

Magnetically Aligned Iron Oxide/Au Nanoparticles Decorated Carbon Nanotube Hybrid Structure as Humidity Sensor

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ABSTRACT

Functionalized carbon nanotubes (f-CNTs), particularly CNTs decorated with nanoparticles (NPs), are of interest due to their synergic effects, such as surface enhanced Raman scattering (SERS), plasmonic resonance energy transfer (PRET), magneto-plasmonic, magneto-electric, and magneto-optical effects. In general, the research has focused on a single type of NP, such as a metal or metal oxide, that has been modified on a CNT surface. However, in this study, a new strategy is introduced for the decoration of two different NP types on CNTs. In order to improve the functionality of modified CNTs, we successfully prepared binary NPs decorated CNTs: iron oxide/Au (IA) NP-decorated CNTs (IA-CNTs) are created through two simple reactions in DI water, without high temperature, high pressure or harsh reducing agents. First, CNTs were dispersed using sonication in DI water with Au³⁺ ions. During this step, positive Au ions were attached to the surface of CNTs due to pi electrons. Subsequently, gallic acid (3,4,5-trihydroxyl benzoic acid) modified iron oxide NPs

(GA-IONP) were added into the Au ion/CNT mixture in order to reduce the Au ions to Au NPs on the CNT surfaces. GA possesses antioxidant effects; therefore, GA-IONPs become oxidizable NPs. GA-IONPs acted as a reducing agent during the second reaction and were automatically attached to the surface of CNTs via pi-pi interactions between the GA and CNTs; and, magnetic and electro conductive IA-CNTs were obtained. The physicochemical properties of IA-CNTs were characterized by UV/Vis spectroscopy, FT-IR, SQUID, TEM and SEM. In this study, humidity monitoring was demonstrated using IA-CNTs. Magnetic IA-CNTs were aligned on interdigitated platinum electrodes under external magnetic fields to create a humidity-sensing channel, and its electrical conductivity was monitored. As the humidity increased, the electrical resistance of the sensor also increased. In comparison with various gases, for example, H₂, O₂, CO, CO₂, SO₂ and dry air, the IA-CNT-based humidity sensor exhibited high selectivity performance. IA-CNTs also responded with heavy water (D₂O), and the mechanism of humidity detection was established with the D₂O sensing performance. Lastly, the humidity from human out-breathing was monitored by this system. Therefore, this unique IA-CNT exhibited potential application for gas detection materials.

Keywords: Aligned magnetoplasmonic CNT, Au/Fe₃O₄ nanoparticles decorated CNTs, Binary nanoparticles decorated CNT, Magnetic field alignment, Oxidizable iron oxide, Humidity detection

1. Introduction

Humidity detectors have been widely used in various fields from human well-being to industrial process.^{1,2} They have also been highly investigated owing to their fuel cell or battery applications. H₂O is released in the cell during operation; and, many researchers have been tried to monitor the humidity with high selectivity against oxygen (O₂) and hydrogen (H₂)³⁻⁵

In general, numerous polymer-based humidity sensors have been developed due to their swelling property in humid conditions.^{6,7} The swelling effect of polymer in a water environment, therefore, could be monitored by measuring the change in electrical conductivity and mechanical properties. In other words, humidity can be detected by translating physical and/or chemical changes into measurable electrical signals.⁸⁻¹⁰ However, polymer materials may get damaged and shrink in size when it is exposed to high levels of humidity for long periods of time.¹¹⁻¹³ Thus, the humidity sensing layer can easily get delaminated from the substrate by a swelling induced structure change.

Recently, functionalized carbon nanotubes (f-CNTs) based materials have been employed as gas and humidity sensing platforms because of their enhanced electrical and mechanical properties.¹⁴⁻¹⁷ In addition, nanoparticles decorated CNTs (NP-CNTs) have been highlighted due to its synergic properties such as surface enhanced Raman scattering (SERS), plasmonic resonance energy transfer (PRET), magneto optical effect (MO effect) and so on.¹⁸⁻²³ Furthermore, these kinds of NP-CNTs have been applied in various fields, not only in gas sensing platform²⁴⁻²⁶ but also in solar cells,^{27,28} secondary ion batteries,^{22,27} and nano biomedical applications.^{20,29,30}

Several methodologies have been developed to create unique NP-based f-CNTs:: chemical vapor deposition (CVD),^{25,31-33} chemical reduction process,^{20,24} high temperature/pressure assisted synthesis,^{34,35} electrochemical deposition,³⁶ soft/hard template method,³⁶ and DNA hybridization method.³⁷ Although many preparation strategies have been suggested, they are still very limited because of the complexities of these methods, the difficulty in controlling these methods, and remnant byproducts from unexpected chemical reactions. In addition, a single type of nanoparticle decorated CNTs can be prepared by using the above mentioned methods; however, they are not often suitable for binary types of nanoparticle decorated CNT preparations. The synthesis of binary types of nanoparticle decorated CNT is more complex and still faces several challenges.³⁸⁻⁴⁰

