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## Novel electromechanical actuation based on spongy graphene paper

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### Abstract

Spongy graphene paper with inside foldable corrugated structure is fabricated by electrothermal reduction of the oxygen-containing groups inside RGO paper. Reversible macroscopic length contraction of the spongy graphene paper with strain of 2.4% under 10V voltage is exhibited, mostly attributed to the deformation of corrugated structures.

### Full Text

#### Abstract

Spongy graphene paper with an internal foldable corrugated structure is fabricated through electrothermal reduction of oxygen-containing groups within reduced graphene oxide (RGO) paper. The resulting material exhibits reversible macroscopic length contraction with a strain of 2.4% under a 10 V voltage stimulus, an effect primarily attributed to deformation of the corrugated structures.

### Introduction

Electric actuator materials and structures that convert electrical energy into mechanical energy have attracted considerable research interest due to their wide-ranging applications in robotics, sensors, switches, and artificial muscles across both macroscopic and microscopic domains. Various materials, such as carbon nanotubes (CNTs) and graphene, have been extensively developed for actuators owing to their remarkable electrical, thermal, and mechanical properties. In addition to serving as electrochemical actuators through charge injection in electrolyte environments and as conductive components in other actuator systems, graphene and its derivatives have recently been investigated as novel actuator materials that exhibit distinctive negative thermal expansion (contracting upon heating), in contrast to conventional materials. Graphene possesses

an intrinsic negative coefficient of thermal expansion (CTE) due to negative in-plane lattice deformation, a property utilized in electrothermal microactuators. Graphene oxide (GO) papers also display reversible contraction/expansion upon heating/cooling, resulting from rapid transport of water molecules attached to oxygen-containing functional groups on GO sheets—a phenomenon described as pseudo-negative CTE. However, graphene's intrinsic negative CTE is relatively small ( $\sim 10$   $^{\circ}\text{C}$ ), limiting large actuation displacement, particularly at the macroscale. Meanwhile, GO paper's large pseudo-negative CTE ( $\sim 10$   $^{\circ}\text{C}$ ) is strongly affected by ambient humidity, and GO's poor electrical properties restrict its utility in electric actuators. Therefore, developing novel graphene materials and structures with large actuation performance, particularly in air, is highly desirable for electric actuator design.

Recently, our group demonstrated that a graphene membrane with a parallel structure could achieve volume variations as large as 98% under low voltage stimulation. This substantial deformation motivates further development of high-performance electric actuation driven by special structures. Spongy graphene materials with internally loose, porous structures have garnered significant attention for applications in pollution sorption, supercapacitors, and sensors. The more loosely packed structures in spongy graphene provide abundant cavities and facilitate larger structural deformation compared with typical tightly packed layered graphene materials, making spongy graphene a promising candidate for exceptional actuation performance.

In this work, we report progress on spongy graphene (sG) paper electric actuators, focusing on the low-voltage deformation mechanism and resulting macroscopic actuation performance. The sG paper actuator, featuring an internal foldable corrugated structure, is designed and fabricated through electrically induced rapid thermal reduction of oxygen-containing functional groups inside RGO paper. The sG paper actuator demonstrates large, rapid contraction along the length direction and expansion in thickness under low voltage, likely due to deformation of the foldable corrugated structures caused by interlayer gas expansion and the collective effect of graphene sheets with intrinsic negative CTE. A macroscopic length contraction with 2.4% strain is achieved for the sG paper actuator under 0.1 Hz, 10 V voltage stimulation, with the actuation amplitude reaching maximum within 0.5 s. The negative CTE of this sG paper along the length direction is estimated to be approximately  $-10$   $^{\circ}\text{C}$ , while the positive CTE along the thickness direction is about  $10^3$   $^{\circ}\text{C}$ .

