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Paper-based Volatile Organic Compound Sensor using Multi-Walled Carbon Nanotubes on a Polytetrafluoroethylene Membrane

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Abstract

In this research, a paper-based volatile organic compound (VOC) sensor using multiwalled carbon nanotubes (CNTs) on a polytetrafluoroethylene (PTFE) membrane was successfully fabricated. The optimum of CNT amount and the responses to VOC vapors were investigated. Firstly, CNTs were functionalized with oxygen-containing function groups by oxygen plasma for 30 min, followed by dispersing the functionalized CNTs in ethanol with a concentration of 0.01 mg/mL. Finally, the paper-based sensor was fabricated by vacuum filtration of CNT suspension. The amounts of CNTs on a membrane were controlled by the volume of the CNT suspension in the range of 20 – 40 mL. The film resistance decreased with a volume of CNT suspension. The CNT sensor formed from 30 mL of CNT suspension exhibited the optimum amount of CNT for VOC sensing. Moreover, the paper-based sensor shows the highest response to methanol and the lowest response to benzene. Such a different sensitivity is essentially due to the different polarities of VOC molecules. These results imply a potential use of CNT on a paper as a low-cost, flexible, portable and disposable VOC sensor.

Keywords: Carbon nanotube, Volatile organic compound, Paper, Sensor

1. Introduction

Due Gas sensor technology has played an important role in the environmental monitoring. To date, the commercial gas sensors are mainly based on metal oxide semiconductors (MOS) which have been developed to detect gases and volatile organic compound (VOC) with a detection limit down to the parts per millions (ppm) level. [1,2] However, the main disadvantages of MOS-based gas sensors are nonselectivity, slow response, and high operating temperature (> 200 °C). The ideal gas sensor requires high sensitivity, high selectivity, fast response, long-term stability and low power consumption. Carbon nanotubes (CNTs) is an allotrope of carbon family which have attracted considerable attention as alternative sensing materials because of their superior characteristics in structural, electrical, optical, mechanical and thermal properties. [3] CNTs have shown a potential use for gas sensing application due to their well-organized nanostructure, large specific surface area and electrical properties. CNT-based sensors have demonstrated high response to oxidizing gases down to the parts per billion (ppb) level under room-temperature operation. [4-7] Nevertheless, the most gas sensors are prepared on the rigid substrate such as a silicon wafer and a printed circuit board. With recent advancements in the field of wearable devices based on Internet of Things (IoT), flexible sensor systems with biocompatibility and disposable properties and inexpensive process have gained significance. One approach for overcoming the challenges is paper-based sensors. Paper-based sensors using single-walled CNTs

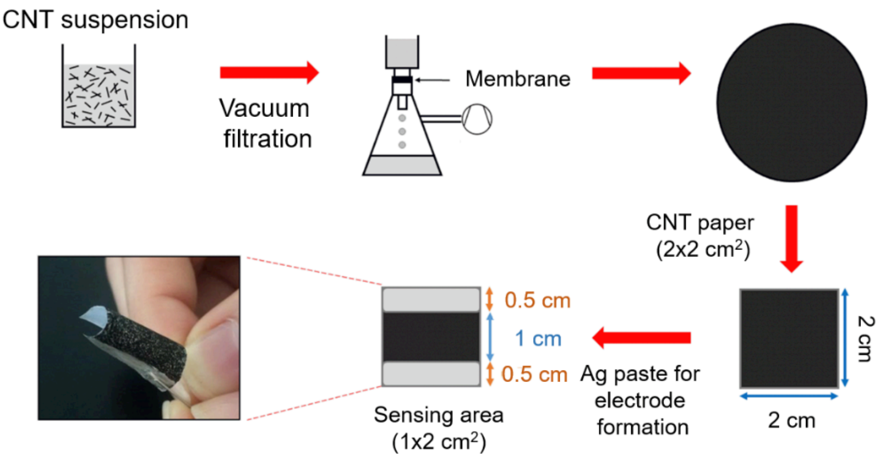

Fig. 1. Schematic diagram of fabrication of a paper-based VOC sensor using CNTs.

(SWNTs) have been demonstrated as humidity, ammonia sensor and volatile organic compound (VOC) sensors with a higher sensitivity than that of on a glass substrate. [8-10] However, the CNT amount dependent VOC sensing properties of a paper-based sensor has not been fully explored.

In this research, paper-based VOC sensor using multi-walled carbon nanotubes (CNTs) on a membrane filter was fabricated. The optimum CNT amount and the responses to VOC vapors were investigated. The amounts of CNTs on a paper were controlled by the volume of the CNT suspension. The CNT sensor formed from 30 mL of CNT suspension exhibited the optimum amount of CNT for VOC sensing. Moreover, the CNT-based sensor on a paper shows the highest response to methanol and the lowest response to benzene.

