Robust and Flexible Micropatterned Electrodes and Micro-Supercapacitors in Graphene–Silk Biopapers

Ruilong Ma, Daniel Gordon, Gleb Yushin, and Vladimir V. Tsukruk*

Robust and flexible micro-supercapacitors based upon a graphene oxide–silk layered bionanocomposite is reported. Generation of micropatterned electrodes with sub-micrometer spatial resolution is accomplished using a novel resist-stenciling technique, enabling the transfer of complex microcircuit designs to a graphene oxide–silk layered substrate as chemically reduced features microfeatures across wafer-length scales. Resist-stenciling can produce micropatterned reduction features with over ten times the feature density compared to techniques such as laser-scribing or screen printing. As a proof-of-concept, resist-stenciling is used to fabricate the first 2D micro-supercapacitors integrated into a layered graphene bionanocomposite. These demonstrate a specific capacitance of $\approx 128 \text{ F g}^{-1}$, good capacitance retention under charge cycling (87.5% after 2000 cycles), and repeated mechanical bending without failure. Resist-stenciling leverages tools currently in use by the microelectronics industry to enable the scalable, high-resolution conversion of layered nanocomposites into microelectronic circuit, storage, and sensing elements.

1. Introduction

The world is seeing a proliferation of distributed networks of miniaturized sensors and computers.[1] Connecting and powering these ubiquitous devices presents new challenges not met by current fabrication technologies. For instance, devices interfaced on clothing, on skin, or in the human body need to be soft and flexible, while conventional electronics are hard and rigid, unable to maintain performance to accommodate bending arising from bodily motion.[2] Additionally, renewable and readily available sources of energy (including light, wind, wasted energy in body motion, mechanical vibrations, and heat) cannot provide constant power, and are also distributed in nature. One promising avenue is the development next-generation energy-storage devices that are flexible to accommodate diverse use scenarios; and sufficiently small and low-cost to be ubiquitously placed to connect energy harvesters with sensing and computational components.[3]

Graphene oxide (GO) is a prospective candidate material for flexible conductors and energy storage. GO can be exfoliated from earth-abundant graphite using solution-scalable methods, and can adopt a wide gamut of mechanical and electronic properties via its reduction or surface modification.[4–6] The structure of GO consists of a monolayer hexagonal network of sp$^2$ hybridized carbon interspersed with sp$^3$ carbon bearing oxygen-containing functional groups, with hydroxyl and epoxy groups at the basal plane, and carboxy and carboxyl groups at sheet edges.[7] The removal of these oxygenated groups via reduction processes can produce an increase in conductivity by several orders of magnitude (up to $10^3 \text{ S m}^{-1}$ in graphene oxide–silk fibroin, GO–SF, composites), opening a route toward applications in flexible energy storage.[8–10] Much work has also focused on the assembly of nanocomposites, whereby GO acts as 2D “bricks” bound by 1D polymeric binders to yield nacre-like structures designed for superior mechanical properties, including extreme tensile strength (526.7 MPa in GO–chitosan),[11] Young’s modulus, toughness (13.9 MJ m$^{-3}$ reduced graphene oxide–silk fibroin, GO–SF),[12] and stretchability (up to 10.1% in GO–polyvinyl alcohol).[13] Synergistic effects arise from confined networks of intermolecular interactions to produce materials with superior mechanical properties in composites otherwise comprised of soft constituent components.[14–17] However, the investigation of layered graphene composites has been largely confined to structural applications.[6,7] Advanced multiplex functions can be introduced into graphene-based composites via directed assembly techniques such as layer-by-layer (LbL) assembly.[18,19] However, few works have explored multifunctional applications as microelectronic components.[20]

Exploration into introducing electrical conductivity into GO via reduction reactions began in earnest in the last decade,[7] and have yielded a plethora of chemical and physical methods. Chemical methods include reduction of GO by diverse reductants such hydrazine,[21,22] melamine,[23] anodic metals,[24,25] ascorbic acid,[26] while physical methods include reduction by thermal annealing,[27,28] electrochemistry,[29,30] microwave pulses,[31] and light irradiation.[32–34] However, most works focus on the indiscriminate, areal reduction of GO. These methods cannot localize the generation of conductive reduced GO features within the critical dimensions required by modern microelectronics, with current generation package substrates approaching sub-10 µm line width/space, and image pixels of camera phones at 1.5 µm.[35–37] High resolution, patterned reduction of graphene oxide on the single-micrometer length scale have been reported...
using strategies such as laser scribing,[38–40] ion beam conversion,[41–43] or contact by hot probe.[44] While these techniques can achieve reduced GO features with critical dimensions of approaching 100 \( \mu \)m for laser scribing, 20 nm for ion beam, and 12 nm for hot probe, ultimately, they are based on serial techniques that cannot scale for high-volume manufacturing across wafer- and panel-sized substrates.

