



Facile and scalable fabrication of chemiresistive sensor array for hydrogen detection based on gold-nanoparticle decorated SWCNT network

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ABSTRACT

We report a facile and scalable process to fabricate chemiresistive hydrogen sensors based on the single-walled carbon nanotube (SWCNT) network decorated with metal nanoparticles (NPs). In order to obtain the statistical and reliable results in the detection, 100 unitary sensing array are fabricated on a single chip at one go. Two device structures were studied; one coated on top of the SWCNT network (SWCNCN) and the other sandwiched by Au-NPs (the Au/SWCNCN/Au structure). The sensor response of the Au-NP decorated SWCNCN was found to be ~ 3.6 and 18.5 times superior to that of the Cu- and Sn-NP coated SWCNCN, respectively, at room temperature. Sensing response of the sensor was further improved 3 times from 16.1 to 50% by using the sandwiched structure of Au/SWCNCN/Au. Based on reproducible electrical responses and statistical understanding, we also found that the enhancement of sensing response is proportional to the increase of the change in resistance by the Au-NP decoration.

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1. Introduction

Carbon nanotubes (CNTs) are believed to have the potential to create previously-unexpected applications in conventional micro-scopic devices due to its extraordinary physical and electrical properties [1–3]. In particular, because of its high surface-to-volume ratio and hollow cylindrical structure with every atom on the surface, the electrical characteristics of single-walled CNT (SWCNT) are affected strongly by tiny surface perturbations. Therefore, this ability makes it a promising candidate for various types of sensing applications [4–6]. Furthermore, recent studies on the development of hybrid structures, such as metal nanoparticle (NP)-coated SWCNT have devoted to explore the newly emerging applications, including electrical devices, bio-chemical sensors, catalysis, fuel cells, etc. [7–13].

Metal oxide and semiconducting materials have been used widely in the applications of gas sensing. It usually requires a

thermally isolated micro-hotplate to meet the high operating temperature, which leads to high power consumption and complex processing steps. On the other hand, SWCNT-based gas sensors show good sensitivity to a range of gas molecules at room temperature by itself or with appropriate chemical/physical tailoring on SWCNTs [14–16]. Especially, metal nanoparticle decorated SWCNTs have received a great deal of attention for the sensors showing high sensitivity and selectivity [17–19]. However, the process to build up the sensor still remains to be improved in terms of manufacturability and production. In this paper, we propose a tractable post-processing strategy and judicious electrode structure. Our strategy meets the following requirements: (1) mask-free process, (2) low temperature process, (3) reliable and reproducible sensor responses, and (4) the scalability and compatibility with well-established micromachining processes. A SWCNT network (SWCNCN) was formed on the fabricated test chip, in which concentric electrodes were embedded, using a dip-coating process. Metal-NPs were then deposited by thermal evaporation, requiring no additional photolithography process, during the SWCNT coating and metal-NP coating. The goal of the present work is to provide a facile and scalable fabrication chemiresistive sensor array, based on tractable post-processing strategy and judicious electrode

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structure, rather than to demonstrate practical applicability of the sensor in real environment. Hence, dry N_2 gas was used as a carrier gas to exclude the effect of other reactive gas molecules, especially oxygen and water, and no attempt is made at optimizing electrode spacing and coating density of SWCNN.

We examined the sensing ability of a gold nanoparticle (Au-NP)-decorated SWCNN toward hydrogen gas at room temperature ($\sim 20^\circ\text{C}$) by comparing the sensor responses with the decoration of copper (Cu) and tin (Sn) nanoparticles. The sensor response of the Au-NP decorated SWCNN was found to be superior to that of the Cu- and Sn-NP coated SWCNN. In order to further improve the sensing response, a SWCNT network sandwiched vertically by Au-NPs (*i.e.*, the Au/SWCNN/Au structure) is proposed. This structure is able to provide the high surface coverage of Au-NPs on the sidewalls of SWCNTs, thus leading to the enhanced sensing response.

2. Experimental

2.1. Preparation of SWCNT solution

The SWCNTs (ASP-100F produced by Iijin Nanotech) were sonicated in nitric acid at 50°C for 30 min to purify and simultaneously exfoliate them from the bundles [20]. The SWCNTs were then neutralized with deionized (DI) water and trapped on a membrane filter (Millipore, $0.2\ \mu\text{m}$ pore size, 47 mm diameter) by vacuum filtration. The SWCNTs on the filter were dried in a vacuum oven at 80°C for 2 days. 1,2-dichlorobenzene (1,2-DCB) was used as a solvent to prepare SWCNT colloidal solutions. Finally, the prepared SWCNTs were highly dispersed in 1,2-DCB by sonication for 10 h.