2. Experimental details

2.1 Preparation of CNT suspension

Firstly, multiwalled CNT (NANOCYL, a diameter and a length in the ranges of 9.5 nm and 1-2 µm, respectively) were treated by oxygen plasma to functionalize their walls with oxygen-containing function groups. For plasma treatment, 1 g of CNTs was treated using an expanded plasma cleaner (Harrick Scientific) at an RF frequency of 13.56 MHz and a power of 29.6 W for 30 min. Next, the functionalized CNTs were sonicated with ethanol at a concentration of 0.01 mg/mL for 3 h to prepare CNT suspension.

2.2 Fabrication of gas sensor device

The CNT suspension was deposited on a commercial PTFE membrane (Omnipore^{TM} Membrane Filters, an average pore size of 0.2 µm) by a vacuum filtration method and dried under room temperature. The amount of CNT and the thickness of CNT film on a membrane were controlled by the volume of the CNT suspension varying at 20, 25, 30, 35 and 40 mL (hereinafter referred to as CNT-20, CNT-25, CNT-30, CNT-35 and CNT-40 respectively). After vacuum filtration, the paper-based CNT sensor was cut into a size of 2×2 cm^2. The silver paste was coated on the CNT paper and was used for contact electrodes. The distance between two electrodes was about 1 mm, thus the sensing area was approximately 1×2 cm^2. A schematic view of the sensor fabrication process is shown in Fig. 1.

2.3 Characterization techniques

The morphologies of the CNTs on a PTFE membrane were characterized by field emission scanning electron microscopy (FESEM; JEOL JSM-7800F). The FESEM observation was carried out in a high vacuum mode with a base pressure of approximately 1×10^{-4} Pa and an acceleration voltage of 1 kV without any surface treatment with metal coating. The current-voltage (*I-V*) characteristics were measured in the voltage range -3 to 3 V by using two-point probe technique.

2.4 Gas sensor measurement

The sensor response to VOC vapors (including vapors of methanol, acetone and benzene) were investigated at room temperature by recording the electrical resistance using a FLUKE NetDAQ during cycles of alternating supply of dry N_2 gas and VOC vapors. The sensors were placed in a stainless steel chamber and N_2 gas was used as baseline and carries gases. VOC vapor was introduced into the chamber by bubbling liquid VOC with N_2 carrier gas at a flow rate of 1.0 lpm for 600 s. The sensors were recovered by purging with 3.0 lpm of N_2 for 600 s. The sensor response (*SR*) was defined as $SR = (R_{VOC}-R_0)/R_0$, where R_{VOC} and R_0 are the resistances of the sensor after and before VOC exposure. To compare the responses of all the sensors, the sensor responses were normalized by the VOC concentration. The normalized sensor response (*NSR*) was defined as the ratio between the sensor response at a time of 1200 s (SR_{1200}) and the VOC concentration (C_{VOC}): $NSR = SR_{1200}/C_{VOC}$..

3. Results and discussion

3.1 Morphology and electrical properties of paper-based VOC sensor using CNTs

The FESEM images of bare and CNT-coated membranes using different volumes of CNT suspension are shown in Fig. 2. Fig. 2(a) shows the pore structure of a membrane. Fig. 2(b-f) clearly indicates the presence of dispersed CNTs along the microfibrillar structure of a membrane. CNTs were dispersed not only over the top surface, but also in the pores of the membrane. For CNT-20, the CNTs tangled along the microfibrillar shape of the membrane, keeping the nearly original morphology of the membrane, showing the highest porosity (Fig. 2(b)). When the amount of the CNT suspension increased, the thickness of the CNT tangled on the microfibrils increased and gradually closed the pore of the membrane. As a result, when the CNT suspension reached as high as 40 mL, the membrane lost its microfibrillar structure and was wholly filled with the dense CNT network (Fig. 2(f)).

Next, the electrical properties of the CNT-coated paper were investigated. The *I-V* curves of the CNT paper show a linear behavior (data not shown), implying the Ohmic contact between CNT paper and silver electrodes. The initial resistance of CNT paper versus a volume of CNT suspension is shown in Fig. 3. The initial resistances of CNT-20, CNT-25, CNT-30, CNT-35 and CNT-40 were 1286, 618, 576, 496 and 310 Ω, respectively. The resistance of CNT paper exponentially decreased with a volume of CNT suspension.

