Graphene-Based Actuators**

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The development of new mechanical actuators that convert external stimuli such as thermal, light, electrical, or chemical energy to mechanical energy depends on the development of new materials. Reversible mechanical actuators based on carbon nanotubes (CNTs) and hydrogel polymers have suggested applications in robotics, sensors, mechanical instruments, microscopy tips, switches, and memory chips.[1–7] Recently, electromechanical resonators composed of single- and multilayer graphene sheets were reported.[8] We present here a novel macroscopic graphene-based actuator that shows actuation that depends on variation of humidity and/or temperature. The actuator is a free standing ''paper-like'' material made by sequential filtration of CNT, and then graphene oxide, aqueous colloidal suspensions.

''Paper-like'' materials composed of stacked graphene oxide platelets produced by simple filtration of an aqueous graphene oxide suspension exhibited good mechanical properties, with a modulus of about 40 GPa and a fracture strength of about 130 MPa.[9] Chemical modification of graphene oxide paper with divalent ions can enhance its mechanical properties.[10] Based on these results that show excellent mechanical properties of individual graphene sheets and of paper-like materials composed of them, we have tried to make mechanical actuators by using graphene oxide platelets.

Graphite oxide (GO) is generated by oxidation of graphite and contains a wide range of oxygen functional groups, such as hydroxyl and epoxy groups on the basal plane and carboxylic acid groups at the edges, which make the GO hydrophilic.[11,12] The oxygen functional groups in the GO, which contains a layered structure of graphene oxide platelets, allow dynamic intercalation of water molecules into the gallery between the layers.[13] The interlayer distance between the graphite oxides reversibly varies from 6 to 12 Å depending on the relative humidity, with increased interlayer distance as the relative humidity increases.[13,14] Graphene oxide paper contains a layered structure similar to, but not identical to, GO (the coherence length in the paperlike material is 6–7 platelets,[9,10] whereas the crystal can have many stacked layers); the graphene oxide paper would contain the same chemical functional groups as GO.[9,10] We thought that materials using the graphene oxide paper as a building block could mechanically respond to changes in humidity and/or temperature by changes in the amount of interlamellar water between the graphene oxide platelets.

The use of two different building blocks as a means to fabricate asymmetric materials has proved to be a useful approach for producing mechanical actuators.[15] We created bilayer ''paper'' samples composed of a layer of crisscrossed multi-walled CNTs (MWCNTs) and then of a layer of graphene oxide platelets. CNTs have been intensively studied for their potential use in micro/nanoelectromechanical systems (MEMS/NEMS), sensors, composites, and actuators.[1–5,16] Both graphene and CNTs are composed of the same basic structure, extended aromatic sp^2 carbon networks, and this structural compatibility may provide for a stable interface between these two layers.

Bilayer paper samples were successfully fabricated by sequential filtration of COOH-functionalized MWCNTs and then graphene oxide platelets from an aqueous suspension (Figure 1a). Both surfaces of the circular bilayer paper were flat at the macroscopic level. Reverse sequential filtration, however, produced scattered islands of MWCNT bundles on the graphene oxide layer.

The surface of the graphene oxide layer was dark brown and electrically insulating (Figure 1b and Supporting Information (SI)). On the other hand, the surface of the MWCNT layer was black, shiny, and electrically conductive (Figure 1c and SI). This asymmetry could open the possibility of applications in wrapping and as storage materials. Based on scanning electron microscopy (SEM) observations, the surfaces of the graphene oxide layer and of the MWCNT layer do not seem to cross contaminate each other (Figure 1e, f). The bilayer paper is quite flexible, as can be seen in Figure 1d. The thickness of each layer was measured with SEM from the cross section of the bilayer paper sample (obtained by fracturing it at room temperature with tweezers; Figure 1g), and each was found to be approximately 10-μm thick. The surfaces and cross sections of each layer in the bilayer paper samples exhibited the same morphology as the individually prepared graphene oxide and MWCNT papers.[9,17] The bilayer paper did not delaminate at the macroscale. However, the edge of the fractured paper samples prepared for the aforementioned SEM measurements was slightly delaminated (Figure 1g).

