

# Application of dielectrophoresis to fabrication of carbon nanohorn gas sensor

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## Abstract

This paper describes an electrokinetic fabrication method for a gas sensor composed of single-wall carbon nanohorns (SWCNHs) using dielectrophoresis (DEP). The authors have previously demonstrated that DEP manipulation of carbon nanotubes (CNTs) can be applied to the fabrication of a CNT gas sensor. In the present study, we further explored the possibility of electrokinetic manipulation of SWCNHs. The latter have different structures and properties compared to CNTs. The SWCNHs were synthesized using the ‘arc in water with gas injection’ method. The SWCNH aggregates were dispersed in ethanol and trapped in an interdigitated microelectrode gap under the action of positive DEP. After the DEP process, the ethanol was evaporated and the microelectrode retaining the SWCNHs was exposed to nitrogen dioxide (NO<sub>2</sub>) or ammonia (NH<sub>3</sub>) gas while the electrode impedance was monitored. It was found that conductance of the DEP-fabricated SWCNH sensor increased or decreased upon exposure to ppm-levels of NO<sub>2</sub> or NH<sub>3</sub>, respectively. These results were similar to those previously obtained for CNT gas sensors and suggest that the SWCNH aggregate behaves as a p-type semiconductor. The comparison reveals that intrinsic NO<sub>2</sub> sensitivity of the SWCNHs is lower than that of single-wall CNTs (SWCNTs) but comparable with the intrinsic sensitivity of multiple-wall CNTs (MWCNTs).

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## 1. Introduction

Since the discovery of the C<sub>60</sub> fullerene molecule [1] and the carbon nanotube (CNT) [2], interest in carbon nanomaterials has been grown rapidly. CNTs are especially promising as new materials for a variety of potential applications. As a result of the intense research activity, new types of the carbon nanostructures, such as nanooxions [3] and nanohorns [4–10], have been also discovered. Among the new carbon nanostructures, single-wall carbon nanohorns (SWCNHs) are attracting much attention because of their large surface area and high gas-absorption

capacity which are ideal for gas storage or fuel cell applications [5]. Because no metal catalyst is required for their synthesis, SWCNHs are free from contamination by metallic impurities. Thus far, SWCNHs have been synthesized by the CO<sub>2</sub> laser ablation method [4,5], the ‘arc in liquid’ method [6–8], and some other arc techniques [9,10].

Along with research activity focused on the production of carbon nanomaterials, research in the manipulation and handling of these nanosized materials is becoming important in many applications. Electrokinetic manipulation has been recognized as a useful technique for the separation, alignment, and positioning of CNTs [11–16]. The authors have previously demonstrated a new fabrication method for a CNT-based gas sensor using dielectrophoresis (DEP) [17–21]. DEP describes the electrokinetic

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motion of dielectrically polarized materials in non-uniform electric fields and is currently an active area of research for the manipulation of biological materials such as cells, bacteria and DNA [22]. CNT-based gas sensors have received considerable attention because of their outstanding properties, such as faster response, higher sensitivity, lower operating temperature, and a wider variety of detectable gas than other types of gas sensors [17–21,23–29]. CNT-based gas sensing utilizes the electrical impedance change of the CNTs due to adsorption of gas molecules as the electrical readout. As the dielectrophoretically trapped CNTs bridge over the electrode gap, an electrical connection, which provides a way to measure the CNTs impedance using an external measuring circuit, can be readily achieved. Another advantage of the DEP fabrication is that the number of CNTs trapped between the electrodes can be quantified by impedance monitoring during the DEP process. This feature enables the sensor assembly process to be controlled so that the sensor characteristics become uniform. It also enables one to define the normalized sensitivity of the CNT gas sensor [19–21].

In this study, the DEP method, which has been reported previously as a method for the fabrication of CNT gas sensors, was further extended to the assembly of SWCNH gas sensors. Although the DEP technique has been successfully applied to the manipulation of CNTs, it has not yet been demonstrated that SWCNHs and their aggregates can be manipulated by the same electrokinetic phenomenon. The other motivation for investigating SWCNH gas sensors comes from the large surface area and the high gas absorption capacity of SWCNHs, which suggest that SWCNHs can also be used to make an electronic transducer for gas sensing which may have some advantages over the CNTs such as higher sensitivity. The electrical properties and gas sensing characteristics of SWCNHs are not yet understood because there has been no effective way to assemble them onto a metal microelectrode for electrical signal acquisition. The CNT-based gas sensors have been fabricated mainly by using the catalyst-controlled chemical vapor deposition (CVD) method. Multiple single-wall CNTs (SWCNTs) are grown from patterned metal catalysts on substrates so that they can establish an electrical connection between metal electrodes [23–25]. Because it is difficult to grow SWCNHs using catalyst-controlled CVD, the DEP technique may be useful, especially for SWCNH sensor fabrication. The DEP-fabricated SWCNH sensor reported here was applied to ppm-level detection of nitrogen dioxide ( $\text{NO}_2$ ) and ammonia ( $\text{NH}_3$ ) gas by impedance spectroscopy. The gas sensor characteristics of SWCNHs were compared to those of SWCNTs and multi-wall nanotubes (MWCNTs).

