The gas sensing performances of gas sensors based on the dielectrophoretically manipulated multi-wall carbon nanotubes with various functionalized groups towards NH_3

WANG Hai-bo & FENG Li-li *[1] ,CHEN Hui-ying[2]

[1]Key Laboratory of Urban Stormwater System and Water Environment of Ministry of Education, Beijing Climate Change Response Research and Education Center, Beijing University of Civil Engineering and Architecture, Beijing 100044, P. R. China

[2]College of Life and Environmental Sciences, Minzu University of China, Beijing 100081, P. R. China

*Corresponding author: Beijing University of Civil Engineering and Architecture, Beijing, 100044, P. R. China;fenglili@bucea.edu.cn

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ABSTRACT: Gas sensors based on raw multi-wall carbon nanotubes (raw MWNTs) and functionalized multi-wall carbon nanotubes (MWNTs-x) were fabricated on the chromium-silver-gold microelectrode chips by dielectrophoresis process. The positive dielectrophoresis was observed for the particles of carbon nanotubes. The gas sensing performances of the fabricated gas sensors towards different concentrations of NH_3 were tested at room temperature. It was found that the response time, recovery time and sensitivity of gas sensors towards NH_3 were increased with the increase of NH_3 concentrations. We demonstrated that functionalizing MWNTs does not change the adsorption properties of NH_3 on MWNTs. In addition, We conclude that the interactions between MWNTs and NH_3 such as surface area and small diameter are influential factors for the gas sensing performances of these gas sensors.

Introduction

Recently, carbon tubes (CNTs) has attracted great interest owing to its unique mechanics, electrical and chemical properties. This makes the CNTs a promising material for a variety of potential applications[1]. Previous works have demonstrated that CNTs can detect a wide range of gases at or near room temperature, such as NO_2, NH_3, so it is an ideal candidate for sensing material. CNT-based gas sensing utilizes the electrical resistance change of the CNTs due to adsorption of gas molecules as the electricsl readout. Compared to other gas sensors, CNT-based gas sensors have many outstanding properties such as faster response, higher sensitivity, and lower operating temperature[2].

Many research groups use SWNTs for NO_x[3], Organic vapor[4], O_3[5]detection and MWNTs for SF_6[6], CO[7], H_2S[8,9], H_2 [10,11], VOC[12] detection. The recovery time of SWNTs gas sensors are actually long, although the majority of their performances are better than the traditional ones. MWNTs gas sensors receive little attention due to a low sensitivity. It is a challenge to enhance the reduce the response time and recovery time. We attempt to modify MWNTs and manipulate the MWNTs using dielectrophoretic (DEP) in order to solve these problems.

In this study, the gas sensors based on raw MWNTs and MWNTs-x (-OH, -COOH, $-NH_2$) were fabricated on the chromium-silver-gold microelectrode chips by DEP. The gas sensing performances of the fabricated gas sensors towards different concentrations of NH_3 were tested at room temperature.

Experimental

All MWNTs from the supplier (Cheaptubes, Brattleboro, USA) were synthesized by chemic-al

vapour deposition, which have purities of > 99%. Hydroxylated (OH), carboxylated (COOH) and aminoated (NH_2) MWCNTs were functionalized by plasma treatment and contained 7±1.5 wt% functional groups according to X-ray photoelectron spectroscopy (XPS) and titration results provided by the supplier. The porous characteristics of the MWCNTs materials are shown in table 1.

Table 1 Porous characteristics of the MWNTs materials

Materials	S_{BET}	V_{pore}	D_{pore}
	$m^2 \cdot g^{-1}$	$cm^3 \cdot g^{-1}$	nm
Raw MWNTs	224	1.86	33.2
MWNTs-NH_2	206	2.12	41.2
MWNTs-OH	205	2.31	45.3
MWNTs-COOH	178	1.97	44.2

All MWNTs were suspended in ultrapure water and ultra-sonicated for 20 min. An finger-protruding microelectrode of thin chrome film was patterned on a quartz glass substrate by vacuum evaporation technique. The electrode had 40 μm width and 40 μm the minimum clearance.

The MWNTs suspension was dropped into the microelectrode. The DEP trapping of MWNTs to the microelectrode was performed with ac voltage of 2 MHz frequency and 8 V amplifier (peak to peak value). During the DEP process, the electrode impedance was continuously monitored using microscope (model CN15-T31, Nippon Optical works Co., Ltd, Japan). After a desired time period, the DEP process was stopped and ultrapure was gently dried out at room temperature to prepare the microelectrode retaining MWNTs as a gas sensor. In the gas experiments, NH_3 was employed as a sample gas. The same microelectrode chamber as used in the DEP fabrication process was employed also for the gas sensing experiments. The chamber was firstly filled with air and then NH_3 was introduced. After each sensing cycle, the chamber was flushed with air. The sensor impedance was continuously measured at room temperature using the universal meter (model UT805A, yuanhengtong Co., Ltd, China).

