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Permanent water swelling effect in low temperature thermally reduced graphene oxide

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We demonstrate permanent water trapping in reduced graphene oxide (rGO) after high relative humidity (RH) exposure. For this purpose, we grew graphene oxide films via spin-coating on glass substrates followed by thermal reduction. The electrical resistance of the planar device was then measured. We observed that resistance is significantly increased after water vapor exposure and remains stable even after 250 days in ambient conditions. Various techniques were applied to desorb the water and decrease (recover) the material's resistance, but it was achieved only with low temperature thermal annealing (180 °C) under forming gas (H₂/N₂ mixture). The permanent effect of water absorption was also detected by x-ray photoelectron spectroscopy.

Reduced graphene oxide (rGO) has attracted a strong research interest for gas sensing applications in recent years due to its unique electrical and chemical characteristics^{1,2,3}. Its main advantages among others are good chemical stability over time and ease of functionalization contributing to satisfying selectivity between various analytes⁴. The gas sensing mechanism

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of rGO is generally associated with transfer of electrons to or from the analyte, increasing or decreasing its resistance depending on the reducing or oxidizing nature of the analyte. Lu et al.⁵ reported electron transfer from rGO to low-concentration NO₂, while Hu et al.⁶ suggested electron transfer from NH₃ to rGO. Sensing of water vapor with rGO has been reported in various articles^{7,8,9}, and it has been proposed that the interaction between rGO and water occurs through various mechanisms: 1) electron exchange, 2) proton transport via ionic conductivity and 3) an interlayer swelling effect¹⁰. The latter mechanism has been reported to cause hysteresis and compromise sensor sensitivity to humidity^{11,12}. Swelling occurs when adsorbed water molecules intercalate into graphene oxide layers, thereby increasing interlayer distance and subsequently its resistance.

No report thus far has investigated the long-term effects of swelling on rGO sensor electrical characteristics. Thus, it is unclear whether the swelling effect is permanent. Here, we report that the swelling of rGO after exposure to high relative humidity (RH) (> 85%) results in an increase of rGO resistance that persists for extended periods of time in ambient conditions. It will also be shown that desorption of swelled water molecules from rGO flakes cannot be achieved by thermal annealing at temperatures as high as 180 °C in ambient conditions. This behavior is potentially useful for memory, storage or other water absorbance applications in areas such as construction engineering and hygienic products.

GO films (74 nm thick) were deposited with spin coating on glass substrates, and aluminum contacts were evaporated on top of the GO. This was followed by a thermal reduction process under forming gas (H₂/N₂:5/95). More details on the process parameters are presented elsewhere⁹. The devices were exposed to high RH (>85%) for at least 450 seconds using a cool mist ultrasonic air humidifier (Capriccio T-253). In order to study the behavior of the device

under high RH exposure and in ambient conditions, a constant bias voltage of 7 V was applied to the contacts, and current was measured with a Keithley 2450. To monitor the RH, a commercial humidity sensor HiH-4000-3 was set up along with our device. The hot-probe method¹³ demonstrated that our deposited rGO exhibits p-type semiconducting behavior, consistent with the literature regarding low-thermal annealed GO⁵. Angle-resolved x-ray photoelectron spectroscopy (ARXPS) measurements were performed with a PHI 5500 system on two types of devices: those exposed to and not exposed to high RH. To avoid interference from the glass substrate, chromium (Cr) and gold (Au) was deposited on top of the substrate before GO. The use of Cr is to improve the adhesion of Au. The measurements were taken four months after the high RH exposure date to test the temporal extent of swelling. XPSPeak software was used for peak fitting and identification of chemical components.

Figure 1 shows rGO device sensitivity $(I-I_0)/I_0$ (%) when air (45% RH) and vacuum environments (3×10^{-2} mbar) were alternated. I_0 is the device current at vacuum condition. The sensor current exhibits a clear and rapid decrease upon exposure to humid air (45% RH) with a sensitivity of 9%, and excellent signal repeatability in the alternating vacuum-humid air environment is revealed. This type of device sensitivity is typical for all tested levels of RH up to 70%⁹.