In this paper, we introduce a new strategy for a process for the combination of two different NP types to be decorated on CNTs. It is a simple synthesis method for Iron oxide/Au NPs decorated CNTs (IA-CNTs) in DI water under stirring process without an exposure to any harsh conditions, chemicals, and high temperature/pressure (Figure 1 (D) and Figure S1, supporting information). This reaction involved two-step processes. First, positive Au ions were attached on the surface of CNTs *via* electro static force with pi electrons under the sonication process. Subsequently, oxidizable gallic acid (3,4,5-trihydroxy benzoic acid, GA) modified iron oxide nanoparticles (GA-IONPs) were added into the CNT/Au³⁺ solution. In this step, GA-IONPs were used as a reducing agent to synthesize the Au NPs. The GA possesses an antioxidant effect,^{20,41} thus GA-IONPs can play a role as oxidizable nanoparticles. Au ions were converted to Au NPs on the surface of CNTs by GA-IONPs which were also attached on the surface of CNTs *via* pi-pi interaction. The physicochemical properties of nanocomposites were analyzed using ultraviolet-visible (UV/Vis) spectroscopy,

Fourier transform infrared (FT-IR) spectroscopy, superconducting quantum interference device (SQUID), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Moreover, humidity detection was attempted by aligned IA-CNTs structures. Due to the magnetic property of IA-CNTs, these nanostructures were aligned on the platinum (Pt) based electrical circuit by external magnetic force without soft or hard template or other physical conditions.

In this study, the humidity response of aligned IA-CNTs was monitored by electrochemical impedance spectroscopy (EIS) system, and it exhibited excellent selectivity against several oxide gases such as CO₂, CO, SO₂, O₂, H₂ and dry synthetic air (79 % N₂ + 21 % O₂). In addition, deuterium oxide (Heavy water, D₂O; ²H₂O) was monitored by the aligned IA-CNTs system to establish the binding affinity with water vapor.

2. Materials and Methods

2.1 Materials and instruments

HAuCl₄·3H₂O (99.9%), Gallic acid (GA; 3,4,5-trihydroxyl benzoic acid), FeCl₃, FeCl₂·4H₂O, 25% NH₄OH solution and Deionized water (D.I water) were obtained from Sigma-Aldrich (Oakville, Ontario, Canada). Multi-Walled carbon nanotube (MWCNT, 30~50 nm of diameter and 10~20 μm of length) was purchased from Cheap Tubes Inc. (Cambridgeport, VT, USA). In addition, large diameter MWCNT (110~170 nm of diameter) was also obtained from Sigma-Aldrich. For IA-CNTs alignment, round type magnets (φ; 18 mm and BrMax: 3850 Gauss) were purchased from ABRA Electronics Inc. (Montréal, Québec, Canada). The planar interdigitated Pt electrode was purchased from Synkera (Longmont, CO, USA). The absorbance of GA-IONPs and IA-CNTs was measured by UV/Vis spectroscopy (Cary 50, Varian Inc, Canada). The functional groups of hybrid

nanostructures were monitored by FT-IR spectroscopy (Nexus 470 FTIR, Thermo Instruments, Canada). The magnetic property of nanostructures was analyzed by SQUID (Quantum Design, MPMS XL, USA). The morphologies and size of NPs and CNTs were observed by HR-TEM (Tecnai F20, FEI, USA), SEM (XL30, FEI, USA) and USB digital microscope (UDM; Microview, China). Humidity detection was performed with Electrochemical Impedance Spectroscopy (EIS, SP-150, BioLogic, France).

2.2 Synthesis of GA-iron oxide NPs

GA-IONPs were prepared by co-precipitation process. FeCl_3 (1 mmol, 0.1622 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.0994 g) were dissolved in DI water (20 ml). Then 0.6 ml of 25% NH_4OH solution was added into the mixture and stirred for 10 min to form Fe_3O_4 NPs. Subsequently, GA (1.5 mmol, 0.255 g) powder was poured into the black Fe_3O_4 NPs solution and stirred at 90 °C for 30 min. Due to the binding between GA and Fe in GA-IONPs structure, the solution color changed from black to deep violet. After stirring, GA-IONPs were purified and precipitated with excess acetones, which were finally separated by a magnet.

2.3 Preparation of IA-CNTs

IA-CNTs were synthesized *via* 2 simple steps (Figure S1, supporting information). First, 10 mmol of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (4 mg) and 2 mg of MWCNT were dispersed in 20 ml of DI water under sonication for 30 min. Subsequently, 1 ml of oxidizable GA-IONPs solution (1 mg/ml concentration in DI water) was dropped into the $\text{CNT}/\text{Au}^{3+}$ mixture. After vigorously stirring for 3 hrs, the mixture color turned from black to dark red, and it was an indication that IA-CNTs were obtained. The particles were separated by magnetic force and dried in a vacuum oven.

