Detection of toxic gases using a composite of single-walled carbon nanotubes with polyaniline

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Abstract: We reported on the response behaviours of a composite sensor of SWNTs with polyaniline to detect noxious gases at room temperature. The SWNT-polyaniline composite synthesised were found to be high-quality with good uniformity. A combination of photolithography and a lift-off process was utilised to fabricate 100-nm thick Pd electrodes on drop-cast SWNT-polyaniline composite. The composite-based sensor showed high sensitivities to NH_3 concentration of 35 ppm and CO concentration of 50 ppm at room temperature. The observed sensitivity was 4% and -5.5% for the respective gas species in air. These results indicate that SWNT-polyaniline composite sensors employing Pd electrodes can be a good candidate for a noxious gas sensor that is able to simultaneously detect multiple gases in different modes down to minimal concentrations at room temperature.

Keywords: SWNTs; polyaniline; CO; NH_3; gas sensor.

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1 Introduction

Various gases such as NH_3, CO, including nitrogen oxides and volatile organic compounds are noxious to human. To monitor and prevent air pollution from these harmful gases, it is needed to develop a highly efficient gas sensor that is able to detect such toxic gases simultaneously, but in separate modes. In order to develop the gas sensor, a lot of candidates have been reported, including semiconducting metal oxide (SMO)-based sensor [1–3], surface acoustic wave (SAW) sensor [4], and micro-cantilever sensor. Above all, the SMO-based sensors have many advantages such

as high sensitivity, rapid response, and easy fabrication. However, their operation temperature is generally high, restricting the widespread use. To resolve this problem, single-walled carbon nanotubes (SWNTs) have been considered a leading candidate for several reasons like a high electrical conductivity, high aspect ratio, and large surface area from hollow structure that is favourable for gas adsorption [5–9]. Actually, the SWNTs-based gas sensors have shown outstanding gas sensing properties at room temperature, in particular, high sensitivity and fast response. In spite of these advantages, the SWNTs-based gas sensors have a limitation in commercialisation due to their low selectivity to different gases. Polyaniline is a conducting polymer and can be considered another candidate for gas sensing due to its good properties such as environmental stability, easy synthesis, and room-temperature operability [10]. Interestingly, the conductivity of polyaniline changes with the transition of oxidation state that depends on a protonation degree in accordance with acid doping level. In this paper, we present the sensing behaviours of SWNT/polyaniline composite sensors in the presence of NH_3 and CO gases. The sensor operated reproducibly at room temperature and exhibited noticeable difference in responses to the respective gases.

2 Experimental details

We first patterned palladium (Pd) electrodes on a Si substrate and immediately dispersed SWNT/polyaniline composites on electrodes to avoid a plasma damage of composite in post-patterning method. After photoresist patterns were developed on a Si substrate, a Pd film was deposited on them with a thickness of 100 nm under an ultra-high vacuum. The Pd electrode patterns were shaped through a subsequent lift-off process. Purified SWNTs that were synthesised using an arc-discharge method with 70~90% purity were purchased from Iljin Nanotech Co., Ltd. Other chemicals and sodium dodecyl sulphate (SDS) surfactant were prepared from Sigma-Aldrich and Samchun Chemistry in Korea, respectively. To synthesise SWNT/polyaniline composites, purified SWNTs were first dissolved in distilled water with 0.2 wt% SDS surfactant. After ultra-sonication for 4 h, SWNTs were filtered with Teflon filters using a vacuum pump. Filtered SWNTs were rinsed with distilled water to eliminate SDS surfactant. Chemical oxidative polymerised polyaniline in an aqueous acidic media with 1.33M HCl was added and dissolved in N,N′-dimethyl formamide (DMF) under an inert environment [11]. To synthesise uniform films, the mixed solution of SWNTs and polyaniline was stirred constantly for 24 h at room temperature. Then, the polyaniline-SWNTs films were deposited on a Si substrate by drop-casting. The measurement system to analysis gas sensing property composed of 180 cc sealed chamber, mass flow controllers (MFC) for regulating inflow, and recording system with digital multi-meters. The change of resistance for sensor was observed in real time while each gas was injected into the chamber during 100 s. Then each gas in the chamber was ventilated before starting next gas injection cycle for 100 s. All recorded data using digital multi-meters were kept in a hard disk with a LabView program through a general-purpose interface bus (GPIB).

