Facile Fabrication of Flexible In-Plane Graphene Micro-Supercapacitor via Flash Reduction

Seok Hun Kang, In Gyoo Kim, Bit-Na Kim, Ji Hwan Sul, Young Sun Kim and In-Kyu You

Flash reduction of graphene oxide is an efficient method for producing high quality reduced graphene oxide under room temperature ambient conditions without the use of hazardous reducing agents (such as hydrazine and hydrogen iodide). The entire process is fast, low-cost, and suitable for large-scale fabrication, which makes it an attractive process for industrial manufacturing. Herein, we present a simple fabrication method for a flexible in-plane graphene micro-supercapacitor using flash light irradiation. All carbon-based, monolithic supercapacitors with in-plane geometry can be fabricated with simple flash irradiation, which occurs in only a few milliseconds. The thinness of the fabricated device makes it highly flexible and thus useful for a variety of applications, including portable and wearable electronics. The rapid flash reduction process creates a porous graphene structure with high surface area and good electrical conductivity, which ultimately results in high specific capacitance (36.90 mF cm^{-2}) and good cyclic stability up to 8,000 cycles.

Keywords: Flexible, Graphene, In-plane, Micro-supercapacitor, Photoreduction.

I. Introduction

With the advent of new technologies, there is an increasing demand for microscale energy storage devices that can power next-generation miniaturized electronics such as microsensors, radio frequency identification tags, microelectromechanical systems, and portable wearable devices [1]–[3]. Among various micro energy storage systems, micro-supercapacitors (MSCs) have attracted much research attention owing to their high power density, fast charge/discharge (CD) rates, and long cycle life, which make them more attractive than their battery counterparts [4]–[7]. Progress in micro-fabrication techniques has made the production of MSCs with an interdigital planar structure possible in various ways, including photolithography [3], etching [8]–[10], selective wetting [11], and others [12]–[14]. However, these fabrication techniques are limited to photolithography or etching methods that require complex fabrication steps and are generally costly, which makes them unsuitable for commercial applications. Direct printing techniques, such as spray deposition [4], [15], inkjet printing [16], and micro-extrusion [17], have also been proposed, but they require an additional thermal or chemical reduction step to reduce graphene oxide (GO) ink into conductive electrode material. Thus, a new strategy is required for low-cost, large-scale fabrication of MSCs suitable for device commercialization.

Recently, photoreduction technique was proposed as an alternative method for producing in-plane MSCs. Gao and others [18] first reported a direct laser writing technique that selectively reduces the desired area of hydrated GO film into reduced GO (rGO), thus enabling patterning of interdigitated electrodes for MSCs. Following their work, many laser-induced in-plane MSC fabrication studies using graphene or other nanocomposites have been

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reported [19]–[22]. Although these approaches are promising, the laser scribing technique is still limited to slow scan speeds of micro patterning. A more facile photoreduction approach was proposed by Park and Kim [23], which includes GO reduction with flash light irradiation. Using this approach, rGO can be produced in a cost-effective manner via exposure to flash light irradiation under room temperature ambient conditions. A similar concept was adopted by Xue and others [24] when they used ultraviolet (UV) light as an optical source to reduce GO; however, UV light requires 24 h of irradiation for effective reduction.

In this study, we report a facile fabrication method for an interdigitated graphene MSC with a single flash irradiation, which occurs in only a few milliseconds. This process is even more scalable than laser scribing techniques because it can reduce a large area of GO film instantaneously. By employing a photomask with the desired interdigital pattern, multiple MSCs can be flash-printed with a single flash, which occurs in only a few milliseconds. The scalability of this fabrication technique is limited only by the exposure area of the flash-lamp, which can be easily scaled up by installing multiple lamps. The produced device exhibits specific capacitance of 36.90 mF cm^{-2} at a scan rate of 0.2 mA cm^{-2}, comparable or even superior to those of other graphene MSCs reported in the literature. The all-solid-state MSC demonstrated herein is extremely thin and flexible, thereby showing high electrochemical stability under different bending conditions, which highlights its potential application in portable and wearable electronics.