2.4 Alignment of IA-CNTs on the Pt electrode and humidity detection test

Alignment of CNTs was spotlighted due to its enhanced mechanical and electrical properties. A number of alignment processes were introduced such as polymer mediated injection molding process, mechanical pulling and electric field assisted alignment.⁴²⁻⁴⁵ In this study, aligned IA-CNTs were formed by external magnetic force using two magnetic bars. 10 μ L of IA-CNTs solution (1mg/ml concentration) was dropped onto the Pt electrode which is located on the two magnetic bars (Figure 3 (B)). In order to obtain aligned IA-CNTs, the solvent was dried at room temperature and during this process, IA-CNTs formed as straw structures, which is a result of following magnetic field directions on the substrate surface.

Subsequently, for humidity sensing studies, prototype sensors were prepared by IA-CNTs deposited the Pt-microelectrodes embedded on alumina substrate (5 mm x 5 mm). Pt wires were kept in contact to each microelectrode in the gas-tight chamber. All sensing measurements were taken at room temperature. CO₂ (3000 ppm bal. in Ar), CO (1% bal. in Ar), SO₂ (100 ppm bal. in Ar) (Praxair, Inc. Canada) were purged for selectivity results, where pure N₂ (99.99%) was utilized as diluting gas. The concentration level of the gases varied in controlled manner using a conventional gas flow apparatus and computer regulated mass flow controllers (MCS-100 SCCM-D/5M, 5IN).

For humidity sensing measurements, N₂ gas bubbled through water at various temperatures before purging into the testing chamber. The sensitivity of the sensor was monitored by EIS system. In addition, the selectivity test was carried out against CO₂, CO, SO₂, O₂, H₂ and dry synthetic air (79 % N₂ + 21 % O₂). Similarly, D₂O was used instead of water by bubbling N₂ to demonstrate our working mechanism. In this case, 3 % of D₂O was also detected by the IA-CNTs based sensor to establish the binding affinity between sensing

materials and target gases (H₂O and D₂O). The flow rate was kept constant at 100 sccm. A constant dc voltage of 100 mV was applied (Solartron, SI 1287) to obtain an output current for humid as well as corresponding gases as mentioned above. The gas selectivity is defined as:

$$Selectivity = \frac{R_A - R_G}{R_G} \times 100\% \quad (1)$$

where R_A is electrical resistance when reference base gas air is purged, and R_G is electrical resistance upon the target gases (CO₂, CO, SO₂, O₂, H₂, H₂O and D₂O) passed into the sensor chamber at various concentrations for selectivity tests.

3. Results and Discussion

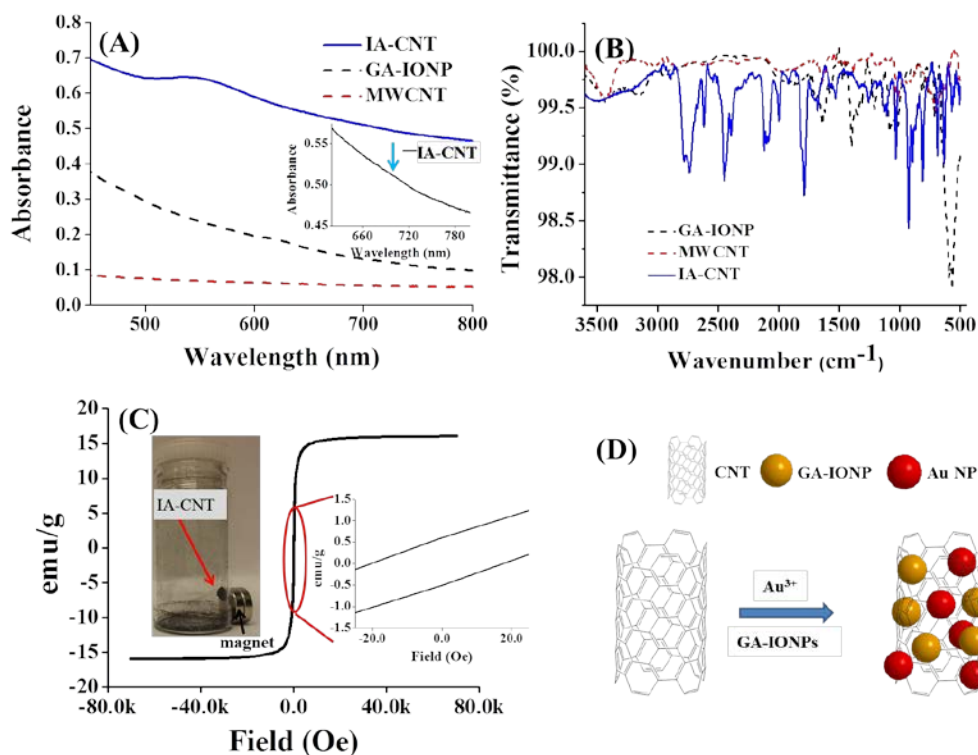


Figure 1. Physicochemical property; (A) UV/Vis spectra, (B) FT-IR spectra of IA-CNTs, GA-IONP and MWCNT, (C) magnetization-hysteresis (M-H) curve of IA-CNTs and (D) Schematic illustration of IA-CNT preparation (non-scalable)

