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Ge, Y, Cao, R, Ye, S orcid.org/0000-0001-5152-5753 et al. (5 more authors) (2018) A bio-inspired homogeneous graphene oxide actuator driven by moisture gradients. Chemical Communications, 54 (25). pp. 3126-3129. ISSN 1359-7345

https://doi.org/10.1039/c8cc00394g

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DOI: 10.1039/C8CC00394G

Journal Name

COMMUNICATION

Bio-inspired homogeneous graphene oxide actuator driven by moisture gradients †

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An actuator driven by moisture gradients has been developed from a homogeneous graphene oxide film, relying on the in-situ formation of bilayer structure induced by water adsorption. This actuator shows efficient and controllable bending motions, coupled with the capability of lifting objects 8 times heavier than itself.

Smart actuators responsive to external stimuli can efficiently convert different forms of energy, such as heat, light, and sound to mechanical movements,[1-5] and hence holding great potential in a varieties of applications including artificial muscles,[6] microrobotics,[7] switches,[8] tissue engineering devices,[9] and motors. In particular, the actuator driven by water/moisture/humidity or their gradients has attracted increasingly growing interest. Indeed, humidity has served as a paramount form of natural energy resources.[12] For instance, pinecones close when wetted (or open when dried), because the variation of environmental humidity leads the aligned layers of nano- and mesoscale to change conformation and undergo bending deformation. Since water is among the most abundant and important resources in the world,[10, 11] it is of great significance to develop actuating systems which are able to convert the energy from humidity/moisture or the gradient thereof into usable energy for tackling the global challenges of energy consumption.

As a novel carbon material, graphene oxide (GO) contains a large number of oxygenated functional groups on the surfaces and edges,[13] and thus hydrophilic and easily dispersible in water as fully exfoliated and individual sheets to form a stable colloidal suspension. GO has been be explored as an excellent component for smart actuation systems driven by water-related trigger, owing to its intriguing physical and chemical features.[14] A number of actuators have been developed based on unique GO-containing stimuli-responsive systems, and have shown potential applications in energy conversion and controllable shape change due to the sensitivity of GO with the moisture.[15-19] They display well-controlled responsiveness and effective energy conversion powered by moisture in a predetermined manner. For example, Cheng et al.[20] prepared the asymmetric structure of graphene and GO fibers via the positioned laser reduction of GO fibers, which displays a predetermined motion in a well-defined manner upon the moisture exposure. Ruoff et al.[21] fabricated a macroscopic actuator based on GO and carbon nanotubes (GO/CNTs) bilayer film, which demonstrates remarkable actuation depending on the variation of humidity. In these cases, it is necessary to involve bilayer structures with different swelling response to achieve the desired actuation. However, bilayer actuators are subject to the poor interlayer attachment and even delamination of the two layers during the locomotion process. Engineering actuators from a homogeneous structure is imperative for solving these issues, but remains in infancy.

Here, we report a facile strategy for fabricating an actuator driven by moisture gradients based on a homogeneous GO film. The success actuation has been realized via the in-situ formation of bilayer structure upon the trigger of GO film by moisture gradient**.** The homogeneous structure has enabled the actuator to be highly sensitive to the stimuli of humidity gradients, alongside display rapid and continuous motion. To the best of our knowledge, this has been the first actuator of a homogeneous GO film driven by water-related trigger.

The fabrication process of the homogenous GO thin film is schematically illustrated in Figure 1a. The GO film was prepared via the vacuum filtration of GO sheets dispersion (The scanning electron microscopy images of GO sheets of two different sizes are shown in Fig S1a and b), as a result of the vacuum-assisted self-assembly of GO sheets.[22] After a drying process in the air, the self-supported, flexible yet strong GO film were peeled off from the acetate fiber Millipore filter.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C8CC00394G

(Figure 1b). This fabrication process is simple, time-saving, and easy to be scaled up. Due to similar performance of GO films with two different sizes (20~30 μm and 6~10 μm) (Figure S1c and d) on the moist substrate, we choose the GO film with larger size (20~30 μm)for further investigation. The X-ray photoelectron spectroscopy (XPS) analysis reveals that the prepared GO film contains a variety of oxygen containing functional groups, such as epoxy groups, carboxylic acid groups, and hydroxyl groups, which can provide abundant active sites for forming hydrogen bonds between GO sheets (figure S2a and b).The cross-sectional scanning electron microscopy (SEM) image of GO film in Figure 1c shows that the GO sheets possess high aspect ratios, and hence able to act as building blocks with the feature of highly ordered structure. [23]

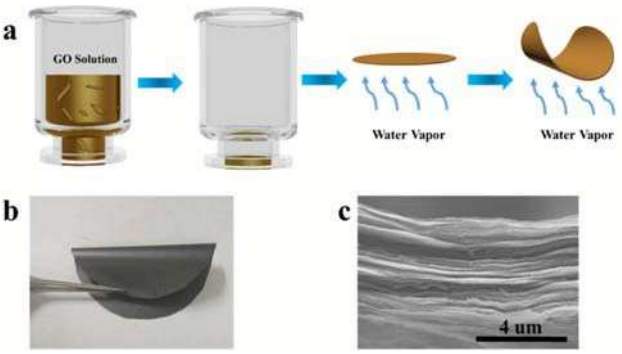

Figure 1. (a) Schematic illustration of the fabrication process of a homogeneous GO thin film which can serve as an actuator. (b) Photograph of flexible GO film produced by filtration of an aqueous graphene dispersion. (c) Cross-sectional SEM image of the layered structure of GO film viewed from a fracture edge.

The GO film has a uniform thickness, which is determined to be ca. 6 μm from SEM images, but 12 μm measured by micrometer caliper. The lower thickness value is due to the low water content by high vacuum of SEM equipment.

We first qualitatively investigated the actuation behaviour of the homogeneous GO thin film in response to the humidity gradients at room temperature. It can be seen from Figure 2a, the GO film bends within one second when placed on the palm, whereas showing no locomotion when put on the palm wearing a glove (Figure 2b). Furthermore, this film bended 3 millimetres down (Figure 2c) by approaching the finger without contact, indicating it is highly sensitive to moisture. Notably, in a sealed chamber saturated by water vapor, the film showed no locomotion (Figure S3), which suggests that it is the moisture gradients, instead of water vapour, that accounts for the observed bending of the GO film, that is, the actuation is triggered by the moisture gradient. In addition, the flips of the GO film take place spontaneously and continuously on a moist paper substrate at 40 °C (Movie S1), with each cycle generally consisting of 6 stages (I- VI) (Fig. 2d). When a GO film is placed on the moist substrate, the bottom face of the film is in contact with the moist substrate, which has higher humidity than the ambient air above the film. As a result, the bottom face absorbed more water vapor than the top face, leading the film

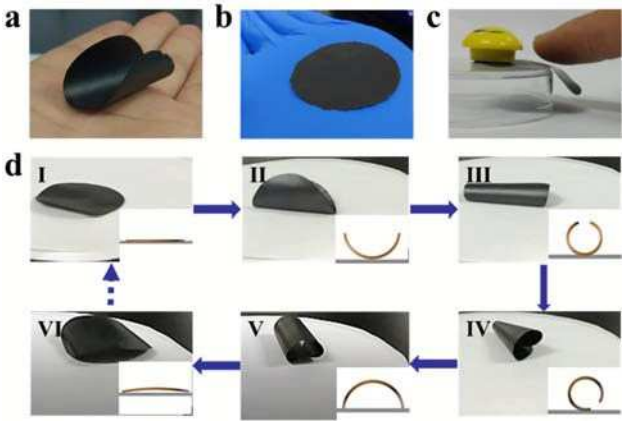

Figure 2. Qualitative investigation of the actuation behaviours of the homogeneous GO film: (a) Bending upward when placed on the bare palm; (b) Showing no bending when placed on the hand wearing glove; (c) Demonstrating rapid bending deflection downward when a finger is close to the film without contact; (d) Flipping locomotion of a GO film on a moist substrate at 40 °C.

to swell asymmetrically and curl away from the substrate (I). Afterwards, the film's centre of mass rises and reaches a critical height (II), at which the film becomes mechanically unstable and consequently topples over (III). Then, repeated and symmetric water adsorption occurred at the film/substrate interface, in cooperation with the water release from the elevated part of the film to produce the movement in the horizontal orientation (IV). Finally, a majority of the contact areas bent up, and the film dropped back to the substrate, with the top face at the initial stage in contact with the moist substrate (V) to start a new cycle (VI). The actuation can be repeated tens of cycles without obvious fatigue.

The flipping frequency is dependent on the film thickness. As shown in Figure S4, a series of investigations have revealed that, the optimal thickness for persisted motion of the film is 12 μm. The thinner films are apt to adhere to the substrate due to the absence of humidity gradient, while thicker films exhibit reduced rolling frequency because ofthe increased stiffness. As can be seen from Movie S1, the flipping frequency of the GO film is about once a second with the thickness of 12 μm at 40 °C, which is comparable to that of PEE-PPy film[12] and PACD@AG film[24] of similar thicknesses.

The flipping frequency also varies with the temperature. It has been found that the optimal temperature is ca. 40 °C. This can be rationalised by the influences of the temperature on the exchange kinetics: at 30 °C, the water evaporation was slow, and the moisture gradient is too small to provide sufficient energy for fast flip. The use of higher temperature (70 °C) brings about larger moisture gradient, but compromised with faster water desorption form the film surface, and thus fails in increasing the rolling frequency efficiently. At the optimal temperature of about 40 °C, the

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dynamic equilibrium with faster water adsorption and desorption was rapidly established (Fig. 2d).

Motivated by the above results that our homogeneous GO film is capable of actuation driven by moisture gradients, we further conducted the quantitative study of the actuation behaviour on a home-built testing device (shown in Figure S5a and Movie S2). The GO film was placed on a solid plastic substrate with a rectangle hole at the center to introduce the water vapor gradients. The GO film was clamped and exposed to moisture from one end.

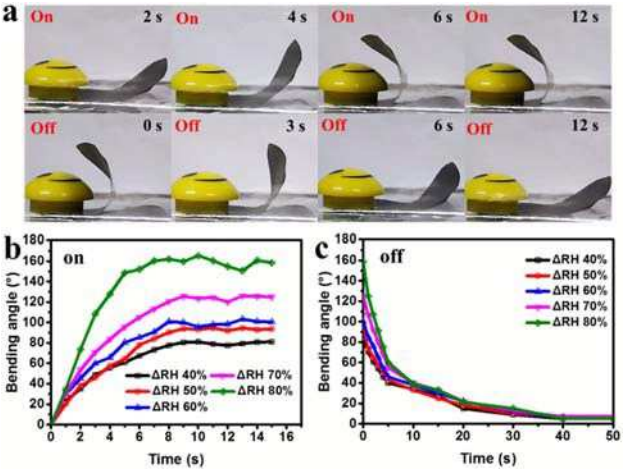

Figure 3. (a) Photos of bending/unbending motion at 20 °C and ΔRH=60%. Time-dependent angle of (b) bending and (c) unbending at different relative humidity differences (ΔRH) with film thickness of 12 μm.

The moisture gradients can be adjusted via tuning the water evaporation rate that is correlated with moisture differences. The final bending/unbending angle of GO film was investigated as a function of moisture differences, and the determination of bending angle is shown in Figure S5b. As shown in Figure 3a, b and c, the average bending speed is greatly larger than the unbending speed because the moisture adsorption of the GO film is faster that the desorption of the GO films. Also, the final bending angle increased gradually from 80° to 160° as ΔRH was increased from 40 to 80%. Upon the trigger by the moisture gradient, the homogeneous GO thin film shows a very rapid response, with a bending speed over 30° s^{-1} , comparable with that of reported bilayer graphene-based actuators (13~18° s^{-1}).[12,22,25] Distinct from the bilayer/multilayer structures, our homogeneous GO actuator can ensure a stable coherent interface. The bending and unbending deformations were highly reversible and reproducible, as demonstrated by the function of the film curvature with the time, upon the exposure to moisture gradients over 10 cycles with on/off switches (Figure S5c).

Figure 4a shows the schematic illustration of the locomotion mechanism of our homogeneous GO thin film. During the trigger by a water gradient from below the film, the bottom part of the hydrophilic GO film absorbs water to expand. Owing to the formation a stronger intermolecular hydrogen bonding interaction, the expansion of thin film only occurs at the bottom layer, giving rise to the swelling difference along the vertical direction. As a result, a unique bilayer structure in this homogeneous thin film in has been generated in-situ, responsible for the observed bending of the GO film.