In this work, we demonstrate the efficient fabrication of a flexible, micro-supercapacitors in a flexible, yet mechanically robust, GO bionanocomposite paper through a novel resist-stenciling technique. This technique employs photolithography to generate a photoresist stencil, coupled with electron beam deposition to localize the placement of chemically reduced features in the bionanocomposite at photolithographic length scales—demonstrating microstructured reduced GO features with sub-micrometer critical dimensions (as small as 0.8 \( \mu \)m). Our method can be generalized to enable the generation of microscale electrodes, antennae, and interconnects in graphene oxide-based composites, opening a route to leverage the incredible breadth of mechanical and electronic properties of GO and its derivative films.

2. Results

2.1. Guiding Metal-Assisted Reduction via Photolithography

Figure 1 shows the process scheme for generating conductive microtraces using resist templating. A typical photolithography process is employed to generate a resist-based mask that protects selective loci of underlying GO–SF from contacting the reductant. Using electron-beam deposition, an anodic metal such as Al is deposited through the resist mask. Here, the patterned resist acts as a conformal stencil to enable the transfer of the reduction pattern onto the underlying layered nanocomposite. GO–SF in contact with the aluminum undergoes controlled reduction as explored in a previous work.[10] The E-beam deposition of other common deposited metals such as Cu and Ti can also induce reduction, though to a lesser extent than by Al as demonstrate in a previous work.[10,45] Stripping the residual resist and washing the GO–SF biopaper lifts off the deposited Al and reveals reduced, conductive features written into the surface of the GO–SF biopaper (Figure 2).

The resist-stenciled method for patterned reduction described here is highly compatible with common photolithography processes. Herein, we successfully generated conductive features using both representative positive and negative tone resist stencils, respectively. Modifications were made (see the Supporting Information) to avoid baking at high temperatures.

Figure 1. Fabrication of conductive microtraces in flexible, tough GO–SF biopapers via photolithography to guide metal-assisted reduction. Inset images show from left to right, optical images at each step of (i) initial photomask, (ii) resist with transferred mask pattern, (iii) deposition of aluminum reductant, and (iv) conductive feature patterned in GO–SF after stripping resist.

Figure 2. a) Photograph showing GO–SF biopaper patterned with an array of micro-supercapacitors. Optical micrographs of micropatterned reduced GO–SF by resist stenciling in b) antenna motifs, and c) grating motifs.
which would cause warpage of the GO–SF biopaper due to mismatching coefficients of thermal expansion between layers and trapped moisture within the GO–SF. Reducing warpage ensured flat contact between the photomask and the resist-coated GO–SF to ensure optimal pattern transfer. The spin-coated resist helped make smooth inherent roughness on the surface of the GO–SF biopaper ($R_t = 52$ nm). Conformal contact between the resist mask and the GO–SF biopaper means the resist stencil acts as a hard stop against the reducing agent contacting protected areas. Other scalable methods of patterned reduction cannot ensure conformal contact. For instance, in shadow masking flash lithography, separation between mask, and GO-based substrate creates broad drop-off of reducing radiation intensity[14] while in stamping, asperities may block contact in surrounding loci to the reductant.[25] While screen printing can create conformal contact between reductant and GO composite surface, the deposited reductant may deform due prior to and during firing to fix the reductant paste shape.[9]

2.2. Characterizing Reduction of GO Component

Figure 2a shows a photograph of a GO–SF biopaper with patterned chemically reduced features. Regions of the biopaper that have undergone reduction change in visual appearance from the dull and brown characteristic of protected GO–SF biopaper to a gray and shiny appearance.[7] Figure 2 shows optical micrographs illustrating the wide variety of accessible geometries of conductive features that can be formed by the patterned reduction process. Using a common negative tone resist system, we obtained conductive features in the GO–SF with line widths as small as 800 nm. This critical dimension of conductive features written into the biopapers in this study was found to be defined by the dimensions of the resist stencil that is generated on top of the GO–SF biopaper. We expect the critical dimension of stencil features can be made even smaller with further optimization of process variables in the exposure, bake, and development steps. However, resist stencil features would be unlikely to match reported resolution limits on ideal substrates like polished Si, due to the biopaper substrate having a higher roughness which interferes with photomask placement during exposure, and lower thermal conductivity which may produce suboptimal bake times that affect resist development profiles.