2.2. Fabrication of the device

Fig. 1 shows the concentric electrode geometry and an optical microscopy image of the test chip. The concentric electrode has an inner electrode (Island Electrode, IE) enclosed by an outer electrode (Enclosing Electrode, EE) in which the SWCNN channel is confined to the area between the two electrodes, as shown in Fig. 1(b). The concentric electrode itself provides a *self-aligned* SWCNT network channel. This self-alignment scheme is simple and quite useful because the SWCNTs can be coated on the entire test chip without the need for cumbersome processes. The Au electrodes ($0.5\ \mu\text{m}$ thickness) with a 10 nm thick titanium (Ti) layer as an adhesive layer formed on the thermally grown silicon dioxide (SiO_2 , 10 nm) using a standard lift-off process. The IE lies as a square with $60\ \mu\text{m}$ on each side and the electrode gap between the IE and EE was $15\ \mu\text{m}$.

2.3. Dip-coating of SWCNN on the device

A schematic diagram depicting SWCNT dip-coating is shown in Fig. 1(c). Prior to the coating, an oxygen plasma treatment was performed on the oxide layer for 5 min to enhance the coating uniformity of the SWCNN. The detailed procedures to achieve a highly uniform SWCNN device by a dip-coating method are explained elsewhere [20]. Briefly, the fabricated chip was immersed in a SWCNT colloidal solution with a concentration of 0.05 mg/mL and pulled out at a constant withdrawal velocity of $3.0\ \text{mm/min}$. During the dip-coating, a SWCNT bundle consists of several individual SWCNT in parallel was deposited on the surface of the oxide surface in the form of a network by the surface tension and capillary condensation between the CNTs and the surface. No additional photo-lithography process was used to remove the SWCNTs covering unnecessary areas due to the concentric electrode, as shown

in Fig. 1(c), which excludes side-effects, such as photo-resist (PR) residue in photo-lithography process.

2.4. Deposition of metal nanoparticles

Decoration of the SWCNT with metals could be accomplished by two techniques, such as reduction–oxidation (redox) reaction and physical vapor deposition (PVD). For redox reaction, it is generally necessary to generate defect sites on SWCNT walls through strong acid pretreatment [21]. Therefore, this method degrades the inherent properties of SWCNTs. On the other hand, PVD methods like thermal evaporation and sputtering, which physically place a metal layer onto SWCNT, have the advantage of controlling the deposition volume and particle size without damaging SWCNTs [22]. Moreover, this method is especially suitable for mass production. In the present study, three types of metal (1 nm-thick Au, Cu and Sn) were deposited on the SWCNN devices by thermal evaporation. Thermal evaporation was performed in an enclosed evaporation chamber (MHS-1800, Muhan vacuum). A SWCNN device was attached to a sample holder in which the SWCNN on a device was perpendicularly oriented to the evaporation incident angle. During evaporation the substrate was rotated to obtain a uniform film thickness distribution. The deposition rate and thickness were monitored using a quartz crystal microbalance (QCM). The deposition rate was $\sim 0.1\ \text{nm/s}$ for all depositions and the vacuum condition was below 10^{-6} Torr.

2.5. Experimental details for hydrogen gas sensing

All the measurements of gas sensing were performed using an Agilent 4156C parameter analyzer and a probe station with multi-electrode arrays, equipped with a gas chamber at 20°C . The sensor was exposed to dry N_2 (500 sccm) for 10 min to record an initial sensor resistance, and then H_2 balanced with N_2 were injected for 15 min to measure the sensing signal. To recover the sensor, N_2 was supplied into the tube for 30 min. The use of dry N_2 as a carrier gas enables us to exclude the effect of other reactive gas molecules, especially oxygen and water.

3. Results and discussion

3.1. Self-gating effect of the SWCNN device

Fig. 2(a) shows an equivalent circuit diagram of the bare SWCNN device, which is basically a transistor with a p-substrate as the back gate. In the concentric electrode, the two electrodes have an asymmetric shape. No gate bias is applied in the following experiments, including I – V characterizations and gas sensing; however, the back gate is coupled capacitively with the IE (drain) and EE (source). In particular, the voltage of the back gate follows the voltage of EE because of the difference in the area of the two electrodes, leading a difference in parasitic capacitance ($C_{ox1} > C_{ox2}$), as shown in the figure. This behavior is called the *self-gating effect*, which is observed frequently in two-terminal devices built on an oxidized silicon (Si) substrate [14] or aqueous solution due to electrical double layers [23,24].

The electrode scheme is beneficial not only to fabricate the *self-aligned* SWCNT network channel but also to evaluate the electrical characteristics of the SWCNN channel. Fig. 2(b) shows the current versus voltage (I – V) characteristics of a representative bare SWCNN device in which the drain voltage is swept from -5 to $+5\ \text{V}$ with the source voltage fixed at $0\ \text{V}$. The bare SWCNN device exhibited asymmetric behavior with the polarity of the V_{DS} . It indicates that, although there were some metallic SWCNTs in the channel, semiconducting SWCNTs comprised a substantial portion of the randomly-distributed SWCNN modulated by the back gate, leading

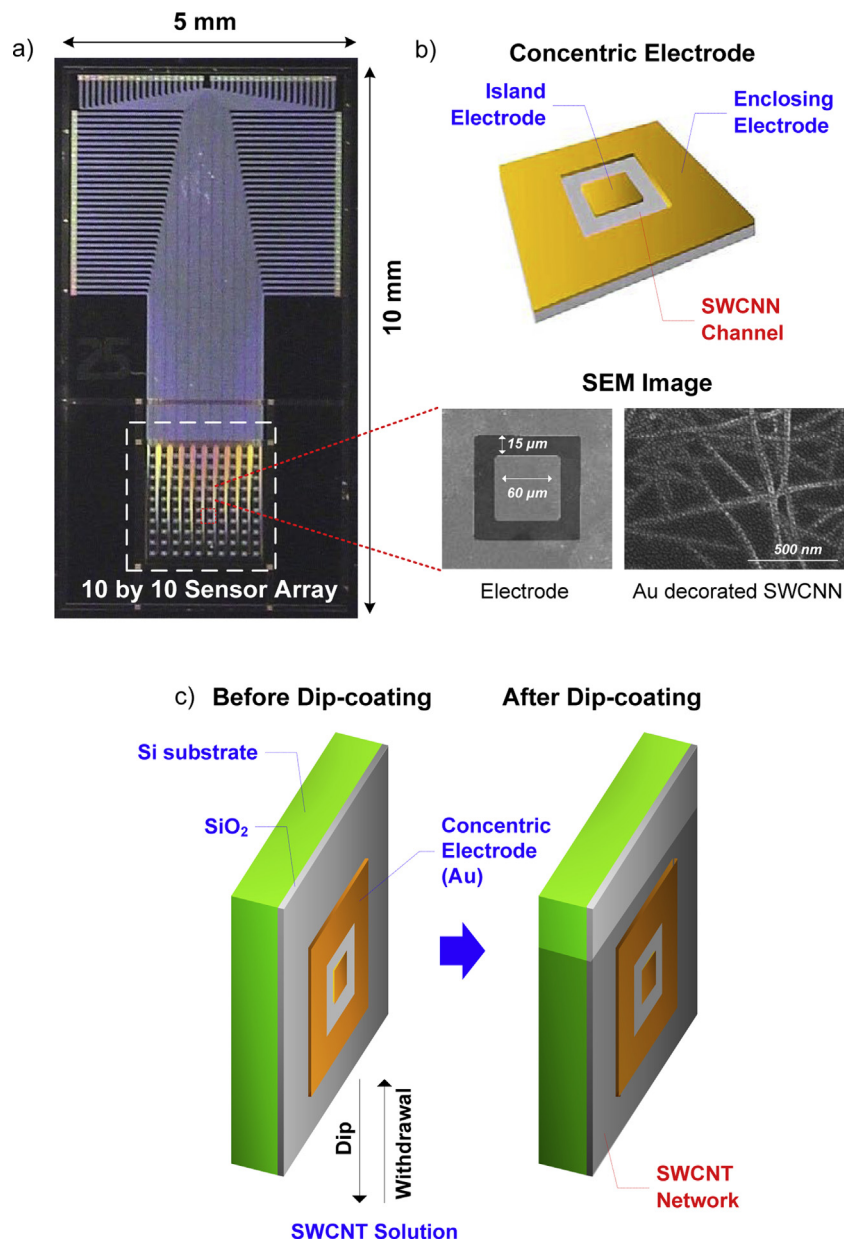


Fig. 1. Schematic diagram of the concentric electrode and SWCNT dip-coating: (a) Optical image of the 10 by 10 sensor array. (b) Conceptual diagram of the concentric electrode composed of an Island electrode and an Enclosing electrode, and their SEM images (space is 15 μm , perimeter is 240 μm). (c) Conceptual diagram of the SWCNT dip-coating process.