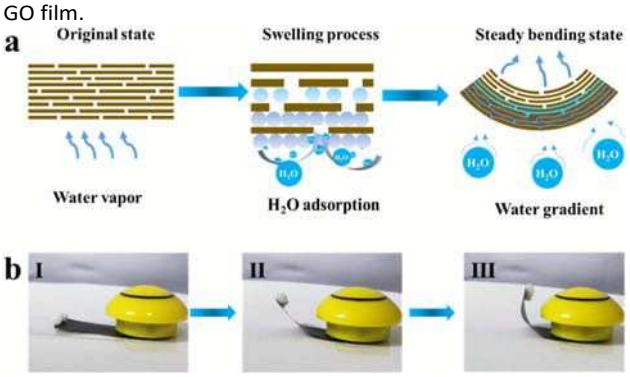

Figure 4. (a) Schematic illustration of the locomotion mechanism of the homogeneous GO thin film actuator. (b) Digital images showing that the film can lift cargo 8 times heavier than itself driven by water gradients.

Following the compete bending deformation of the GO film, the local moisture gradient disappears.[26] The water inside the bottom layer immediately undergoes a desorption which drives the GO film to return to an unbent state. When the moisture gradient appears again, the intermolecular hydrogen bonding interaction is recreated. This dynamic reconstruction/destruction of intermolecular hydrogen bonding by "breathing" water contributes to the reversible expansion/contraction activity of the GO film. For in-depth understanding of this process, XRD measurement was performed under dry ambient condition and bending condition on the moist substrate, to investigate the effect of the intermolecular hydrogen bonding on the interlayer spacing. As shown in Fig S6, the GO film showed a d-spacing of 7.8 Å under ambient condition. After bending on the moist substrate, the d-spacing of lower part of the GO film increased greatly to 10.1 Å, and the upper part increased a little to 8.8 Å. This demonstrates that the water molecules enter the GO layers, resulting in the destruction of π–π interactions and thus the stretching of d-spacing, and the d-spacing closed to moisture is larger than that away from. The reversible swelling and deswelling induced by the absorption and desorption of water endow the as-made film reversible bending/ unbending ability.

Thanks to the capability of fast and sensitive response, the homogeneous GO thin films are promising for fabricating smart actuation device. As shown in Figure 4b, the prepared GO films were cut into rectangular strip of 1 cm × 2 cm, and the cargos (plastic block of larger density) were loaded on one end of the strip. The resultant system was placed on a wet filter paper at 40 ℃. (Movie S3). The GO film in the air of non-uniform humidity can covert the harvested potential energy of the moisture gradient to mechanical work. As a consequence, the device of 4.5 mg, 12 μm-thick film of GO was able to lift

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the cargos of 35.5 mg to the height of 0.8 cm in 8 s with a work output of 0.64 J kg^{-1} and a power density of 0.08 W kg^{-1}.

In summary, we have engineered a moisture gradient-driven actuator of a homogeneous GO film. This actuator shows a highly sensitive and ultrafast response towards the stimuli of moisture gradient, with a bending speed about 30° s^{-1}. It can convert the potential energy in moisture gradients to mechanical work, and has been exploited to produce an actuation device which can lift cargoes 8 times heavier than itself. This work has provided a novel and facile strategy for fabricating efficient actuators based on homogeneous materials, and also insightful ideas for the design and construction of smart actuation systems driven by moisture or the gradient thereof for various potential applications such as soft robots,[15] biosensors,[27] and water-gradient–driven generator.[12] In addition, given the unique optical and electrical properties of GO, one can envision the extension of the concept developed in this work to the engineering of a homogeneous GO film actuator driven by other triggers, such as light and sound, with a wide range of utilities.

We thank the financial support from the National Natural Science Foundation of China (No. 21104050, 11604045), China Postdoctoral Science Foundation (2013M541715, 2014T70541), a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Fundamental Research Funds for the Central Universities, Shanghai Science and Technology Commission 16PJ1400100, 17ZR1440000, and 17JC400700.

Conflicts of interest

There are no conflicts to declare.

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