Since GO swells and shrinks with increases and decreases in relative humidity, we investigated the actuation of the bilayer paper samples as a function of the relative humidity at room temperature (see SI about the method of increasing the relative

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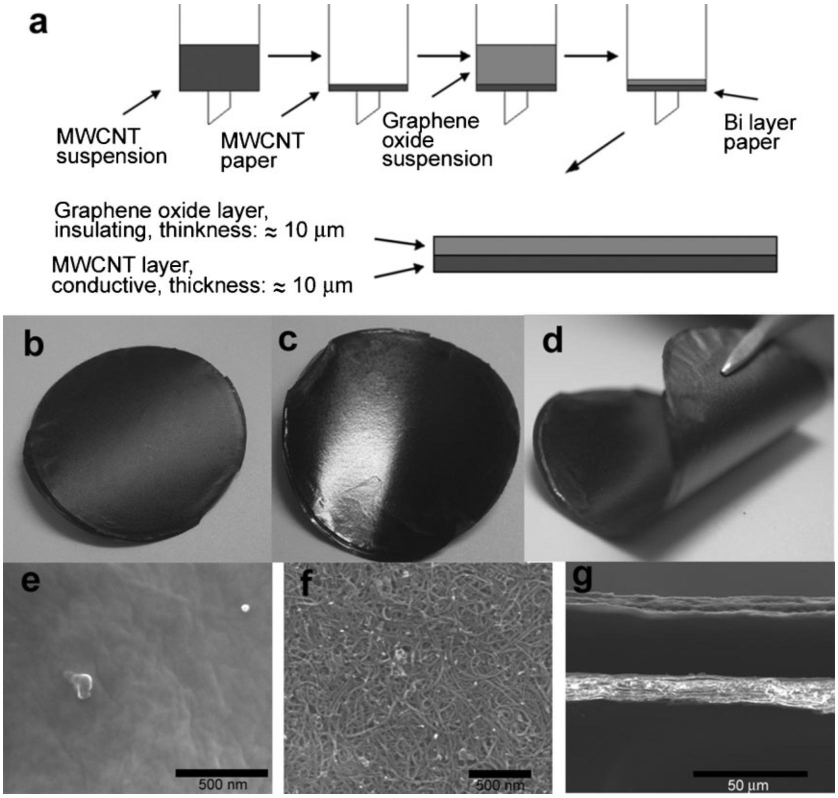

Figure 1. a) Schematic drawing of how the bilayer paper is made. b–d) Photos of both surfaces of the bilayer paper. b) Graphene oxide layer and c) MWCNT layer. d) Curled bilayer paper, outside: graphene oxide layer, inside: MWCNT layer. e–g) SEM images of the surface. e) Graphene oxide layer and f) MWCNT layer. g) SEM image of the cross-section of the bilayer paper; upper layer: MWCNT and lower layer: graphene oxide.

humidity). Notably, the bilayer papers actuated—they curled depending on the relative humidity (Figure 2). At low relative humidity (12%) the bilayer paper rolled up with the MWCNT side facing outward (Figure 2a). As the relative humidity increased, the bilayer paper gradually unrolled, becoming almost flat around a relative humidity of 55% to 60% (Figure 2b, c) at room temperature. As the relative humidity exceeded ≈60%, the bilayer paper started to curl in the opposite direction, with the MWCNT side facing in and the graphene oxide side facing out (Figure 2d, e). The bilayer paper ''completely curled'' at a humidity of 85% with each end of the paper touching each other (Figure 2f). When the bilayer paper was then re-exposed to low room relative humidity, the bilayer paper gradually unrolled, curled in the opposite direction with MWCNT side facing outward, reaching steady state in about thirty seconds (we have not investigated the reversibility of the paper in terms of actuation angle as a function of the relative humidity or temperature; see below).

The bilayer paper samples also showed similar actuation, curling as a function of temperature (see SI). We have found that the bilayer paper is stable under normal in-lab humidity changes on a day-to-day basis for at least 6 months with additional actuation tests for achieving completely curled paper through combined variation of relative humidity and temperature (10 and 20 times, respectively).