## 2. Experimental details

The SWCNHs were prepared by the ‘arc in water with gas injection’ method. This method, which has been

described in detail elsewhere [8], provides a convenient method for synthesizing SWCNHs. To produce the SWCNH powders for the present study, a 80 A, 40 V dc arc discharge was generated between a rod cathode and an anode, which were submerged in de-ionized water. The anode was a graphite rod of 3 mm diameter, and the cathode was a graphite rod of 9 mm diameter with a hole of 7 mm diameter and 15 mm depth. The anode rod was coaxially placed in the cathode hole. The arc discharge was generated between the anode tip and the bottom of the cathode hole. Two narrow holes (2 mm diameter) were drilled through the cathode bottom in order to introduce  $\text{N}_2$  gas flow (21/min) so that the arc-generated carbon vapor could be efficiently transferred to the cold environment cooled by the surrounding water. The SWCNH-containing products were obtained as the floating fine powders on the water surface. A transmission electron microscope (TEM) image of SWCNH aggregates produced by this method is shown in Fig. 1. The TEM observations revealed that the collected powders contained the SWCNH powder as a major component (50–80%) as well as a smaller amount of amorphous carbon. The SWCNH aggregate had a ‘dahlia-like’ (‘dahlia’ is name of a flower) or ‘bud-like’ spherical shape over the range of 50–100 nm in diameter [7,8]. The SWCNH aggregate spheres further coalesced to form a larger powder. It was the SWCNH powders but not ‘individual’ SWCNHs or their aggregates that were manipulated by the DEP. The SWCNHs powder particles were in the micron or sub-micron range. In preliminary experiments performed as a part of this work, we tried to further purify the as-grown SWCNHs by heat

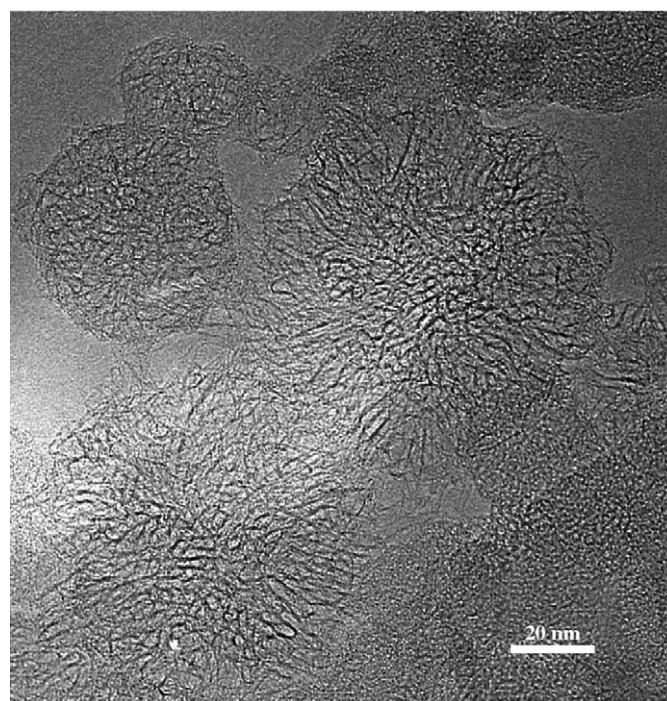


Fig. 1. The transmission electron microscope (TEM) image of SWCNH aggregate produced by the ‘arc in water with gas injection’ method.

treatment in air (400 °C, 4 h). However, there were few changes to the SWCNH purity and the gas sensor characteristics. Along with the SWCNH, the SWCNT and MWCNT were also employed for comparison tests of the gas sensing. The SWCNT and MWCNT were commercially purchased from manufacturers and their details had been described in elsewhere [17–21].

Fabrication method of the SWCNH gas sensor using positive DEP was basically same as that developed by the authors for MWCNT or SWCNT [17–21]. Fig. 2 depicts the experimental apparatus for sensor fabrication. The as-grown SWCNH powders were suspended in ethanol (0.2–2.0 µg/ml final concentration) and ultra-sonicated for 60 min so that they could be isolated from each other. An interdigitated microelectrode of thin chrome film (100 nm thickness) was patterned on a glass substrate (20 mm × 20 mm) by photolithography technique. The electrode finger had a ‘castle-wall’ pattern with 5 mm length and 5 µm minimum clearance. The 20 electrode fingers formed 19 castellated gaps. The castle-wall electrodes were surrounded by a silicon rubber wall to form a chamber (15 µl capacity) in which the SWCNH suspension was introduced. The DEP trapping of SWCNHs to the microelectrode was performed with ac voltage of 100 kHz frequency and 8 V amplitude (peak to peak value) while SWCNHs suspension continuously flowed through the chamber at 0.5 ml/min. During the DEP process, the electrode impedance was continuously measured using a lock-in amplifier (dielectrophoretic impedance measurement, DEPIM). The DEPIM was originally developed by

the authors for electrical detection of bacteria or micro-organisms [30]. The DEPIM instruments were controlled by a personal computer, which also served as a data recorder and analyzer. After the DEP process, the ethanol was evaporated and the microelectrode structure that retained SWCNH powder was employed as a gas sensor.