to asymmetric I – V characteristics. The distinct electrical behavior of the bare SWCNN device can be explained as follows. With a positive V_{DS} ($>0\text{ V}$), holes in the p-type semiconducting SWCNTs accumulate by the low V_{GS} ($\approx 0\text{ V}$), resulting in an increase in current. On the other hand, with a negative V_{DS} ($<0\text{ V}$), holes are depleted by the high V_{GS} ($\approx 0\text{ V}$), decreasing the current. When the SWCNN was fabricated on the glass substrate, we could not observe any asymmetric behavior in I – V characteristics, showing no back gate modulation. From the I – V characteristics in Fig. 2(b), a characteristic index (R_{NET}) was set, which is the resistance at $V_{\text{DS}} = 1\text{ V}$. The histogram in Fig. 2(c) shows the statistical distribution of R_{NET} for 50 bare SWCNN devices, exhibiting a relatively well-controlled distribution in the range from 2 to 9 k Ω . This suggests that the dip-coating of SWCNN on the concentric electrode provides good statistics for uniform reproducible electrical properties.

3.2. Hydrogen sensing response of the SWCNN sensor with metal nanoparticles

Thermal evaporations of Au-, Cu- and Sn-NPs with a thickness of 1 nm were carried out on the bare SWCNN devices, respectively. Thermal evaporation deposits metals on a SWCNT in the form of nanoparticles when the thickness is very small. It is the well-known film growth mechanism in metal deposition, where cohesive bonds between metal atoms are stronger than adhesive bonds between the atoms and substrate [25]. Deposited metal nucleates and grows into individual nanoparticles on SWCNT surface as shown in transmission electron microscopy (TEM) images of Fig. 3(a).

Fig. 3(b) shows the representative I – V characteristics before and after Au-NP deposition, showing a significant increase in current and no gate modulation after the deposition. Deposited metal-NPs on the SWCNT allow the local depletion or accumulation of carriers,

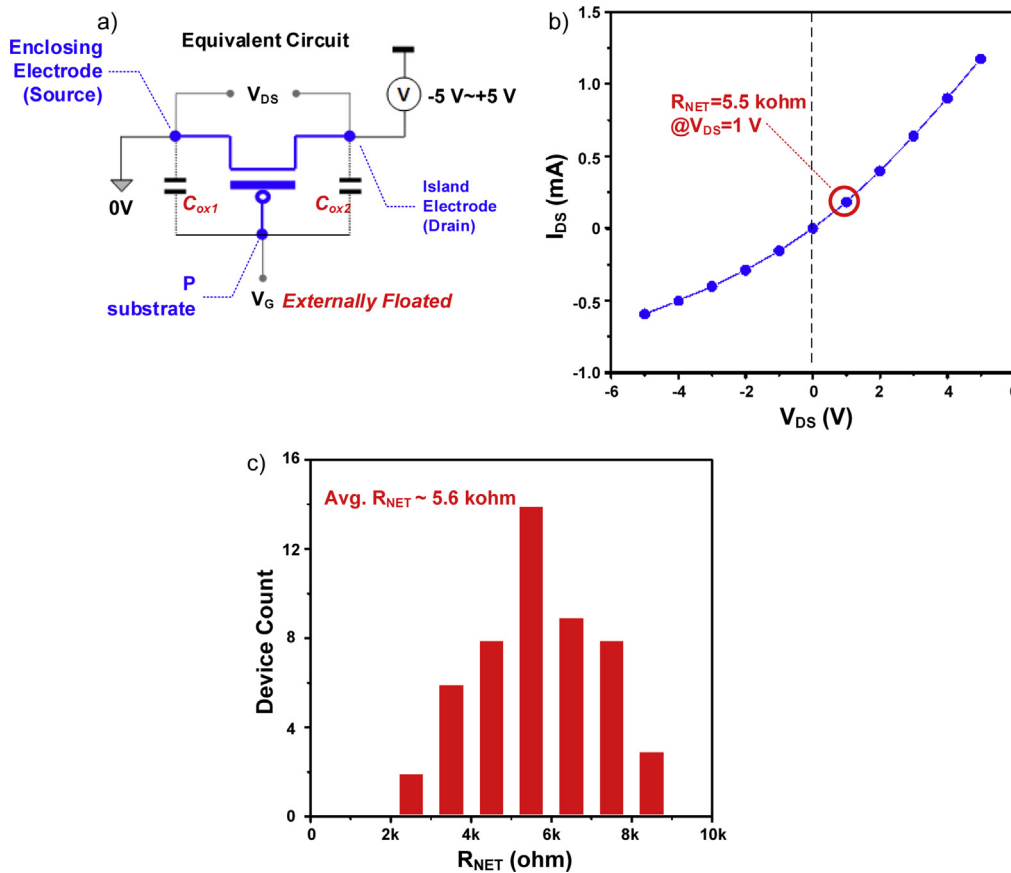


Fig. 2. Equivalent circuit of the fabricated bare SWCNN device and its representative I – V curve. (a) Equivalent circuit of the device in which the p-substrate (back gate) is floated externally but capacitively coupled with the IE (drain) and EE (source). (b) I – V characteristic curve of the fabricated bare SWCNN device, showing asymmetric behavior due to a self-gating effect. (c) Statistical distribution of R_{NET} for the 50 CNN devices (The averaged R_{NET} is measured $\sim 5.6 \text{ kohm}$).

resulting in tuning the electrical characteristics of SWCNTs [26]. In the case of the Au-NP coating, hole carriers would accumulate locally in the vicinity of the Au-NPs on the SWCNT via electron transfer from the SWCNT to the Au-NP because the work function of SWCNT ($\sim 4.8 \text{ eV}$) is smaller than that of Au ($\sim 5.1 \text{ eV}$). This work function difference is attributed to an increase in current as shown in Fig. 3(b). On the other hand, opposite results were observed in the case of the Cu-NP and Sn-NP coatings. The work functions of Cu and Sn ($\sim 4.6 \text{ eV}$ and 4.3 eV , respectively) are smaller than that of the SWCNT, therefore, the hole carriers would deplete locally in the vicinity of the Cu- and Sn-NP on the SWCNT via electron transfer from the Cu and Sn to the SWCNT, resulting in a decrease in current.

To evaluate the statistical effect of the coating on the change in R_{NET} quantitatively, the rate of R_{NET} change (RORC) is defined as $RORC = ((R_{NET_DECORATION} - R_{NET_BARE}) / R_{NET_BARE}) \times 100 (\%)$, where R_{NET_BARE} and $R_{NET_DECORATION}$ denote the R_{NET} before and after metal deposition, respectively. Fig. 3(c) shows that the mean RORC depends on the types of deposited metal-NP for 12 SWCNN devices. As discussed, it is clearly shown that the RORC of the devices keeps track of the work-function difference.

Sensing ability of the metal-NP coated SWCNN was examined as shown in Fig. 4. Fig. 4(a) shows the representative I – V characteristics of the Au-NP coated SWCNN device before and after the exposure to 1000 ppm H_2 in a nitrogen carrier gas. It shows an increase of the R_{NET} (decrease in current from 0.315 to 0.258 mA at 1 V). The increased R_{NET} was also observed as the SWCNNs decorated with Cu- and Sn-NPs upon hydrogen exposure. SWCNTs under ambient conditions are known to be covered with oxygen [27], thus behave like a p-type semiconductor with the majority

charge carrier of hole (Fig. 2(b)). Although the work function difference between SWCNT and the decorated metal nanoparticles changes the electrical resistance of the SWCNT device, the majority carrier of the SWCNTs partially covered with metal-NPs (see TEM images in Fig. 3(a)) is still hole. It is noteworthy in this regard that the resistance of the CNN devices increases after exposure to H_2 gas, which is typical of p-type semiconductors.

Fig. 4(b) shows the mean sensor response depending on the types of deposited metal-NP for the 12 CNN devices. The gas response is defined as the response $= ((R_{NET_H_2} - R_{NET_N_2}) / R_{NET_N_2}) \times 100\%$, where $R_{NET_N_2}$ and $R_{NET_H_2}$ denote the resistance before and after hydrogen exposure, respectively. The sensor response of the Au-NP decorated SWCNN was found to be ~ 3.6 and 18.5 times superior to that of the Cu- and Sn-NP coated SWCNN, respectively. This improved response in the Au-NP decorated SWCNN sensor might be attributed to the different sensing mechanism as the followings. It was reported that hydrogen could adsorb dissociatively on the surface of Au-NPs [28]. Based on the catalytic effects of Au-NP, the sensing mechanism is presumably as the followings. When the SWCNN device is exposed to H_2 , hydrogen molecules are dissociated into atomic hydrogen, leading to a decrease in the work function of Au-NP. The lower work function associated with the H_2 dissociation is beneficial to the transfer of more electrons from the Au nanoparticles to the SWCNN channel, which leads to trap the p-type carriers in the SWCNN, resulting in an increase of resistance of the device. It indicates that the sensing kinetics of the sensor mainly relied on the hydrogen dissociation process over Au-NP. The hydrogen atoms dissolve on the Au surface and rapidly diffuse to the Au/SWCNT interface, which reduces the electronic work function. This plausible detection

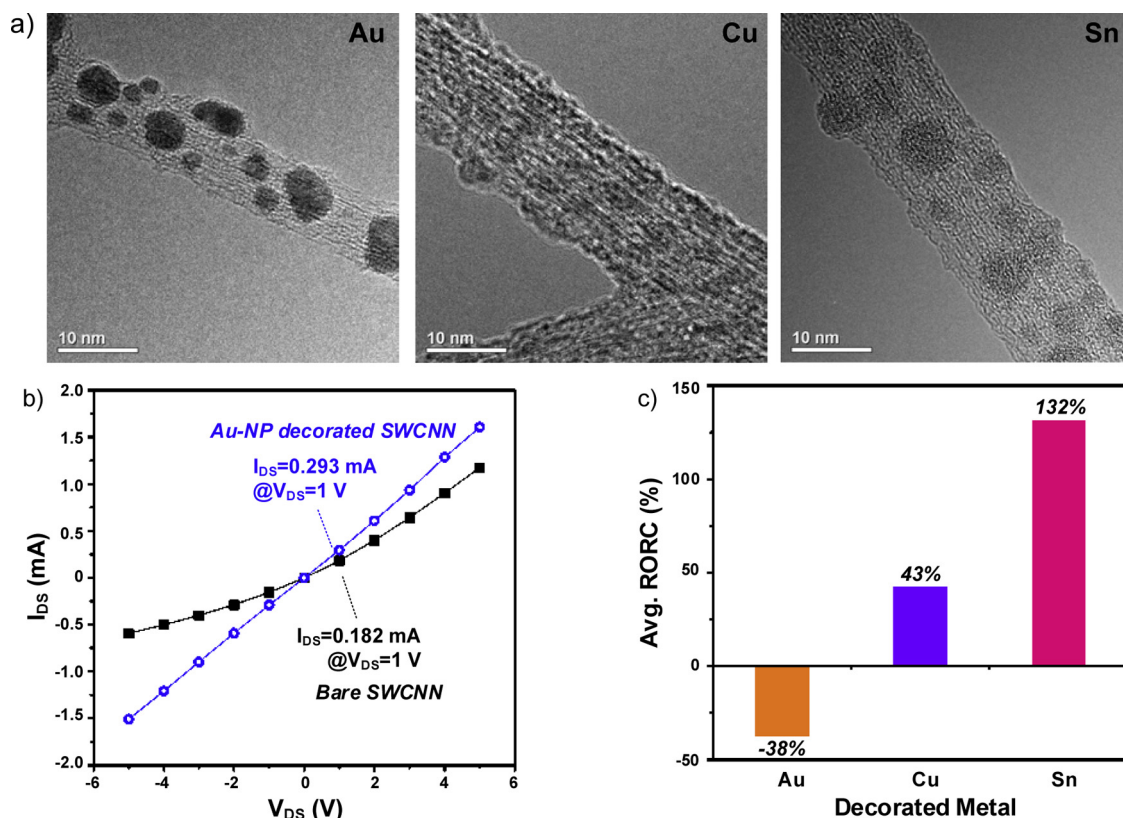


Fig. 3. Change in the electrical characteristics of the CNN device after the metal nanoparticle decoration. (a) TEM images of the metal decorated SWCNT bundle. (b) Representative I - V curves before and after the Au-NP decoration on the bare CNN. (c) The average rate of the R_{NET} change (RORC) before and after Au-, Cu- and Sn-NP coating, respectively.

principle is similar to that reported previously for Pd-NP coated SWCNT devices [11,17,29].

On the other hand, the surface of low-work function metals, such as Cu and Sn, is easily oxidized at ambient condition and generally covered with negatively charged adsorbed oxygen ions [30,31]. When exposed to H_2 gas, the oxygen adsorbates react with H_2 , and produce water molecules. The produced water molecule might be dissociatively adsorbed on the metal surface by forming hydroxyl molecules with assistance of the oxygen adsorbate [32]. We believe that the coverage of water and hydroxyl molecules might reduce reaction sites on the metal surface, thereby providing relatively lower sensing response compared to that of Au-NPs.

3.3. Improvement of sensing response using the Au/SWCNN/Au structure

Coverage of Au-NPs on the surface of SWCNT is one of the most critical factors to improve the sensing performance by providing numerous H_2 receptors, accordingly, we proposed the SWCNN sandwiched by Au-NPs (*i.e.*, Au/SWCNN/Au structure). Fig. 5(a) shows a schematic diagram of the procedure to fabricate the proposed sandwich structure, in which a SWCNN film is vertically interposed between two Au thin films conceptually. 1 nm-thick Au layer was deposited on the bare device by thermal evaporation, followed by the dip-coating of SWCNN. Then, another 1 nm-thick

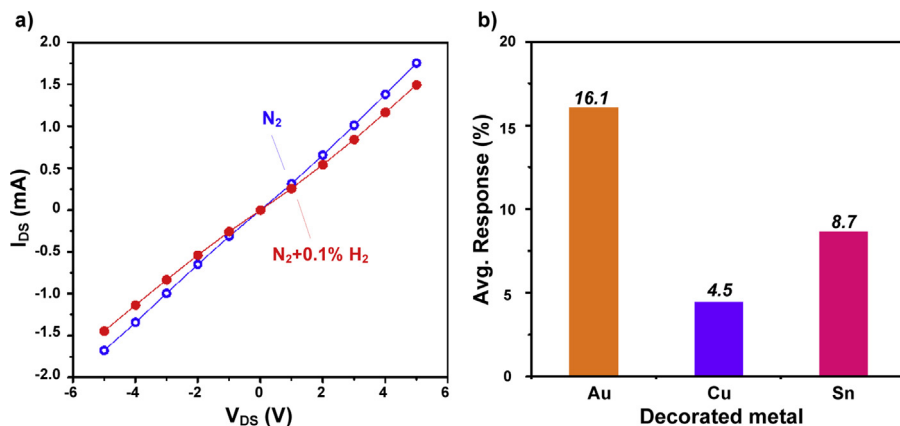


Fig. 4. Change in the electrical characteristics when the device was exposed to 1000 ppm H_2 . (a) Representative I - V characteristics in response to H_2 , (b) the averaged gas response of Au-, Cu-, and Sn-NP coated SWCNN, respectively.

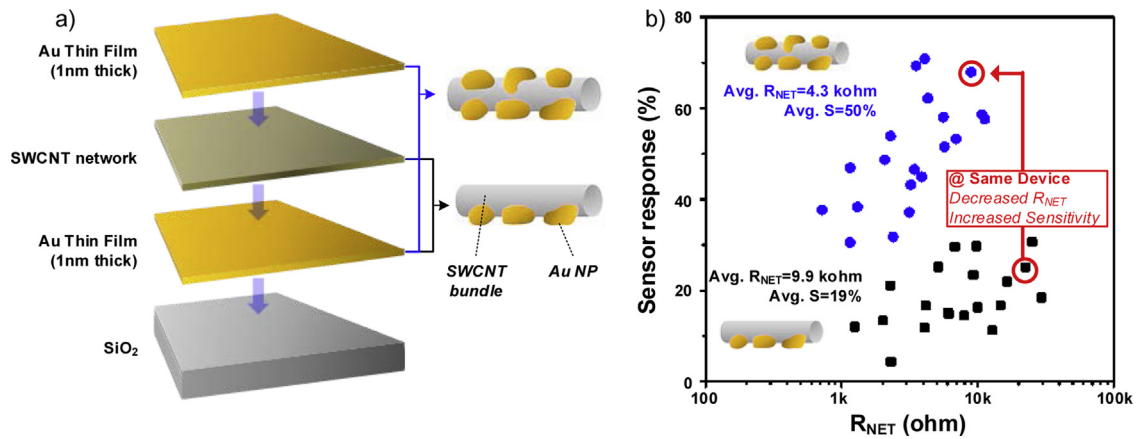


Fig. 5. Increase in the surface coverage of Au-NPs on the SWCNN to enhance the gas response of the sensor. (a) Schematic diagram showing the fabrication procedures. (b) Sensor response change with respect to the R_{NET} of the device.

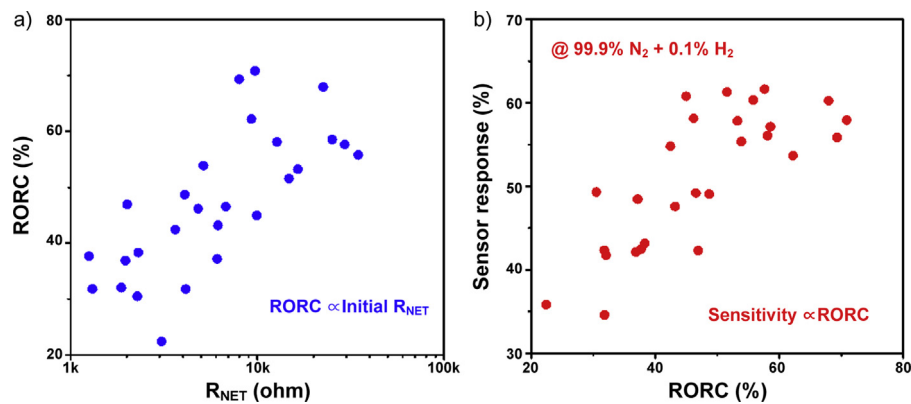


Fig. 6. (a) RORC dependency on the R_{NET} determined by the SWCNT dip-coating step. (b) Relationship between the RORC and the sensor response.

Au layer was deposited on the sensor. Finally, in order to remove the residue of 1,2-DCB, heat treatment was applied to the fabricated specimen in a chamber at 400 °C for 30 min. The applied temperature is higher than the boiling temperature of the solvent (~180 °C). This thermal treatment step is very critical to ensure a sensing ability because no change in electrical characteristics was observed upon exposing the sensor to H_2 gas without heat treatment.

Fig. 5(b) shows the change in the R_{NET} after the second Au deposition step and the sensor responses for 27 devices. Meanwhile the sensor response from the device that has Au-NPs on the bottom of SWCNN (*i.e.*, Au/SWCNN) is comparable to that of Au-NP decorated SWCNN shown in Fig. 4, it is clear that the R_{NET} decreases after the second deposition of Au-NPs on the SWCNN and the sensor response increases as the R_{NET} increases. Moreover, the mean sensor response was improved 3 times from 16.1 to 50% by using the sandwiched structure of Au/SWCNN/Au. It is obvious that the increased coverage of Au-NPs on the SWCNN is attributed to the improvement in hydrogen sensing.

One of the interesting features from Fig. 5(b) is that the sensor response is enhanced and the amount of change in the sensor response is strongly related to the amount of RORC after completing the second Au deposition step. The RORCs are proportional to the R_{NET} determined by the SWCNT dip-coating step, as shown in Fig. 6(a). The R_{NET} is determined mainly by the portion of semiconducting SWCNTs in the conduction path. Therefore, the existence of more semiconducting SWCNTs in the conduction paths leads to a large R_{NET} . The RORC of the fabricated device with a high R_{NET} is larger than that with low R_{NET} by the Au-NP decoration because

the effect of charge transfer *via* the formation of a semiconducting SWCNT-Au hybrid is presumably larger than that of a metallic SWCNT-Au hybrid. Fig. 6(b) shows the relationship between the RORC and sensor response. The SWCNN device with a larger RORC leads to larger response to hydrogen. It indicates that, although the surface coverage is high enough, the sensor response could be limited by the content of semiconducting SWCNT in the SWCNN channel. Therefore, the increase of Au-NP coverage on the SWCNN as well as the content of semiconducting SWCNTs in the SWCNN channel plays an important role in enhancing the sensor performance of the present device.

4. Conclusion

Based on highly scalable and batch-compatible processes, we fabricated the chemiresistive hydrogen sensor using the decoration of Au-NPs on SWCNN. The fabrication procedure is straightforward and can be applied to batch production due to the use of concentric electrodes, CNT dip-coating and the thermal evaporation of metal nanoparticles. The sensor response to hydrogen gas was examined using the SWCNN sensor decorated with Au, Cu and Sn nanoparticles. The sensing ability of the Au-NP decorated SWCNN was found to be ~3.6 and 18.5 times superior to that of the Cu- and Sn-NP coated SWCNN, respectively, at room temperature. The response was further improved 3 times from 16.1 to 50% by using the stacking structure of Au/SWCNN/Au. Based on reproducible electrical responses and statistical understanding, we also found that the enhancement of sensing response is proportional to the increase of the change in resistance by the Au-NP decoration.

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