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An ultrasensitive moisture driven actuator based on small flakes of graphene oxide

Guochuang Xu, Ji Chen, Miao Zhang, Gaoquan Shi*

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

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ABSTRACT

Moisture driven actuators with sensitive and strong actuation performances have important applications in robots, artificial muscles and hygrometers, etc. Here, we report such an actuator constructed by one layer of small flakes of graphene oxide (SGO) with an average lateral dimension of 0.9 μm and another layer of reduced conventional graphene oxide sheets (rCGO). An SGO film can adsorb about 22% (by weight, wt%) of water compared with its own weight by changing relative humidity (RH) from 20% to 50%. This SGO film can generate a contractile stress up to 90 MPa as relative humidity (RH) changed from 100% to 23%. An SGO/rCGO bilayer actuator with a thickness of 2.3 μm displayed an extremely large curvature (about 19.1 cm^{-1}) at an RH of 98%. This actuator also exhibited a high rate of bending (4.4 cm^{-1} s^{-1}) in the first second as RH switched from 75% to 32%. It showed excellent stability (kept unchanged after actuating for 1000 cycles), and was capable of moving an object 30 times heavier than its own weight.

1. Introduction

Actuators are devices that can convert environmental stimulations such as light [1,2], electrical field [3,4], pH value [5,6], temperature [7,8], or moisture [9,10] to mechanical movements. Recently, they have attracted a great deal of attention because of their promising applications in environment-triggered sensors [11,12], self-walking robots [13], artificial muscles [14], and controllable displays [15,16]. Graphene and its derivatives are attractive materials for fabricating high-performance actuators [17,18], mainly due to their atom-thick two-dimensional structures, low weight densities, large specific surface areas, high mechanical strengths and electrical conductivities [19,20]. Furthermore, graphene oxide (GO), one of the most important graphene derivatives, has abundant oxygenated groups, making it be able to change its volume rapidly and reversibly via adsorbing/desorbing water molecules [21,22]. Therefore, GO-based moisture driven actuators have been extensively studied. For example, Sun et al. designed a GO paper with hierarchical structure [23]. In this case, the upward convection flow of solvent during evaporation process induced the formation of GO film with gradient packing density in its cross-section direction. However, the difference of water adsorptions at the both surfaces of this GO film is small, making the actuation force to be weak. Han et al. fabricated a humidity actuator based on reduced GO (rGO)/GO bilayer films prepared by UV irradiation of GO film [24]. The GO layer exhibited reversible contraction/expansion deformations induced by fast adsorption and desorption of water molecules via switching between different RHs. The curvature of the actuator with a thickness of 10.5 μm was measured to be about 1.75 cm^{-1} at an RH of 97%. In these actuators, conventional GO (CGO) sheets were prepared from large flakes of graphite powder (100 or 325 meshes). Smaller GO flakes with higher edge-to-basal plane ratios have more edging functional groups, facilitating adsorb more water molecules to provide a larger volume expansion [25,26]. On the basis of this consideration, we developed a moisture driven bilayer actuator by using SGO prepared from small graphite flakes (12,000 meshes) as the actuation layer and conventional rGO as the supporting layer. It showed reversible ultrasensitive actuation performance, and its actuation process and mechanism have been qualitatively studied for the first time.

2. Experiment

2.1. Materials and instruments

All the solvents were of analytic grade. Scanning electron micrographs were taken out by the use of a field-emission scanning electron microscope (Sirion-200, Japan). The average size of GO sheets was measured by taking account of the largest 100 sheets

* Corresponding author.
E-mail address: gshi@tsinghua.edu.cn (G. Shi).

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in the SEM image of each sample (the tiny sheets are too small to be accurately measured). The size of a GO sheet was calculated by averaging its largest and small transverse widths [25]. X-ray photoelectron spectra (XPS) were carried out by using an ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific) with Al Kα (1486.6 eV); the X-ray source was set at 150 W with a pass energy of 30 eV for high resolution scan. Raman spectra were recorded on a LabRAM HR Raman spectrometer (Horiba Jobin Yvon) with a 532-nm laser. Contact angles were measured by using an OCA 15 Plus Contact Angle Meter (Eastern-Dataphy Inc., Beijing, China).

2.2. Preparation of SGO and CGO dispersions

SGO or CGO dispersion was prepared from 12,000 or 100 meshes graphite powder following a modified Hummers method reported previously in references [27,28].

2.3. Preparation of the rCGO film

CGO dispersion was concentrated to 9.1 mg mL^{-1} by centrifugation. Successively, it was poured into a plastic dish with a size of 47 mm × 27 mm under ambient environment and dried to form a CGO film. Finally, it was reduced by a hydroiodic acid (HI) solution (57 wt%) for 12 h, and washed with ethanol and water in turn to extensively remove residual acid and iodine ions [29].