In the gas detection experiments, NO<sub>2</sub> and NH<sub>3</sub>, which have been successfully detected by CNT gas sensors [17,19–21,23–29], were employed as the target gas. The target gas concentration was controlled by a mass flow controller employing N<sub>2</sub> as a carrier gas. The same microelectrode chamber as used in the DEP fabrication process was employed also for the gas sensing experiments. The chamber was first filled with pure N<sub>2</sub> gas and then the target gas was introduced. The flow rate of N<sub>2</sub> and target was kept constant at 0.2 l/min. The sensor impedance was continuously measured at room temperature and 100 kHz frequency using the same system as that employed during the DEP sensor fabrication.

### 3. Results

Scanning electron microscope (SEM) images of SWCNH powders trapped on the microelectrode are shown in Fig. 3. The SEM observation was conducted after the ac electric field for DEP trap was removed and ethanol was evaporated. These powders were a coalescence of the spherical SWCNH aggregates shown in Fig. 1. In a few tens of minutes after the DEP process was started, aggregations of the SWCNH powder were formed around the electrode corners. The trapped SWCNH powders bridged across the electrode gap. The trapping was probably due to positive DEP because the electric field became higher around the electrode corner. The SEM images also revealed that DEP-trapped SWCNH powders could be firmly retained on the microelectrode even after the ethanol evaporation. This might be due to the large surface areas of the individual SWCNH particles and their aggregates and the resultant physical adhesion to the glass surface. The SWCNH powders were loosely agglomerated, forming porous structures that might be advantageous for efficient adsorption of target gas molecules.

Results of impedance spectroscopy conducted during the DEP trapping of SWCNH powders are shown in Fig. 4. The impedance was analyzed assuming an equivalent circuit of parallel conductance and capacitance [14,17,19–21,30]. Both conductance and capacitance components increased with elapsed time, namely, with more SWCNH powder trapped on the electrode (in the figure, only the conductance component is shown). From Figs. 3 and 4, the conductance increase can be attributed to the DEP-trapped SWCNH powders bridging the electrode gap [14,17]. Assuming an equivalent circuit made of two components, the impedance of trapped SWCNH powders and the impedance of the electrode in the suspending medium (ethanol), the increment from the initial value represents the total conductance or capacitance of the

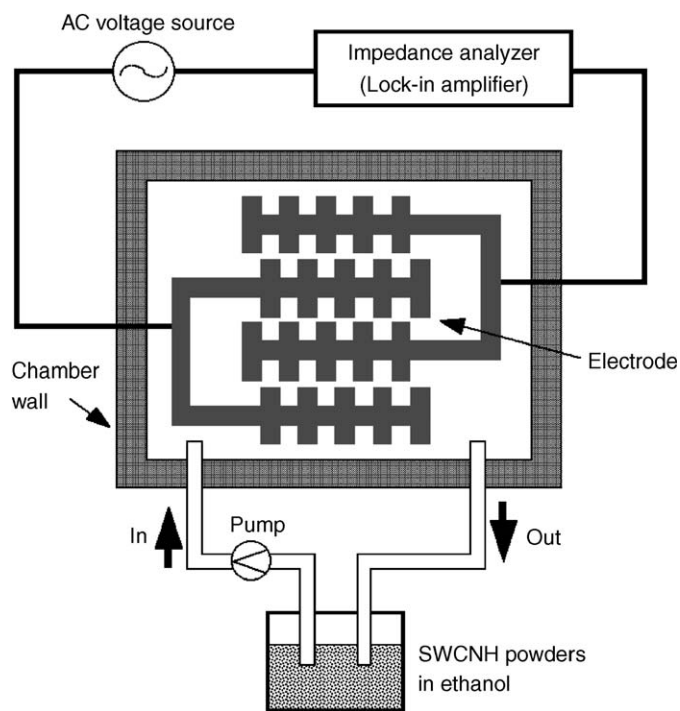


Fig. 2. Schematics of experimental apparatus for the SWCNH gas sensor fabrication using dielectrophoresis.