3.2 Gas sensing characteristics of paper-based VOC sensor using CNTs

To investigate the effect of morphology of CNT paper on sensing performance, the sensor response of each CNT paper to methanol vapor was investigated. Fig. 4(a) shows sensor

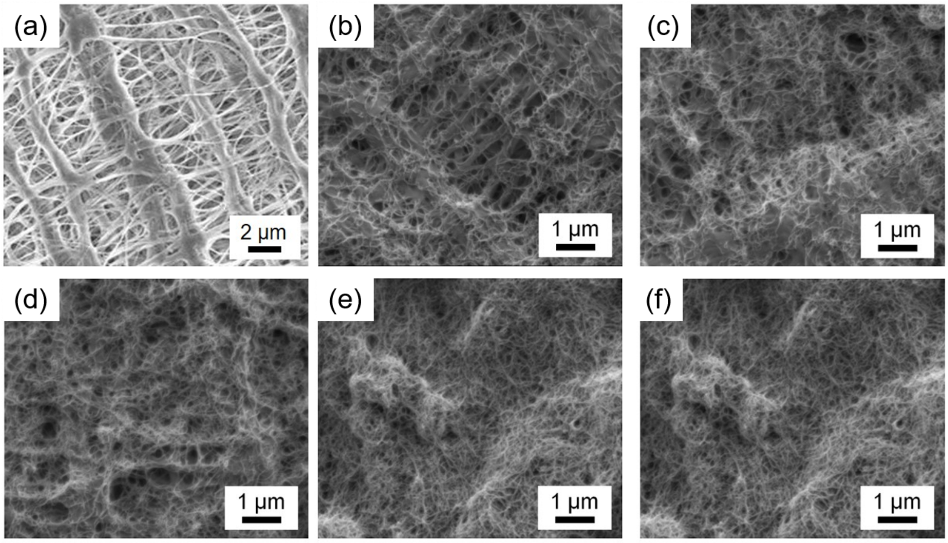

Fig. 2. FESEM images of (a) a bare membrane filter, (b) CNT-20, (c) CNT-25, (d) CNT-30, (e) CNT-35 and (f) CNT-40.

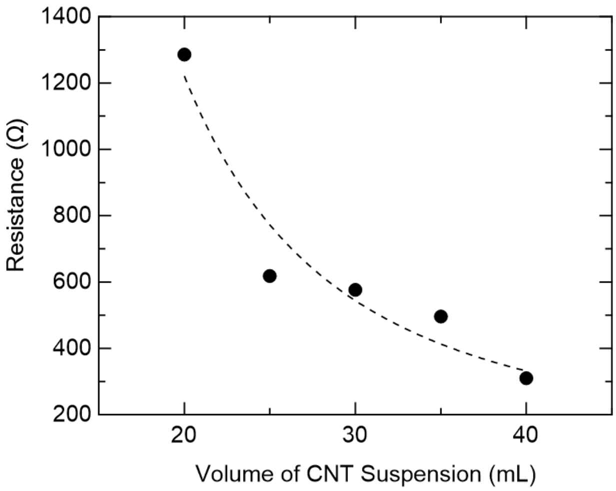

Fig. 3. Resistance of CNT papers prepared from different volumes of CNT suspension.

response as a function of time of CNT paper under an alternating supply of methanol at concentration of 95 parts per thousand (ppt) and N_2 gas for 3 cycles. The electrical resistance of all sensors increased upon methanol exposure and decreased after replacing methanol with N_2 gas. All sensors were hardly recovered to their initial resistances. The reversibility of the sensor can be improved by applying heat or UV exposure, similar to single-walled CNT sensor system. [4, 6, 10] Since the stability and reproducibility are one of the important parameters of sensor, sensor performance of three sensors was compared (data not shown). The results show that the response pattern, response time and recovery time of each paper-based VOC sensors to methanol vapor were almost similar, demonstrating that the CNT paper-based VOC

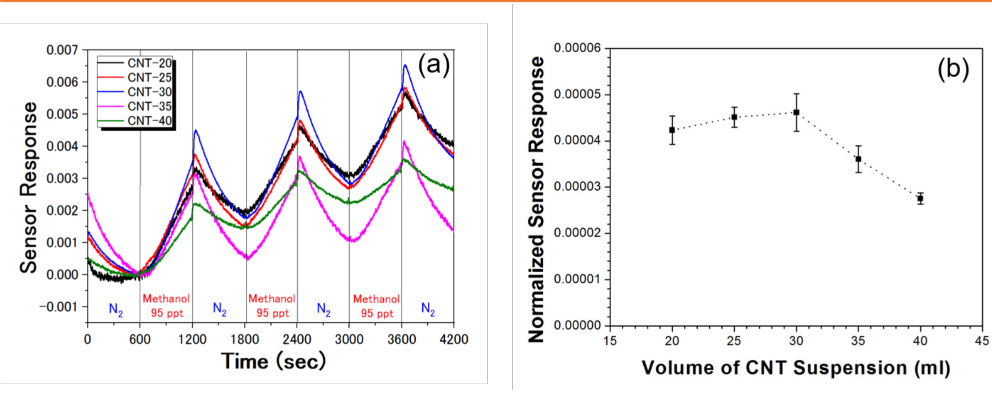

Fig. 4. (a) Sensor response of each paper-based VOC sensors to methanol vapors. (b) Relationship between volume of CNT suspension and normalized sensor response.

sensor is high stable and reproducible. However, the lift time of sensor need to be studied in the future work.