Results and discussion

Dielectrophoretic manipulation of the raw MWNTs and MWCNTs-x

Microscope images of raw MWNTs and MWCNTs-x trapped on the microelectrode are shown in Fig.1.The trapped MWNTs seemed to be aligned along the electric field line and bridged over the electrode tips.

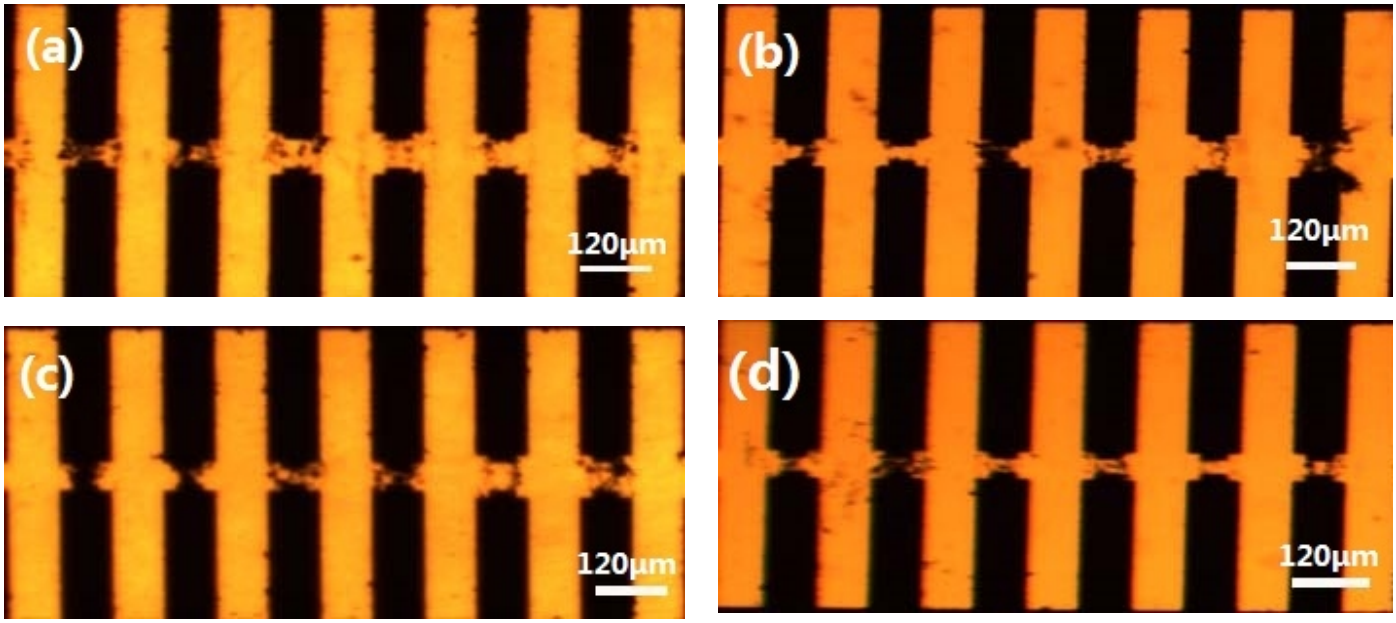

Fig. 1. Microscope images of MWNTs trapped onto microelectrode by positive DEP: (a) raw MWNTs; (b) MWNTs-OH; (c) MWNTs-COOH; (d) MWNTs-NH_2.

Gas sensing performance

The dynamic responses of MWNTs gas sensors exposure to NH_3 with concentrations from 10 ppm to 100 ppm are shown in Fig.2.

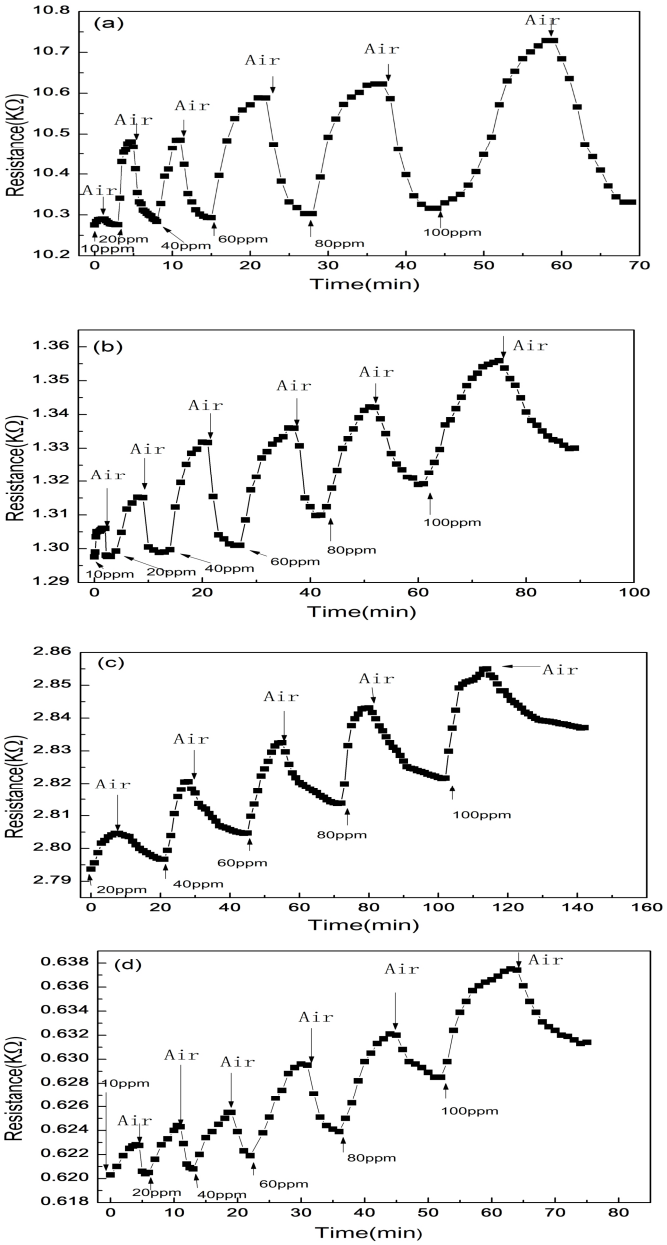

Fig.2. Dynamic response of MWNTs to different concentrations of NH_3 : (a) raw MWNTs; (b) MWNTs-OH; (c) MWNTs-COOH; (d) MWNTs-NH_2.

In order to examine effects of the MWNTs modified with different functional groups (-OH, -COOH, -NH_2), four sensors were fabricated. The sensitivity (S) of the sensor is defined as $S = \Delta R/R_0 \times 100\%$, where ΔR is the resistance change after NH_3 exposure and R_0 is the initial resistance. When the sensor was exposed to NH_3, the resistance increased for all MWNTs sensors. The resistance increase of MWNTs by NH_3 exposure suggested that MWNTs, MWNTs-OH, MWNTs-COOH and MWNTs-NH_2 were p-type semiconductors. The charge transfer between NH_3 and MWNTs results in a reduced hole density in MWNTs, and thus an increased resistance[13]. It was found that the response time, recovery time and sensitivity of gas sensors towards NH_3 were increased with the increase of NH_3 concentrations. When the NH_3 was replaced with air, the resistance returned to the initial value.

Fig.3. plots the sensitivity and response time of MWNTs and MWNTs-x gas sensors measured

in the NH_3 concentration rang of 10-100 ppm. We demonstrated that functionalizing MWNTs does not change the adsorption properties of NH_3 on MWNTs. Raw MWNTs sensor showed a 1.14% reversible resistance change to 10 ppm NH_3 with a response time of 30 s. Higher sensitivity of raw MWNTs is observed because of the lager surface area and small diameter that allows faster diffusion of gas into the MWNTs. The smaller diameters give a shorter response time because diffusion into small-diameter cylinders is fast. The normalized sensitivity of the MWNTs sensor is five times higher than that of the MWNTs-COOH sensor.

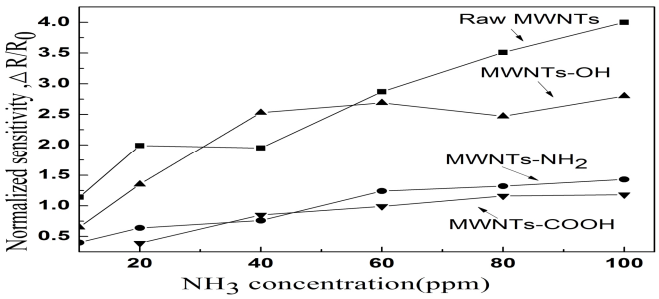

Fig.3. The sensitivity comparison of raw MWCNTs, MWCNTs-OH, MWCNTs-COOH, MWCNTs-NH_2 gas sensors.

Conclusions

A MWNTs-based NH_3 sensor was successfully manipulated by positive DEP on the chromium–silver-gold microelectrode chips. The gas sensing performances of the fabricated gas sensors towards different concentrations of NH_3 were tested at room temperature. It was found that the response time, recovery time and sensitivity of gas sensors towards NH_3 were increased with the increase of NH_3 concentrations. We demonstrated that functionalizing MWNTs does not change the adsorption properties of NH_3 on MWNTs. Raw MWNTs sensor showed a 1.14% reversible resistance change to 10 ppm NH_3 with a response time of 30 s.

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