Human-Finger Electronics Based on Opposing Humidity-Resistance Responses in Carbon Nanofilms

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Carbon nanomaterials have excellent humidity sensing properties. Here, it is demonstrated that multiwalled carbon-nanotube (MWCNT)- and reduced-graphene-oxide (rGO)-based conductive films have opposite humidity/electrical resistance responses: MWCNTs increase their electrical resistance (positive response) and rGOs decrease their electrical resistance (negative response). The authors propose a new phenomenology that describes a “net”-like model for MWCNT films and a “scale”-like model for rGO films to explain these behaviors based on contributions from junction resistances (at interparticle junctions) and intrinsic resistances (of the particles). This phenomenology is accordingly validated via a series of experiments, which complement more classical models based on proton conductivity. To explore the practical applications of the converse humidity/resistance responses, a humidity-insensitive MWCNT/rGO hybrid conductive films is developed, which has the potential to greatly improve the stability of carbon-based electrical device to humidity. The authors further investigate the application of such films to human-finger electronics by fabricating transparent flexible devices consisting of a polyethylene terephthalate substrate equipped with an MWCNT/rGO pattern for gesture recognition, and MWCNT/rGO/MWCNT or rGO/MWCNT/rGO patterns for 3D noncontact sensing, which will be complementary to existing 3D touch technology.

1. Introduction

As the market for industrial flexible electronics that sense and control environmental humidity grows,[1,2] so does the demand for carbon nanomaterials with excellent humidity-sensing properties.[3–5] Carbon nanomaterials, especially those made of carbon nanotubes (CNTs) and/or reduced graphene oxide (rGO), exhibit larger surface-to-volume ratios, faster response times, and more reproducible performance at lower cost than more traditional humidity-sensing materials, such as ceramics (e.g., Al₂O₃ and ZnO),[6,7] semiconductors (e.g., GaN, SnO₂, and In₂O₃)[8,9] and polymers (e.g., polyelectrolytes and conducting polymers),[10,11] making them more appealing for large-scale manufacture and deployment.[12–14]

Theoretical calculations and experimental demonstrations on humidity-sensing of nanomaterials[15–17] have led to one generally accepted explanation of their behavior based on Anderson’s proton conductivity model.[18,19] In this model, water molecules are absorbed by nanomaterials through physical diffusion or hydrogen bonding, which generates hydronium ions (H₃O⁺) that become charge carriers.[20,21] Experimental results show that water molecules are observed to increase the electrical conductivity of n-type nanomaterials and to decrease the electrical conductivity of p-type nanomaterials.[22,23] Although CNTs behave similarly to p-type nanomaterials and rGOs behave similarly to n-type nanomaterials in terms of their resistance response to humidity,[24,25] we cannot simply conclude that these materials should be grouped accordingly.[26,27] Categorization of these materials requires that we also consider the microstructure of each.
material. This type of investigation will further clarify how water molecules affect the resistance response and ultimately the electrical conductivity of these materials.

Here, we develop a new phenomenology to explain the converse humidity/resistance responses of CNT- and rGO-based films and explore their potential applications.

First, we demonstrated the opposite humidity/resistance of CNT films and rGO films under identical conditions: CNTs increase their resistance (positive response) and rGOs decrease their resistance (negative response). Then, a “net”-like model for CNTs and a “scale”-like model for rGOs are introduced to explain these trends, combining the changes in intrinsic resistance of the particles and junction resistance between the particles (Figure 1).

Second, we experimentally verify the proposed phenomenology via investigating the influence of the number of junctions on the humidity/resistance response using multiwalled CNTs (MWCNTs) of different lengths (intrinsic resistance is regarded as constant). To evaluate the effect of the intrinsic resistance of the particles, we can study rGO-based films with different thermal reduction times (the number of junctions is constant).

Third, we prepare a type of humidity-insensitive materials: an MWCNT/rGO-based hybrid film via adjusting the MWCNT/rGO ratio, which has a near-zero relative change in resistance with changing humidity.