Besides change in visual appearance after guided reduction by resist stencil, Figure 3 shows independent confirmation of chemical conversion by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy analyses. XPS reveals that the C/O ratio increases in regions exposed by the resist stencil to $3.6 \pm 0.2$, whereas protected regions retain the C/O ratio of $2.3 \pm 0.1$ matching the C/O ratio of the as-prepared biopaper.[25] This increase in the C/O ratio supports the partial removal of oxygen-containing moieties from the surface of GO–SF biopaper exposed by the resist stencil. The C1s spectra collected was deconvoluted into peaks centered around binding energies of 284.7, 286.5, and 288.5 eV; corresponding to carbon in the chemical states C–C, C–O, and C=O/O=O–C=O, respectively. Deconvoluted spectra show that the biopaper protected by the resist stencil has a significant fraction of surface carbon in higher binding energy chemical states, characteristic of carbon in oxygenated moieties represented in common models of GO.[7] Surface carbon in the biopaper unprotected by the resist stencil shifts toward lower energy chemical states indicative of sp$^3$ and sp$^2$ carbon–carbon bonds.

Figure 3b shows Raman spectra collected from biopaper points protected and unprotected by the resist stencil. The D- and G-bands (centered at 1350 and 1600 cm$^{-1}$, respectively) from graphitic materials are clearly visible in each case. Regions unprotected by the resist stencil and exposed to the Pt metal reductant show a simultaneous decrease in D-band width and increase in relative D-band peak intensity from 0.92 to 1.19. This increase in D-to-G band peak intensity is indicative of graphitization associated with GO reduction.[46] We use this change in relative peak intensity to map the areal extent of reduction (Figure 3c,e), with lighter colors signifying chemical reduction and corresponding to regions exposed by the resist stencil. Raman mapping reveals that features in the resist stencil such as fine 0.8 µm width lines. Examination of Raman mapping of line patterns (Figure 3c,e) also reveals an abrupt transition in peak intensity ratio with a width that corresponds with the stencil pattern line width of 10 and 0.8 µm respectively.

2.3. Integrated Micro-Supercapacitors on GO–SF Biopapers

We demonstrate the application of resist stencil-guided chemical reduction by fabricating integrated, nonflammable micro-supercapacitors into flexible GO–SF biopapers with enhanced mechanical robustness. Interdigitated electrode pairs are fabricated across the surface of GO–SF biopapers (Figure 2a), as small as $9 \times 10^{-4}$ mm$^2$ in footprint area, and having 2 µm interdigitated finger width and gap separation (Figure S2, Supporting Information). While pristine GO on its own has properties that promote energy storage such as high specific surface area and surface moieties that promote pseudocapacitive Faradic reactions, its performance as an active material is limited by low electrical conductivity due to the presence of oxygenated moieties that disrupt the sp$^2$ basal plane.[8,47] While the presence of interspersed SF in GO–SF biopapers promote GO flake spacing, it further lowers the conductivity to $=1 \times 10^{-2}$ S m$^{-1}$.[16] On the other hand, metal-assisted reduction increases electrical conductivity of GO–SF by over six orders of magnitude up to $1.5 \times 10^{-2}$ S m$^{-1}$.[10] As a control, Pt wires secured with a spacing of 2.4 mm by micromanipulators across protected GO–SF show negligible integrated area and capacitance by cyclic voltammetry (CV) testing (Figure S4, Supporting Information).

Here, resist stenciling enables the rational placement of microstructured reduced GO–SF features as interdigitated fingers and busbars to facilitate charge collection, and electric double layer formation across the large area at the patterned electrode surface and edges. We showcase the fabrication of interdigitated microelectrodes with as small as 2 µm fingers, and $9 \times 10^{-4}$ mm$^2$ footprint (Figure S2, Supporting Information).