## Fabrication and Characterization

RGO papers are fabricated by casting GO aqueous solution to form GO papers, followed by hydroiodic (HI) acid reduction. This method provides high electrical conductivity of approximately 210 S/cm and excellent flexibility (figure S1) for the RGO paper compared with other fabrication approaches. Because the HI acid reduction proceeds from the outer surface of the GO paper inward, the reduction degree can be tuned by controlling the reduction time. Consequently,

oxygen-containing functional groups may remain inside the RGO paper after short reduction times, which is crucial for sG paper fabrication. Here, the RGO paper is reduced in HI acid for 10 minutes, and the XRD pattern of the resulting RGO paper ( $2\theta = 10.9^\circ$ ) in figure S2a confirms the presence of remaining oxygen-containing functional groups.

The sG paper with internal corrugated structure is fabricated through electrically induced thermal reduction of oxygen-containing functional groups inside the RGO paper. Figure 1a [Figure 1: see original paper] illustrates the fabrication process schematically. When an appropriate voltage is applied to the RGO paper, rapid expansion of gaseous species from residual oxygen-containing functional groups occurs due to electrically induced thermal reduction, causing interlayer expansion within the RGO paper and forming sG paper with corrugated structures. Cross-sectional SEM images reveal the internal microstructures of sG papers (figures 1d-1e). For comparison, cross-sectional SEM images of GO and RGO papers (figures 1b-1c) show well-packed layered sheets, with thickness decreasing from 9  $\mu\text{m}$  to approximately 5  $\mu\text{m}$  due to removal of oxygen-containing functional groups. Figure 1d shows a cross-sectional SEM image of sG paper fabricated under 10 V, clearly revealing much more loosely packed graphene sheets with corrugated cavities. Applying a higher voltage (12 V) produces even larger corrugated structures with bigger internal cavities, demonstrating that the corrugated structures can be tuned by applied voltage (figure 1e). Voltages below 10 V do not produce sG paper, indicating a threshold voltage is required for electrothermal reduction. XRD patterns and Raman spectra of RGO and sG papers (figures S2b and S3) further confirm thermal reduction of oxygen-containing functional groups in the RGO paper.

## Actuation Performance

The sG paper exhibits electrically induced length contraction behavior (figures 2a-2c). To enable current flow and facilitate measurement, the sG paper is cut into a U-shape configuration with both ends fixed to electrodes, allowing it to shrink upward along the length direction under voltage stimulation so that actuation strain can be directly estimated from the measured contraction displacement (figure 2a). The actuated displacement is measured simultaneously using a laser displacement sensor. Because the sG paper is too thin for reliable laser targeting, a 60 mg tag paper is attached to the bottom of the U-shaped sample to enable clear recording of contraction displacement. Under 0.1 Hz, 10 V square wave voltage, the 27 mm-long U-shaped sG paper generates macroscopic periodic contraction and recovery with a displacement amplitude of 0.66 mm (figure 2b), corresponding to a length strain of 2.4% using the simple formula  $\Delta L/L$  and demonstrating a fast response within 0.5 s (a video of this process is provided in the Supporting Information). The actuation frequency closely matches the applied voltage frequency. Actuation strains under 10 V square wave voltage at various frequencies are shown in figure S4; actuation remains observable at frequencies up to 20 Hz. For comparison, the electric

actuation of RGO paper without corrugated structure was also tested. Figure 2c shows the actuated displacement of sG paper (blue curve) and RGO paper (black curve) under identical 0.1 Hz, 5 V square wave voltage. The sG paper's actuated displacement is approximately six times larger than that of RGO paper, highlighting the crucial role of corrugated structure in electric actuation performance. The temperature change of sG paper during actuation (red curve in figure 2c [Figure 2: see original paper]) tracks the displacement variation, confirming that actuation is indeed related to electrically induced thermal energy. The current generated under 10 V actuation increases to 87 mA, comparable to other electrothermal actuators operating at voltages as high as 40 V.

The sG paper also exhibits thickness expansion under electrical stimulation. For displacement measurement, an sG paper strip is firmly fixed on a glass substrate with electrodes connected at both ends (figure 3a [Figure 3: see original paper]). Under 0.1 Hz square wave voltage (0-3 V), the sG paper's thickness displacement increases rapidly when voltage is applied (figure 3b). No thickness displacement is observed in RGO paper under the same conditions, confirming that thickness expansion arises from the internal corrugated structure.