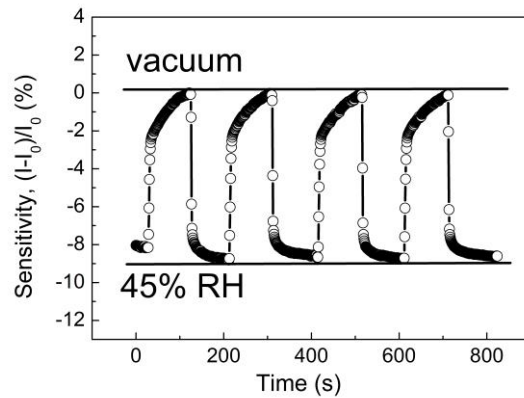


FIG. 1. Current response, $(I-I_0)/I_0$ (%), for fabricated rGO sensor as a function of time in alternating vacuum-air (RH: 45%) environment.

The behavior of the device before, during and after high RH ($> 85\%$) exposure is displayed in Figure 2. Initially, rGO current remains stable while the RH in the chamber is unmodified at 32%. As soon as RH is increased above 85%, the current abruptly increases by 190%. Before the RH recovers to 32%, the current decreases by 100% (compared to the initial value) and stabilizes over time. This permanent current decrease after high RH exposure reveals permanent effects that could be attributed to mechanisms associated to either water trapping inside the rGO flakes and/or damage of the rGO flake structure during water absorption and desorption.

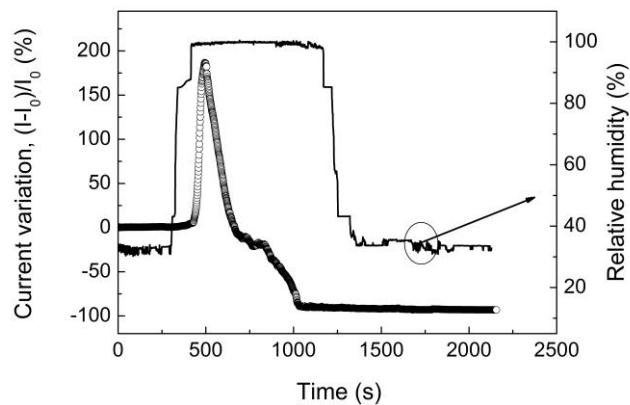


FIG. 2. Evolution of rGO current before, during and after high relative humidity exposure. Left axis represents rGO current and right axis the relative humidity level in the test chamber. I_0 is the current at ambient conditions (before the high relative humidity exposure).

In order to identify the mechanism responsible for this effect, ARXPS was conducted on samples with and without high RH exposure 9 months after the device fabrication and humidity exposure date. Figure 3 shows O1s XPS spectra of rGO on Au, not exposed to high RH (a), (b) and (c) in comparison to a device exposed to high RH (d), (e) and (f) for different sample tilt angles. The binding energy (BE) of oxygen within H_2O can assume different values depending on the physical state (gas or liquid phase) and the material to which H_2O is physisorbed¹⁴. However, it has been reported that within GO or rGO layers, the BE of O1s within H_2O appears at around 535 eV to 536 eV^{15,16}.

The sample tilt angle determined if the observed chemical state lies at the surface of the device (lower angles) or deeper within (higher angles). Peak deconvolution revealed that water chemisorption is present in the devices exposed to high RH in comparison to those not exposed. For devices not exposed to high RH, two O1s components are present. The first with a BE of 532 eV is attributed to C-O bonds and the second with a BE of ~533 eV corresponds to C=O. Meanwhile, rGO devices exposed to high RH exhibit three components, the ones described above and one additional peak with BE at ~535 eV, which is attributed to water molecules. Figure 3(d) to 3(f) demonstrate that the water component increases in intensity and area in the depth of the device. Table I shows the parameters from Gaussian peak fitting for the device exposed and not exposed to high RH, and for every sample tilt angle. Bond content was calculated by considering the integrated areas for each peak under the spectra. The water content is ~6% for the 45° and 55° degrees and 8.85% for the 35° degrees.

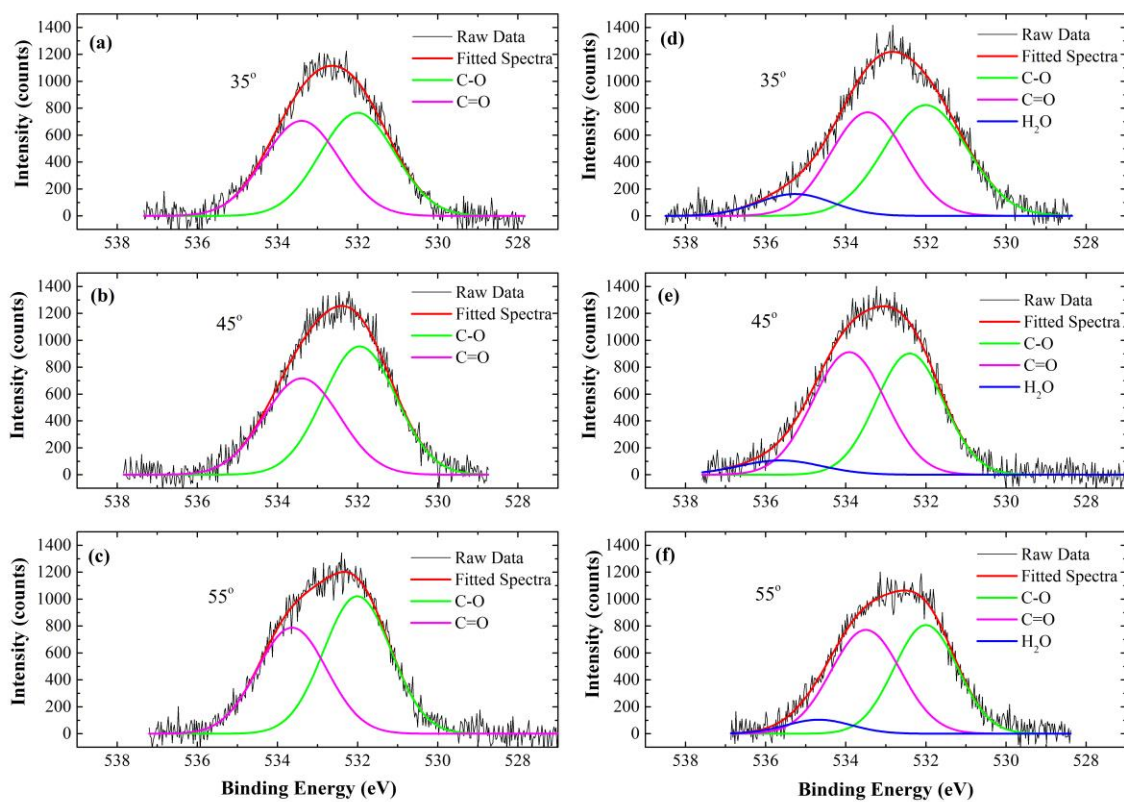


FIG. 3. XPS O1s spectra in various sample tilt angles for reduced graphene oxide devices not exposed to high relative humidity (a), (b) and (c) and devices exposed to high relative humidity and remained for 9 months at ambient environment (d), (e) and (f).

Table I: XPS O1s component parameters for reduced graphene oxide devices not exposed to high relative humidity and devices exposed to high relative humidity, for three different sample tilt angles.