Solid state micro-double layer capacitors (EDLCs) were fabricated by swelling the produced and patterned GO–SF paper in
an aqueous 6 \textit{m} KOH solution to induce ionic conductivity and effectively fabricate a silk gel electrolyte. Reduced portions of the paper serve as electrodes, while the electronically insulative portion in between the electrodes serves as a separator. Using CV, we investigate the charge storage behavior of the micropatterned GO–SF.

EDLCs with a rather thick (400 \textmu m width) busbars collecting current from interdigitated and still relatively thick (200 \textmu m) width fingers (Figure 4a, inset), forming symmetric electrodes. The separator membrane portion was designed to exhibit serpentine shape and a relatively large width of 200 \textmu m (Figure 4a, inset). Note that “regular” commercial devices typically utilize thinner (75–50 \textmu m) electrodes and thinner (10–25 \textmu m) separators to achieve higher power capabilities. We utilized larger dimensions for simplicity sufficient for this proof-of-concept device fabrication.

As a control, Pt wires secured with a spacing of 2.4 mm by micromanipulators across protected GO–SF show negligible integrated area and capacitance by CV testing (Figure S4, Supporting Information). At a scan rate of 10 mV s$^{-1}$, the specific capacitance ($C_{sp}$) of fabricated devices reach $\approx 130$ F g$^{-1}$, which is comparable with many reduced GO-based and activated carbon-based electrodes reported previously (up to $\approx 150$ F g$^{-1}$ in aqueous KOH-based gel electrolytes)\cite{48-51}. Distortion from the perfect horizontal rectangular shape of an ideal EDLC CV (Figure 4b) might be expected due to large electrode and separator dimensions and the associated increased contribution of the electrolyte resistance as well as other factors.\cite{52}
Figure 4 illustrates the effects of increasing the equivalent series resistance ($R_S$) and increasing the leakage current (or decreasing the leakage resistance, $R_L$) on the shape of the cyclic voltammogram curve, given a simple equivalent circuit model of an EDLC. Clearly, in the experimental curves, a significant equivalent series resistance is revealed. Runaway electrolyte decomposition at extreme potentials (discussed more below) may be described as a form of current leakage current, but cannot be described with a constant resistance $R_L$. (Given the large equivalent series resistance and significant current runaway at extreme potentials, we do not try to deconvolute the magnitude of any potential difference-independent/constant leakage resistance.)

More specifically, such distortions may generally be associated with (i) kinetic limitations (e.g., insufficiently fast ion transport from the bulk of the electrolyte to the graphene surface to form a double layer), particularly evident at faster sweep rates; (ii) leakage current (e.g., due to insufficiently high electric resistance of the GO–SF composite or parasitic side reactions); (iii) electrolyte decomposition (particularly at higher voltages) and (iv) various redox processes (e.g., pseudocapacitance reactions). Reducing electrode/separation layer dimensions by, for example, 4 times or more (to approach typical dimensions in commercial EDLCs) should enhance the rate performance of the device by over 16 times and reduce the contribution of the electrolyte resistance to the slope observed in the CV curves by 4 times. Based on the low electrical conductivity in GO–SF layer, which should be reduced further upon silk swelling in the electrolyte we expect that its contribution to the leakage current to be insignificant. The sharp current increase observed at above 0.7 V in our symmetric EDLCs is associated with water decomposition and is typical for KOH-based aqueous electrolyte solutions.\textsuperscript{49} We do not observe a clear redox peaks within 0.6 V. However, this does not necessarily mean that the contributions of Faradaic reactions and pseudocapacitance is negligible because in many cases the pseudocapacitive materials exhibit very broad CV peaks.\textsuperscript{53}

In order to observe accelerated aging we tested cycle stability of the produced EDLC at a relatively high maximum voltage of 1 V (compared to 0.6 V commonly used in academic studies to avoid decomposition of water, electrode drying, and formation of microgas bubbles that further reduce access of electrolyte to
the inner electrode surface area. Still the observed stability of micro-EDLCs fabricated in GO–SF was quite reasonable. The device retained ~88% after 2000 charge cycles, which is in-line with laboratory-fabricated EDLCs with gel electrolytes cycled in a similar voltage range.\textsuperscript{[49]} Slight decrease in capacitance retention after thousands of charge–discharge cycles is a common phenomenon in supercapacitors. As charge is cycled through operation, there may be changes to electrode surface morphology or to the electrode porosity. Either of these phenomena may decrease the accessible surface area to the electrolyte, reducing the double-layer effect. Yet, it is inferior to EDLCs based on regular aqueous electrolytes, cycled within a lower voltage window and commonly comprising excess of electrolyte, which may show similar capacity retention after over 100 000 cycles or more.