Figure 4(b) shows the normalized sensor response of CNT paper to methanol vapor. The sensitivity of CNT paper to methanol determined from the normalized sensor response was in the following order: CNT-30 > CNT-25 > CNT-20 > CNT-35 CNT-40 (Fig. 4(b)). CNT-30 sensor exhibited the highest sensitivity to methanol vapor. These results may be attributed to the optimum porosity and largest effective surface area for CNT-30 to methanol adsorption. The decrease in the sensitivity of the CNT-40 could be attributed to decreasing the porosity of membrane due to the excessive amounts of CNTs. The methanol molecule hardly diffuse into the densely interconnected CNTs or interstitial sites of CNTs which is the optimum path for charge transfer compared to other sites such as surface, groove and pore. [11]

Next, the sensor performance of a paper-based VOC sensor using CNTs to polar and nonpolar molecules were investigated. Fig. 5 shows the normalized sensor response of CNT-30 to vapors of methanol, acetone and benzene. The magnitude of sensor response of CNT-30 to VOC vapors were in the following order: methanol > acetone > benzene. The sensing mechanism to VOC vapors can be described in terms of the dielectric constant, which involves the solvent polarity of VOCs. The solvent polarity is in the following order: methanol > acetone > benzene. Normally, CNTs can be metallic or semiconducting depending its chirality. Semiconducting CNTs always exhibit as p-type with holes as the majority carriers. During exposure of VOC vapor to CNTs, molecule with higher polarity can hold moving holes and interrupt the movement of holes along the p-type CNTs, resulting in a large increase in resistance and thus an increase in sensor response. [7, 12-14] The trend of the sensor response of CNTs to methanol, acetone and benzene corresponds with the VOC polarity. A low resistivity to nonpolar molecules such as benzene can be overcome by functionalization with polymer. [15]

The advantage of the CNTs paper-based VOC sensor proposed in this work is a promising approach for the low-cost, flexible, portable and disposable VOC sensor. Moreover, the CNTs paper-based VOC sensor can operate under room-temperature condition and low power consumption. However, its limit detection should be studied in the future work. However, the range of concentration is still high. There is a room to improve its sensitivity down to ppm level using nanocomposites as the graphene system. [16] The high sensitivity to VOC detection offers a potential for portable real-time medical diagnostics. Not only VOC sensor,

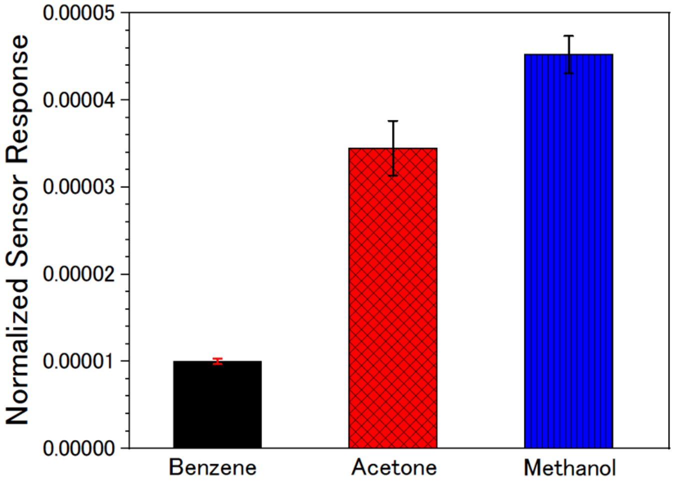

Fig. 5. (a) Comparison of sensor response of CNT-30 to vapors of benzene, acetone and methanol.

CNT on a membrane is conceivable to use for the separation of aqueous-organic solvent system. [17]

4. Conclusion

A paper-based VOC sensor was successfully fabricated by forming network of CNTs on a membrane using vacuum filtration technique. The network of CNTs was formed along the microfibrillar structure of the filter membrane. The amounts of CNTs on a paper were controlled by the volume of the CNT suspension. The 30 mL of CNT suspension is the optimum volume to fabricate paper-based sensor using CNTs for a detection of VOC vapor. Moreover, the paper-based sensor highly responded to methanol, acetone and benzene, respectively. The sensitivity to VOCs directly depended on the dielectric constant. Methanol, the highest polarity, showed the highest sensor response, whereas benzene, the nonpolar molecule, showed that lowest sensor response. These results imply a potential use of CNT on a paper as a low-cost, flexible, portable and disposable VOC sensor.

Acknowledgement

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