Tilt angle	Bonds	Humidity	Peak	Intensity	FWHM	Bond %
35°	C-O	Yes	532	823.037	2.45	49.74
		No	532	765.515	2.2	51.96
	C=O	Yes	533.45	768.94	2.18	41.4
		No	533.4	706.112	2.2	48.03
	H ₂ O	Yes	535.27	162.515	2.2	8.85%
		No	-	-	-	-
45°	C-O	Yes	532	901.772	1.98	44.74
		No	532	954.529	2.14	56.19
	C=O	Yes	533.91	911.514	2.13	48.79
		No	533.39	716.77	2.22	43.8
	H ₂ O	Yes	535.63	106.178	2.42	6.46
		No	-	-	-	-
55°	C-O	Yes	532	807.088	1.87	45.93
		No	532	1021.17	1.97	55.65
	C=O	Yes	533.5	771.32	2.04	47.98
		No	533.63	787.613	2.04	44.34
	H ₂ O	Yes	534.67	103.98	1.92	6.08
		No	-	-	-	-

To study the desorption of trapped water within rGO flakes after device exposure to high RH, several tests were carried out while the device current was monitored: 1) heating at 180 °C for 1 h under vacuum, 2) heating at 100 °C for 1 h in ambient environment and 3) heating at 70 °C for 16 h under vacuum. None of these conditions succeeded in increasing the device current to the initial value (before high RH exposure).

In order to better comprehend the additive effect of high RH exposure and whether the current eventually improves with time at ambient conditions, the device current was monitored for a long period of time. Figure 4 shows device current versus time for a device that was subjected to two consecutive high RH exposures for 450 seconds each. The device was measured and stored at ambient conditions. It is observed that after each high RH exposure, the current decreases and remains at that value for 250 days. After this period, an annealing procedure (180 °C for 30 min under forming gas, 5% H₂ in N₂) was performed and current was eventually increased at a lower level than the initial value.

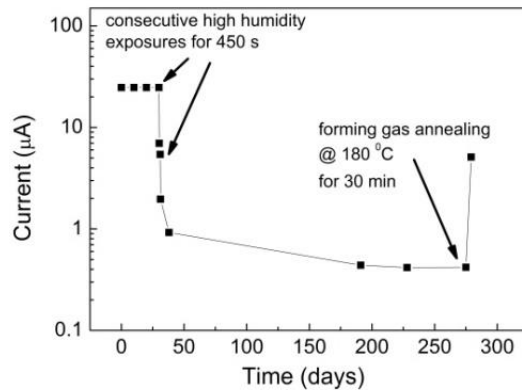


FIG. 4. Device current monitored versus storage time in ambient environment after two consecutive high relative humidity exposures (450 s each). Forming gas annealing at 180 °C for 30 min was performed at the end.

From the above results, we conclude that when rGO devices are exposed to low/medium levels of RH, H₂O serves as an electron donor. Therefore, the hole concentration is reduced in the p-type rGO, and its resistance increases¹⁰. In contrast, at high RH, the adsorbed water molecules may be ionized and thus, ionic conductivity causes a decrease in resistance¹⁰ which is revealed by an increase in current shown in Figure 2. In parallel, H₂O molecules enter the material and intercalate between its layers, increasing the resistance (swelling effect) shown by the current decrease in Figure 2. We can assume that these two mechanisms are antagonistic and eventually the swelling effect prevails due to its slower kinetics in the bulk rGO material. Furthermore, it has been shown that this swelling effect is permanent and remains even when the device is heated up to 180 °C at vacuum conditions or up to 100 °C in air. It was shown that water desorption is enhanced during thermal annealing under a forming gas environment at 180 °C. However, it was observed that the initial device current value cannot be recovered, most likely due to damage to the rGO flakes that occurs during water desorption from the material.

In summary, rGO devices demonstrated a permanent water trapping effect upon exposure to high RH for at least 450 s at room temperature. Device current decreased after such exposure and did not recover even after 250 days in ambient conditions. In addition, the existence of trapped water molecules inside the rGO layer was detected with XPS analysis. Finally, it was demonstrated that water intercalation has an additive nature and is readily monitored by the device current. We believe that this kind of material behavior could be useful for various memory, construction engineering and medical applications.

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