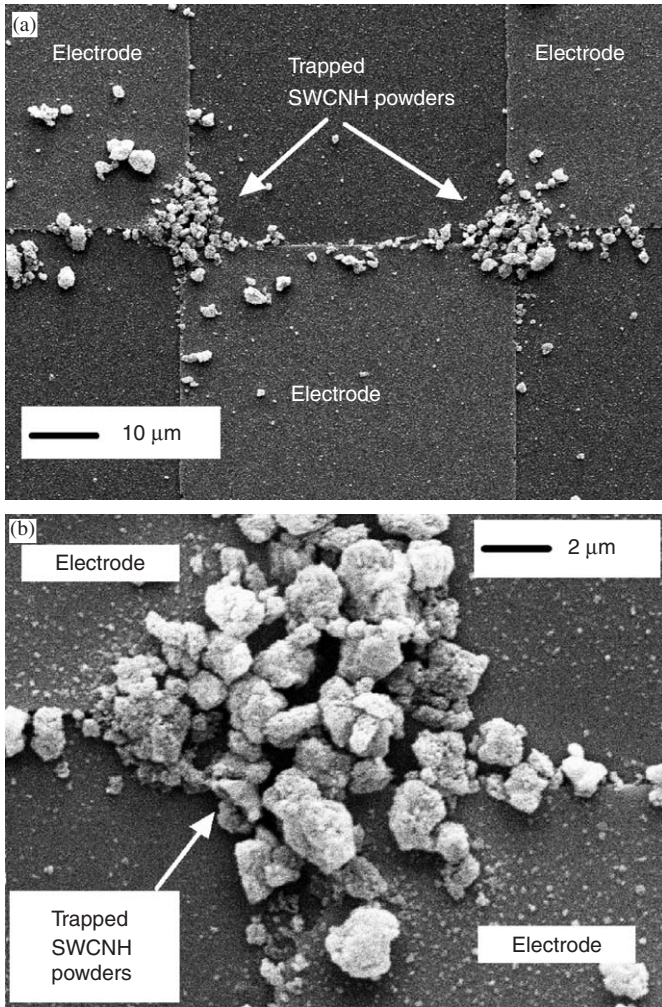


Fig. 3. The scanning electron microscope (SEM) images of SWCNH powders trapped onto a castellated microelectrode by dielectrophoresis for 1 h. Amplitude and frequency of the electrode energizing potential was 8 V (peak to peak) and 100 kHz, respectively. (a) Low magnification. (b) High magnification.

trapped SWCNH powders [17,30]. In the figure, results for SWCNTs and MWCNTs obtained under an identical condition (nanomaterial concentration, electrode potential, etc.) are also depicted for comparison. The conductance of SWCNH powders increased more slowly than those of CNTs.

When the conductance increased to a desired value  $G_T$ , the DEP process was terminated and ethanol was evaporated to prepare the SWCNH gas sensor. As summarized in Fig. 5, the conductance  $G_0$  measured after ethanol evaporation was higher than  $G_T$  measured in ethanol. This suggests that electrical contact between the metal electrode and the SWCNH powder is poor in ethanol similar to the CNTs [16,17]. Based on the relationship shown in Fig. 5, the initial conductance of the SWCNH gas sensor  $G_0$  could be controlled as desired by the real time monitoring of  $G_T$  during the DEP process. Fig. 6 depicts temperature dependency of the SWCNH sensor conductance measured in  $N_2$  gas. The conductance increase at

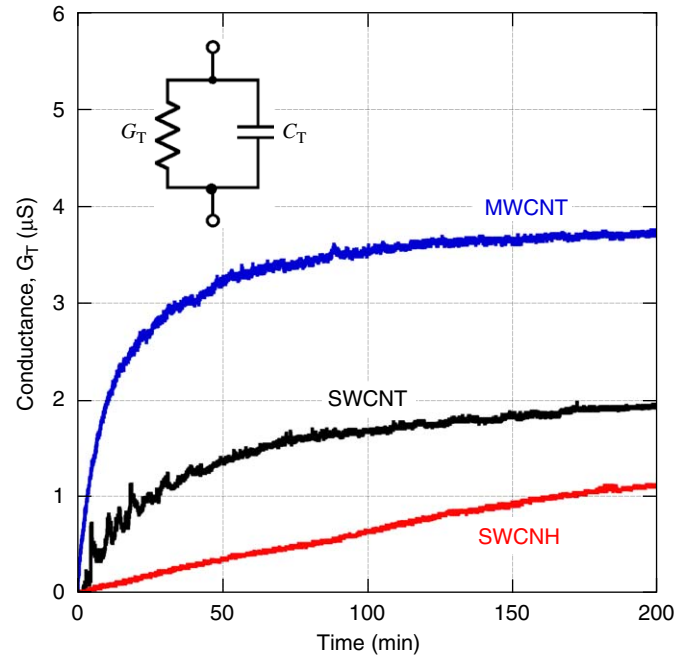


Fig. 4. Temporal increase of the electrode conductance  $G_T$  measured during the DEP trapping process of SWCNHs, MWCNTs and SWCNTs under an identical condition. The inset shows an equivalent circuit of trapped nanomaterials.