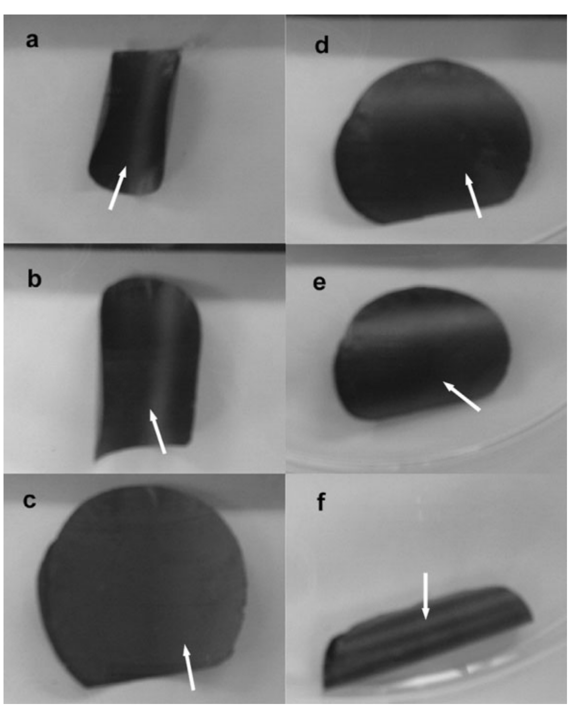

Figure 2. Actuation of the bilayer paper sample as a function of relative humidity (%), a) 12, b) 25, c) 49, d) 61, e) 70, and f) 90. White-arrowed side: surface of graphene oxide layer.

The water uptake of the hydrophilic graphene oxide paper was confirmed by thermal gravimetric analysis (TGA; see SI). The TGA curve of the graphene oxide paper, prepared separately, showed a 17% weight loss before 100 °C, from evaporation of water molecules.[18,19] Conversely, a MWCNT paper did not exhibit weight loss in this temperature region, indicating that the MWCNT paper does not absorb water molecules. Consequently, although the behavior of both papers as a function of the relative humidity or temperature has not been fully understood, we think that the actuation of the bilayer paper might be induced by this different amount of interlamellar water of both layers depending on the relative humidity or temperature (see SI for proposed mechanism).

In conclusion, we prepared a bilayer paper, composed of adjacent graphene oxide and MWCNT layers with the thickness of the graphene oxide and MWCNT layers approximately 10 µm each, and demonstrated the first case of a macroscopic graphene-based actuator. The papers curl depending on humidity and/or temperature. Although the mechanism of the actuation is not yet understood, we think that this actuation of the bilayer paper is highly interesting and further applications for gas sensors could be promising. Furthermore, given the excellent electrical and mechanical properties of the graphene sheets, we believe that future work on this graphene-based actuator will lead to development of a wide range of mechanical actuators, including MEMS and NEMS.

Experimental Section

Method: GO was synthesized from natural graphite (SP-1, Bay Carbon, MI) by the modified Hummers method.[20] Colloidal suspensions (30 mg of GO per 10 mL of water) of individual graphene oxide platelets in purified water (17.4 MΩ resistance) were prepared with the aid of ultrasound (Fisher Scientific FS60 ultrasonic cleaning bath) in 20-mL batches. Aqueous colloidal suspensions of MWCNTs were prepared by probe sonication of the mixture with COOH-functionalized CNTs (10 mg of MWCNT in 150 mL of water, NANOLAB, >95%, diameter: 15 ± 5 nm, length: 5–20 μm) and hexadecyltrimethylammonium bromide (100 mg for 10 mg of MWCNTs, >99% from Fluka) for 24 h. Both homogenous graphene oxide and MWCNT paper samples were made by filtration of the resulting colloidal suspension through an Anodisc membrane filter (47 mm in diameter, 0.02-μm pore size, Whatman, Middlesex, UK). The bilayer paper was produced by sequential filtration of MWCNTs and then graphene oxides, aqueous colloidal suspensions suspension through an Anodisc membrane filter (47 mm in diameter, 0.02-μm pore size, Whatman, Middlesex, UK). The resulting bilayer papers were rinsed by addition of purified water and filtered 3 times. After the filtration, the papers were suction-dried for half a day, followed by a thorough wash, soaked in purified water for half a day each time (3 times) before being peeled from the filter.

Instruments: The secondary electron images of the bilayer paper sample were taken with an FEI Quanta-600 FEG Environmental SEM using a voltage of 10 to 15 keV. Temperature measurements were made with ThermoTrace 15006 from DeltaTRAK. Relative humidity was measured with Caliber III by WESTERN. The TGA of the paper samples was measured by PERKIN-ELMER TGA with $1\ ^{\circ}\ min^{-1}$ heating rate in the air flow.

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