Finally, we explore how the converse resistance response to humidity by MWCNT-based and rGO-based films can be applied to human-finger electronics via simple pattern designs: (1) gesture recognition using an MWCNT/rGO pattern and (2) 3D noncontact sensing using MWCNT/rGO/MWCNT or rGO/MWCNT/rGO patterns.

2. Results and Discussion

2.1. Differences in Resistance Responses to Humidity

To explain why MWCNT- and rGO-based films have a converse resistance response to humidity, we fabricated conductive patterns (2.5 mm × 1.5 mm) of each with comparable thicknesses (MWCNT: 71 ± 10 nm, rGO: 63 ± 6 nm) on polyethylene terephthalate (PET) substrates (Figure S1, Supporting Information). Humidity was controlled by adjusting the distance between the finger and the conductive film, as seen in Figure 1a.

Figure 1b shows that resistance of the default-sized CNT-2 films increases with increasing humidity. The relative change in resistance ($\Delta R / R_0 = (R_1 – R_0) / R_0$, where $R_0$ and $R_1$ are the original and updated resistance, respectively) of MWCNT films increases gradually and reaches 6.8% when the distance between the finger and the film is 1 mm. At this distance, humidity sensitivity is 0.078 RH$^{-1}$ (Sensitivity $= \delta(\Delta R / R_0)\cdot \delta(RH^{-1})$). The resistance of rGO films decreases with increasing humidity in Figure 1b. At the same distance from the finger (1 mm), the resistance of the
The rGO film decreases by 5.6% where the humidity sensitivity is \(-0.064 \text{ RH}^{-1}\). Video S1 (Supporting Information) demonstrates the resistance response of each film in real time.

We investigated the microstructure of each film using scanning electron microscopy (SEM) (as shown in the insets of Figure 1b). Total electrical resistance depends on the within particle resistance (intrinsic, $R_{\text{intrinsic}}$) and the resistance between particles (at junctions, $R_{\text{junction}}$). This is represented schematically by the electrical circuit shown in Figure 1c and can be expressed with Equation (1)

$$\sum \Delta R = \Delta R_{\text{intrinsic}} + \Delta R_{\text{junction}}$$

We found that the differences in the macroscopic electrical responses of each film can be explained by the relative contributions of intrinsic resistance versus resistance at junctions. As moisture absorption increases, each film responds with a different resistance. The intrinsic resistance response involves the formation of hydronium ions (H$_3$O$^+$), which behave as charge carriers that tend to decrease the intrinsic resistance (negative resistance). This is a reversible mechanism: the concentration in hydronium ions will increase with the water absorption but decreases as the relative humidity of the environment decreases. The reversibility of water adsorption mechanisms and differences between bound and free water were examined for other materials. Resistance at junctions involves the intercalation of water molecules at the interface between nanoparticles, which increases the interparticle distance, causing a switch from ohmic-type to ohmic/capacitive-type behavior that increases resistance at junctions (positive resistance) (electrical double layer, $C_{\text{EDL}}$).

We found that the macroscopic resistance of MWCNT films is mainly dependent on resistance at junctions ($R_{\text{junction}} \gg R_{\text{intrinsic}}$), and we illustrate the phenomenology via a point-connect net model shown in Figure 1c. As water absorption increases resistance at junctions, a positive resistance response is observed. Alternatively, we found that, dependent on thermal reduction time, the macroscopic resistance of rGO films depends on either intrinsic resistance or resistance at junctions ($R_{\text{junction}} \gg R_{\text{intrinsic}}$). We illustrate this via a surface-contact scale model shown in Figure 1c. In this model, rGO particles stack layer by layer over a large overlapping area, lowering the overall effect of resistance at junctions. Prior to any thermal reduction time, the absorption of water molecules by rGO particles creates hydronium protons, which reduces the intrinsic resistance, resulting in a negative resistance effect. However, with longer thermal reduction times, the electrical conductivity of the rGO particles improves, making the macroscopic resistance mainly dependent on resistance at junctions. Because in this case, water absorption increases resistance at junctions, a positive resistance response is observed, similar to what is observed for MWCNT films.