2.4. Fabrication of SGO/rCGO actuator

In order to increase the hydrophilicity of rCGO membrane, its surface was treated by oxygen plasma for 2 min. Then, a concentrated SGO suspension (8.1 mg mL^{-1}) was casted on the surface of pretreated rCGO membrane. After drying in air, an SGO/rCGO bilayer film was obtained (Fig. S1).

2.5. Actuation tests

An SGO/rCGO bilayer film was cut into beams with a size of 3 mm × 1 mm for actuation tests at a temperature of 20 °C. The bending degree of the actuator was expressed by its curvature (Fig. S2), which is related to the length and the deformation of actuator. The contractile stresses of SGO and CGO films were tested on a model 3342 Instron universal testing machine. The specimen has a size of 15 mm × 5 mm. The RHs were controlled by a humidifier using saturated aqueous solutions of CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, NaCl, KCl, and K_2SO_4 as modulating regents.

3. Results and discussion

Single-layer SGO and conventional GO (CGO) sheets were prepared from graphite powders with particle sizes of 12,000 and 100 meshes. The SGO sheets have an average lateral dimension of 0.9 μm, and that of CGO sheets was measured to be as large as 19 μm (Fig. 1). The X-ray photoelectron spectrum (XPS) of SGO indicates its C/O atom ratio is 1.7, slightly lower than that of CGO (2.1) (Fig. S3). This is mainly due to that SGO has more edges caped with carboxyl groups.

The water adsorption capacity of an SGO film was monitored by a precision balance, showing that it can adsorb about 22 wt% of water compared with its own weight as RH changed from 20% to 50% (Fig. 2a). However, a CGO film with the same shape and size can adsorb only 12.6 wt% of water. The water adsorption capacity of SGO film is also superior to those of many polymers used for fabricating moisture driven actuators [30]. The superior water adsorptive property of SGO is partly attributed to its low C/O ratio (1.7) or high oxygen content. For comparison, an SGO film was thermally reduced by heating at 180 °C for 40 min, and it was nominated as rSGO. rSGO has a higher C/O ratio of 2.6 than that (1.7) of SGO, making the former can adsorb much less water (Fig. S4). Furthermore, the small dimensions of SGO sheets with more oxygenated groups at their edges also improved their water adsorbing capability. The contractile stress generated in an SGO or CGO film was measured by using a mechanical analyser. In this case, an SGO or CGO film in air with an RH of 100% (offered by a humidifier) was preloaded with a force of 0.5 mN to keep it to be straight. When the humidifier was moved away, the RH of air was changed to 23%. As a result, the SGO film generated a contractile stress as high as 90 MPa caused by its shrinking and stiffening upon water desorption (Fig. 2b). This value is about 3.5 times that of a CGO film (27 MPa), and 260 times higher than that of mammalian skeletal muscle (~0.35 MPa) [31]. As shown in Fig. 2c, a thinner SGO film delivered its maximum contractile stress within a shorter time because of a faster rate of desorbing water. The shrinkage and expansion of an SGO film can be repeated for many times, and the

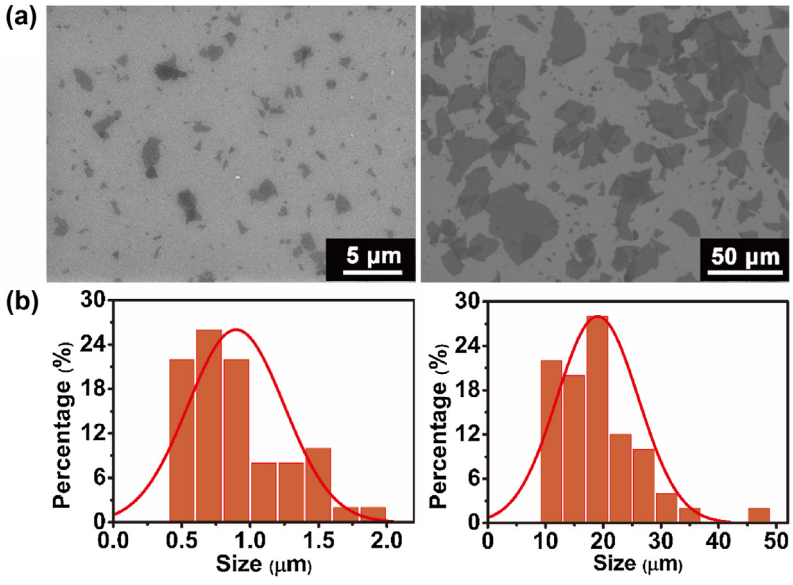

Fig. 1. (a) SEM images of SGO (left) and CGO (right) sheets. (b) The histograms of size distributions of SGO (left) and CGO (right) sheets; each histogram was obtained by counting the largest 100 sheets in the SEM image of corresponding sample.