online 16 March 2010

Keywords:
Carbon nanotubes ;·Gas sensors
Sensitivity
Functionalization
SF_6
Dissociation
Partial discharge

ABSTRACT

The detection of dissociated gas species, generated either by plasma or partial discharge, is of great interest because the dissociated species can alter inherent potential of a gas: for example, the insulating characteristics of SF_6. Here we report that the sensitivity of carbon nanotubes (CNTs) about dissociated species of SF_6 substantially increases by functionalizing with benzene. The sensors were prepared by the dielectrophoretic deposion of CNTs on microelectrodes. The target analytes were chemisorbed on the benzene-functionalized CNTs, and the sensors also could be regenerated by annealing at around 400 °C. The sensor response was analytically described by the modified Langmuir isotherm model. Through the density functional theory calculations, we identified that SOF_3 was particularly influential on the electronic structure of the benzene-functionalized CNTs whereas SOF_1, SOF_2, SO_2F_2, and HF showed negligible effects. The proposed functionalization methodology provides insight into how to increase sensitivity of carbon nanotube sensors for the detection of dissociated SF_6 species.

1. Introduction

Carbon nanotubes (CNTs) are allotropes in which carbon atoms are covalently bonded in cylindrical structures [1,2]. Their unique properties as sensor elements have received considerable attention, and successful detection of various gases, organic vapors, and radicals has been reported [3–12]. Sensitivity has been further enhanced by applying selective binding ligands [13,14], oxidation defects [15] and chemical functionalization [16] although nanotube sensors exhibit high intrinsic sensitivity due to the large surface-to-volume ratios and molecular compositions consisting of surface atoms only [3,16,17].

The detection of dissociated gas species, generated by plasma [8–10] or partial discharge [11,12], is of interest to researchers from various fields [18]. The dissociated species, such as radicals and ions, may be exploited to adjust material properties [9,10]. In some cases, they are harmful to equipment performance and, thus, need to be precisely controlled. One notable example is the decomposed species of sulfur hexafluoride (SF_6). The compressed SF_6 gas has been used as an electrical insulating medium in high power electrical devices such as gas-insulated switchgears [19]. The detection of SF_6 dissociation in the early stage is important since decomposed by-products can cause electrical break down of the equipments.

Partial discharge of SF_6 in the presence of oxygen and water molecules generates decomposed and oxidized species, including SOF_2, SOF_3, SOF_4, SO_2F_2, SO_2, HF, and SF_4, and carbon nanotube sensors have been employed to detect these species [11,12,19–21]. In this study, we significantly improved the sensitivity of CNTs by functionalizing with benzene. The adsorbed species on the tube surface were analyzed by density functional theory and experimentally confirmed by Fourier transform infrared spectroscopy (FT-IR). Modified Langmuir isotherm models were applied to interpret the sensor response.

2. Experiments

2.1. High voltage chamber setup

A schematic of the experimental setup is shown in Fig. 1 [11]. High voltage was supplied to a needle electrode (4 mm gap, stainless steel) where partial discharge was generated. The chamber was initially at air atmospheric environment and then vacuumized to 14.67 Pa. Then SF_6 (99.9999% purity) was introduced at an absolute

* Corresponding author at: School of Mechanical Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440-746, Republic of Korea. Tel.: +82 31 290 7456.
E-mail addresses: inthesky6@skku.edu (H. Kang), lice_haha@hanmail.net (S. Lim), noejung@dku.edu (N. Park), kychun@skku.edu (K.-Y. Chun), sbaik@me.skku.ac.kr (S. Baik).

0925-4005/$ – see front matter.
doi:10.1016/j.snb.2010.03.028

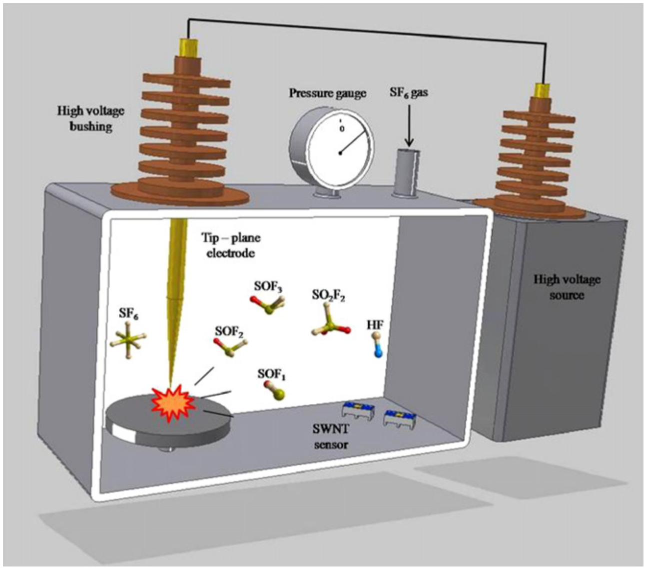

Fig. 1. Schematic of the experimental setup. Partial discharge is generated at the tip-plane electrode where SF_6 is dissociated into radicals and ions.

pressure of 140 kPa. Carbon nanotube sensors operating at room temperature were placed 10 cm away from the needle electrode.