## Actuation Mechanism

Given that thermal energy drives sG paper actuation, thermomechanical analysis (TMA) was employed to directly investigate the thermal expansion properties of sG paper (figure S5). The sG paper exhibits negative thermal expansion along the length direction and positive thermal expansion along the thickness direction, consistent with electric actuation behavior. The length CTE of sG paper is measured to be as large as  $-10 \text{ }^\circ\text{C}^{-1}$ , while the thickness CTE from  $37^\circ\text{C}$  to  $70^\circ\text{C}$  is about  $10^3 \text{ }^\circ\text{C}^{-1}$ .

As noted, graphene materials exhibit negative CTE properties for two main reasons: in-plane thermal contraction of graphene sheets and water molecule transport between GO sheets. Due to the absence of oxygen-containing functional groups in sG paper (figure S2), water molecule transport likely contributes negligibly to electric actuation. Furthermore, our investigations show that electrically induced length contraction and thickness expansion in sG paper are related to the internal corrugated structure. A possible actuation mechanism is illustrated in figure 3c. Within the sG paper, corrugated structures consist of tightly bound graphene sheets at joints with internal fusiform cavities (red dashed circle in figure 3c), resembling a foldable construction that readily deforms under external force and recovers due to graphene's elasticity and flexibility. Under electrothermal stimulation, corrugated structure edges shrink through the collective effect of graphene sheets with intrinsic negative CTE, causing inward folding along the length direction. This deformation simultaneously produces thickness expansion, driving actuation of the entire sG paper. Additionally, thermal expansion of gas molecules from reduction of oxygen-containing functional groups during sG paper fabrication and adsorption of surrounding gas in confined fusiform cavities may contribute to corrugated structure deformation.

When voltage is applied, gas sealed inside fusiform cavities expands through Joule heating, generating pressure perpendicular to the graphene layer plane that causes thickness expansion and consequent length contraction. Electric actuation of sG paper in vacuum further confirms gas effects on actuation (figure S6). Therefore, sG paper actuation primarily results from corrugated structure deformation—the corrugated structure essentially serves as an engine driving sG paper actuation under low voltage. This structure-driven actuation in graphene materials is particularly noteworthy and has not been previously reported. To further confirm this mechanism, a clear video record of structure deformation-driven actuation under electrical stimulation is provided in the Supporting Information. For direct observation, sG paper was fabricated at higher voltage to produce larger surface-accessible corrugated structures (figure 1e). When voltage is applied, these structures plump up, driving contraction of the entire sG paper in the plane direction; when voltage is removed, the structures and sG paper recover to their original state. Further study is needed to fully elucidate the detailed deformation mechanisms of the corrugated structures.

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### Figure Captions

Figure 1. (a) Schematic drawing of the electric-induced inner heating fabrication of sG paper from RGO paper. (b-e) Cross-sectional SEM images of (b) GO paper, (c) RGO paper by HI acid reduction, (d) sG paper, and (e) sG paper fabricated by higher voltage.

Figure 2. Electric-induced contraction of sG paper along length direction: (a) Schematic setup of the electric actuation displacement test of the U-shape paper. (b) Actuated displacement (black curve) of the U-shape sG paper under 0.1 Hz square wave voltage (0-10 V) (blue curve). (c) Actuated displacement of the U-shape sG paper (blue curve) and RGO paper (black curve) as well as temperature variation of sG paper (red curve) under applied 0.1 Hz square wave voltage (0-5 V).

Figure 3. (a) Schematic setup for measuring thickness displacement of sG paper. (b) Displacement of sG paper along thickness direction under 0.1 Hz square wave voltage. (c) Schematic diagram of corrugated structure-causing actuation process for sG paper under applied voltage. The red dashed circle shows corrugated

structure in sG paper.

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