The optical absorbance was measured by UV/Vis spectroscopy to confirm the surface plasmonic property of IA-CNTs. (Figure 1. (A)). The plasmonic absorption was taken at a place around 550 nm, and the spectrum was broaden. It indicated that large size of Au NPs (over 50 nm) was synthesized on the MWCNT surfaces, and the size distribution of NPs was not homogeneous. In this experimental process, GA-IONPs were used as a reducing agent in preparation of Au NPs, and surfactant was not used for stabilization of the NPs. Thus the size of the particles was not homogenous in comparison with other strong reducing agents, such as sodium borohydride (NaBH_4) and hydrazine, heating or high pressure. However, this plasmonic absorption band proved that Au NPs can be successfully synthesized through only GA-IONPs without any reducing agents (such as NaBH_4 , hydrazine), heating, high pressure and so on. In addition, weak absorbance band (shoulder) was measured at around 700 nm. (inset in Figure 1. (A)). It established the longitudinal plasmon coupling interaction that occurred between adjacent Au NPs due to the delocalized π -electron cloud on the surface of MWCNTs.^{20,46} In the GA-IONPs and MWCNT case, the plasmonic band were not shown. On the other hand, weak absorption peak was analyzed in GA-IONPs spectrum at around 620 nm. As it was mentioned in the experimental section, synthesized GA-IONPs were purple; thus peak was induced by binding between GA and IONPs.

The functional groups of nanomaterials were characterized by FT-IR spectroscopy (Figure 1. (B)). First of all, The vibration band of Fe-O appeared at around 570 cm^{-1} in the spectra of GA-IONPs and IA-CNTs. The carboxylic groups of IA-CNTs and GA-IO NPs were measured at 1675 cm^{-1} and 1640 cm^{-1} , respectively. The peaks at around 1524 cm^{-1} corresponded the aromatic bonds of IA-CNTs (blue spectrum in Figure 1 (B)). The magnetic property of IA-CNTs was analyzed by SQUID measurement at room temperature from -80

kOe to 80 kOe (Figure 1 (C)). The magnetic-hysteresis (M-H) relationship exhibited nonlinear and reversible hysteresis loop (Figure 1 (C)). From the inserted magnetization curve in Figure 1 (C), remanence effect was shown around -0.5 emu/g and 0.6 emu/g when the applied magnetic field was zero. In addition, the coercive force of IA-CNTs was measured to be approximately - 20 Oe and 17 Oe. The photograph in Figure 1 (C) shows the movement of IA-CNTs with an extra magnet. The black powder indicated IA-CNTs and it could be located on the wall of vial because of the magnet. The magnetization curve of GA-IONPs was shown in Figure S2 (supporting information). In this case, the remanence effect was - 2.0 emu/g and 2.1 emu/g, and the coercive force was - 12 Oe and 10 Oe, which means that the magnetization property was maintained after a decoration reaction.

