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Ultraflexible in-plane Micro-Supercapacitors by Direct Printing of Solution-Processable Electrochemically Exfoliated Graphene

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Key words: printing, in-plane, micro-supercapacitors, electrochemically exfoliated graphene, energy storage

With portable and miniaturized electronic devices becoming increasingly pervasive in our daily lives, there is a growing demand for lightweight, flexible, and highly efficient micro-scale energy storage devices.^[1] Current commercially available thin-film batteries, which incorporate micro-scale power sources into electronics and micro-systems, suffer from various limitations, such as a short cycle life, abrupt failure, poor low-temperature kinetics, and safety concerns associated with using lithium.^[2] Moreover, the integration of batteries

with electronic circuits is challenging and often limits the miniaturization of the entire system.

^[3] This effect occurs because the necessary energy-storage components scale down in size poorly and are not well suited for the in-plane geometries of integrated micro-fabrication processes. Recently, in-plane micro-supercapacitors (MSCs) have emerged as potential candidates to complement or even replace micro-batteries in various applications because they can provide a high power density, a fast charge/discharge rate, and a long cycle life.^[4] Advanced progress in micro-fabrication technology has enabled on-chip MSCs in an interdigitated planar form.^[2c, 3, 5] All-solid-state MSCs that do not use a liquid electrolyte can be directly implemented as embedded energy-storage devices for portable and wearable microelectronics systems. However, the conventional fabrication techniques for MSC devices rely primarily on photolithography or on oxidative channel-etching methods to define patterns on substrates, which are difficult to apply to the construction of cost-effective and flexible devices for commercial applications. To overcome the obstacles surrounding scalability, high-cost and flexibility, new strategies to manufacture MSCs efficiently on flexible substrates are highly appealing.

Direct printing techniques, including spray deposition and inkjet printing, offer a promising protocol for future roll-to-roll production of MSC arrays, which can be rapidly processed onto both plastic and paper substrates at low temperature and over large areas. As a key component for printing techniques, the selected ink should be stable, low-cost and easily printable on appropriate substrates; it should display excellent electrical properties, without the need for aggressive post-treatments. Graphene is well suited for use in printable supercapacitors because of its large theoretical surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), excellent electrical conductivity, high intrinsic areal capacitance ($21 \text{ } \mu\text{F cm}^{-2}$ for a single layer), theoretical gravimetric capacitance (550 F g^{-1}), and mechanical robustness.

In this work, we demonstrate novel and directly printable in-plane MSCs on paper and ultra-thin polyethylene terephthalate (PET) substrates. Graphene ink with a concentration of 0.8 mg mL^{-1} was obtained by electrochemically exfoliating graphite under mild conditions. Such a graphene dispersion was stable in volatile 2-propanol (IPA) for at least 4 weeks. A hybrid ink composed of electrochemically exfoliated graphene (EG) and an electrochemically active poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) formulation (Clevios PH1000) was subsequently prepared. By spray coating the EG/PH1000 hybrid ink through a shadow mask with the designed MSC device geometry, the direct printing of MSCs was realized. The fabricated MSC on a paper substrate offered a significant areal capacitance as high as 5.4 mF cm^{-2} , which is among the best reported performances of graphene based MSCs, and exhibited an excellent rate capability with a capacitance retention of 75% when operated from 10 to 1000 mV s^{-1} . We further demonstrated that light-emitting diodes (LED) could be readily illuminated by MSC arrays that were printed on a paper substrate. Moreover, using a PET ($2.5\text{-}\mu\text{m}$ -thick) substrate for the formation of the printed hybrid film resulted in an ultra-thin MSC that exhibited “ultraflexibility,” thus making it suitable for the next-generation flexible micro-electrochemical energy storage devices.

EG was produced with a two electrode system (**Figure 1a**) using platinum as the counter electrode and a pre-treated graphite foil as the working electrode (Supporting Information). Initially, high voltage pulses ($+10 \text{ V}$) were applied to expand the graphite, as shown in Figure 1a. Afterward, 30 minutes of low voltage ($+3 \text{ V}$) was applied for direct exfoliation. After washing of the exfoliated product, the collected EG powder was dispersed in IPA by sonication for 30-40 min. Thus, EG ink with a high concentration of 0.8 mg mL^{-1} was readily obtained. The ink remained stable for 4 weeks without visible agglomeration. Atomic force microscopy (AFM) revealed the flat graphene morphology of the nanosheets (Figure 1b). The typical cross-section of a single graphene sheet shows an average thickness of 1.82 nm

(statistically from 100 nanosheets by AFM measurement,^[6] as shown in Figure S1), which is about twice of the thickness of monolayer graphene sheet on a Si wafer (0.6-0.9 nm), suggesting that the EG sheets are dominated by double layers^[7]. The morphology of the EG sheets was further investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Note that the lateral sizes of over 95% of the EG sheets were smaller than 2 μm (Figure 1c and d), which is ideal for most printing techniques because larger graphene sheets might block the nozzle.^[8] The selected area electron diffraction (SAED) exhibited a typical 6-fold symmetric pattern with stronger diffraction from the (1-210) plane than from the (0-110) plane, indicating the high crystallinity of a bilayer graphene sheet (Figure 1e).^[9] As presented in Figure S2 and Figure 1f, X-ray photoelectron spectroscopy (XPS) revealed a low oxygen-atom content (13%) in EG. The dominant oxygen species were attributed to the C–OH group at 285.5 eV, which is due to oxidation of the graphite electrode during the low-voltage exfoliation process, and also explains the good dispersibility of EG in IPA. Raman spectroscopy of the EG sheets on SiO₂/Si substrates (Figure 1g) revealed that the intensity of the G peak was almost two times that of the D peak. The derived I_D/I_G value (0.60) is much smaller than that of chemically or thermally reduced graphene oxide (~1.1–1.5), indicating a lower degree of defects and thus better electronic conductivity for EG.

The low boiling point of IPA and the high stability of EG ink are beneficial for the direct spray coating or ink-jet printing of graphene for MSC electrode patterning. **Figure 2a** depicts the general procedure for the mask-assisted spray deposition method for the direct printing of MSC devices and “arrays” (several devices connected in a series manner) on paper or PET substrates. Firstly, EG ink was spray-coated onto paper substrates covered by the shadow mask (both finger and channel widths were 1000 μm , and the length was 2 cm).^[10] Subsequently, a gel electrolyte of poly(vinyl alcohol) (PVA)/H₂SO₄ was drop-casted onto the

finger electrodes and allowed to solidify overnight (inset of Figure 2c). After that, an all solid state EG-based MSC with in-plane geometry was obtained. One advantage of producing the MSC device on paper is that the porous structure of paper can lead to a large capillary force that acts on the ink. The strong capillary force enables a large contact surface area between the graphene sheets and the paper substrate after the ink is absorbed and the solvent evaporates. By adjusting the amount of EG ink and the number of spray coating cycles, the thickness of the patterned micro-electrodes was easily controlled. As shown in Figure 2a, the corresponding R_s of the EG based MSC patterns on SiO_2 and paper substrates reached as low as $15\ \Omega\ \text{sq}^{-1}$, which is comparable to the carbon nanotube paper obtained from a rod-coating method (with the same film thickness of approximately $1.5\ \mu\text{m}$).^[11] Moreover, the R_s of the MSC electrode film perfectly maintained its original value after being bent to a radius of 5 mm 500 times (Figure S3), demonstrating a great potential for flexible MSC devices.^[10]

To examine the electrochemical properties, we carried out cyclic voltammetry (CV) of the MSCs based on spray-coating 3 mL of EG ink (a film thickness of approximately $0.5\ \mu\text{m}$), as shown in Figure 2b and c. The device delivered an areal capacitance of $800\ \mu\text{F}\ \text{cm}^{-2}$ at a scanning rate of $1\ \text{mV}\ \text{s}^{-1}$, whereas only 40% of this capacitance remained after scanning at $100\ \text{mV}\ \text{s}^{-1}$. The performance of such an EG-based MSC is mainly attributed to the capacitive nature of the electric double-layer in EG. To enhance the capacitance of the printed MSC, a hybrid ink containing EG and the electrochemically active PH1000 was fabricated. The hybrid ink could be stable for at least four weeks without visible agglomeration, since PH1000 can also act as surfactant due to its conjugated aromatic chains which can strongly anchor onto the graphene surface via π - π interactions without disrupting the electronic structure of graphene (Figure S5). In a typical experimental procedure, 5 mL of the EG dispersion in IPA ($1\ \text{mg}\ \text{mL}^{-1}$) was mixed with 0.5 mL of the PH1000 aqueous solution (1–1.3 wt%). This was followed by a mild sonication and gentle stirring, thus,

forming a homogenous EG/PH1000 hybrid ink. The morphology study suggested that the polymer chains of PH1000 strongly interacted with the graphene surface via a non-covalent functionalization, which was responsible for the high stability of the hybrid ink.^[10] The pseudocapacitive MSC device that was based on the EG/PH1000 film was fabricated by spray-coating 3 mL of the hybrid ink, and other procedures were kept the same as those for the pure EG-based MSCs. As shown in **Figure 3** a-e and Figure S4, CV experiments were performed at scan rates ranging from 5 to 5000 mVs⁻¹. Compared with pure EG-based MSCs, the devices based on the EG/PH1000 hybrid ink exhibited an exceptionally enhanced electrochemical performance with a nearly rectangular CV shape, even at a scan rate of 1000 mV s⁻¹, which is indicative of the pronounced capacitive behavior inherent to the EG/PH1000 hybrid. An areal capacitance of 1080 $\mu\text{F cm}^{-2}$ at scan rate of 10 mV s⁻¹ was delivered, and there was no obvious capacitance change when the scan rate increased to 100 mV s⁻¹. Moreover, the device exhibited capacitance retention of 75% when operated at 1000 mV s⁻¹, which indicated that a capability for fast charging and discharging. The superior rate capability over pristine EG film based device can be attributed to the improved conductivity of the EG/PH1000 hybrid film (Figure S5). Such a high rate capacitance outperformed most of the reported graphene based MSCs.^[3, 12] The device also exhibited excellent cycling stability with ~90% capacitance retention after 5000 charge/discharge cycles. (Figure S4d, measured at scan rate of 100 mV s⁻¹).

We further optimized the areal and volumetric capacitances of the device with different film thicknesses. When spray coating 10 mL of the EG/PH1000 hybrid ink, the thickness of the MSC electrode pattern reached up to 2 μm . Remarkably, a maximum areal capacitance of 5.4 mF cm⁻² was achieved at 1 mV s⁻¹ (**Figure 4a**), which is superior to most of the reported values for graphene or porous carbon based MSCs (summarized in Table S1), e.g., reduced graphene oxide (RGO) MSCs from the direct laser writing of GO films using a standard

LightScribe DVD burner (2.32 mF cm^{-2} , thickness $\sim 8 \text{ }\mu\text{m}$)^[3], RGO microelectrodes by laser reduction and patterning of GO films (0.51 mF cm^{-2} , thickness $\sim 20 \text{ }\mu\text{m}$)^[5a] onion like carbon (1.7 mF cm^{-2} , thickness $\sim 7 \text{ }\mu\text{m}$)^[5b], and a methane plasma reduced RGO film ($80.7 \text{ }\mu\text{F cm}^{-2}$, thickness $\sim 15 \text{ nm}$)^[4]. Meanwhile, a volumetric capacitance of 27 F cm^{-3} at 1 mV s^{-1} was also delivered, and well comparable to the above mentioned state-of-the-art MSCs.

To further demonstrate the possible practical application of directly printable MSCs based on EG/PH1000, MSC arrays were fabricated by connecting four separately printed MSC devices in series (Figure 4b). To our delight, the charged MSC arrays could readily power an LED, demonstrating the great potential of MSCs as a portable and flexible micro-power supply. More interestingly, to meet the industrial requirements for scale-up production of MSC arrays, an ink-jet printing technique was also developed in this work. As shown in Figure 4c, the stable pristine EG ink was loaded into the cartridge of a commercial inkjet printer. By designing the MSC electrode geometry on the computer, we could easily print MSC arrays, which contained 10 individual MSC devices on standard A4 paper, with a commercially available printer; the whole process took only several minutes.

Ultra-thin MSCs based on EG/PH1000 hybrid films were also manufactured to demonstrate the MSCs as potential wearable micro-energy storage units. To this end, ultra-thin PET foils with a thickness of $2.5 \text{ }\mu\text{m}$ were employed as the substrate. For the convenience of device fabrication, the ultra-thin PET foils were attached to PDMS-coated rigid glass slides. By adhering the ultra-thin PET foils to the supports, all subsequent processing steps including spray-coating of the EG/PH1000 hybrid ink and assembling the device were exactly the same as for processing on paper (Figure 2a). Afterward, the as-fabricated ultra-thin MSC device was carefully peeled off of the supporting PDMS without causing any damage to the device. By spray coating 5 mL of the EG/PH1000 hybrid ink, the thickness of the obtained hybrid film was approximately $1 \text{ }\mu\text{m}$. The MSC device delivered a maximum areal capacitance of 2

mF cm^{-2} at 5 mV s^{-1} (**Figure 5a**), which is higher than those of reported graphene-based MSCs;^[4-5] however, this value is lower than the device fabricated on the paper substrate because of the limited thickness. As shown in Figure 5b, the total thickness of the fabricated MSC device including the thickness of the substrate and solid-state electrolyte is less than $5 \mu\text{m}$, which is much thinner than a human hair, showing great potential for “ultra-flexible” device architectures. Interestingly, the ultra-thin MSC device can be attached to a human finger or other body parts (Figure 5b), which demonstrates tremendous flexibility and compatibility with artificial intelligent devices, such as wearable electronics that undergo bending and stretching. To evaluate the mechanical stability of such an ultra-thin MSC device for flexible energy storage, we further examined the areal capacitance retention of an as-fabricated device after 1000 cycles of a bending test (Figure 5c, bending radius of 5 mm). The resulting device measured at a scan rate of 100 mV s^{-1} exhibited stable performance with only a slight capacitance loss of 1.5%. This mechanical stability even outperformed a device fabricated on regular PET substrates (Figure 5d, after 1000 cycles of bending with a radius of 7 mm), which showed a capacitance loss of more than 2% at scan rate of 100 mV s^{-1} . Remarkably, even with random twisting and folding (similar conditions to wearing the device on a human finger), the device presented only a slight capacitance loss of 1% compared with the flat state, demonstrating the “ultra-flexibility” and highly stability of the ultra-thin MSC (inset in Figure 5c).

In conclusion, we demonstrated novel directly printable in-plane MSCs on paper substrates using an electrochemically exfoliated graphene ink and a hybrid ink with an electrochemically active conducting polymer. The fabricated MSCs on paper substrates offered a significant areal capacitance as high as 5.4 mF cm^{-2} , which is superior to that of state-of-the-art graphene-based MSCs. Furthermore, we developed an “ultra-flexible” MSC device by employing ultra-thin PET substrates, which exhibited excellent flexibility. By

further optimization of the electrochemically exfoliation process of graphene and employing conductive polymers with higher pseudo-capacitance might improve the MSC device performance. Our work may pave the way for the future development of scalable high performance portable and wearable power supplies.

Experimental Section

Experimental Details including Materials, EG Production, printing of EG/PH1000 hybrid inks, and MSC device fabrication and characterization are listed in supporting information.

Supporting Information

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

Acknowledgements

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Figures and Figure Captions

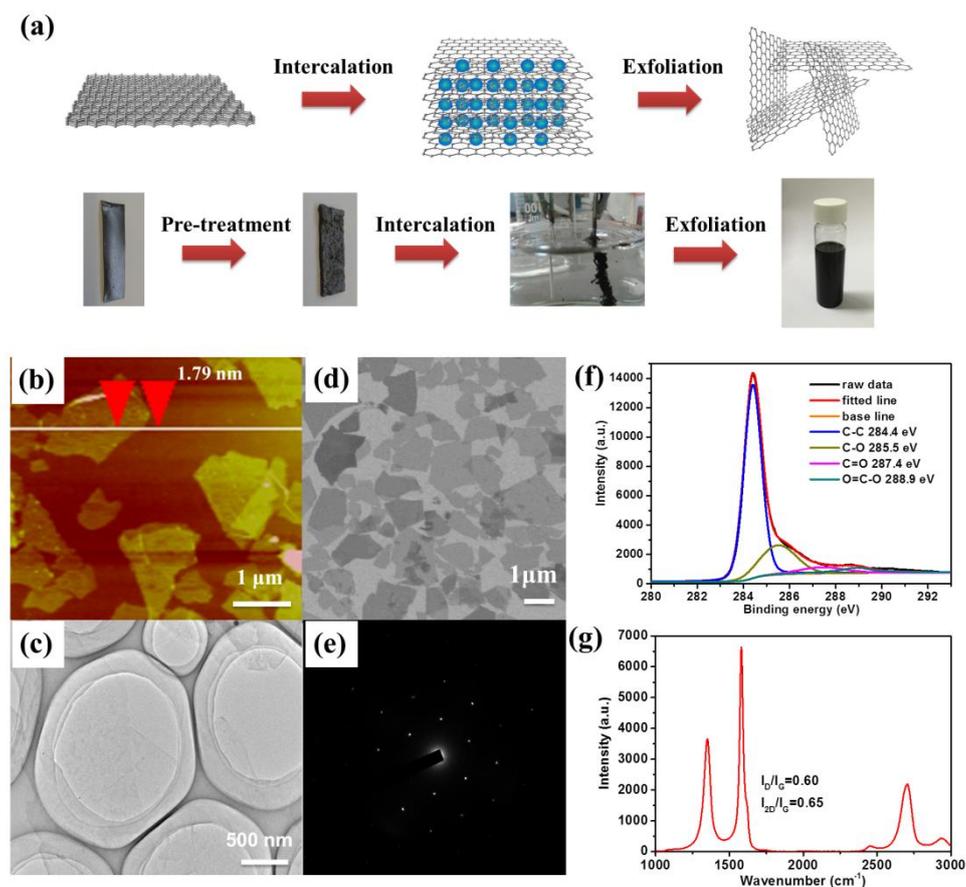


Figure 1. (a) Schematic illustration of the electrochemical exfoliation of graphene and photographs of the graphite foil volume change during exfoliation. (b) An AFM image of the EG sheets on SiO₂. (c) A TEM image of the EG sheets. (d) An SEM image of the EG sheets on SiO₂. (e) An SAED pattern of bilayer graphene. (f) High-resolution XPS of the C 1s spectrum for EG. (g) The Raman spectrum of a selected area of EG with the ratios of I_D/I_G and I_{2D}/I_G peaks indicated.

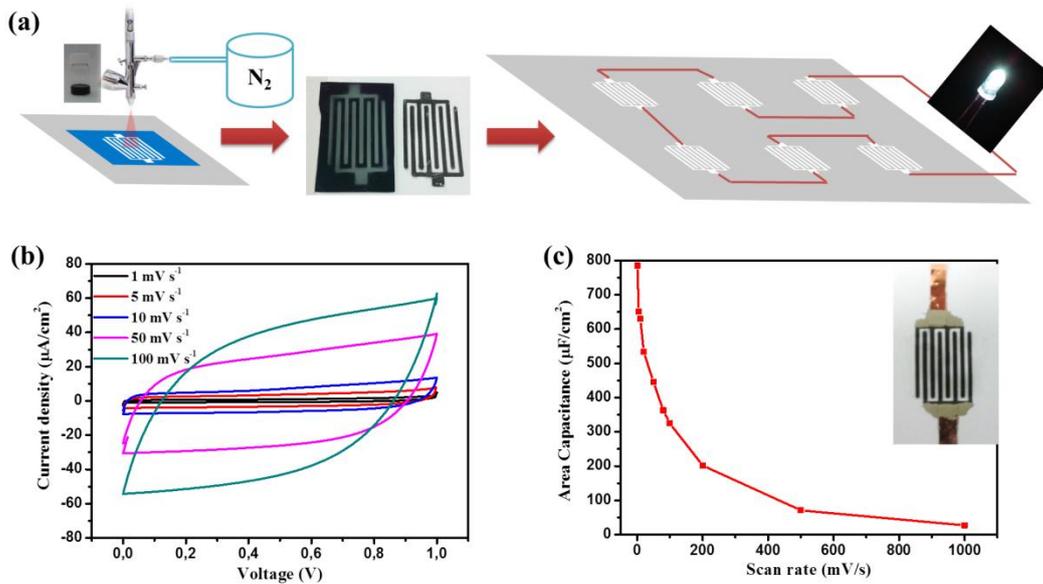


Figure 2. (a) Schematic illustration of the mask-assisted spray deposition method for the direct printing of single and arrayed MSC devices; pictures of EG-based MSC patterns on SiO₂ and paper substrates. (b) Cyclic voltammetry curves of a pristine EG ink (total amount 3 mL) MSC on a paper substrate at scan rates of 1 mV s⁻¹ to 100 mV s⁻¹. (c) The evolution of areal capacitance versus scan rate, the inset shows a digital image of the as fabricated MSC device on normal printing paper.

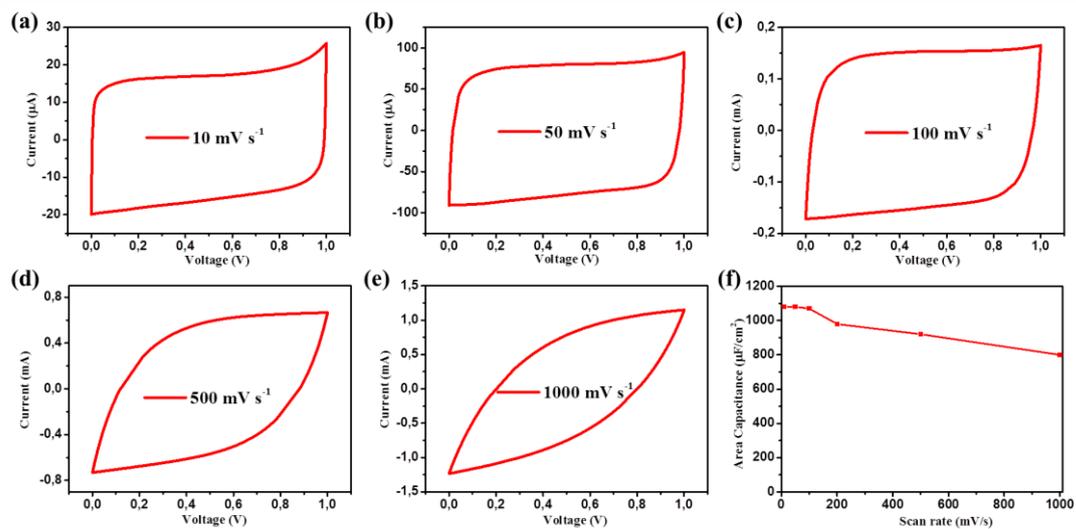


Figure 3.(a-e) Cyclic voltammetry curves of an EG/PH1000 hybrid ink (total amount 3 mL) MSC on a paper substrate with scan rates ranging from 10 to 1000 mV s⁻¹, and (f) the evolution of areal capacitance versus scan rate.

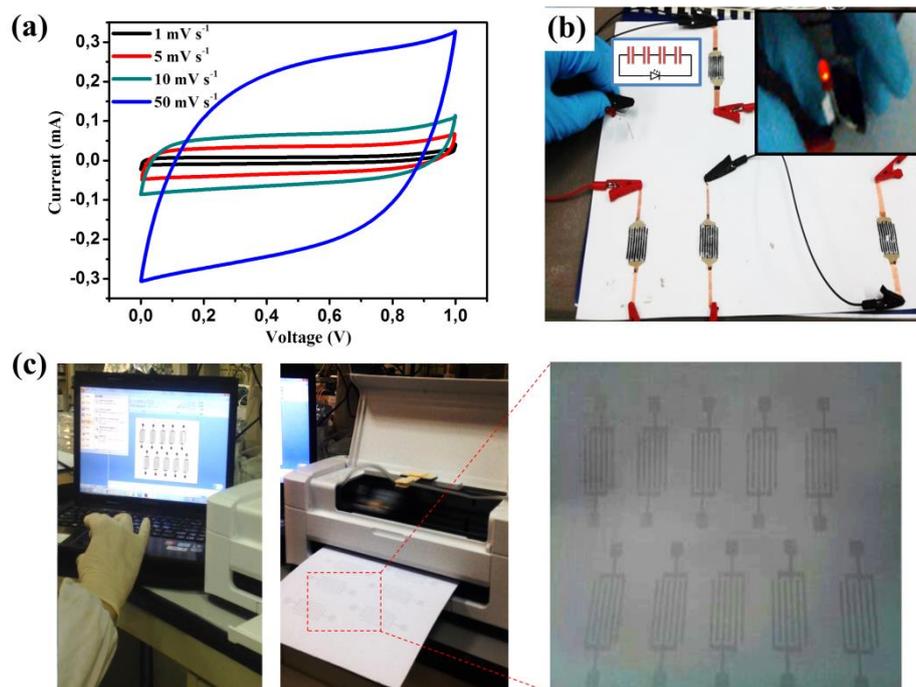


Figure 4. (a) Cyclic voltammetry curves of an EG/PH1000 hybrid ink (total amount 10 mL) MSC on a paper substrate at scan rates of 1 mV s^{-1} to 50 mV s^{-1} . (b) A charged MSC array containing 4 single devices can power an LED. (c) Inkjet printing of custom designed MSC arrays from a “home computer and printer” using pristine EG ink.

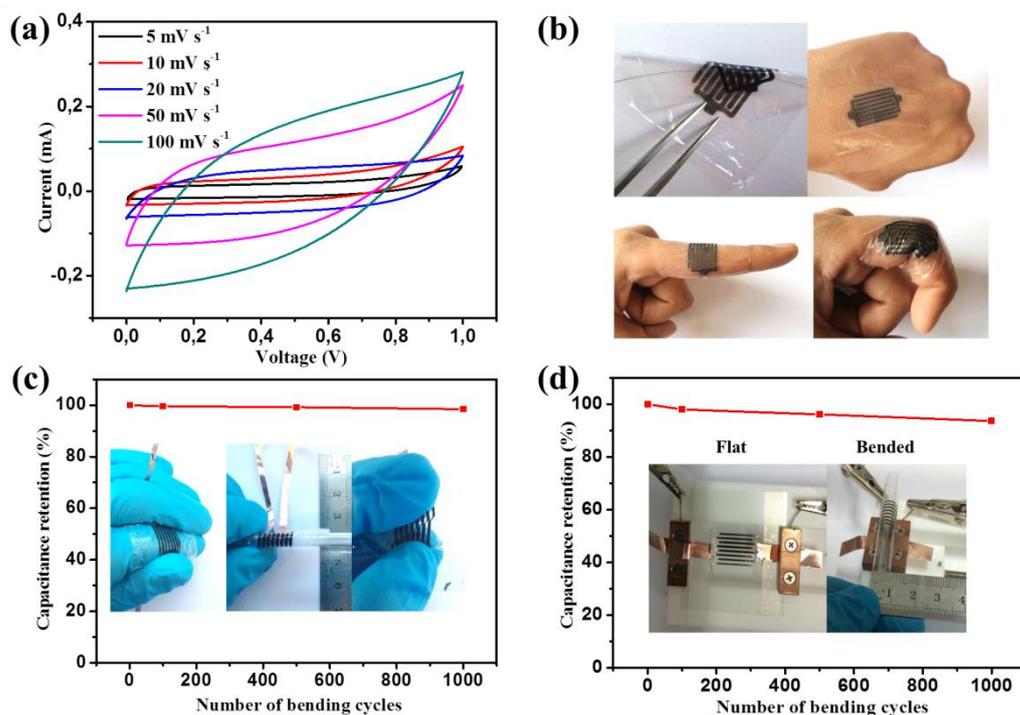


Figure 5. (a) Cyclic voltammetry curves of an EG/PH1000 hybrid ink (total amount 10 mL) MSC on an ultra-thin PET substrate at scan rates of 1 to 100 mV s^{-1} . (b) Ultra-thin and flexibility demonstrations of the fabricated MSC device indicating that the device is thinner than a human hair, wearable on the human hand, and capable of conforming to bent fingers. The MSC capacitance retention after 1000 cycles of the bending test using (c) ultra-thin and (d) regular PET substrates. The insets show flat, bent and deformable states of the MSC.

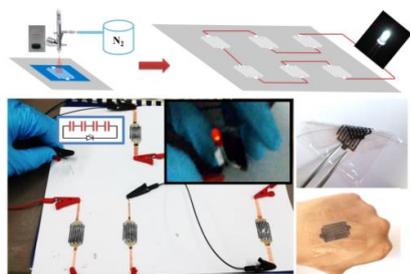
A novel direct printing approach for in-plane micro-supercapacitors (MSCs) fabrication is demonstrated. Solution processed graphene/conductive polymer hybrid inks are utilized. The fabricated MSCs on paper substrates offer significant areal capacitance and excellent rate capability. An ultra-thin MSC on PET (2.5- μm -thick) substrate exhibits “ultraflexibility,” making it suitable for the next-generation flexible micro-electrochemical energy storage devices.

Keyword: printing, in-plane, micro-supercapacitors, electrochemically exfoliated graphene, energy storage

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Supporting Information

Ultraflexible in-plane Micro-Supercapacitors by Direct Printing of Solution-Processable Electrochemically Exfoliated Graphene

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Experimental Section

Materials:

Graphite foil was purchased from Alfa Aesar. Clevios PH1000 (1.3 wt %) was purchased from Heraeus Clevios GmbH. Airbrush (Infinity CRplus) was purchased from Harder & Steenbeck GmbH. Ultrathin PET foils were supported by Pütz GmbH + Co. Folien KG.

EG Production:

EG was produced as previously reported. Briefly, graphite foil, platinum wires, and 0.1 M H₂SO₄ solutions were used as working electrodes, counter electrodes, and electrolytes, respectively. Initially, high voltage pulses (+10 V) were applied to expand the graphite, as shown in Figure 1a. Afterward, 30 minutes of low voltage (+3 V) was applied for direct exfoliation. After washing of the exfoliated product, the collected EG powder was dispersed in IPA by sonication for 30-40 min. Thus, EG ink with a high concentration of 0.8 mg mL⁻¹ was readily obtained.

Printing of EG/PH1000 hybrid inks for MSC device fabrication:

A custom-made shadow mask was employed to define the required MSC pattern, with 4 digital fingers on each side. The diameter of the airbrush nozzle was 0.15 mm, and the spray coating pressure was fixed at 3 bar nitrogen gas. The distance between the substrate and the airbrush nozzle was 10 cm. To achieve a homogeneous film, each spray process was conducted in a gentle manner. After each spray, a pause of 20 s should be taken for the film to be dried. The hybrid film will be heated 90 °C in the oven overnight to remove residual solvent before use. R_s was measured by a standard four-point probe system with a Keithley 2700 Multimeter (probe spacing: 0.635 mm, $R_s = 4.5324$ V/I). We utilized cyclic voltammetry (CV) to test the MSC device, with potential window 0-1 V, and the capacitance values were calculated from the CV data according to the following equation:

$$C_{device} = \frac{1}{\nu(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV$$

Where ν is the scan rate, V_f and V_i is are the integration potential limits of the CV curve. $I(V)$ is the voltammetric discharge current. Specific area capacitance was calculated according to:

$$C_{area} = C_{device}/A$$

where A is the total area of the device.

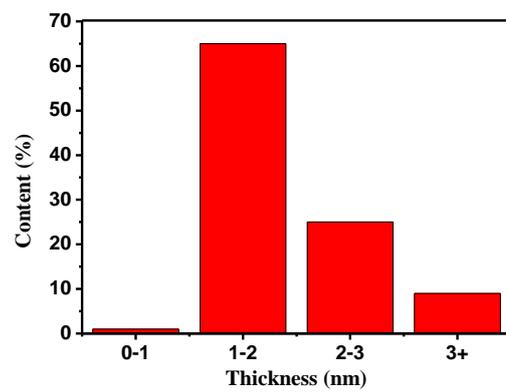


Figure S1. Graphene sheet thickness distribution.

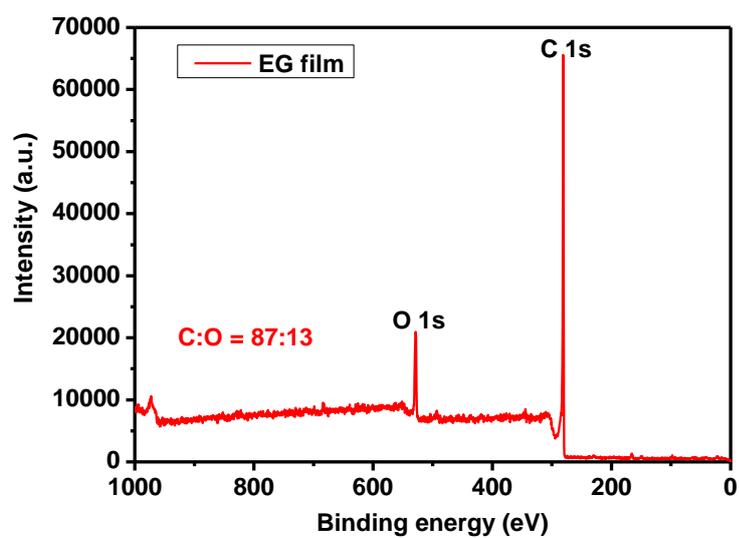


Figure S2. XPS spectrum of an EG film recorded over a range of 0-1000 eV.

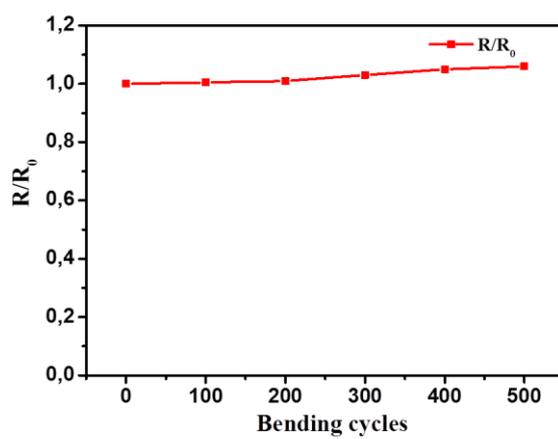


Figure S3. Change in R/R_0 with 500 bending cycles.

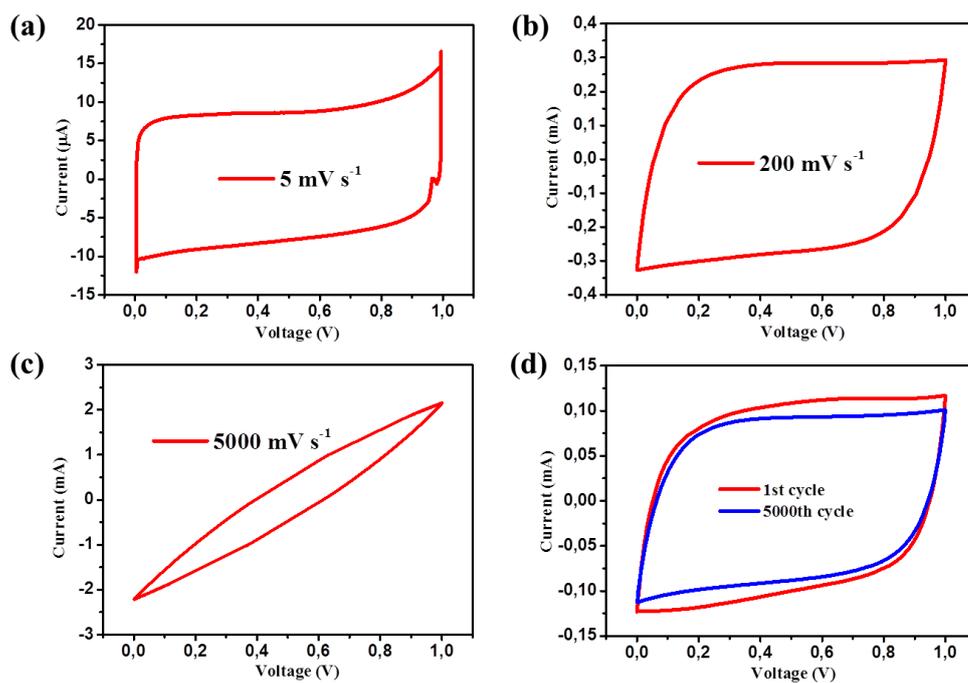


Figure S4. CV curves of an EG/PH1000 hybrid ink (total amount 3 mL) MSC on a paper substrate based at (a-c) scan rates of 5, 200 and 5000 mV s⁻¹, and (d) 1st and 5000th cycle measured at a scan rate of 100 mV s⁻¹.

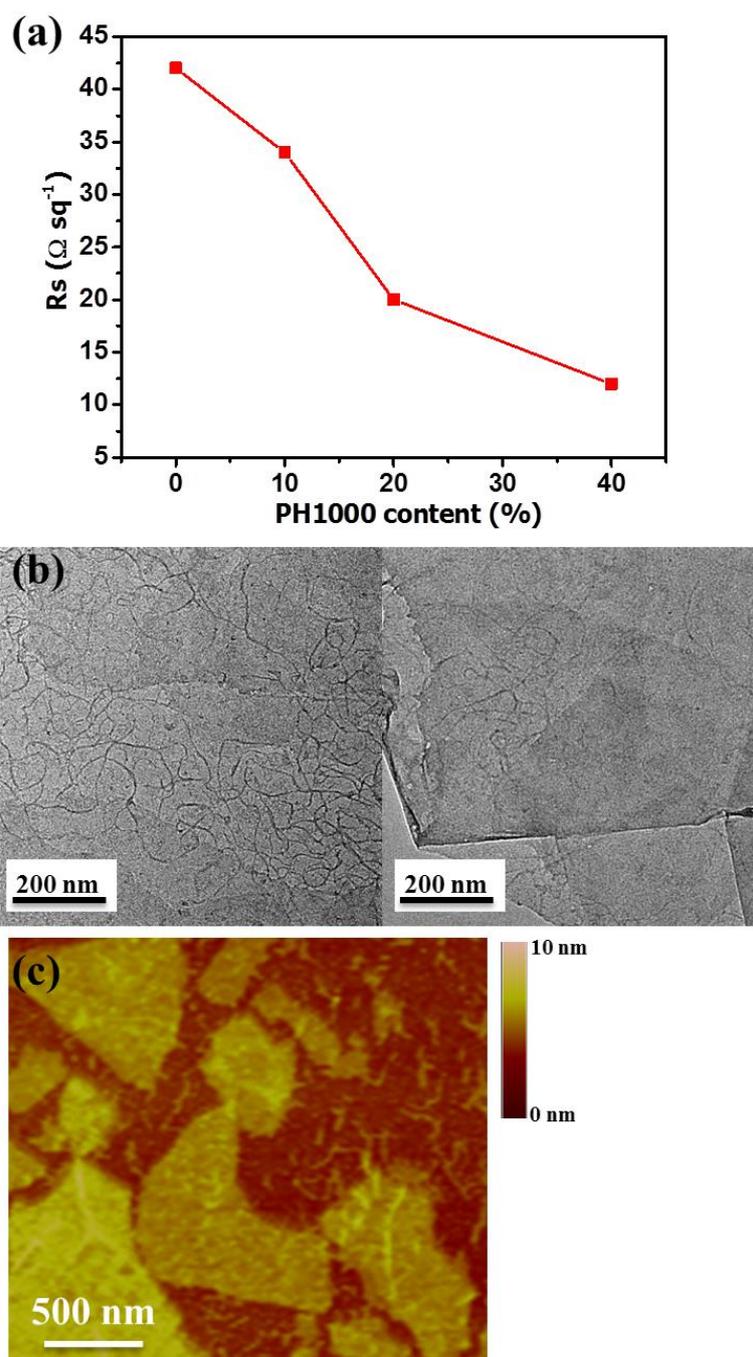


Figure S5. (a) Sheet resistance plot of EG/PH1000 hybrid films with different PH1000 content (film thickness $\sim 1.2 \mu\text{m}$). (b) TEM and (c) AFM images of EG/PH1000 hybrid.

Table S1. Compare with state-of-the-art graphene based MSCs performance, in regards of areal capacitance, volumetric capacitance, active material film thickness and measuring conditions.

	C_{area}	C_{vol}	Active material	Film thickness	Measuring condition(electrolyte, potential window, and scan rate)	
1	$< 2 \text{ mF cm}^{-2}$					Before 2011
2	1.7 mF cm^{-2}	1.3 F cm^{-3}	onion-like carbon film	$7 \mu\text{m}$	Organic electrolyte, 0-3 V, 1 V/s	Reference 5b
3	0.51 mF cm^{-2}	3.1 F cm^{-3}	laser reduced graphene oxide film	$20 \mu\text{m}$	Aqueous electrolyte, 0-1 V, 20 mV/s	Reference 5a
4	2.32 mF cm^{-2}	3.05 F cm^{-3}	laser reduced graphene oxide film	$8 \mu\text{m}$	PVA-H ₂ SO ₄ , 0-1 V, 16.8mA/cm ³	Reference 3
5	$80.7 \mu\text{F cm}^{-2}$	17.9 F cm^{-3}	Graphene oxide thin film by methane plasma treatment	15 nm	PVA-H ₂ SO ₄ , 0-1 V, 10 mV/s	Reference 4
6	5.4 mF cm^{-2}	27 F cm^{-3}	EG/PH1000 hybrid film	$2 \mu\text{m}$	PVA-H₂SO₄, 0-1 V, 1 mV/s	This work