2.2. Preparation of CNT sensors

Single-walled carbon nanotubes (SWNTs) produced by the arc-discharge method were obtained from Iljin Nanotech. Nanotubes were suspended in sodium dodecyl sulfate aqueous solution (SDS, Sigma–Aldrich, 436143, 1 wt.%) by ultra-sonication (BRANSONIC 5510R-DTH) for 20 min at 540 W and ultra-centrifugation (Beckman coulter LE-80K) for 4 h at $170{,}000 \times g$ [22]. Finally, the supernatant was carefully decanted. Nanotube sensors were prepared by the dielectrophoretic deposition method [8,11]. Microelectrodes were fabricated by a conventional photolithographic method. Titanium (5 nm) and gold (200 nm) layers were thermally deposited (EVACO-41SC, DR Vacuum) on a SiO_2–Si substrate as top electrodes. A drop of nanotube suspension (10 μl) was placed on the electrode after applying alternating current electric field at a frequency of 10 MHz and a peak-to-peak voltage of 8 V using a function generator (Agilent 33220A). The droplet was blown off after 10 min, and the function generator was turned off. The conductance change of the nanotube sensor was monitored using a data logger (Agilent 34970A). For benzene functionalization, SWNTs were dispersed in benzene (Sigma–Aldrich, 12550, 0.1 wt.%) by ultra-sonication for 20 min at 540 W without any surfactant. The upper solution was decanted, and benzene-functionalized nanotube sensors were prepared by dielectrophoresis using identical conditions.

2.3. Sample preparation for FT-IR measurement

The small penetration depth of microscope attenuated total reflectance (ATR, HYPERION) of FT-IR analysis (Bruker IFS-66/s) was carried out. The imaging accessory made of a germanium crystal source, which has a contact radius of 0.6 mm, was used for the small penetration depth of the microscope ATR method. A drop of nanotube suspension (5 μl) was air-dried on an aluminum-coated silicon substrate for the FT-IR analysis since the number of dielectrophoretically deposited tubes was not large enough to obtain clear FT-IR signal [19].

3. Results and discussion

3.1. Partial discharge detection response of CNT sensors

A magnified SEM image of carbon nanotube sensor is shown in Fig. 2(a). Fig. 2(b)–(d) compare carbon nanotube characteristics before and after the benzene functionalization. As shown in Fig. 2(b), a benzene peak [23] at 1590 cm^{-1} could be observed after

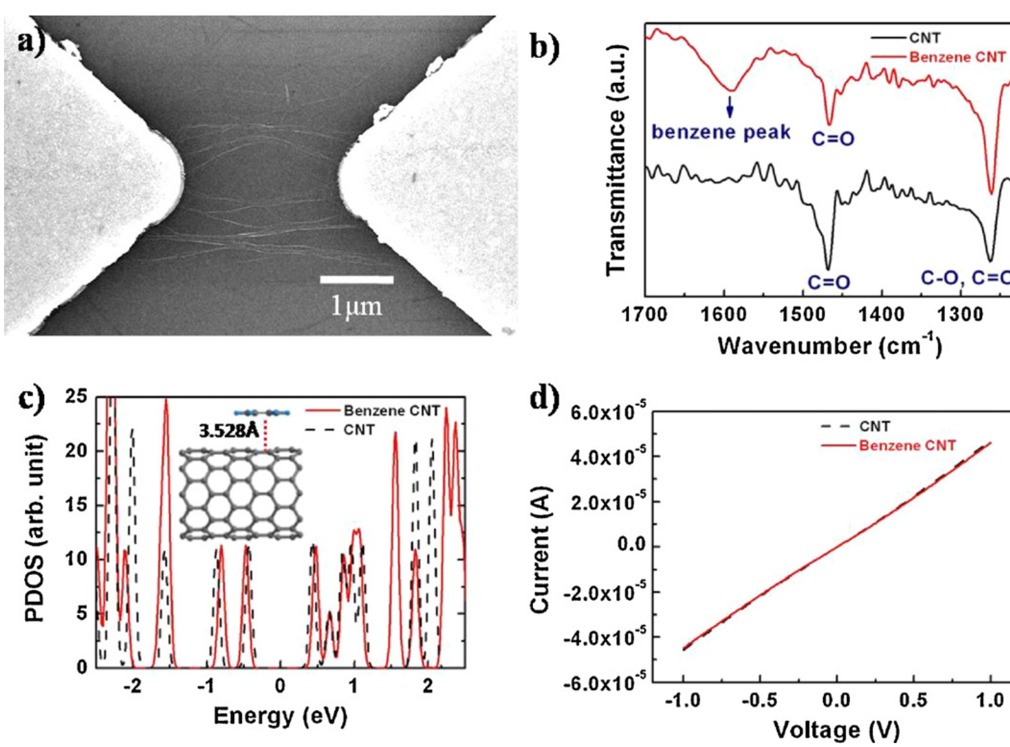

Fig. 2. Characterization of CNTs before and after the benzene functionalization (a) SEM image of the dielectrophoretically deposited benzene-functionalized CNTs, (b) FT-IR analysis before and after the benzene functionalization, (c) comparison of the density of states and (d) comparison of the current–voltage characteristics.