3 Result and discussion

Figure 1 shows a Scanning Electron Microscopy (SEM) image of the composite showing SWNTs randomly distributed in polyaniline matrix. Rough surfaces of SWNT/polyaniline composite may be advantages to gas adsorption due to increased surface area. Polyaniline doped with HCl is transformed to become a high conductivity structure, which is caused by charge transfer according to cationic radical generation in polyaniline as a result of the addition of HCl, as shown in Figure 2(a). The structure-transformed polyaniline mixed with SWNTs behaves like a p-type semiconductor, where majority carriers are holes. When the SWNT/polyaniline composite is exposed to NH_3 that plays as an electron donor, the resistance of the composite is increased due to a reduction of its majority carrier density, as stated in Figure 2(b). Another reason for this resistance increase of the composite can be sought from protonation of NH_3 to NH^{4+} activated by donation of H^+ of polyaniline. This process decreases the number of carrier-hopping sites of polyaniline, resulting in an increase in its resistance. On the other hand, the resistance of the composite is decreased when the SWNT/polyaniline composite is exposed to CO gas. A positive charge in carbon atom of CO gas is transferred to polyaniline. This produces the protonation of polyaniline and the conductivity of both polyaniline and SWNT/polyaniline composite is increased, as mentioned in Figure 2(c).

Figure 1 A SEM image of the assembled SWNT-polyaniline composite

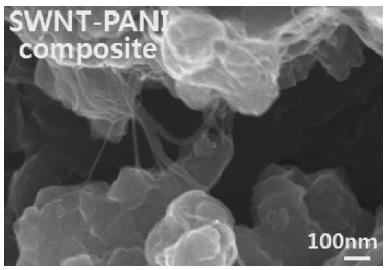

Figure 2 A schematic about sensing mechanism to each gases. (a) A doping process of polyaniline with HCl and (b) mechanism of response to CO gas, (c) mechanism of response to NH_3 gas about SWNT/polyaniline composite (see online version for colours)

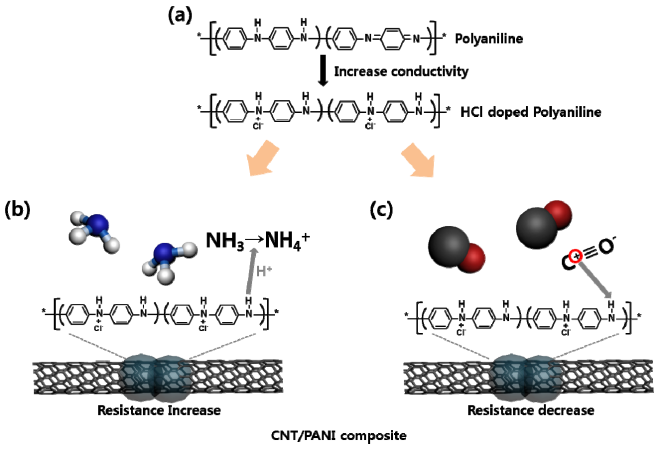

Figure 3 shows responses of the SWNT/polyaniline composite sensor to NH_3 and CO gases at room temperature. The sensitivity of the composite sensor to a specific gas species is defined as

$$\text{Sensitivity (\%)} = \frac{R_{gas} - R_0}{R_0} \times 100 \quad (1)$$

where R_{gas} is the resistance of the composite after exposure to a gas and R_0 is the initial resistance before an exposure. Figure 3(a) exhibits cyclic responses of the sensor in the presence of 35 ppm NH_3 gas. The points of gas injection and removal are marked with arrows in the figure. Repeating gas absorption and desorption processes at intervals of 100 s, the sensor shows reversible responses with a moderate response time and good reproducibility. The sensitivity and response time of the SWNT/polyaniline composite sensor is calculated to be about 4% and 65s, respectively. The response time is measured as the time to reach 90% of the total change of resistance upon exposure to a gas [12].