Micropatterned GO–SF EDLCs also demonstrate high mechanical robustness. Whereas layered composites, such as pristine GO paper, show low wet strength and will swell and fall apart in aqueous solution—the SF binder preserves the integrity of the GO–SF biopapers in the electrolyte (Figure S3, Supporting Information). This enables the micro-supercapacitors fabricated in GO–SF biopapers to undergo repeated 90° bending (bend radius as little as ~1 mm) without tearing. CV profiles show that the GO–SF still preserve a large integrated area, retaining 82.2% ± 7.1% of original capacitance after 10 bending cycles, and 77.0% ± 8.9% capacitance after 20 bending cycles (Figure 4d). We believe the decreased EDLC performance to arise from bending causing closure of pores on the surface of the reduced GO–SF microelectrodes, decreasing the total electrode surface and ability to support the electrical double layer. However, we note that the capacitance retention is significantly higher for the second set and subsequent sets of bending. This presents a tradeoff whereby the capacitance retention during device operation can be tuned high at the expense of rated capacity by “priming” the GO–SF micro-supercapacitors via prebending.

Unlike the previously reported macroscopic EDLCs, the flat and flexible micro-EDLCs generated by resist-stenciling can readily integrate into miniaturized packages and into current generation 2D integrated circuits. We expect that \( C_{\text{eq}} \) of GO–SF micro-EDLCs could be further increased with optimization of electrolyte, to enhance microelectrode double layer coverage; and the inclusion of transition metal oxide nanoparticles (such as VO\(_x\), CoO, NiO, Fe\(_2\)O\(_3\), RuO\(_2\), or MnO\(_2\)) to enhance contribution from pseudocapacitance.\textsuperscript{[8]} In the latter example, highly conductive graphene features generated by resist-stenciling can enhance the traditionally low conductivity associated with oxide-based pseudocapacitive materials.

3. Conclusion

We report for the first time the fabrication of sub-micrometer chemically reduced features in a graphene oxide–silk bio-nanocomposite. We accomplish this through guiding the electron-beam deposition of reductant using a photore sist stencil–generating conductive micropathways in GO with feature density over an order of magnitude higher than previously reported techniques such by laser-scribing or screen printing. Because this novel technique for GO reduction leverages common wafer- and panel-level scale techniques in the micro-electronics industry, it can achieve an unprecedented combination of resolution and manufacturing scalability.

The successful transfer of complex electronic circuits into a layered GO biocomposites opens the possibility of robust, tough, yet flexible, electronic components to be assembled from Earth-abundant, low-embedded energy materials such as silkworm silk and graphite. We showcase here that complex reduction features in GO–SF in the form of antenna, wire interconnects, and energy storage devices, as flexible micro-electric double layer capacitors with high specific capacitance of ~130 F g\(^{-1}\). The GO–SF micro-supercapacitors are extremely robust—they do not short-circuit and do retain their capacitance after repeated mechanical bending and charge cycling. This work opens a route for flexible nanocomposites to be converted into microelectronic substrates and interconnects that can enable the proliferation of ubiquitous sensing and computing.

4. Experimental Section

**Vacuum-Assisted Lbl Assembly of GO–SF Biopapers:** SF binder was extracted from the cocoon of the *Bombyx mori* silk worm in accordance with protocols pioneered by Kaplan and co-workers.\textsuperscript{[34]} Briefly, *B. mori* cocoons were cut and boiled in 0.02 m H\(_2\)CO\(_3\) for 30 min, then washed three times with ultrapure (18.2 M\(\Omega\)cm) water to yield degummed silk fibers. Silk fibers were solubilized in 9.3 m LiBr (at 1:10 wt. ratio of silk fiber to LiBr solution) at 60 °C for 2 h. The solubilized SF was dialyzed against water to yield an aqueous stock solution of SF in water at a concentration of 50 mg mL\(^{-1}\). GO flakes were exfoliated according to the method of Hummers’ from natural graphite powder (325 mesh, Alfa Aesar, USA) and diluted by ultrapure water to 5 mg mL\(^{-1}\).\textsuperscript{[53]} To the GO dispersion was stirred the SF suspension to yield 3% dry weight SF. The GO–SF was collected onto a membrane filter (Pall Versapor, acrylic copolymer, 0.2 µm pore size) via a vacuum filtration setup to yield GO–SF biopapers with a flat side (filter side), and a rough side (air side).