II. Experimental Section

1. Flash Reduction of Interdigital Electrodes

A solution of 6 g L^{-1} GO (Grapheneall Co. Ltd., product no. GO_A400) was coated on a 100 μm-thick polyethylene terephthalate (PET) film using a film applicator and dried under room temperature ambient conditions for 24 h to produce a GO-coated PET film. A stainless steel photolithography mask of the desired interdigital pattern was custom-ordered. The photolithography mask was used to selectively expose GO to xenon irradiation from flash lamp equipment (NovaCentrix, pulse forge 1300). The photoreduction conditions were optimized by controlling various parameters of the flash lamp equipment, including the voltage, pulse width, exposure energy, and exposure time (Fig. S3).

2. Fabrication of All-Solid-State Flexible Supercapacitor

The flash-reduced interdigital pattern was directly used as an electrode for the all-solid-state flexible in-plane supercapacitor. A small amount of Ag paste was applied to the two ends of the interdigital pattern to ensure electrical contact between the electrode and current collector. Cu alligator clips were clipped onto the Ag paste area to serve as current collectors. Kapton tape was applied to the top of the alligator clips and Ag paste area, covering four sides of the interdigital pattern. Note that Kapton tape should completely cover the Ag paste area so that the gel electrolyte does not come in contact with the Ag paste. A polyvinyl alcohol (PVA)-H_2SO_4 gel electrolyte, prepared by mixing PVA, H_2SO_4, and deionized water in a ratio of 1 g: 1 g: 10 mL at 80 °C for 1 h, was drop-casted on top of the flash-reduced GO (FrGO) pattern confined by Kapton tape and dried in a vacuum desiccator to enhance the infiltration of electrolyte.

3. Material Characterization

The microstructure and elemental analysis of FrGO were investigated using field-emission scanning electron microscopy (SEM, SU8230, Hitachi). Electrical conductivity measurements were carried out using a four-point probe station (Dasoleng Co., Ltd.). The material surface was characterized using X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific), high-resolution powder X-ray diffractometry (Smartlab, Rigaku), and high-resolution Raman spectroscopy with a 514-nm laser source (LabRAM HR Evolution Visible–NIR, Horiba). The electrochemical performance of the fabricated flash-printed MSCs (FP-MSCs) was investigated by measuring the cyclic voltammetry (CV), galvanostatic CD, and electrochemical impedance spectroscopy (EIS) using the PARSTAT MC electrochemical workstation (Princeton Applied Research). All the measurements were performed under room temperature ambient conditions.

4. Calculations

The capacitance of the FP-MSC was calculated by analyzing its galvanostatic discharge after IR drop using the following equation:

$$C = \frac{I \times \mathrm{d}t}{-\mathrm{d}V}, \quad (1)$$

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where C is the cell capacitance in Farad, I is the discharge current, t is the time of discharge, and V is the voltage after the IR drop. The areal capacitance of a single electrode (mF cm^{-2}) was calculated using the following equation:

$$C_A = 4 \times \frac{C}{A}, \quad (2)$$

where A is the area of the FrGO electrode. The factor of 4 adjusts the cell capacitance of two electrodes to the capacitance of a single electrode. The volumetric capacitance of a single electrode (mF cm^{-3}) was calculated by dividing the areal capacitance by the average thickness t of the FrGO electrode.

$$C_V = 4 \times \frac{C}{A \times t} = \frac{C_A}{t}. \quad (3)$$

The energy density (mWh cm^{-3}) was calculated using the following equation:

$$E = \frac{C \times (\Delta V)^2}{2 \times 3,600 \times A \times t}, \quad (4)$$

where ΔV is the voltage drop after the IR drop.

The power density (mW cm^{-2}) was calculated using the following equation:

$$P = \frac{(\Delta V)^2}{4R_{ESR} \times A}, \quad (5)$$

where R_{ESR} is the equivalent series resistance given by:

$$R_{ESR} = \frac{V_{drop}}{2I} \quad (6)$$

and V_{drop} is the IR drop at the beginning of the galvanostatic discharge profile.

III. Results and Discussion

The fabrication process of the FP-MSC is schematically illustrated in Fig. 1(a). A thin GO film was prepared by coating viscous GO dispersions on a flexible PET substrate and drying it under room temperature ambient conditions. The dried GO film was selectively exposed to xenon pulse irradiation by masking the film with a shadow mask of a predesigned interdigital pattern. The high-energy xenon light causes a rise in the local temperature of the exposed GO surface, resulting in photo-induced thermal reduction of the oxygen functional groups. Removing the shadow mask revealed a black interdigitated FrGO pattern on the gray GO surface. Flash reduction occurs in only a few milliseconds and multiple patterns can be fabricated simultaneously (Fig. S1), making this process more scalable than other MSC fabrication techniques, such as photolithography, direct printing, and laser scribing. In conventional sandwich-type supercapacitors, an additional assembly step is required to separate two electrodes with an insulating separator. However, using this approach, the non-reduced region of GO between two interdigitated FrGO patterns can retain the insulating property of GO and thus, it can be used as a separator to divide the two FrGO patterns. Consequently, FrGO patterns can be used directly as electrodes for an in-plane configurational supercapacitor, which further simplifies the fabrication of such MSCs. Cu clips were used as current collectors and Ag paste was applied to ensure electrical contact between the electrode material and current collectors. Subsequently, a polyimide (Kapton) tape was used to define the interdigitated area and to cover and protect the current collectors from the electrolyte contact. A PVA-H_2SO_4 gel electrolyte was drop-casted on the confined area to create an all-solid-state flexible in-plane supercapacitor (Fig. 1(b)).

Optimization of the photoreduction conditions is crucial for achieving both high conductivity and high capacitance of the FP-MSC. A photograph of the xenon flash lamp equipment and the time-resolved power profile are shown in Fig. S2. Generally, the electrical resistance of the FrGO decreases with the increase of voltage, energy, and the number of flashes (Fig. S3). However, if the parameters mentioned above are set too high, the high-energy xenon light causes ablation of the GO film, which reduces the amount of FrGO that can be used as electrode material. The optimal conditions were determined experimentally to fabricate a high performance FP-MSC.

Figure 2 shows the photograph and SEM images of the FrGO. A clean interdigitated pattern of the FrGO (200 μm width, 200 μm spacing, 10 mm length) was formed within a few milliseconds of exposure to xenon light

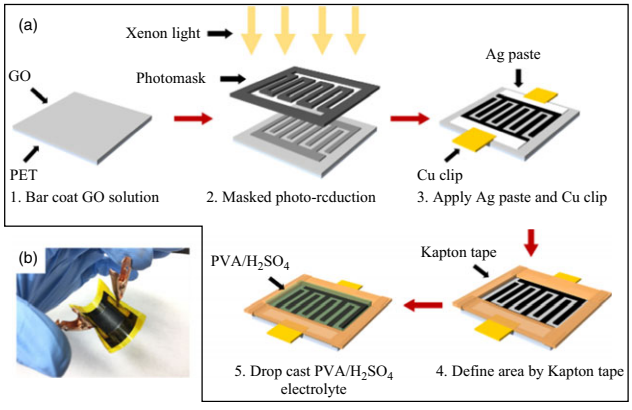

Fig. 1. (a) Schematic illustration of the fabrication process of FP-MSC and (b) photograph image of a flexible FP-MSC.

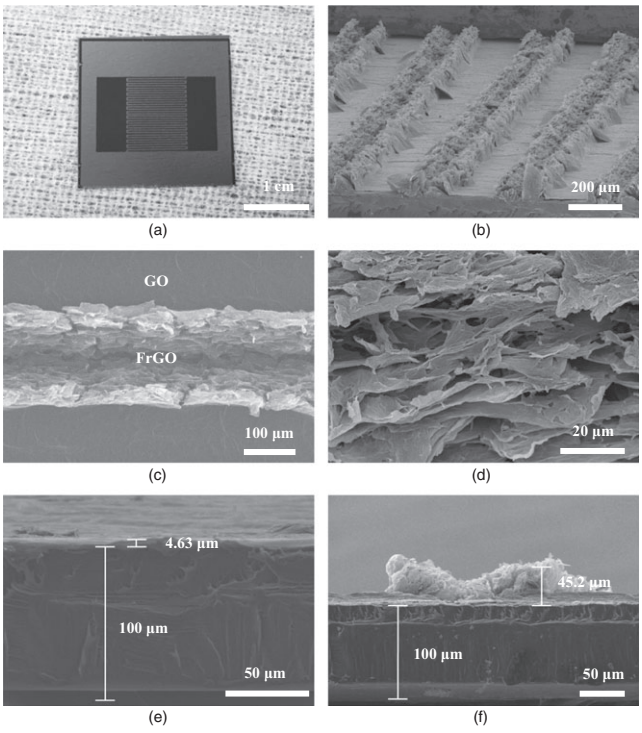

Fig. 2. (a) Photograph of the FrGO interdigital electrode. SEM images of FrGO interdigital electrode shown in (b) tilted view, (c), (d) top view, and (e), (f) cross-sectional view.

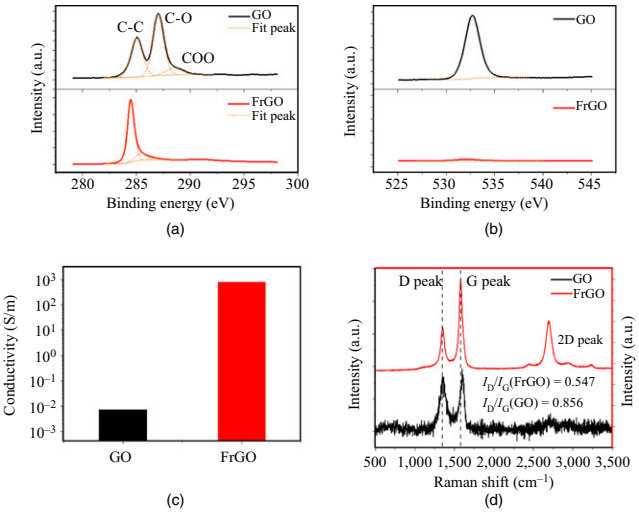

Fig. 3. Material characterization of untreated GO and FrGO. (a) C1s and (b) O1s XPS spectra; (c) conductivity comparison using a four-point probe; (d) Raman spectroscopy results.

(Figs. 2(a)–(c)). High magnification of the FrGO region indicates the formation of a porous structure owing to the rapid reduction of oxygen functional groups and the subsequent release of gas by-products during the flash reduction (Fig. 2(d)). Analysis of the cross-section of the film reveals an increase of the thickness of the GO film from 5 μm to 45 μm (Figs. 2(e) and (f)) after reduction. Such volume expansion is favorable for a supercapacitor electrode as it creates a highly porous rGO structure capable of facilitating electrolyte infiltration. Energy-dispersive X-ray spectroscopy (EDS) mapping of an FrGO finger pattern in Fig. S4 reveals the successful reduction of oxygen element and the strong presence of C element in the FrGO region. The dark region in the center of the FrGO finger could not be analyzed using EDS mapping owing to the difference in height. The presence of sulfur is most likely due to the impurities present in the purchased GO dispersion.

Successful reduction of FrGO was confirmed using various material characterization methods. XPS profiles (Figs. 3(a) and (b)) show the distinct disappearance of oxygen peaks resulting from the reduction of oxygen functional groups. The level of reduction was quantified by calculating the C/O atomic composition ratio of XPS profiles before and after photoreduction. The C/O ratio drastically increases from 1.76 to 63, indicating a high degree of reduction and removal of oxygen functional groups. The restoration of graphitic lattice owing to reduction is reflected by a significant increase of film conductivity (Fig. 3(c)). The four-point probe measurement of untreated GO and FrGO revealed the electrical conductivity of 7.14×10^{-3} S m^{-1} and 7.91×10^{2} S m^{-1}, respectively, showing an increase of conductivity by a magnitude of five. Owing to its high electrical conductivity, FrGO can be used directly as electrode material without additional reduction treatment.

Raman spectroscopy in Fig. 3(d) further confirms the high degree of reduction of GO after exposure to flash irradiation. Three characteristics peaks of graphene can be observed at 1,350 cm^{-1}, 1,580 cm^{-1}, and 2,700 cm^{-1} corresponding to D, G, and 2D peaks, respectively. Typically, in the Raman spectrum of graphene, the G peak represents the in-plane bond-stretching motion of C sp_2 atoms and the D peak represents disruption in the carbon lattice symmetry [25]. The prominent D peak in the Raman spectra of untreated GO indicates the presence of a structural disorder induced by the presence of residual oxygen functional groups on the carbon basal plane [26]. The D peak is significantly diminished after exposure to flash light irradiation, indicating the removal of oxygen functional groups and the restoration of graphene lattice symmetry. The intensity ratio between the D and G peaks (I_D/I_G), which is commonly used to quantify the level of reduction, is decreased from 0.856 to 0.547 after flash irradiation, indicating successful reduction of GO. The

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appearance of a sharp 2D peak at 2,700 cm^{-1} also indicates the formation of few-layer graphene after flash reduction [27].

Owing to the high electrical conductivity and porous structure of the FrGO, the FrGO pattern can be directly used to fabricate an in-plane MSC by drop-casting PVA-H_2SO_4 gel electrolyte. As shown in Fig. 4(a), the fabricated FP-MSC exhibits CV curves that are nearly rectangular in shape, indicating capacitive behavior under scan rates from 10 mV s^{-1} to 500 mV s^{-1} (higher scan rates shown in Fig. S5). Galvanostatic CD profiles exhibit an ideal triangular shape (Figs. 4(b) and (c)), indicating electric double-layer storage mechanism. The FP-MSC device exhibits high areal capacitance of 36.90 mF cm^{-2} at a scan rate of 0.2 mA cm^{-2}. This value is far superior to those reported in the literature for carbon-based electric double-layer capacitor MSCs, including laser-reduced MSCs, which exhibit capacitance values of 1 mF cm^{-2} to 2 mF cm^{-2} [19], [21], [28]. The high capacitance value can be attributed to the porous structure of the FrGO resulting from the rapid reduction process and the high reduction depth of xenon irradiation. The volumetric capacitance of a single electrode calculated using the thickness of the FrGO region is 9.01 F cm^{-3} and the energy density of the device is 0.30 mWh cm^{-3}. These values are lower than those reported in the literature owing to the low-density porous architecture resulting from flash reduction. However, the volumetric capacitance is often an overestimate of the actual device capacitance for micro devices and the FP-MSC possesses sufficient capacitance for practical application to power miniaturized electronics.

The FP-MSC displays excellent stability (Fig. 4(e)) under repeated CD cycles. The capacitance initially increases for the first 3,000 cycles, reaching 110% of its initial value. A possible explanation of this phenomenon was reported previously in the literature as "electro-activation" [29]. The authors suggested that intercalation of electrolyte ions between graphene sheets during the initial charge cycles increases the spacing between the sheets, which improves the accessibility of electrolyte ions to graphene surface. This phenomenon was confirmed by Beidaghi and Wang, who showed that electro-activation did not occur for rGO composite electrodes when carbon nanotubes were used as spacers between rGO sheets [15]. The capacitance of the FP-MSC remains at 87% of its initial value even after 8,000 cycles of repeated CD, indicating excellent cyclic stability.

The power performance of the FP-MSC was investigated by measuring the EIS in the frequency range of 10 mHz to 100 kHz (Fig. 4(f)). The electrochemical

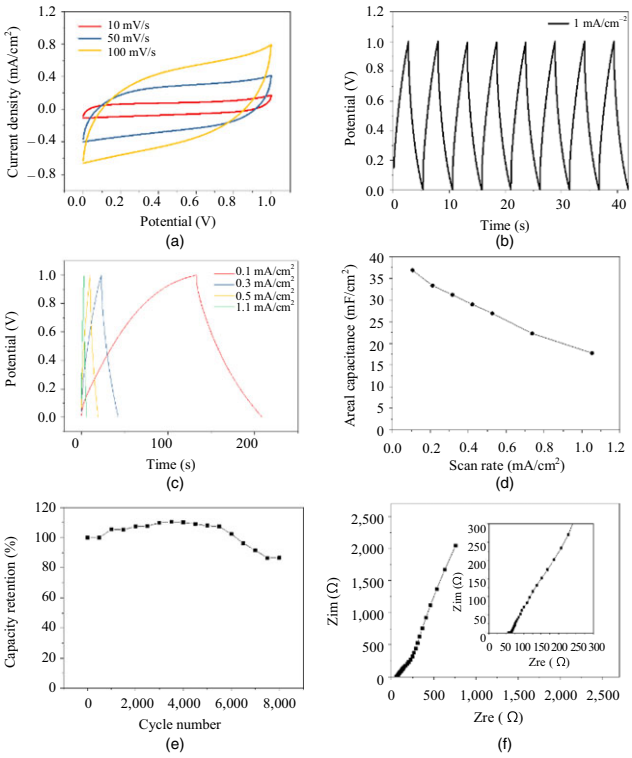

Fig. 4. Electrochemical analysis of the FP-MSC. (a) CV curves at various scan rates, (b) CD curves measured at a scan rate of 1 mA cm^{-2}, (c) CD curves at various scan rates, (d) areal capacitance measured at different discharging rates, (e) Capacity retention during 8,000 cycles of repeated, CD at a rate of 1 mA cm^{-2}, and (f) EIS spectra: the inset shows a magnified view in a low-frequency range.

series resistance estimated by calculating the real axis intercept of the low-frequency impedance spectrum was 54.5 Ω. This value is also reflected by the equivalent series resistance (ESR) calculated using the IR drop at the beginning of galvanostatic discharge, which was calculated to be 58.6 Ω. Generally, solid electrolytes exhibit lower ionic conductivity than liquid electrolytes. The ESR values of the in-plane all-solid-state supercapacitors fabricated using gel electrolytes reported in literature were above 50 Ω [11], [30]. Considering the intrinsic limitation of solid gel electrolytes, the FP-MSC shows good electrolyte diffusion characteristics owing to the volume expansion of the FrGO electrode during the rapid reduction process, which allows facile electrolyte ion transport. The areal power density of the FP-MSC calculated using the ESR was 4.28 mW cm^{-2}.

Owing to the thin nature of the device, the FP-MSC shows outstanding stability against mechanical bending motion. To test the flexibility of the device, CV was measured for the FP-MSC bent to various angles. Even

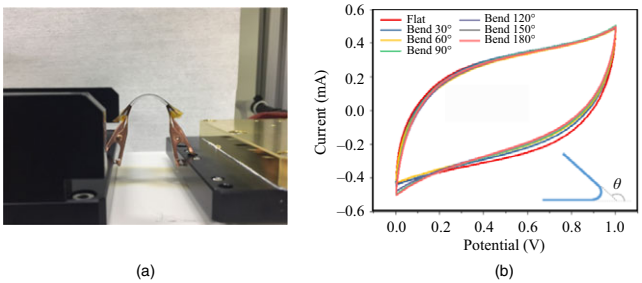

Fig. 5. (a) Photograph of FP-MSC in a bent state and (b) CV curves of the FP-MSC at various bend angles measured at a scan rate of 50 mV s^{-1}.

when the device is bent to 180°, the FP-MSC shows no obvious degradation in performance, as shown in Fig. 5(b). Even at a high bending angle of 180°, the capacitance remains at 90% of its original value. The excellent flexibility of the device makes the FP-MSC promising for portable and wearable electronics.

IV. Conclusion

In summary, a facile fabrication method of a flexible in-plane graphene MSC using xenon irradiation was proposed. Multiple rGO interdigital electrodes can be fabricated within a few milliseconds of flash irradiation and can be directly used as MSC electrodes in in-plane configuration without requiring additional thermal/chemical treatment or the addition of conductive additives or polymer binder. Such a device exhibits high areal capacity, high energy and power densities, and superior cycling stability up to 8,000 cycles. The microscale thickness of the entire device makes it durable against severe mechanical bending motion, with negligible performance degradation even at critical bending angles. This simple and cost-effective method of fabricating MSC devices can be promising for the commercialization of MSCs for next-generation miniaturized electronics.

V. Associated Content

Photograph of multiple FrGO electrodes, photograph and time-resolved power profile of xenon flash lamp equipment, optimization of photoreduction conditions, EDS mapping images of FrGO electrode, and CV curves at high scan rates.

Acknowledgements

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Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's web-site:

Fig. S1. Photograph image of multiple FrGO patterns printed with a single flash. The fabrication process can be easily scaled up by employing a larger photomask.
Fig. S2. (a) Photograph image of the Xenon flash lamp equipment and (b) Time resolved power profile of the Xenon flash light.
Fig. S3. Optimization of the photo reduction conditions for enhanced electrical conductivity of FrGO. (a) Resistance vs. voltage at a constant pulse time, (b) Resistance vs. voltage at a constant energy, and (c) Resistance vs. the number of flashes at a constant voltage, pulse time, and energy.
Fig. S4. (a) SEM image of a FrGO finger. (b) Allocated pixels for EDS mapping of the FrGO finger. EDS mapping of the (c) C element, (d) O element, (e) S element, and (f) the overlay of C, O, S elements.
Fig. S5. CV curves at scan rates of 100 mV s^{-1}, 300 mV s^{-1}, and 500 mV s^{-1}.

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