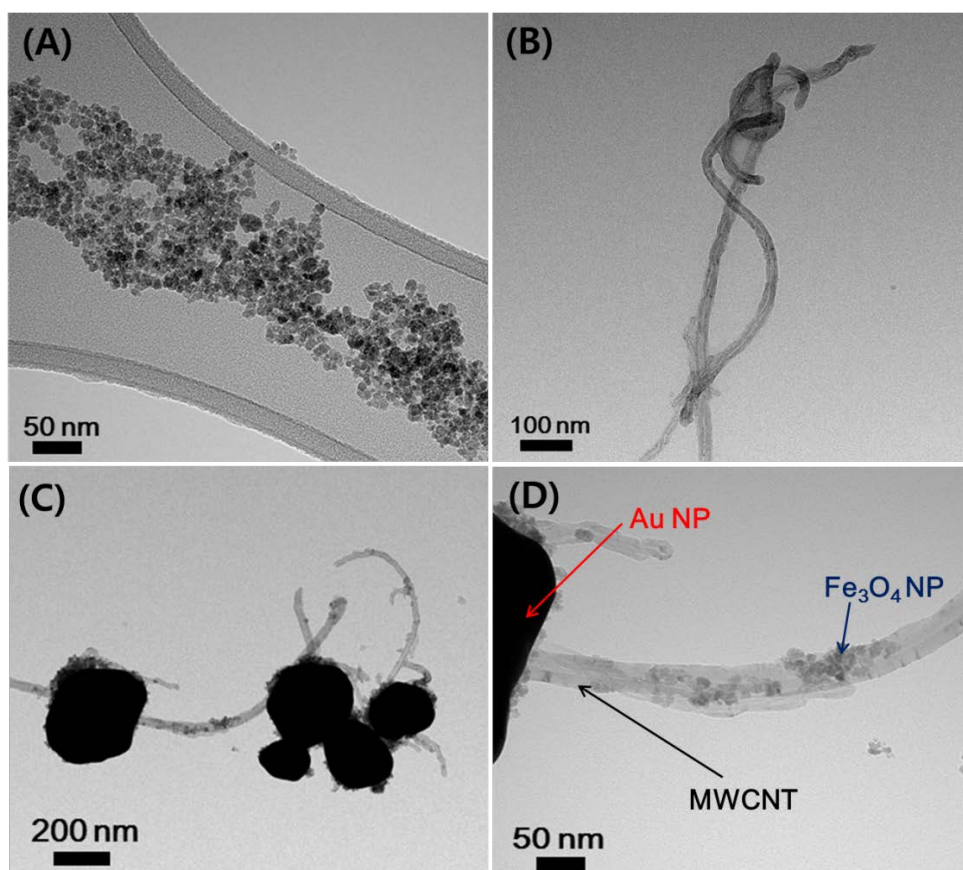


Figure 2. TEM images of (A) GA-MNP, (B) MWCNT, (C) IA-CNT (low mag) and (D) IA-CNT (high mag).

The morphology of GA-IONPs, MWCNT and IA-CNTs was observed by HR-TEM. Figure 2 (A) shows GA-IONPs, and their average size was approximately 13 nm. These particles are well dispersed due to GA modification. In the case of organic acid binding reaction with iron oxide NPs, it is well known that carboxylic group of organic acid can attach with iron oxide surface. Thus carboxylic group of GA can bind with iron oxide, and tri hydroxyl groups can prevent aggregation between iron oxide NPs via electrical static repulsion. In addition, tri hydroxyl group of GA possesses anti-oxidant effect; therefore, Au ions can be converted to Au NPs by GA-IONPs. MWCNTs were observed in pre-decoration step and the clean surface of MWCNT was shown (Figure 2 (B)). After the 2 step reactions, Au and GA-IONPs on the MWCNT were clearly observed in Figure 2 (C) and (D). The surface electrical density of Au is higher than iron oxide NPs; black dots indicate Au NPs and pale gray dots indicate iron oxide NPs. Since a surface stabilizer for Au NPs was not used in this reaction, the size of the Au NPs was slightly big: around 200 nm. In addition, GA-IONPs were well dispersed on the MWCNT and their size was almost the same with pre-reacted particles.

The alignment of the IA-CNTs was visualized by SEM and digital microscope observation. In the pre-alignment case, the IA-CNTs were randomly dispersed on the Si substrate (Figure 3 (A)). On the other hand, to induce the alignment of IA-CNTs, a nanocomposite solution was dropped on the Si wafer surface where it was located in the center of two magnets (Figure 3 (B) and Figure S3). In this case, the magnetic field was generated inbetween two magnets, so IA-CNTs could be aligned following the external magnetic field during solvent evaporation without a soft or hard template such as polymer or anodic aluminum oxide (AAO). Figure 3 (C) and Figure S4 (A) (supporting information)

showed alignment of IA-CNTs in parallel. In this case, aligned IA-CNTs were formed as straw-bundle structures on the substrate due to the magnetic force interaction and surface tension during water evaporation process. Furthermore, the cross-alignment of IA-CNTs was attempted via the same procedure. Firstly, IA-CNTs were aligned in parallel on the Si substrate, and then it rotated 90-degree which means that aligned IA-CNTs were perpendicular to the magnetic field. Subsequently, IA-CNTs solution was dropped on the first

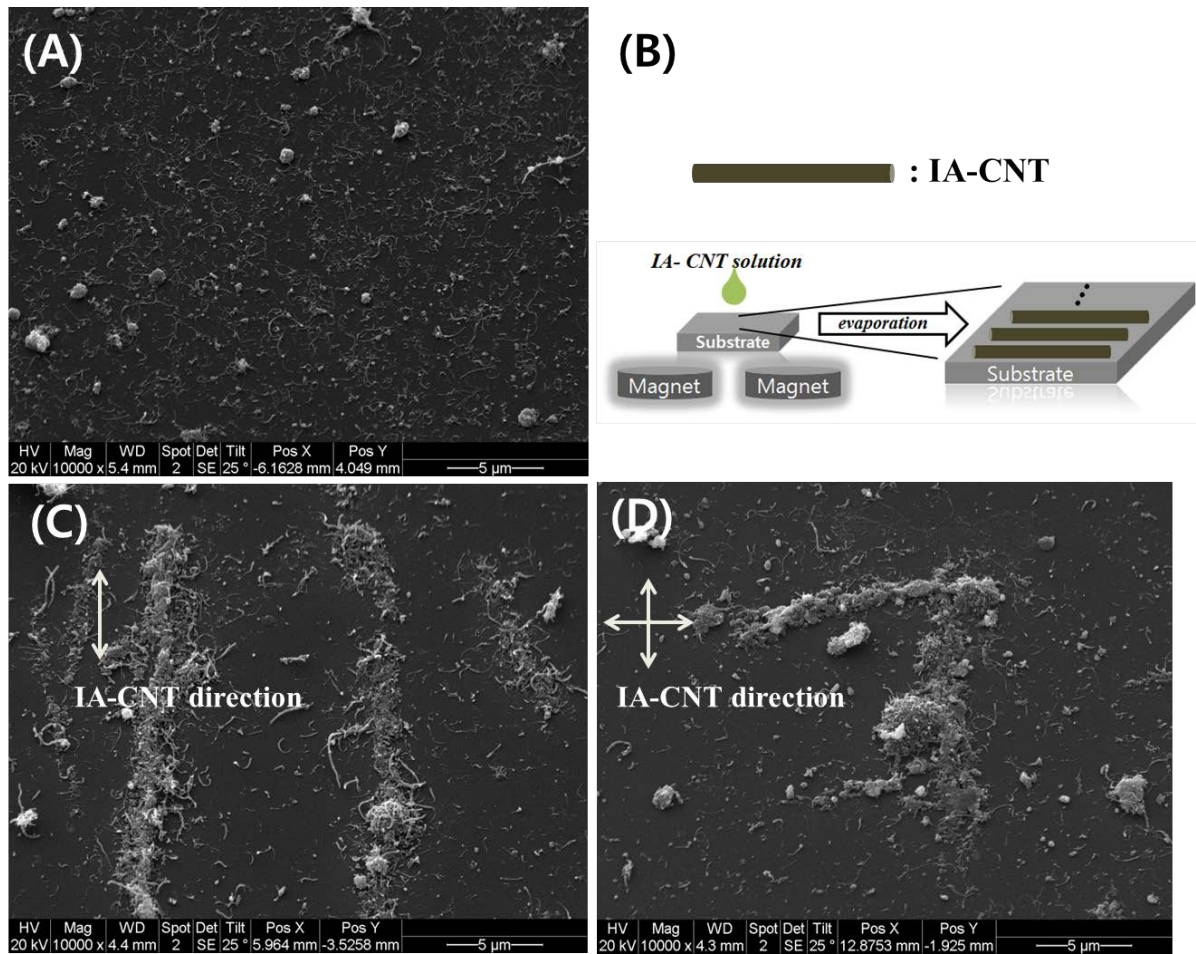


Figure 3. (A) SEM image of pre-aligned IA-CNTs, (B) illustration of IA-CNTs alignment process, (C) SEM image of parallel aligned IA-CNTs and (D) SEM images of cross aligned IA-CNTs

aligned IA-CNTs layer. The cross-aligned IA-CNTs were also observed by SEM and UDM (Figure 3 (D) and Figure S4 (B), supporting information). In addition, large diameter IA-CNTs were also prepared and aligned by the same procedure. The alignment structures were depicted with SEM (Figure S5, supporting information). These observations proved that the decoration process could occur without CNT size limitation and IA-CNTs can be simply aligned to any direction by an external magnetic field.

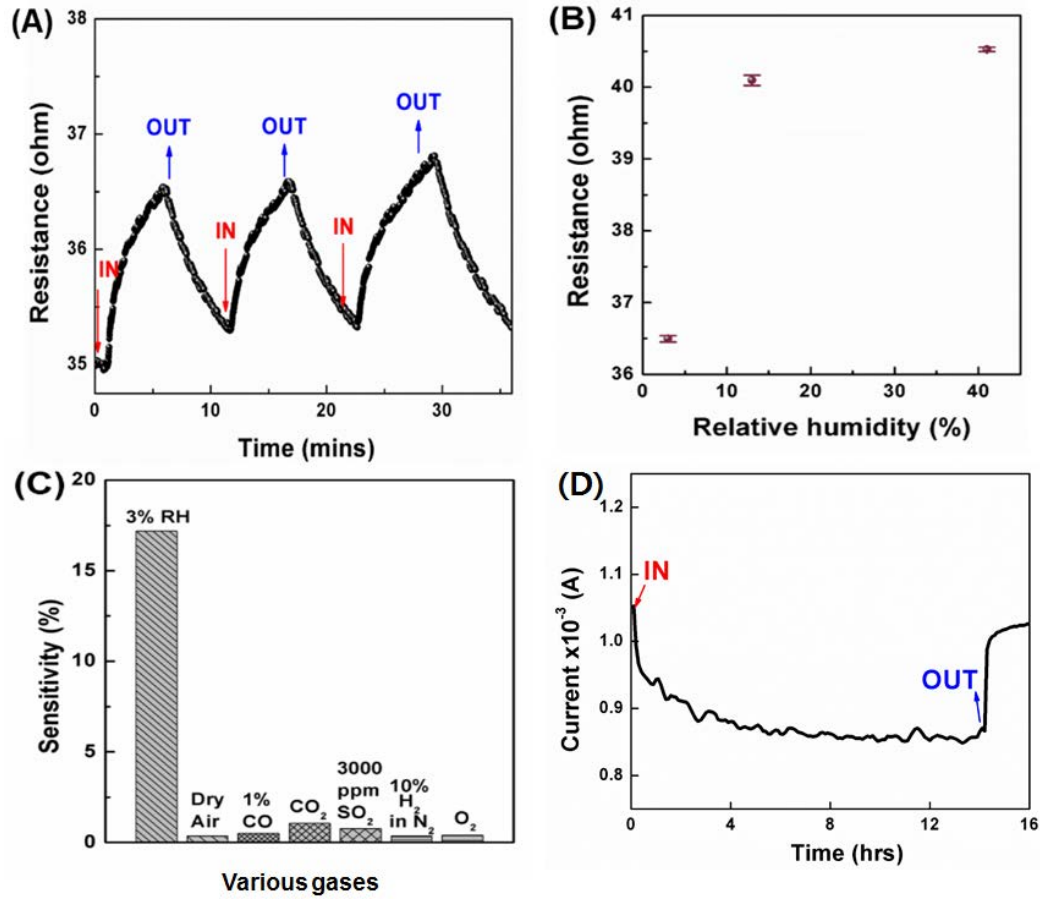


Figure 4. (A) Dynamic response of IA-CNTs under 3 % RH at 25 °C, (B) RH dependent sensitivity test (3 %, 13 %, 41 %), (C) selectivity test under the influence of various gaseous species (dry air, CO, CO₂, SO₂, H₂, and O₂) and (D) Response and recovery transients of IA-CNTs under 3% RH in N₂ for long-term stability tests (~ 16 hrs) at 25 °C (pure N₂ used as bal. gas; 0.1V applied dc voltage; 100 sccm total gas flow rate)

In order to demonstrate humidity detection, IA-CNTs were aligned and deposited on the Pt electrode with external magnetic force. In this case, aligned IA-CNTs were used for a humidity sensing channel. Dynamic response of IA-CNTs with 3 % humidity was monitored by EIS system. When H₂O vapor was introduced into the sensing channel, the resistance of IA-CNTs increased. In contrast, when H₂O vapor was removed, the resistance tends to recover to its initiation state (Figure 4 (A)). Moreover, the response and recovery transients were consistent with similar following cycles exhibiting high reproducibility. Depending on humidity contents, response of IA-CNTs varied (Figure 4 (B)). High relative humidity (RH) induced high resistance of IA-CNTs. In the 3 % RH case, the resistance of IA-CNTs was around 36.5 ohm, but the resistance reached about 40 ohm and 41 ohm at 13 % and 41 %, respectively. Since only a small amount ($\sim 10 \mu\text{g}$) of IA-CNTs was deposited on the Pt electrode, the resistance values between 13 % and 41 % did not differ significantly. However, if a large amount of IA-CNTs was deposited on the electrode, the response variation could increase.

The selectivity test was demonstrated on various gases such as CO₂, CO, SO₂, O₂, H₂ and dry synthetic air (Figure S6, supporting information). All the gases with various concentrations were exposed to IA-CNTs gas sensing channels. In addition, the selectivity of IA-CNT based humidity sensor was expressed using equation (1) and exhibited in Figure 4 (C). In Figure 4 (C), the selectivity was very high towards humid gas obtained by bubbling N₂ through a water bubbler at room temperature (i.e., 3% RH). However, a significant change in current (at 0.1 V) was not found in the case of other gaseous species (CO₂, CO, dry synthetic air (21% O₂ in N₂), H₂, SO₂) that passed through the same gas-tight cell at various concentrations under the same conditions (25 °C and 100 sccm total gas flow). The other

gases were also balanced in N₂ gas. The selectivity of IA-CNTs sample was compared to various gaseous species by calculating the changes in resistance of the material (at different ppm level) i.e. sensitivity according to equation (1). As shown in Figure 4 (C), aligned channel responded with only H₂O vapor with ~17 % sensitivity. The detection test was carried out for a long term, it took more than 15 hrs with 3 % relative humidity (in Figure 4 (D)) at room temperature. In this case, the removal of 3% RH generated a rapid recovery signal (electric current), which was close to the original value ($\sim 1.05 \times 10^{-3}$ A) as before the sample in contact with humidity. These results are very promising and lead towards further advancement of IA-CNTs sensor into a highly selective and durable humidity sensor.

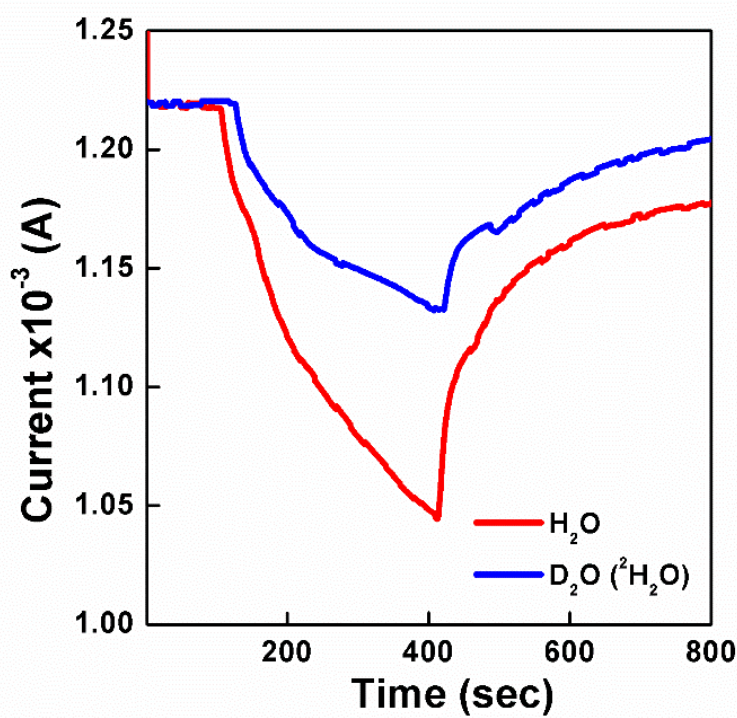


Figure 5. Response and recovery behavior of IA-CNTs under the influence of 3 % H₂O and D₂O (²H₂O). (Applied voltage = 0.1V; total flow rate = 100 sccm)

In the D₂O (²H₂O) case, the current of sensing channel decreased 1/2 the scale less than H₂O. It means the interaction between IA-CNTs and normal water or heavy water is different

in behavior. The interaction between water molecules and IA-CNTs is still not clear and the mechanism should be taken to a further study. Nonetheless, our study established that hydrogen type of water can be distinguished by IA-CNTs sensing channel (Figure 5). One of the humidity detection mechanism hypotheses on IA-CNT was related to hydrogen bonding.^{47,48} In FT-IR spectrum of IA-CNT (in Figure 1 (B)), two OH vibrations were observed around 3250 cm^{-1} (weak) and 3514 cm^{-1} (strong) from iron oxide and CNT. This part of IA-CNT could induce hydrogen bonding with H_2O and D_2O . Furthermore, hydrogen bonding force between H_2O or D_2O could be different with IA-CNT, so they may be distinguished by this system.⁴⁹⁻⁵¹ Similar to other gases (except 3% RH), H_2 gas also did not show significant changes on exposure to IA-CNTs (Figure 4C). This result and further investigations could lead us to find the potential mechanism of IA-CNT's sensing behavior.

Humidity in human breath was successfully detected via IA-CNTs sensing system. In this case, our breath was blown to IA-CNTs channel (Supporting video 1). Interestingly, the electrical resistance dramatically changed by blowing breath out into the IA-CNT coated tiny sensor (Figure 6 and Supporting video 1). In the video, the response is shown in terms of current (applied voltage = 0.1V), whereas in Figure 6, it is shown in terms of resistance values. Breathing-out is represented by the arrows where a fast response can be observed. In addition, a fast recovery can also be seen when breathing-out stopped. This result shows that IA-CNT can be potentially applied as a miniaturized humid sensor with a fast response, high sensitivity, and high selectivity at room temperature.

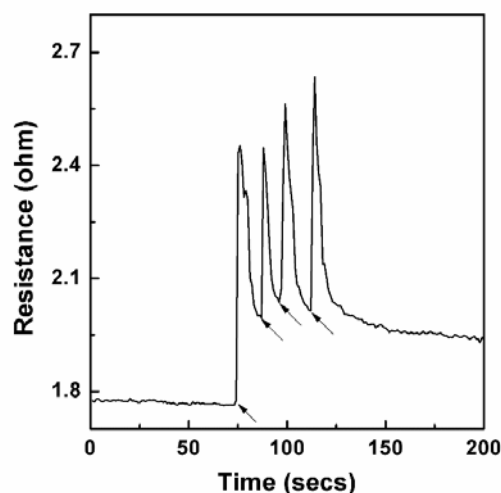


Figure 6. Humidity detection through human breathing

Conclusion

IA-CNTs were successfully synthesized via an oxidizable GA-IONPs assisted synthesis method, which does not require high temperature or pressure as well as harsh reducing agents. This hybrid material was synthesized through 2 simple steps in DI water. In addition, IA-CNTs were simply aligned on the substrate following the external magnetic field without any hard or soft template. Crossed structures of IA-CNTs were formed in layer through a layer deposition on the substrate. In order to perform humidity sensing applications, IA-CNTs were deposited on the Pt based electrode to monitor the electrical changes. Interestingly, the functionalized CNTs did not respond to various gases such as CO₂, CO, SO₂, dry air (79 % N₂ and 21 % O₂ mixture). However, it showed excellent sensing selectivity with humidity. Thus, these hybrid CNTs possess a high potential in nano-electronic fields through simple alignment process, and they can be applied for humidity sensing platform.

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Supporting information

The supporting figures are schematic illustrations for preparations of IA-CNT, Hysteresis curve of GA-IONPs, Alignment process, Digital microscope image of aligned IA-CNT, SEM images of large size IA-CNT and detection selectivity data of IA-CNT. This information is available free of charge via <http://pubs.acs.org/>

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