Figure 3 The real-time response of the SWNT-polyaniline based gas sensor to (a) 35 ppm NH_3 gas, (b) 50 ppm CO gas at room temperature and (c) sensitivity comparison of two gases (see online version for colours)

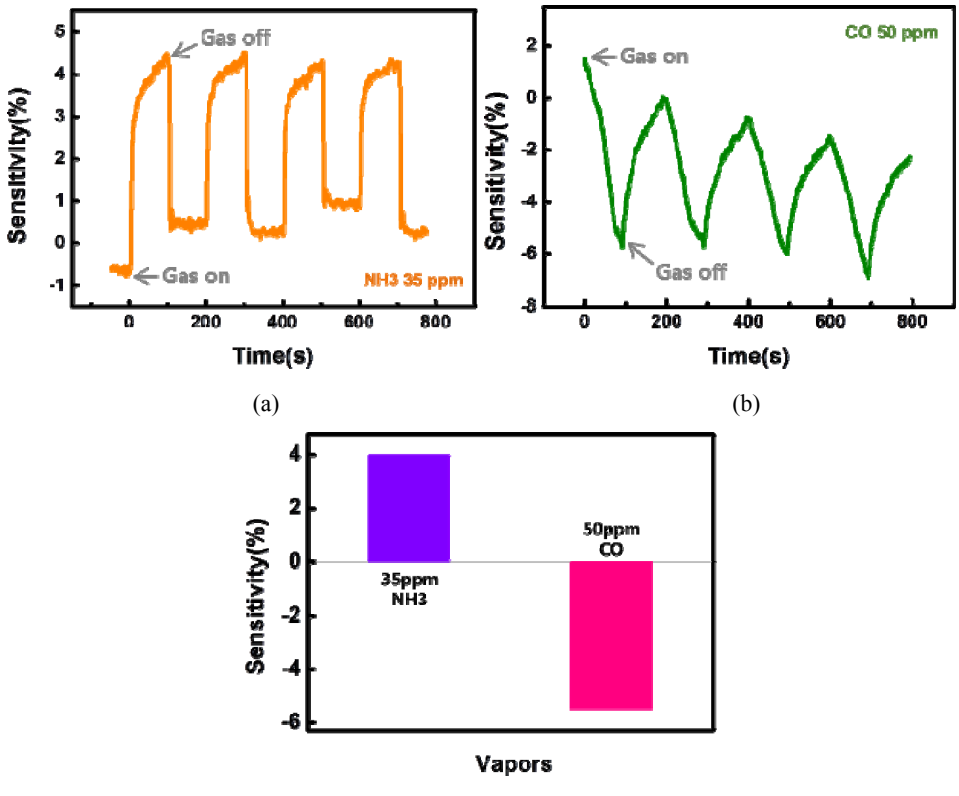

Figure 3(b) shows the sensitivity of the composite sensor to 50 ppm CO gas. Like the case of NH_3, the sensor looks reproducible and reversible, even though some extent

of baseline shift is observed. The sensitivity and response time of the sensor are found to be –5.5% and 62.5 s. Although the magnitudes of both the sensitivity and response time are similar for two kinds of gases, the signs of the sensitivity are opposite to each other. This arises from the difference in interactions of the respective gases with the SWNT/polyaniline composite, as discussed above. Figure 3(c) graphically summarises this difference. These results indicate that the SWNT/polyaniline composite has a potential to reliably detect minute amounts of NH_3 and CO gases at the same time.

4 Summary

In summary, we studied the response behaviours of SWNT/polyaniline composite sensors to NH_3 and CO gases. The sensor exhibited a high sensitivity and good reproducibility even at very low concentrations of gases. The resistance of the composite sensor increased in the presence of NH_3, while it decreased when exposed to CO. These Interesting results were attributed to the difference in interactions of the SWNT/polyaniline composite with the respective gases. Our results suggest that the SWNT/PANI composite is a promising material to be used for sensing very small amounts of multiple gases at the same time.

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