2.2. The Phenomenology of the Resistance Responses to Humidity

To validate our phenomenological explanation of the observed responses, we estimated the contribution of each resistive component (junction resistance and intrinsic resistance) on each film.

2.2.1. Contribution of Junction Resistance to the Overall Resistance Response to Humidity

We investigated the contribution of resistance at junctions to the overall resistance response of MWCNTs to humidity using tubes of different lengths, $L_1$, $L_2$, and $L_3$ (such that $L_1 > L_2 > L_3$), to fabricate the corresponding conductive films, CNT-1, CNT-2, and CNT-3: shorter MWCNTs create films with more junctions. Note that these MWCNTs have the same surface functional group (−COOH) and the same O:C ratio (41 ± 1 wt% in Figure S2a, Supporting Information), any difference in intrinsic resistance among these conductive films was presumed to be negligible.

We found that films created from shorter MWCNTs had higher capacitance values than films created from longer MWCNTs, within the tested range of frequency, and greater sheet resistance (Figure 2a), ranging from 1.8 MΩ in CNT-1 to 18 MΩ in CNT-3 (inset of Figure 2a). These two observations testify to the much higher number of junctions in films made with short CNTs.

Figure 2b shows the relationship between the resistance response of films made from CNT-1, CNT-2, and CNT-3 to humidity. Results show that variations in resistance changed proportionally with increasing environmental humidity: when the humidity increased from 43% (room RH = 41.3%) to 86.9%, the relative change in resistance increased from 4.7% to 6.6% to 14.2% for CNT-1, CNT-2, and CNT-3, respectively. Macroscopic change in electrical resistance is therefore largely dependent on the number of junctions in an MWCNT, which has been presented in the corresponding microstructures in the inset of Figure 2b and the net model in Figure 2c. In addition, the sensitivity to humidity decreased gradually with increasing humidity. This can be explained by the basic response of junctions to humidity; indeed, the effective resistance of these junctions is expected to vary exponentially with increasing distance between particles. When the junction begins to absorb humidity, resistance changes quickly because any small separation between particles induces a large exponential change in resistance; however, when the humidity becomes quite high, the particles are already separated well enough so changing the distance between them has little influence on the electron transfer (and subsequently resistance) between them.

2.2.2. Contribution of Intrinsic Resistance to the Overall Resistance Response to Humidity

To evaluate the contribution of intrinsic resistance to the overall resistance response of films to humidity, we investigated rGO-based conductive films manufactured with different thermal reduction times. According to previous reports during the reduction process, the number of hydrophilic functional groups (e.g., epoxy, hydroxyl, and carboxyl) on the surface of rGO particles gradually decrease, along with the number of defects. Thus, thermal reduction is a simple way to specifically modify the intrinsic resistance of the particles.
Based on the results in Figure 2d (inset), the sheet resistance decreased from 52 MΩ (4 h) to 2.1 MΩ (8 h) to 0.285 MΩ (12 h). We attribute this decreased resistance to a decrease in the number of defects as functional groups are eliminated from the surface of rGO particles. We also observed higher values of capacitance in rGO particles that underwent a shorter reduction time (Figure 2d), which is consistent with a decrease in the number of hydrophilic functional groups with reduction time.

It also has been found that there is nearly no change in microstructure with longer reduction time (inset of Figure 2e); however, as shown in Figure 2f, after 4, 8, and 12 h of reduction time, the deionized (DI) water contact angle increased from 12° to 57° to 98°, respectively. Figure 2e summarizes these experimental results, which confirm our prediction that reduction time determines variation in intrinsic resistance because the number of hydrophilic functional groups decreased with increased reduction time. After 8 h of reduction at 150 °C, the rGO film’s gradual negative change in resistance reached zero but then switched to a positive resistance response, similar to MWCNTs. The predominant contributor to macroscopic resistance switches from intrinsic resistance to resistance at junctions. Meanwhile, we also monitored this process by tracking the O:C ratio, as shown in Figure 2e and Figure S2b (Supporting Information).

These results led us to conclude that resistance at junctions is central to the response to humidity by MWCNT-based conductive films. In addition, resistance of rGO-based conductive films is initially governed by the intrinsic resistance of the particles, but after longer periods of thermal reduction time, resistance at junctions dominates. These experimental results support our simple phenomenology: Note that we did not observe the increase in conductance of MWCNT films in higher humidity environments that has been previously reported. This may be because the moisture introduced by a human-index finger as the source of humidity is probably not enough to induce a percolated network of hydronium protons.

2.3. Application to Humidity-Insensitive Materials

We constructed one humidity-insensitive MWCNTs/rGO hybrid conductive films through adjusting the mass ratio between MWCNTs and rGO to produce a single film with an optimized response to resistance when exposed to humidity. Our objective was to achieve near-zero relative change in resistance (∆R/R₀) independent of changing humidity, which we define as less than 0.3%.

A CNT-2-based conductive film and an rGO-based conductive film sintered at 150 °C for 6.5 h were chosen for demonstration due to their similar sheet resistance (4.2 ± 0.5 MΩ sq⁻¹) (Figure 3a); their microstructures are presented in Figure 3b and Figure S3 (Supporting Information). Plots illustrating their response to humidity were generated and fitted according to experimental results. When the mass ratio meets Equation (2), the relative change in resistance of a CNT-2/rGO-based conductive film will be zero. According to calculations, the best mass ratio is 0.625 (RH = 56%). The feasibility of this strategy was further confirmed by...
experiments, showing that the balance point is located at \( \approx 0.6 \), which is highly consistent with the calculated value 0.625 (Figure 3c).

\[
M \cdot R_{\text{CNT-2}} \cdot Y_{\text{CNT-2}} + N \cdot R_{\text{rGO}} \cdot Y_{\text{rGO}} = 0
\]  

(2)

where \( M \) and \( N \) are the masses of MWCNT and rGO, \( R_{\text{CNT-2}}, Y_{\text{CNT-2}} \), and \( R_{\text{rGO}}, Y_{\text{rGO}} \) are the original resistance and the relative change in resistance to humidity, respectively.

The current–voltage curves shown in Figure 3d confirm the insensitivity of this new material toward humidity: the curves of the CNT-2/rGO-based film (ratio = 0.6) nearly overlap with or without a humidity source (human-index finger). Pure CNT-2 and pure rGO films clearly displayed opposite and observable responses to humidity. We further confirmed these results using human breath that contained a RH of 92% \( \pm \) 3%, which produced consistent and stronger evidence of the phenomena (Figure 3d).

This humidity-insensitive performance of the prepared CNT-2/rGO film was further verified through its real-time resistance response to human finger and breath, respectively (Figure 3e). It can be found that, compared with CNT-2 and rGO films, the variations in resistance of CNT-2/rGO to human finger and breath are within the range of \( \pm 0.3\% \) of its original resistance, which meet the condition of humidity insensitivity.
insensitive materials we defined above. More details can be found in Video S1 (Supporting Information).

2.4. Application to Gesture Recognition

Two films (8 mm long and 4 mm wide, 1/2 length for CNT-2, 1/2 length for rGO) were combined on a PET substrate (Figure 4a) to create a gesture recognition device by exploiting the opposite resistance responses of MWCNT and rGO networks to humidity.[37,38] This transparent flexible device is presented in Figure 4a, and their microstructure can be seen in Figure S4 (Supporting Information).

The efficiency of the device was confirmed, as shown in Figure 4b,c and Video S2 (Supporting Information), by moving a human-index finger from CNT-2 to rGO networks to generate first a positive resistance response (defined as peak-A) followed by negative resistance response (defined as peak-B) and vice versa. The final relative change in resistance at each time point is the combined result of the resistance response to humidity of each film; this is further demonstrated by the 3D illustration based on a Gaussian function in Figure S5 (Supporting Information). The real-time resistance-variation profile shows that response periods were always less than 1 s, a completely acceptable rate for practical applications. The subsequent transparent, flexible device can recognize human-finger gestures in a noncontact mode effectively.

2.5. Application to 3D Noncontact Sensing

A transparent flexible pattern of equal sections of rGO sandwiched a section of CNTs (rGO/CNT-2/rGO) was fabricated on an 8 mm × 4 mm PET substrate (Figure 4d). Here, our objective was to determine whether this system would be suitable for 3D noncontact sensing (Figure 4d).[37,39,40] Because fingertips have a spherical shape, humidity is not introduced uniformly over the area covered by the three conductive films. Thus, when the human-index finger approaches the connected rGO/CNT-2/rGO film, the CNT portion of the film will sense its humidity before the rGO portion of the film. Thus, when the combination of these two changes in resistance cancel each other out, resistance reaches zero, and
if the resistance from the rGO becomes stronger, resistance reaches the negative zone, defined as peak-B. As the finger is slowly removed, resistance immediately returns toward the positive zone, indicating stronger resistance from the CNTs, defined as peak-C. Therefore, each introduction and removal of the finger (finger displacement) causes three peaks (two positive and one negative) that correspond to three signals.

Figure 4e shows that the profile is very regular from one cycle to the next, with similar positive/negative peak values and response times for each period (=1.3 s). Consistency in response time demonstrates that results have great repeatability and stability, which can also be seen in Video S3 (Supporting Information). For a single-period profile, three peaks (two positive peaks and one negative peak) are clearly identifiable. A single-period profile is further demonstrated via 3D illustration based on a Gaussian function in Figure S6 (Supporting Information).

Finally, we investigated the influence of finger displacement speed on the generated profile (Figure 4f). Results show that when displacement speed increases from 2.7 to 2.1 to 1.1 s per period, a clear gradual decrease in peak intensity appears. This could be expected because as finger displacement speed increases, the films have less time to absorb water molecules, resulting in a smaller change in resistance. However, the profile of peaks remains distinct even when the displacement speed is 1.1 s per period, indicating that the response rate is high and suitable for application to human-finger electronics for 3D noncontact sensing.

3. Conclusion

Our investigation of the opposite resistance responses to humidity by two carbon-based conductive films revealed that MWCNT-based films produce a positive resistance response whereas rGO-based films produce a negative resistance response as well as the switched humidity/resistance response of rGO via thermal reduction. We proposed a phenomenology that explains this behavior through a “net”-like model for MWCNTs and a “scale”-like model for rGOs. We expect that the humidity-insensitive rGO/MWCNT hybrid conductive films we developed will greatly improve stability to humidity of actual carbon-based electrical devices. In addition, our transparent, flexible device demonstrates promise for application to human-finger electronics, especially for 3D noncontact sensing but perhaps in complement with existing 3D touch technology. Further investigations are necessary to improve the conductivity of carbon-based conductive films and to explore more avenues for their application to flexible electronics.

4. Experimental Section

Materials: Carboxyl-group (−COOH)-functionalized MWCNTs of different lengths were purchased from Cheap Tubes, Inc. including CNT-1: length = 10–50 μm, CNT-2: length = 3–30 μm, and CNT-3: length = 0.5–2 μm, with the same outer diameter of 8–15 nm and over 95 wt% purity. Graphene oxide ink (0.1 mg mL−1) was prepared in the lab from purified natural graphite (SP-1, Bay Carbon) by the Hummers method with the plate diameter of 0.2–1.5 μm, as shown in Figure S7 (Supporting Information). Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT/PSS) aqueous dispersion (1.3 wt%, Clevios PH1000) was purchased from HC Starck, Inc. PET films were purchased from Teonex Inc. with a thickness of 125 μm. DI water was used in all experimental processes.

Fabrication of MWCNT and MWCNT/rGO Inks and MWCNT/ rGO-Based Patterns: MWCNT inks were prepared using MWCNTs (200 mg), PEDOT/PSS aqueous dispersions PH1000 (1 g) and DI water (19 g). The effective concentration of MWCNTs in the final solution was 10 mg mL−1. This mixture was then homogenized using a Brason 8510 bath sonicator (Thomas Scientific) for 1 h followed by the exfoliation of MWCNTs using an ultrasonic processor (Cole-Parmer) at 20 kHz and 500 W for 40 min in an ice bath to prevent overheating and damage to the MWCNTs and the PEDOT:PSS layer. The resultant ink was then diluted in DI water to the desired final concentration of 0.1 mg mL−1; CNT-2 and CNT-3 inks were prepared similarly. CNT-2 ink was used as the default size for producing MWCNT films. Typical inks are shown in Figure S7 (Supporting Information) with their Raman plots, as well as their microstructures in Figure S8 (Supporting Information).

CNT-2/rGO inks were prepared by adding different volumes (0, 1, 2, 3, 4, and 5 mL) of CNT-2 ink (0.1 mg mL−1) to the rGO ink (0.1 mg mL−1, 5 mL). This preparation was homogenized using a Brason 8510 bath sonicator (Thomas Scientific) for 0.5 h. Inks with different mass ratios (CNT-2:rGO of 0, 0.2, 0.4, 0.6, 0.8, and 1.0) were prepared.

Carbon-based conductive films were prepared by drop casting on a PET substrate. Specifically, PET films were treated with oxygen plasma at 100 W for 60 s to improve the hydrophilicity of the substrate. Next, the as-prepared inks (pure CNT-2, pure rGO, and CNT-2/ rGO) were dropped onto a rectangular Teflon frame using a Thermo Scientific Finnpipette (0.2–2 μL) with a controlled surface concentration of 1 μL cm−2. Before the Teflon frame was peeled off, these inks were baked on a hotplate at 100 °C for 30 min. The entire process was performed gently to achieve a homogeneous film.

CNT-2/rGO hybrid patterns with different mass ratios (CNT-2:rGO of 0, 0.2, 0.4, 0.6, 0.8, and 1.0) were obtained by the same method with a thermal reduction time of 6.5 h at 150 °C on a hot plate. rGO-based conductive patterns with different conductivities were obtained by adjusting the thermal reduction time from 0 to 24 h at 150 °C on a hotplate. The default thermal reduction time was 6.5 h. Typical CNT-2- and rGO-based conductive films are shown in Figure S1 (Supporting Information).

Characterization and Measurements: The surface microstructure of the prepared carbon-nanoparticle-based films was examined by SEM (Quanta 600, FEI Company) and by profilometry (Veeco Dektak 150 operating at a scanning speed of 0.167 μm s−1). Energy-dispersive X-ray spectroscopy (EDS) was performed for surface elemental analysis using an EDS detector operating at 20 kV. Static contact angle measurements (VCA video contact angle system, AST Products, Billerica, MA) of DI water were performed using the sessile drop method to evaluate surface wettability. Raman spectra of the surface of MWCNT and GO were collected using a LabRAM Aramis Raman spectrometer (Horiba, Ltd.) on casted films using a 473 nm laser for structural analysis. An LCR (inductance (L)-capacitance (C)-resistance (R)) meter (E4982A, Agilent Technologies) was used with frequencies ranging from
20 Hz to 2 MHz to measure capacitance. A semiconductor characterization system (4200-SCS, Keithley company) and a Cascade Microtech (Summit-11600 AP) microprobe station for resistance/humidity stability evaluation via I−V curves were also used. A multimeter (Agilent 34401A) that allowed data to be recorded on a PC was used to map the real-time resistance response to humidity.

Note that a human-index finger was used as the humidity source. To ensure precise control of the environmental conditions, humidity and temperature around the finger were thoroughly mapped using a humidity meter (TM325, Dickson), as shown in Figure S9 (Supporting Information). Environmental humidity was defined according to the distance (using a ruler) between the index finger and the sample. This method is effective for verifying the efficiency of these devices intuitively in practical applications of human-finger electronics. The default room relative humidity and temperature were 41.3% and 25.2 °C, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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