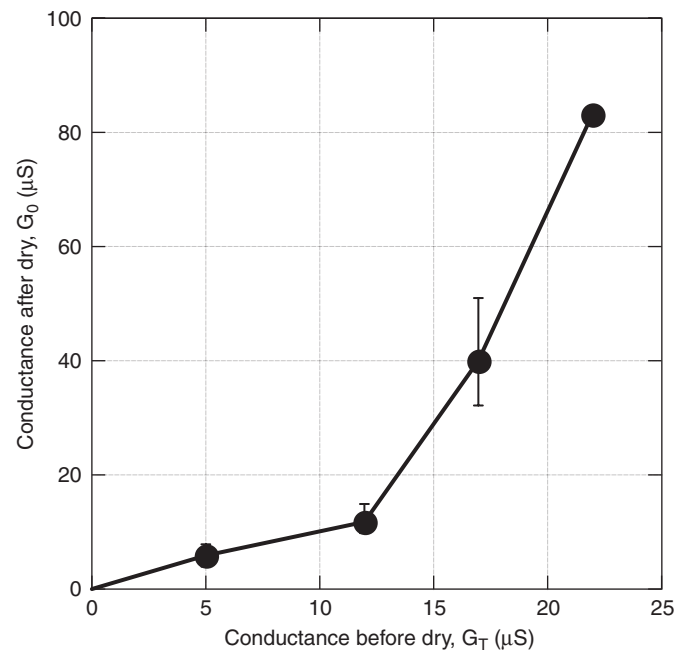


Fig. 5. Relationship between the SWCNH conductances measured before ( $G_T$ ) and after ( $G_0$ ) ethanol evaporation.

higher temperature suggests that the SWCNH sensor behaves as a semiconductor. The temperature dependency was fully reversible.

Fig. 7 shows the conductance response of the SWCNH sensor to 1 ppm  $NO_2$  measured at room temperature. The responses of SWCNT and MWCNT sensors are also

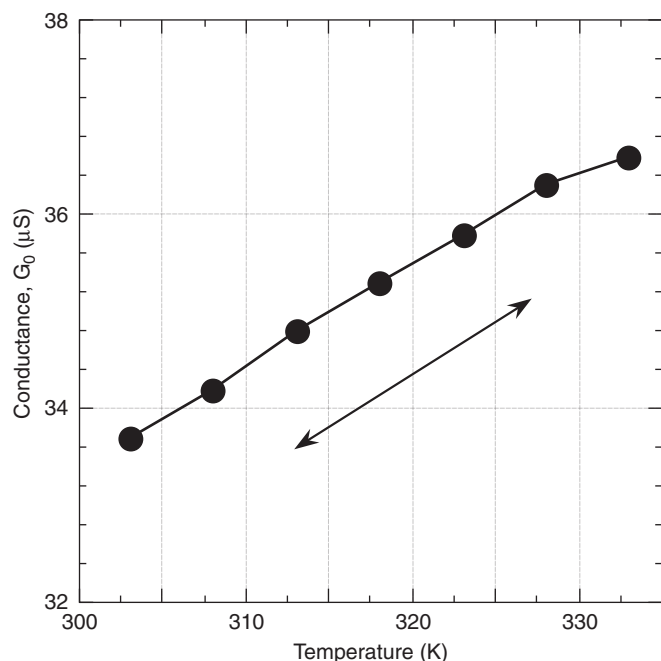


Fig. 6. Reversible temperature dependency of the electrical conductance of the DEP-trapped SWCNHs measured in  $N_2$  gas.

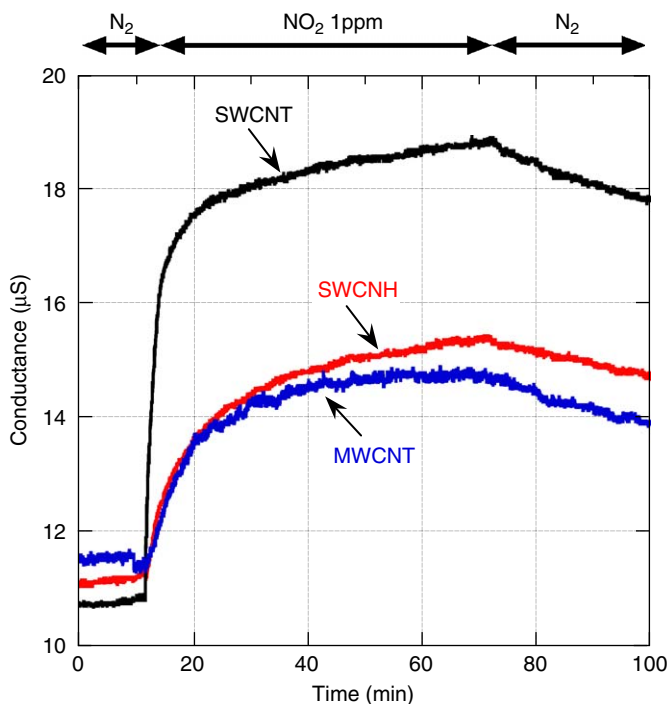


Fig. 7. Conductance response of the SWCNH, MWCNT and SWCNT gas sensors to 1 ppm  $NO_2$  gas measured at room temperature.

illustrated for comparison. These three sensors were fabricated so that the initial conductance  $G_0$  became almost identical to each other (about  $10 \mu S$ ). The conductance of all sensors increased after exposure to  $NO_2$ . When the gas was changed back to  $N_2$ , the conductance began to decrease slowly. The conductance increase of

CNTs by  $NO_2$  exposure has been attributed to the electronic interaction between the chemisorbed  $NO_2$  molecules and p-type semiconducting CNTs [23–27,29]. Figs. 6 and 7 suggest that the SWCNHs may also behave as p-type semiconductor. In order to check this point, we carried out  $NH_3$  detection tests as shown in Fig. 8. In contrast to  $NO_2$ ,  $NH_3$  exposure decreased the conductance of SWCNH and CNT sensors. This result also indicates that SWCNHs behave as p-type semiconductor just like CNTs. That is, the electron transfer from p-type CNTs to oxidative  $NO_2$  molecules results in increased positive hole density and the resultant increase in electrical conductance of CNTs. On the other hand, reducing  $NH_3$  molecules may decrease positive hole density and the conductance of CNTs [23–29]. The same idea can be applied to gas sensing mechanism of the SWCNH sensor when p-type behavior of SWCNHs and their aggregates is assumed.

Similar to the CNT gas sensors, the SWCNH sensor could be repeatedly used after it was reset to the initial conductance by  $N_2$  gas purging or ultraviolet beam illumination [31].

The structure of an individual SWCNH is basically similar to that of a SWCNT. That is, both are composed of a rolled-up, single graphene sheet. In spite of the similarity, their electrical conduction properties do not have to be same because their chiralities, which are known to strongly influence band gap energy of SWCNT [32], may vary depending on their shapes (e.g., whether the shape is a cone or a cylinder). Furthermore, highly packed aggregate formation of SWCNHs may also affect the electronic properties due to their mutual interaction. The p-type

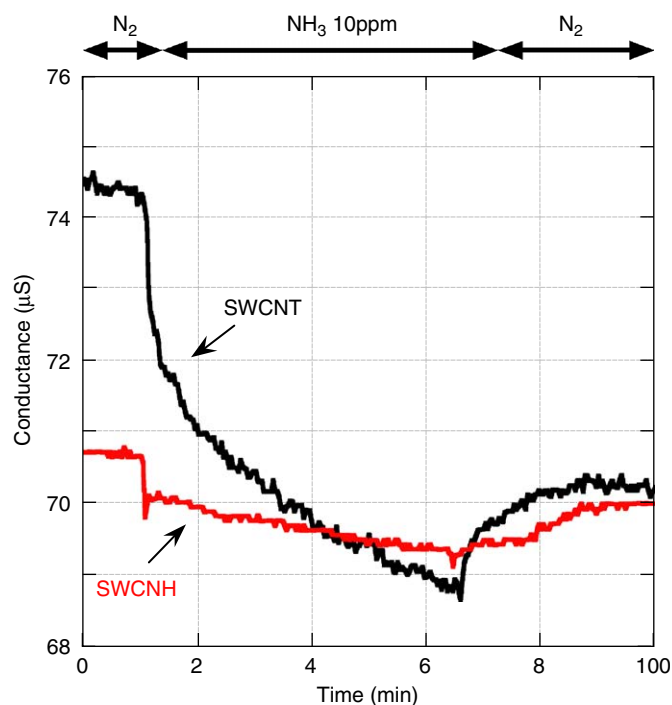


Fig. 8. Conductance response of the SWCNH and SWCNT gas sensors to 10 ppm  $NH_3$  gas measured at room temperature.

behavior of SWCNHs aggregates was newly found in the present study based on the gas sensing characteristics.

Now these results lead us to an interesting question of whether the SWCNH sensors have higher sensitivity than do the CNT sensors. In a previous study, the authors have already compared  $\text{NO}_2$  sensitivity of SWCNT and MWCNT sensors [19–21]. It was found that the apparent sensor response to  $\text{NO}_2$  increased almost proportionally with the initial conductance  $G_0$  for both CNT sensors. The initial conductance  $G_0$  became higher as the number of DEP-trapped CNTs increased. The sensor response normalized by the initial conductance is equal to relative conductance change of single CNT caused by  $\text{NO}_2$  adsorption, which should be constant depending only on the intrinsic CNT properties but not on the number of CNTs [19–21]. The initial conductance dependency of the SWCNH sensor response to 1 ppm  $\text{NO}_2$  was investigated and is depicted in Fig. 9 together with data for the SWCNT and MWCNT sensors. Since the conductance increase did not saturate (see Fig. 7), these sensors were calibrated using the conductance response after 9 min exposure to  $\text{NO}_2$  gas (defined as  $\Delta G$  below). The linear dependence of  $\Delta G$  on  $G_0$  was confirmed not only for the CNT sensors but also for the SWCNH sensors. According to the electrode configuration and size, the number of electrode gaps in which SWCNH powders were trapped was about two thousands. Although the DEP-fabricated aggregates did not form a wide and uniform layer, the SWCNH aggregates in the gaps were electrically connected in parallel. The large number of parallel connections may average and mask the variance in the conduction path or the resultant conduc-

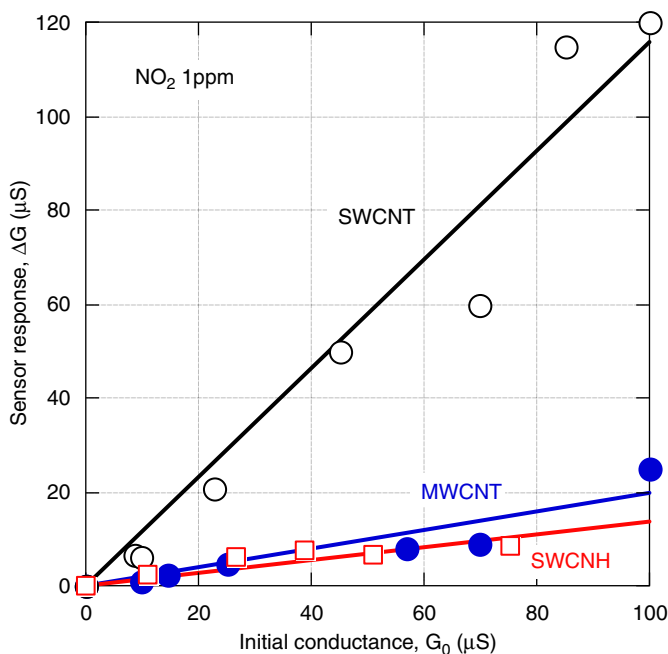


Fig. 9. Relationship between the initial conductance  $G_0$  of the SWCNH, MWCNT and SWCNT gas sensors and the sensor response  $\Delta G$  after 9 min exposure to 1 ppm  $\text{NO}_2$  gas.

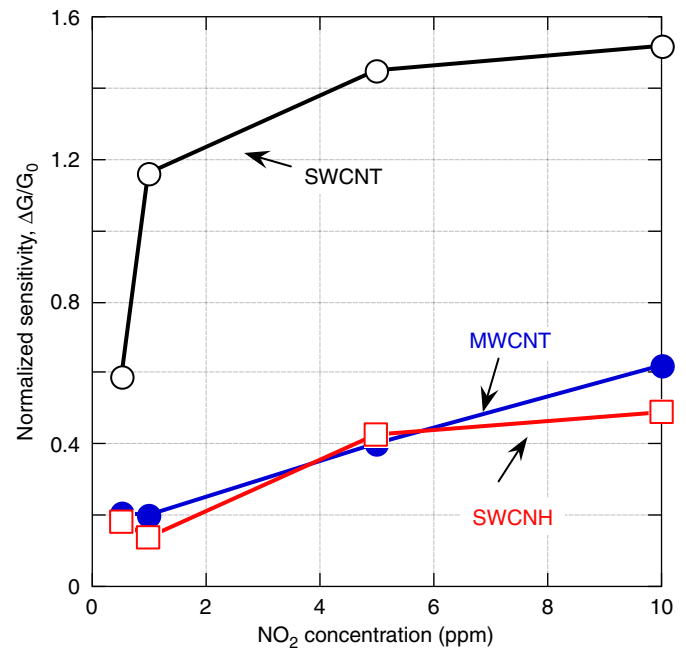


Fig. 10. Normalized sensitivity of the SWCNH, MWCNT and SWCNT gas sensors,  $\Delta G/G_0$ , measured for various  $\text{NO}_2$  concentrations.

tance. This might be the reason why the DEP-fabricated gas sensors had reproducible characteristics stable enough to be normalized by the initial conductance. The normalized sensitivity  $\Delta G/G_0$  of the SWCNH sensor is almost comparable with that of the MWCNT sensor and lower than the SWCNT sensor. As shown in Fig. 10, the normalized sensitivity  $\Delta G/G_0$  increased with  $\text{NO}_2$  concentration for all sensors. The normalized sensitivity of the SWCNT sensor was 2–6 times higher than that of the SWCNH and the MWCNT sensors.

#### 4. Discussion

As shown in Fig. 3, the SWCNH powders could be manipulated by positive DEP and firmly trapped in the microelectrode gap. The DEP-trapped SWCNH powder formed an electrical connection between the electrodes and thus increased the electrode conductance depending on the number of horns. However, the conductance increase for the SWCNH powders was lower than that for the CNTs (see Fig. 4). There are two possible explanations for the lower conductance of the DEP-trapped SWCNH powders. A CNT has a high aspect ratio, and the longitudinal length is almost comparable to the electrode gap (5 μm). This means that an individual CNT, which tends to align with the electric field, can make contact with the two electrodes at both ends to establish an electrical connection. On the other hand, the dimension of the SWCNH powder is in micron or sub-micron range and smaller than the electrode gap (see Fig. 3). As a result, many SWCNH powders need to be connected in series to establish an electrical connection between the electrodes. The contact resistance



between the SWCNH powders may be one cause of the lower conductance increase. Another possible reason is smaller DEP force acting on the SWCNH powders than the CNTs. Yamamoto et al. [11] found that the CNT with a high aspect ratio can experience a higher electrostatic force than carbon particles in a high frequency ac electric field probably due to the larger dipole moment. The lower DEP force will result in a smaller number of the SWCNH powders becoming trapped in the electrode gap and a smaller conductance increment during the DEP trapping.

As shown in the comparison of Figs. 9 and 10, the normalized sensitivity  $\Delta G/G_0$  of the SWCNH to  $\text{NO}_2$  is smaller than that of the SWCNT. Since there is little data available on the electronic properties of the SWCNH, it is difficult to completely explain the reason at this stage in our research. The lower sensitivity of the MWCNT sensor compared to that of the SWCNT sensor has been attributed to lower content of the semiconducting tubes, which are responsible for gas sensing [19–21,29]. The present results seem to suggest that the SWCNHs contain fewer semiconducting components than do SWCNTs, although both of them are composed of a single graphene sheet. The highly packed structure of the SWCNH aggregates and powders also seem to affect the electronic properties due to mutual interaction. The high contact resistance between SWCNH powders can be also one of the reasons for the lower sensitivity because it may mask subtle conductance increase of SWCNHs as a result of the series connection. As far as sensitivity is concerned, it seems that the SWCNH offers a little advantage over the use of CNTs in a gas sensor transducer. However, the SWCNH may have other advantages, such as high purity and cost-effective mass production [4,8].

The DEP fabrication method may provide greater benefits for the SWCNH gas sensor than for the CNT sensors for the following reasons. Up to now, the CNT gas sensors have been fabricated by two different methods by several researchers. In one method, multiple CNTs are directly grown on the electrode via CVD [23–25]. The position of the CNT growth can be controlled by metal catalysts, which are deposited on the electrode in advance. However, the direct growth method cannot be applied to SWCNH sensor fabrication because the SWCNHs cannot be grown by catalyst-controlled CVD. The other fabrication method is based on random deposition of pre-synthesized CNTs onto a metal electrode [26–29]. For example, MWCNTs prepared by pyrolysis were suspended in water and pipetted onto the electrode followed by drying process [26,27]. Due to their high aspect ratio, it is expected that some of CNTs may happen to bridge over the electrode gap and establish the electrical connection. On the other hand, there seems to be little chance of obtaining such an electrical connection between the microelectrodes with sub-micron-sized SWCNH powders. Additional tests were conducted to determine whether the SWCNH and SWCNT sensors could be fabricated by the random deposition method. In order to increase the probability of

the electrical connection formation, these carbon nanomaterials were suspended in ethanol at higher concentration (10  $\mu\text{g}/\text{ml}$ ) than the concentration used in DEP fabrication. The suspension droplet (200  $\mu\text{l}$ ) was placed on the microelectrode and ethanol was gently evaporated. For the SWCNT suspension, the electrical connection between the electrode fingers was formed with an initial conductance  $G_0$  of about 2  $\mu\text{S}$ , which was lower than that obtained by the DEP fabrication method. The SEM observation revealed that some SWCNTs were actually retained and formed random bridges between the electrodes. Thus deposited SWCNHs could detect  $\text{NO}_2$  gas and their response was comparable to that of the DEP-fabricated sensor with the same initial conductance. However, the sensor initial conductance  $G_0$ , which had a strong influence on the sensor response as shown in Fig. 9, could not be controlled by the random deposition method. On the other hand, no electrical connection was established for the SWCNH suspension even after repeated trials. Thus the SWCNH powders, which potentially had comparable  $\text{NO}_2$  sensitivity to SWCNTs, could not be placed between the electrode gap by the random deposition method.

## 5. Conclusions

Electrokinetic manipulation of the SWCNH was demonstrated using positive dielectrophoresis (DEP) in the ac electric field. The SWCNH powders were attracted to the high field region and firmly trapped in the microelectrode gap. The SWCNH-retaining microelectrode could detect ppm-levels of  $\text{NH}_3$  and  $\text{NO}_2$  gas at room temperature. The conductance change caused by these gases suggests that a SWCNH behaves as a p-type semiconductor. The SWCNH sensor had lower normalized sensitivity to these gases than the SWCNT sensor. Since it is difficult to control the location of the SWCNH growth using catalysts, as well as to establish the electrical connection across the electrode gap by random deposition of the SWCNH, the DEP may be a promising technique for the manipulation of SWCNHs during device fabrication. In order to realize the practical use of the SWCNH gas sensor, some technical issues, such as selectivity or faster response, must be further investigated. The authors are currently working on these subjects.

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