**Fabricating of Resist Stencil to Guide Biopaper Reduction:** The rough side of the GO–SF biopaper was mounted against a glass slide by glue stick. A patterned photore sist layer acts as a stencil to protect regions from GO reduction. In a typical experiment, negative-tone NR9-1500 py (Futurrex, Frankling, NJ, USA) was diluted in cyclohexanone and spin-coated onto the GO–SF biopaper. The Al-coated GO–SF was dampened deposited via E-beam deposition (Mark 50, CHA Industries) onto the GO–SF biopaper. Residual Al was removed by washing the GO–SF biopaper in 0.1 m HCl, and ultrapure water to yield GO–SF biopapers.

**Generation of Conductive Microtraces in GO–SF Biopapers:** Electrochemical reduction of exposed GO–SF was undertaken by using a metal-assisted reduction technique based on methods previously reported by the lab.\textsuperscript{[9,10]} A 500 nm thick layer of Al, an anodic metal, was deposited via E-beam deposition (Mark 50, CHA Industries) onto the resist-stenciled GO–SF biopaper. The Al-coated GO–SF was dampened with ultrapure water (18.2 M\(\Omega\)cm), and clamped between PTFE blocks to undergo reduction for 4 h, generating a depth of reduction feature of 1.2 µm as determined in a previous work.\textsuperscript{[10]} The Al-coated GO–SF is agitated in acetone to strip the residual resist, and lifting off large regions of coated Al. Residual Al was removed by washing the GO–SF biopaper in 0.1 m HCl, and ultrapure water to yield GO–SF biopapers.
The mass of the reduced GO–SF active material was determined by scan rate, and mass of active material. Voltammetric charge was reduction depth is 1.16”. Cyclic bending/unbending was performed for patterned GO–SF within a biographene paper, energy storage, microcapacitors, micropatterned conductive regions in the negative pattern of the GO–SF Biopaper. The reduction patterned biopaper was soaked in 6 M KOH for 1 h under vacuum to allow for intercalation of electrolyte. The electrode from the author.

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors would like to thank the financial support from the Air Force Office for Scientific Research (FA9550-17-1-0297) and National Science Foundation (Award No. NSF-1538215).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
biographene paper, energy storage, microcapacitors, micropatterned conductive regions with micropatterned conductive regions in the negative pattern of the photomask. 

Characterizing-Reduced Features in GO–SF Biopapers: Reduced features on GO–SF biopapers were imaged by optical microscopy using a Leica DM 4000, and by low-voltage cold field emission scanning electron microscopy (Hitachi SU8230). Verification of chemical reduction was done by X-ray photoelectron spectroscopy (Thermo Scientific K-alpha), and Raman spectroscopy (Alpha-WiTec Alpha 300R, 532 nm laser).

Fabricating and Characterizing Micro-Supercapacitors Integrated into GO–SF Biopaper: Conductive features were fabricated in the shape of interdigitated electrode pairs using resist stenciling to guide the reduction of GO–SF biopaper. The reduction patterned biopaper was soaked in 6 M KOH for 1 h under vacuum to allow for intercalation of electrolyte. The electrode busbars were clamped against Pt wires and connected to potentiostat (VersaSTAT 3, Princeton Applied Research) for CV characterization at different scan rates (10, 50, 100, 200, 500, and 1000 mV s⁻¹). Cᵣₑ was evaluated by voltammetric charge divided by potential window, scan rate, and mass of active material. Voltammetric charge was determined by sum of integrated area of anodic and cathodic sweeps. The mass of the reduced GO–SF active material was determined by expression: active material area × reduction depth × GO–SF density, where reduction depth is 1.16 μm, and reduced GO–SF density of 1.8 g cm⁻³. Cyclic bending/unbending was performed for patterned GO–SF within a hinge (bend angle 90°, bend radius =1 mm) at 100 mV s⁻¹.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Received: August 5, 2018
Revised: September 25, 2018
Published online: