

www.acsnano.org

Scalable Fabrication of Photochemically Reduced Graphene-Based Monolithic Micro-Supercapacitors with Superior Energy and Power Densities

Sen Wang,^{†,‡} Zhong-Shuai Wu,^{*,†} Shuanghao Zheng,^{†,‡,§} Feng Zhou,[†] Chenglin Sun,[†] Hui-Ming Cheng,^{#,||} and Xinhe Bao^{†,§}

[†]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

[‡]University of Chinese Academy of Sciences, 19 A Yuquan Road, Shijingshan District, Beijing 100049, PR China

[§]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

[#]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, PR China

^{II}Tsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, 1001 Xueyuan Road, Shenzhen 518055, PR China

Supporting Information

ABSTRACT: Micro-supercapacitors (MSCs) hold great promise as highly competitive miniaturized power sources satisfying the increased demand of smart integrated electronics. However, single-step scalable fabrication of MSCs with both high energy and power densities is still challenging. Here we demonstrate the scalable fabrication of graphene-based monolithic MSCs with diverse planar geometries and capable of superior integration by photochemical reduction of graphene oxide/TiO₂ nanoparticle hybrid films. The resulting MSCs exhibit high volumetric capacitance of 233.0 F cm⁻³, exceptional flexibility, and remarkable capacity of modular serial and parallel integration in aqueous gel electrolyte. Furthermore, by precisely engineering the interface of



electrode with electrolyte, these monolithic MSCs can operate well in a hydrophobic electrolyte of ionic liquid (3.0 V) at a high scan rate of 200 V s⁻¹, two orders of magnitude higher than those of conventional supercapacitors. More notably, the MSCs show landmark volumetric power density of 312 W cm⁻³ and energy density of 7.7 mWh cm⁻³, both of which are among the highest values attained for carbon-based MSCs. Therefore, such monolithic MSC devices based on photochemically reduced, compact graphene films possess enormous potential for numerous miniaturized, flexible electronic applications.

KEYWORDS: graphene, photochemical reduction, monolithic, micro-supercapacitors, supercapacitors, energy storage

The rapid development of miniaturized electronic devices has essentially stimulated the urgent demand of microscale power sources that can be directly integrated with them.¹⁻⁷ Recently, micro-supercapacitors (MSCs) with impressive power density, large storage capacity, and superior cycling lifetime are arising as a class of nextgeneration on-chip energy storage devices.^{8–11} So far, the research of the state-of-the-art MSCs has greatly advanced through the elaborated screening of nanostructured materials,^{9,12–15} selection of matching electrolytes,^{10,16} development of thin-film technologies,^{17–20} and precise design of device geometries.^{21–24} Nevertheless, the overall improvement of both scalability and performance for MSCs are still far from satisfactory. 25

Recently, graphene has attracted intensive attentions for engineering planar MSCs.^{26–29} This is because graphene-based planar MSCs can sufficiently utilize the intriguing features of graphene, like two-dimensional thinness and high surface area (2630 m² g⁻¹) for maximizing energy storage.^{28,30–33} Moreover, electrolyte ions can rapidly transport between planar electrode fingers to offer high power capability.⁸ Nevertheless,

Received: February 27, 2017 Accepted: March 28, 2017 Published: March 28, 2017



Figure 1. Fabrication of PRG-MSCs with various tailored planar geometries. (a) Schematic showing the one-step fabrication process for PRG-MSCs with different geometries of parallel interdigital, concentric circular, two parallel strips, and folding line fingers (from the left to right). (b) Photoreduction mechanism of TiO₂ nanoparticle-assisted reduction of a GO film under ultraviolet irradiation. (c) Low-magnification SEM image of a PRG film, showing a clear boundary between GO/TiO₂ and PRG film without and with photoreduction. Inset: photograph of patterned PRG film. (d) C 1s XPS of PRG and GO/TiO₂ film. (e) XRD patterns of PRG and GO/TiO₂ film on quartz glass. (f–k) Various PRG-MSCs with different sizes and diversified shapes of (f) parallel interdigital fingers, (g) concentric circular, (h) two parallel strips, (i) folding line, (j) circular interdigital, and (k) small-size planar interdigital fingers, scale bar of (f) is 250 mm, scale bar of (g–k) is 500 μ m. (l) 9 parallel interdigital PRG-MSCs with the geometries of (m) concentric circular (six MSCs), (n) two parallel strips (four MSCs), and (o) folding lines (eight MSCs), respectively, connected on one single PET substrate, scale bar is 1 mm.

efficient reduction and precise patterning of graphene oxide (GO) are still of considerable importance for scalable fabrication of high-performance MSCs. In general, graphenebased MSCs are created by conventional lithographic microfabrication,^{10,34} inkjet printing,^{35,36} screen printing,³⁷ laser-irradiation assisted method.^{21,38–40} The lithographic microfabrication, combining UV photolithography and a wet or dry etching process, is a well-established microfabrication technique and highly favorable for manufacturing high-resolution micrometre-sized patterns.^{10,34} However, this technique usually involves multiple separated steps of such as spin-coating of photoresist, soft baking, masked irradiation, development,⁴¹ O₂ plasma etching,42 and chemical or thermal reduction of GO films,^{26,28} resulting in the complicated processes and low efficiency of device assembly in a large scale. Further, high cost of lithographic equipment is another major limitation for fabricating low-cost MSCs.⁴¹ Inkjet printing and screen printing are the simple, cost-effective printing methods for efficient

patterning on various substrates,^{35,36} but a stable ink of GO or reduced GO (rGO) exhibiting good compatibility with the printed substrate is a stringent requirement.³⁷ Similar to lithographic technique, an additional reduction process of GO to rGO with chemical or thermal treatment is very necessary before or after printing.⁴³ Further, MSCs show relatively low power density and poor frequency response due to the usage of surfactant or polymeric binder in the ink.¹⁹ Laser-irradiation assisted method, e.g., laser writing,¹⁶ laser-scribing,²¹ is efficient and scalable for simultaneous reduction and flexible patterning of GO films, which is a huge advance on single-step, simplified production of MSCs. But, regardless of high cost, a major disadvantage is that the MSCs displayed limited volumetric capacitance of ~ 3.1 F cm⁻³ because of low packing density of the reduced graphene films.^{16,21} Unlike the above routes, photochemical reduction of GO with various catalysts (e.g., TiO_{2} , ⁴⁴ ZnO, ⁴⁵ WO₃, ⁴⁶ H₃PWO₄₀ ⁴⁷) under UV irradiation represents the distinguished advantages of high efficiency, low

cost, tunable reduction degree, flexible patterning, and superior integration of graphene-based microdevices.^{44,48} Despite enormous efforts made, single-step scalable production of graphene-based MSCs with photocatalytic strategy has not yet been reported.

Here we demonstrated the scalable fabrication of flexible and high-performance graphene-based monolithic MSCs by photochemical reduction and patterning of GO/TiO₂ hybrid films. Notably, the MSCs obtained displayed high volumetric capacitance of 233.0 F cm⁻³, outstanding flexibility, and remarkable capacity of modular serial and parallel integration. More importantly, by precisely engineering the interface of electrode with electrolyte, we developed high-rate graphenebased MSCs using a hydrophobic electrolyte of ionic liquid, working well at a high scan rate of 200 V s⁻¹, two orders of magnitude higher than those of conventional supercapacitors. The MSCs showed high volumetric power density of 312 W cm⁻³ and energy density of 7.7 mWh cm⁻³, both of which are among the highest values achieved for carbon-based MSCs.

RESULTS AND DISCUSSION

Figure 1a and Figure S1 in Supporting Information illustrate the fabrication process of planar MSCs based on photoreduced graphene oxide (PRG) hybrid films, denoted as PRG-MSCs (see Methods). First, a thin film of GO/TiO_2 nanoparticles was obtained by vacuum filtration of a stable dispersion containing GO sheets (0.05 mg mL⁻¹) and TiO₂ nanoparticles in diameter of $5-10 \text{ nm} (0.025 \text{ mg mL}^{-1})$, followed by transferring onto a flexible polyethylene terephthalate (PET) substrate. The thickness of the PRG films can be adjusted by the volume of the used dispersion. Second, a 500 W high-pressure Hg lamp was used for synchronous photoreduction and patterning of GO films with the help of a photomask by UV irradiation for 4 h. In this process, the photogenerated electrons transfer from the TiO₂ nanoparticles to GO sheets, resulting in efficient reduction of the GO film and restore of the sp²-C network (Figure 1b). Third, a thin layer of gold was deposited on the top surface of PRG patterns as current collectors, and a suitable external electrolyte, e.g., H₂SO₄/poly(vinyl alcohol) (H₂SO₄/ PVA), ionic liquid, was slowly dropped on the project area of the microdevice. Finally, planar PRG-MSCs were obtained.

After UV irradiation, a dramatic change in color from light brown for a pristine GO film to black for a patterned PRG film was observed (Inset of Figure 1c), suggesting efficient reduction of the GO film. This result was further confirmed by the morphological and structural analysis. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed the uniform and flat morphology of PRG film with a porous structure, in which TiO₂ nanoparticles as nanospacers significantly prevent the restacking of graphene sheets (Figure 1c and Figure S2). X-ray photoelectron spectroscopy (XPS), Xray diffraction (XRD) patterns, and Raman spectra disclosed a substantial decrease of O/C ratio from 0.48 to 0.23 (Figure 1d, Figure S3 and Table S1),⁴⁹ a substantial weakened peak as well as a reduced *d*-spacing distance from 8.2 to 6.6 Å (Figure 1e, Figure S4), and a slight increase of I_D/I_C ratio from 0.98 to 1.02 (Figure S5 and Table S1), respectively. And PRG film with a thickness of 63 nm displayed an electrical conductivity of 0.7 S m^{-1} (Figure S6). Notably, unlike conventional microfabrication techniques, this photoreduction methodology does not require precise equipment, expensive materials, postprocessing or clean room operations.⁴⁸ More importantly, it enables the flexible patterning of GO films for shape-tailored planar MSCs in

different desirable device geometries and sizes, e.g., interdigital fingers, concentric circular, parallel strips, folding line fingers, circular interdigital (Figure 1f-k). Special emphasis is given to a PRG-GO-PRG patterned structure for the construction of monolithic MSCs, in which the GO film can act as a good ionic conductor and electrolyte separator,⁵⁰ and the PRG patterns can be directly used as binder-free electrodes. Moreover, this technique is completely flexible and readily scalable. For instance, a large number of PRG-MSCs with different geometries and shapes can be efficiently produced, and serially interconnected for modular integration on a single flexible PET substrate without need of additional metal-based interconnects and contacts, as described in Figure 11-o. Therefore, this inexpensive, single-step photoreduction strategy holds great potential for scalable production of cost-efficient, flexible and miniaturized graphene-based MSCs.

To demonstrate the superior performance, we first constructed PRG-MSCs based on eight interdigital PRG fingers (film thickness of 63 nm) using a polymer gel of H_2SO_4/PVA electrolyte. The electrochemical performance of PRG-MSCs was then examined at scan rates from 2 mV s⁻¹ to 50 V s⁻¹ through cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) profiles (Figure 2). Notably, PRG-MSCs



Figure 2. Electrochemical characterization of PRG-MSCs (finger and interspace widths of 1 mm, length of 14 mm). (a,b) CV curves of PRG-MSCs obtained at different scan rates of (a) 0.05-2 V s⁻¹ and (b) 5-50 V s⁻¹. (c) Change of the volumetric capacitance (C_V) and areal capacitance (C_A) of PRG-MSCs versus scan rate. (d) Cycling stability of PRG-MSCs. Inset: GCD profiles performed at a current density of 0.02 mA cm⁻².

exhibited typical double-layer capacitive behavior with a nearly rectangular CV shape, even at a high scan rate of 15 V s⁻¹ (Figure 2a,b), indicative of exceptional performance. Furthermore, it was calculated that areal capacitance and volumetric capacitance of PRG-MSCs recorded at 2 mV s⁻¹ were 1.5 mF cm⁻² and 233.0 F cm⁻³ (Figure 2c), respectively. Both of them were much higher than those of the most reported carbon-based MSCs, such as 0.32 mF cm⁻² and 71.6 F cm⁻³ for methane plasma rGO,⁸ 5.6 mF cm⁻² and 180 F cm⁻³ for carbide-derived carbon,¹⁰ 0.28 mF cm⁻² and 0.76 F cm⁻³ for vertically aligned carbon nanotubes,⁵¹ 2 mF cm⁻² and 29.4 F



Figure 3. Flexibility of all-solid-state PRG-MSCs. (a) Photographs of PRG-MSCs tested under different bending angles. (b) CV curves of PRG-MSCs obtained at different bending angles, at 200 mV s⁻¹. (c) Capacitance ratio as a function of bending angle. Inset: optical images of the device in flat and bending states. (d) Cycling stability of PRG-MSCs under constant bending state. Inset: GCD curves obtained at a current density of 0.1 mA cm⁻².



Figure 4. Electrochemical characterization of PRG-MSCs in EMImNTF₂ electrolyte. (a) The scheme of PRG-MSCs (top right), molecular structure of EMImNTF₂ (top left), and contact angle of EMImNTF₂ on the surface of a PRG film (bottom). (b,c) CV curves of PRG-MSCs measured at different scan rates of (b) 0.1-10 V s⁻¹ and (c) 20-200 V s⁻¹. (d) The discharge current *versus* scan rate. (e) GCD profiles obtained at different current densities of 0.01-0.5 mA cm⁻². (f) Complex plane plot of PRG-MSCs. Inset: a magnified curve in high-frequency region. (g) Phase angle *versus* frequency of PRG-MSCs. (h) Areal capacitance and volumetric capacitance of PRG-MSCs . (i) Volumetric capacitance of PRG-MSCs *versus* scan rate measured in three electrolytes of ionic liquid.

cm⁻³ for laser written GO film,¹⁶ 9.9 mF cm⁻² and 7.6 F cm⁻³ for onion-like carbon,¹² 40 mF cm⁻² and 29.4 F cm⁻³ for rGO/ carbon nanotube,⁵² 14.7 mF cm⁻² and 19 F cm⁻³ for laser-scribed graphene,²¹ (Table S2). Moreover, our PRG-MSCs also

showed outstanding rate capability and cyclability. For instance, high capacitances of 1.1 mF cm⁻² and 167.0 F cm⁻³ were maintained for PRG-MSCs even operated at a high scan rate of 1 V s⁻¹ (Figure 2c). Meanwhile, our device retained ~100% of

initial capacitance after 10 000 cycles (Figure 2d), and kept almost unchanged after a month, demonstrating the capability of stored charges for a significant period (Figure S7).

We also constructed classical sandwich supercapacitors (PRG-SSCs) based on two PRG film electrodes sandwiching H_2SO_4/PVA gel electrolyte (Figure S8), and compared the performance with PRG-MSCs. Obviously, PRG-MSCs exhibited larger capacitances and better capacitance retention than those of PRG-SSCs (Figure S9), demonstrative of the superiority of the planar geometry over the stacked one.^{26–29} In addition, our photochemical strategy is highly flexible for manufacturing high-resolution planar PRG-MSCs with tailored device size and geometries, *e.g.*, concentric circular (Figure 1, Figure S10).^{53,54}

Furthermore, it should be emphasized that optimum irradiation time for modulating the reduction degree (Figure S11) and thickness of PRG film (Figure S12), are key factors for maximizing the performance.⁵⁵ The areal capacitance from 0.1 to 2.7 mF cm⁻² and volumetric capacitance from 5.3 to 174.5 F cm⁻³ were obtained at 100 mV s⁻¹ with increasing irradiation time from 0 to 4 h. Afterward, the areal and volumetric capacitances remained almost invariable, which were well explained by electrochemical impedance spectra (Figure S11b). It is also revealed that the areal capacitance can be improved, e.g., from 4.8 to 7.6 mF cm^{-2} for PRG-MSCs obtained at 20 mV s⁻¹, by increasing the thickness of film electrode from 2 to 4.5 μ m (Figure S12). Additionally, it is mentioned that the TiO₂ nanoparticles in PRG film can serve as not only (i) efficient photocatalysts to promote the reduction of GO,^{44,48,56} and (ii) a highly pseudocapacitve material⁵⁷ providing additional capacitance contribution, but also (iii) nanospacers distributing between graphene layers that can significantly prevent the restacking of adjacent graphene nanosheets (Figure S2c,d),⁵⁸ resulting in the performance enhancement of PRG-MSCs (Figure S13).

Flexible, thin, lightweight energy storage devices on chip are becoming more and more important for portable and wearable electronics such as roll-up displays, e-paper, smart sensors, and transparent radio frequency identifications.^{59,61} To demonstrate the mechanical robustness of our microdevices, we examined CV measurement of PRG-MSCs under different bending angles from 0 to 180° (Figure 3a). Remarkably, all the CV curves presented almost the same box-like shape, and ~93.7% of the initial capacitance in the flat state remained even at a highly bending state of 180° (Figure 3b,c), suggestive of outstanding structural integrity and mechanical flexibility of our microdevices. Moreover, PRG-MSCs showed excellent electrochemical stability, maintaining nearly 100% of capacitance retention after 4000 cycles under a constant bending state of ~180° (Figure 3d).

Electrolyte is widely considered as a critical influencing factor for both capacitance (C_s) and working voltage (V), determining energy density (E) of a supercapacitor in term of the equation, $E_{\rm max} = 1/2 C_s V^{2.62,63}$ In view of this, we further investigated the effect of three high-voltage ionic liquids of 1-ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImNTF₂), 1-butyl-3-methylimidazolium hydrogen sulfate (BMImHSO₄), and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) on the capacitance of PRG-MSCs (Figure 4, and Figure S14–S17).

Through screening, we found that PRG-MSCs using a hydrophobic ionic liquid of $EMImNTF_2$ as electrolyte exhibited outstanding electrochemical performance with a wide electro-

chemical window of 3.0 V, as confirmed by CV curves obtained at $0.1-200 \text{ V s}^{-1}$ (Figure 4b and 4c) and GCD profiles attained at 0.01–0.5 mA cm⁻² (Figure 4e). It was noted that the CV curves of the resultant PRG-MSCs presented a nearly symmetrical rectangular shape even at a high scan rate of 50 V s⁻¹, indicative of pronounced capacitive behavior. Accordingly, an approximate linear dependence of discharge current versus scan rate was observed (Figure 4d). Remarkably, our microdevices can be rapidly charged and discharged up to 200 V s^{-1} while keeping significant capacitance (Figure 4b,c), demonstrative of ultrahigh instantaneous power. This scan rate (200 V s^{-1}) is at least 20 times higher than those of PRG-MSCs measured in BMImHSO₄ (10 V s^{-1}), and EMImBF₄ (1 V s^{-1}) (Figure S14, S15). To the best of our knowledge, this value is at least two orders of magnitude higher than those of conventional ionic-liquid based supercapacitors,⁶⁴ and is well comparable to aqueous-based MSCs reported to date. Electrochemical impedance spectroscopy (EIS) confirmed the fast ion transport within the interdigital electrodes of PRG-MSCs, exhibiting a straight line closed the Z'' axis at low frequency, and a small equivalent series resistance (ESR) of 36.8 Ω in high-frequency region (Figure 4f). The dependence of the phase angle on the frequency for PRG-MSCs is presented in Figure 4g. The characteristic frequency f_0 at a phase angle of -45° is ~61 Hz for PRG-MSCs. Therefore, the corresponding time constant τ_0 ($\tau_0 = 1/f_0$) was calculated to be only 16.4 ms, which is much lower than those of the supercapacitors using active carbon (700 ms),⁶⁵ vertically aligned graphene (250-290 ms),^{66,67} liquid-mediated graphene (200-73 ms),²⁷ and well comparable to the reported high-power supercapacitors based on vertically aligned carbon nanotubes (21 ms),68 and planar MSCs based on onion-like carbon (26 ms)⁶⁵ and laser-scribed graphene (19 ms)⁶⁰ (Table S2). Furthermore, PRG-MSCs in EMImNTF₂ provided exceptional areal capacitance of 0.53 mF cm^{-2} and volumetric capacitance of 84.7 F cm^{-3} at 50 mV s^{-1} , respectively (Figure 4h). Although these values are lower than those of PRG-MSCs in aqueous electrolyte, they are still much higher than those working in BMImHSO4 and EMImBF4 (Figure 4i). More importantly, PRG-MSCs in EMImNTF₂ exhibited superior rate capability. For instance, a high volumetric capacitance of 66.3 F cm⁻³ was obtained at 1 V s⁻¹, and 14.2 \hat{F} cm⁻³ was maintained even at a rate of 200 V s⁻¹ for PRG-MSCs in EMImNTF₂. In a marked contrast, PRG-MSCs at 1 V s⁻¹ offered a low capacitance of only 6.3 F cm⁻³ in EMImBF₄, and 20.9 F cm⁻³ in BMImHSO₄. This is mainly attributed to the porous structure of the layered PRG film (Figure S2), which cooperatively merges the merits of strongly coupled hydrophobic TiO₂ nanoparticles and graphene with a fully accessible surface area, compatible with hydrophobic EMImNTF₂ electrolyte, as confirmed by the contact angle measurement (only $\sim 5.3^{\circ}$) (Figure 4a, Figure S16 and S17). The nanochannels between the adjacent graphene sheets supported by the TiO₂ pseudocapacitve nanospacers offer feasibility for fast diffusion of ionic liquid in the parallel direction, then maximizing the accessible surface area for charge storage. In light of the above facts, we believe that PRG-MSCs in EMImNTF₂ are very promising for high-energy and highpower microscale supercapacitors.

More importantly, our PRG-MSCs could be directly interconnected in series and parallel configurations without additional metal-based interconnects and contacts, correspondingly, to increase desirable output voltage and capacitance (Figure 5). The integrated PRG-MSCs exhibited a very good



Figure 5. Integration of PRG-MSCs. (a) CV curves of five PRG-MSCs connected in series at 100 mV s⁻¹, (b,c) GCD profiles of (b) five PRG-MSCs connected in parallel and (c) in a combination of 2 series and 2 parallel, at a current density of 0.1 mA cm⁻² in H_2SO_4/PVA electrolyte. (d) CV curves at 10 V s⁻¹ and (e) GCD profiles at 0.1 mA cm⁻² of two serial PRG-MSCs, and (f) CV curves at 10 V s⁻¹ of two PRG-MSCs connected in parallel in EMImNTF₂ electrolyte.

control over the operating voltage and capacitance in both H_2SO_4/PVA gel electrolyte (Figure 5a–c) and EMImNTF₂ electrolyte (Figure 5d–f). For instance, five serial all-solid-state PRG-MSCs (Figure 5d,e), in comparison with the single device (0.8 V in H_2SO_4/PVA and 3.0 V in EMImNTF₂), demonstrated a sufficient voltage extension of ~4.0 V and ~6.0 V, respectively. Further, tandem MSCs connected in 2 series and 2 parallel fashion displayed simultaneous improvement of both voltage and current outputs (Figure 5c). Therefore, these miniaturized MSCs hold great promise as an efficient microscale power source to satisfy certain applications that require high operating currents and voltages in a short time frame.^{69,70}

Large volumetric energy and power densities of microscale energy storage devices are highly required for wearable and flexible electronics.^{27,71} Ragone plot related to volumetric energy and power densities of our PRG-MSCs in different electrolytes was compared with commercially available energy storage devices, as shown in Figure 6. Our PRG-MSCs offered a maximum volumetric energy density of 7.7 mWh cm⁻³ in EMImNTF₂, which is five times higher than those measured in aqueous electrolyte, e.g., 1.5 mWh cm⁻³ in H_2SO_4/PVA electrolyte, and higher than those of most reported carbonbased MSCs, such as 2.1 mWh cm^{-3} for laser-scribed graphene²¹ 2.5 mWh cm⁻³ for methane plasma rGO,⁸ 3.2 mWh cm⁻³ for carbide-derived carbon,¹⁰ 0.3 mWh cm⁻³ for vertically aligned carbon nanotubes,⁵¹ 2.3 mWh cm⁻³ for inkjetprinted carbon,⁷² and 1.6 mWh cm⁻³ for onion-like carbon,¹² and comparable to lithium thin-film batteries (≤ 10 mWh cm⁻³).⁶⁰ More importantly, PRG-MSCs delivered a high power density of 312 W cm⁻³ within an extremely short discharging time of only 15 ms, which is well comparable to electrolytic capacitor (Figure 6) and most reported high-power MSCs so far.

CONCLUSIONS

In summary, we developed a photoreduction strategy for the simplified, scalable fabrication of flexible and high-performance graphene-based monolithic MSCs with diversified planar



Figure 6. Ragone plot of PRG-MSCs in different electrolytes compared with PRG-SSCs and commercially available energystorage systems. Our PRG-MSCs exhibit superior power delivery of electrolytic capacitors and high energy density of lithium thin-film (LTF) batteries.

geometries and tailored size by direct photoreduction and patterning of GO hybrid film. This photoreduction technique is readily scalable and completely compatible with the device manufacturing, and also capable of flexible patterning and integration, which can sufficiently create a large number of shape-tailored planar MSCs in various desirable geometries and size, with micrometre to even submicrometre resolution. The microdevices showed multiple features of excellent flexibility, scalability integration, and superior electrochemical performance, e.g., high volumetric power density of 312 W cm^{-3} outstanding energy density of 7.7 mWh cm⁻³, and fast charge and discharge rate of up to 200 V s^{-1} in EMImNTF₂. It is worthy to note that the performance of these MSCs could be further improved by developing high-capacitance electrochemically active materials, selecting high-voltage ionic liquid electrolytes, applying efficient film manufacturing processes, and engineering high-resolution device configuration. We

believe that this photoreduction strategy is very promising for the direct mass production of multifunctional shape-tailored MSCs to meet the stringent requirements of forthcoming flexible and wearable electronic devices.

METHODS

Fabrication of PRG-MSCs. The GO was prepared by modified Hummer's method, as reported in our previous work.^{73–75} First, 5 mg GO was added into the 100 mL dispersion of TiO₂ nanoparticles by sonciation for 30 min, and then formed a stable mixed solution with a GO concentration of 0.05 mg mL⁻¹ and TiO₂ concentration of 0.025 mg mL⁻¹. Afterward, 10–100 mL dispersion was filtrated to form a thin film on a cellulose membrane (pore size 0.22 μ m). Subsequently, the resulting film was directly dry-transferred on PET substrate with the assistance of a power compressing machine (769YP-15A) under the pressure of 14 MPa. Note that the thickness of GO/TiO₂ films is readily adjustable via the change of the volume of the dispersion. Then, a 500 W high-pressure Hg lamp was used for the efficient photoreduction and patterning of GO/TiO₂ films with the help of a customized photomask under UV irradiation for 4 h at ambient conditions. During this process, the lamb was positioned in a cold trap and kept a distance of ~ 10 cm from the films to keep the temperature (YM-GHX-V, Shanghai Yuming Industrial Co., Ltd.), and the PRG-MSCs with tailor-shaped planar geometries could be readily replicated by using desirable photomasks with different planar geometries and sizes (see Figure 1 in the manuscript). Next, a thin layer of 45 nm gold was evaporated on PRG film with a rate of ~ 1 Å s⁻¹ and a chamber pressure of ~4.5 \times 10⁻⁴ Torr. After the removal of the mask, a polymer gel electrolyte of PVA/H2SO4 (or other electrolytes, e.g., EMImNTF₂) was carefully drop-casted onto the surface of PRG-MSCs and solidified overnight. Finally, PRG-MSCs were achieved.

The PRG-SSCs were fabricated using H_2SO_4/PVA electrolyte sandwiched between two same PRG films electrodes supported on 45 nm-thick Au coated PET substrates, as schematically illustrated in Figure S8. The gel electrolyte was fabricated by adding 1 g PVA (M = 67 000) in 10 mL H_2SO_4 (0.5 M) and heating up to 85 °C for 1 h under vigorous stirring.

Materials Characterization. Materials characterization was conducted by SEM (JEOL JSM-7800F), AFM (Veeco nanoscope multimode II-D), XRD patterns (X'pert Pro), Raman spectra (LabRAM HR 800 Raman spectrometer), XPS (Thermo ESCALAB 250Xi), topography instrument (Dektak TX), and contact angle measurements (KRUSS, DSA100). For the electrical conductivity measurement, 45 nm gold-sputtered film with an empty gap of 1 mm was thermally evaporated on a PET substrate. Then, GO/TiO₂ film was transferred on this gap and allowed to dry at 80 °C for several hours. After that, the resistance of the GO/TiO₂ film after UV irradiation was measured, and electrical conductivity was calculated in the term of I-V curves and film thickness.

Electrochemical Characterization. The electrochemical performance of all devices was carried out by CV test from 2 mV s⁻¹ to 200 V s⁻¹, GCD profiles from 0.05 to 1 mA cm⁻² and electrochemical impendence spectroscopy recorded in the frequency range of 0.01 Hz ~ 100 kHz with a 5 mV ac amplitude on a CHI 760E electrochemical workstation. The assembly and electrochemical measurement experiments of PRG-MSCs using ionic liquid electrolytes were performed in a high-purity argon-filled glovebox.

Calculation. The capacitance values were calculated from the CV data according to the following eq 1:

$$C_{\text{electrode}} = \frac{4}{\nu(V_f - V_i)} \int_{V_f}^{V_i} I(V) \, \mathrm{d}V \tag{1}$$

where $C_{\text{electrode}}$ is denoted as the capacitance contribution mainly from graphene electrodes, ν is the scan rate (V s⁻¹), V_f and V_i are the integration potential limits of the voltammetric curve, and I(V) is the voltammetric discharge current (A).

Specific capacitance was calculated in term of the area or volume of the device according to the following formula:

$$C_A = \frac{C}{A} \tag{2}$$

$$C_V = \frac{C}{V} \tag{3}$$

where C_A (F cm⁻²) and C_V (F cm⁻³) refer to the areal capacitance and volumetric capacitance, respectively. $A_{\text{electrode}}$ and $V_{\text{electrode}}$ are the total area (cm²) and volume (cm³) of the electrodes, respectively. A_{device} is the entire projected surface area of the device, including the area of microelectrodes and the interspaces between them. V_{device} was calculated by taking into account the whole volume of the device, including the volume of PRG electrodes, the interspaces between the electrodes, current collector, and electrolyte.

The energy density and power density of PRG-MSCs shown in Ragone plot were calculated based on the volumetric capacitance of the device ($C_{V,\text{device}}$) measured under the same dynamic condition from the discharge curves of cyclic voltammetry. The energy density of the device was obtained from the following eq 4:

$$E = \frac{1}{2} \times C_{V,\text{device}} \times \frac{\Delta V^2}{3600} \tag{4}$$

where *E* is the energy density (Wh cm⁻³), $C_{V,\text{device}}$ is the volumetric capacitance obtained from eq 3 and ΔV is the discharge voltage range (*V*).

The power density of the device was calculated from the eq 5:

$$P = \frac{E}{\Delta t} \times 3600 \tag{5}$$

where *P* is the power density (W cm⁻³), and Δt is the discharge time (in seconds).

ASSOCIATED CONTENT

0

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b01390.

Figures S1–S17; Tables S1 and S2 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: wuzs@dicp.ac.cn.

ORCID 🔍

Zhong-Shuai Wu: 0000-0003-1851-4803 Xinhe Bao: 0000-0001-9404-6429

Author Contributions

Z. S. Wu, C.L. Sun, H.M. Cheng, and X.H. Bao proposed and supervised the overall project. S. Wang did the photoreduction of GO-based films, fabrication and electrochemical measurement of MSCs. S. Wang and Z. S. Wu analyzed the data. S. H. Zheng and F. Zhou participated in the architecture design of different planar MSCs, the preparation of electrolytes and the characterization of the related materials. S. Wang, Z. S. Wu, C. L. Sun, H. M. Cheng and X. H. Bao wrote the paper. All authors discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant 51572259), National Key R&D Program of China (Grants 2016YBF0100100, 2016YFA0200200), Natural Science Foundation of Liaoning Province (Grant 201602737), Thousand Youth Talents Plan of China, and DICP (Grant Y5610121T3).

REFERENCES

(1) Gates, B. D. Flexible Electronics. Science 2009, 323, 1566-1567.

(2) Rogers, J. A.; Someya, T.; Huang, Y. G. Materials and Mechanics for Stretchable Electronics. *Science* **2010**, 327, 1603–1607.

(3) Cima, M. J. Next-Generation Wearable Electronics. Nat. Biotechnol. 2014, 32, 642-643.

(4) Beidaghi, M.; Gogotsi, Y. Capacitive Energy Storage in Micro-Scale Devices: Recent Advances in Design and Fabrication of Micro-Supercapacitors. *Energy Environ. Sci.* **2014**, *7*, 867–884.

(5) Liu, C.; Li, F.; Ma, L. P.; Cheng, H. M. Advanced Materials for Energy Storage. *Adv. Mater.* **2010**, *22*, E28–E62.

(6) Harada, S.; Honda, W.; Arie, T.; Akita, S.; Takei, K. Fully Printed, Highly Sensitive Multifunctional Artificial Electronic Whisker Arrays Integrated with Strain and Temperature Sensors. *ACS Nano* **2014**, *8*, 3921–3927.

(7) Zheng, S.; Tang, X.; Wu, Z.-S.; Tan, Y.-Z.; Wang, S.; Sun, C.; Cheng, H.-M.; Bao, X. Arbitrary-Shaped Graphene-Based Planar Sandwich Supercapacitors on One Substrate with Enhanced Flexibility and Integration. *ACS Nano* **2017**, *11*, 2171–2179.

(8) Wu, Z.-S.; Parvez, K.; Feng, X. L.; Müllen, K. Graphene-Based In-Plane Micro-Supercapacitors with High Power and Energy Densities. *Nat. Commun.* **2013**, *4*, 2487.

(9) Wu, Z.-S.; Feng, X.; Cheng, H.-M. Recent Advances in Graphene-Based Planar Micro-Supercapacitors for On-Chip Energy Storage. *Natl. Sci. Rev.* **2014**, *1*, 277–292.

(10) Chmiola, J.; Largeot, C.; Taberna, P. L.; Simon, P.; Gogotsi, Y. Monolithic Carbide-Derived Carbon Films for Micro-Supercapacitors. *Science* **2010**, *328*, 480–483.

(11) Wang, K.; Zou, W. J.; Quan, B. G.; Yu, A. F.; Wu, H. P.; Jiang, P.; Wei, Z. X. An All-Solid-State Flexible Micro-Supercapacitor on A Chip. *Adv. Energy Mater.* **2011**, *1*, 1068–1072.

(12) Pech, D.; Brunet, M.; Durou, H.; Huang, P. H.; Mochalin, V.; Gogotsi, Y.; Taberna, P. L.; Simon, P. Ultrahigh-Power Micrometre-Sized Supercapacitors Based on Onion-Like Carbon. *Nat. Nanotechnol.* **2010**, *5*, 651–654.

(13) Dinh, T. M.; Achour, A.; Vizireanu, S.; Dinescu, G.; Nistor, L.; Armstrong, K.; Guay, D.; Pech, D. Hydrous RuO₂/Carbon Nanowalls Hierarchical Structures for All-Solid-State Ultrahigh-Energy-Density Micro-Supercapacitors. *Nano Energy* **2014**, *10*, 288–294.

(14) Si, W.; Yan, C.; Chen, Y.; Oswald, S.; Han, L.; Schmidt, O. G. On Chip, All Solid-State and Flexible Micro-Supercapacitors with High Performance Based on MnO_x/Au Multilayers. *Energy Environ. Sci.* 2013, *6*, 3218–3223.

(15) Ferris, A.; Garbarino, S.; Guay, D.; Pech, D. 3D RuO_2 Microsupercapacitors with Remarkable Areal Energy. *Adv. Mater.* 2015, 27, 6625–6629.

(16) Gao, W.; Singh, N.; Song, L.; Liu, Z.; Reddy, A. L. M.; Ci, L. J.; Vajtai, R.; Zhang, Q.; Wei, B. Q.; Ajayan, P. M. Direct Laser Writing of Micro-Supercapacitors on Hydrated Graphite Oxide Films. *Nat. Nanotechnol.* **2011**, *6*, 496–500.

(17) Wu, Z.-S.; Parvez, K.; Li, S.; Yang, S.; Liu, Z. Y.; Liu, S. H.; Feng, X. L.; Müllen, K. Alternating Stacked Graphene-Conducting Polymer Compact Films with Ultrahigh Areal and Volumetric Capacitances for High-Energy Micro-Supercapacitors. *Adv. Mater.* **2015**, *27*, 4054–4061.

(18) Chang, J.; Adhikari, S.; Lee, T. H.; Li, B.; Yao, F.; Pham, D. T.; Le, V. T.; Lee, Y. H. Leaf Vein-Inspired Nanochanneled Graphene Film for Highly Efficient Micro-Supercapacitors. *Adv. Energy Mater.* **2015**, *5*, 1500003.

(19) Liu, Z.; Wu, Z.-S.; Yang, S.; Dong, R.; Feng, X.; Müllen, K. Ultraflexible In-Plane Micro-Supercapacitors by Direct Printing of Solution-Processable Electrochemically Exfoliated Graphene. *Adv. Mater.* **2016**, *28*, 2217–2222.

(20) Kim, S. K.; Koo, H. J.; Lee, A.; Braun, P. V. Selective Wetting-Induced Micro-Electrode Patterning for Flexible Micro-Supercapacitors. *Adv. Mater.* **2014**, *26*, 5108–5112. (21) El-Kady, M. F.; Kaner, R. B. Scalable Fabrication of High-Power Graphene Micro-Supercapacitors for Flexible and On-Chip Energy Storage. *Nat. Commun.* **2013**, *4*, 1475.

(22) Kim, D.; Shin, G.; Kang, Y. J.; Kim, W.; Ha, J. S. Fabrication of a Stretchable Solid-State Micro-Supercapacitor Array. *ACS Nano* **2013**, 7, 7975–7982.

(23) El-Kady, M. F.; Ihns, M.; Li, M. P.; Hwang, J. Y.; Mousavi, M. F.; Chaney, L.; Lech, A. T.; Kaner, R. B. Engineering Three-Dimensional Hybrid Supercapacitors and Microsupercapacitors for High-Performance Integrated Energy Storage. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 4233–4238.

(24) Meng, F. H.; Ding, Y. Sub-Micrometer-Thick All-Solid-State Supercapacitors with High Power and Energy Densities. *Adv. Mater.* **2011**, 23, 4098–4012.

(25) Beidaghi, M.; Gogotsi, Y. Capacitive Energy Storage in Micro-Scale Devices: Recent Advances in Design and Fabrication of Micro-Supercapacitors. *Energy Environ. Sci.* **2014**, *7*, 867–884.

(26) Wu, Z.-S.; Parvez, K.; Winter, A.; Vieker, H.; Liu, X.; Han, S.; Turchanin, A.; Feng, X.; Müllen, K. Layer-by-Layer Assembled Heteroatom-Doped Graphene Films with Ultrahigh Volumetric Capacitance and Rate Capability for Micro-Supercapacitors. *Adv. Mater.* **2014**, *26*, 4552–4558.

(27) Yang, X. W.; Cheng, C.; Wang, Y. F.; Qiu, L.; Li, D. Liquid-Mediated Dense Integration of Graphene Materials for Compact Capacitive Energy Storage. *Science* **2013**, *341*, 534–537.

(28) Niu, Z. Q.; Zhang, L.; Liu, L. L.; Zhu, B. W.; Dong, H. B.; Chen, X. D. All-Solid-State Flexible Ultrathin Micro-Supercapacitors Based on Graphene. *Adv. Mater.* **2013**, *25*, 4035–4042.

(29) Wu, Z.-K.; Lin, Z.; Li, L.; Song, B.; Moon, K.-s.; Bai, S.-L.; Wong, C.-P. Flexible Micro-Supercapacitor Based on *In-Situ* Assembled Graphene on Metal Template at Room Temperature. *Nano Energy* **2014**, *10*, 222–228.

(30) Yoo, J. J.; Balakrishnan, K.; Huang, J. S.; Meunier, V.; Sumpter, B. G.; Srivastava, A.; Conway, M.; Reddy, A. L. M.; Yu, J.; Vajtai, R.; Ajayan, P. M. Ultrathin Planar Graphene Supercapacitors. *Nano Lett.* **2011**, *11*, 1423–1427.

(31) Liu, W. W.; Feng, Y. Q.; Yan, X. B.; Chen, J. T.; Xue, Q. J. Superior Micro-Supercapacitors Based on Graphene Quantum Dots. *Adv. Funct. Mater.* **2013**, *23*, 4111–4122.

(32) Liu, W.; Lu, C.; Wang, X.; Tay, R. Y.; Tay, B. K. High-Performance Microsupercapacitors Based on Two-Dimensional Graphene/Manganese Dioxide/Silver Nanowire Ternary Hybrid Film. *ACS Nano* **2015**, *9*, 1528–1542.

(33) Wang, S.; Zheng, S.; Wu, Z.-S.; Sun, C. Recent Advances in Graphene-Based Planar Micro-Supercapacitors. *Sci. Sin. Chim.* **2016**, 46, 732–744.

(34) Wei, L.; Nitta, N.; Yushin, G. Lithographically Patterned Thin Activated Carbon Films as A New Technology Platform for On-Chip Devices. *ACS Nano* **2013**, *7*, 6498–6506.

(35) Choi, K.-H.; Yoo, J.; Lee, C. K.; Lee, S.-Y. All-Inkjet-Printed, Solid-State Flexible Supercapacitors on Paper. *Energy Environ. Sci.* **2016**, *9*, 2812–2821.

(36) Pang, H.; Zhang, Y. Z.; Lai, W. Y.; Hu, Z.; Huang, W. Lamellar $K_2Co_3(P_2O_7)_2$ ·2H₂O Nanocrystal Whiskers: High-Performance Flexible All-Solid-State Asymmetric Micro-Supercapacitors *via* Inkjet Printing. *Nano Energy* **2015**, *15*, 303–312.

(37) Hu, H.; Pei, Z.; Ye, C. Recent Advances in Designing and Fabrication of Planar Micro-Supercapacitors for On-Chip Energy Storage. *Energy Storage Mater.* **2015**, *1*, 82–102.

(38) Peng, Z. W.; Ye, R. Q.; Mann, J. A.; Zakhidov, D.; Li, Y. L.; Smalley, P. R.; Lin, J.; Tour, J. M. Flexible Boron-Doped Laser-Induced Graphene Microsupercapacitors. *ACS Nano* **2015**, *9*, 5868– 5875.

(39) Lin, J.; Peng, Z.; Liu, Y.; Ruiz-Zepeda, F.; Ye, R.; Samuel, E. L. G.; Yacaman, M. J.; Yakobson, B. I.; Tour, J. M. Laser-Induced Porous Graphene Films from Commercial Polymers. *Nat. Commun.* **2014**, *5*, 5714.

(40) Huang, H.-C.; Chung, C.-J.; Hsieh, C.-T.; Kuo, P.-L.; Teng, H. Laser Fabrication of All-Solid-State Microsupercapacitors with Ultra-

high Energy and Power Based on Hierarchical Pore Carbon. *Nano* Energy **2016**, *21*, 90–105.

(41) Wu, Z.-S.; Parvez, K.; Feng, X. L.; Müllen, K. Photolithographic Fabrication of High-Performance All-Solid-State Graphene-Based Planar Micro-Supercapacitors with Different Interdigital Fingers. *J. Mater. Chem. A* **2014**, *2*, 8288–8293.

(42) Wu, Z.-S.; Yang, S.; Zhang, L.; Wagner, J. B.; Feng, X.; Müllen, K. Binder-Free Activated Graphene Compact Films for All-Solid-State Micro-Supercapacitors with High Areal and Volumetric Capacitances. *Energy Storage Mater.* **2015**, *1*, 119–126.

(43) Sun, G. Z.; An, J.; Chua, C. K.; Pang, H. C.; Zhang, J.; Chen, P. Layer-by-Layer Printing of Laminated Graphene-Based Interdigitated Microelectrodes for Flexible Planar Micro-Supercapacitors. *Electrochem. Commun.* **2015**, *51*, 33–36.

(44) Williams, G.; Seger, B.; Kamat, P. V. TiO_2 -Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. ACS Nano 2008, 2, 1487–1491.

(45) Akhavan, O. Photocatalytic Reduction of Graphene Oxides Hybridized by ZnO Nanoparticles in Ethanol. *Carbon* **2011**, *49*, 11– 18.

(46) Qin, J. W.; Cao, M. H.; Li, N.; Hu, C. W. Graphene-Wrapped WO₃ Nanoparticles with Improved Performances in Electrical Conductivity and Gas Sensing Properties. *J. Mater. Chem.* **2011**, *21*, 17167–17174.

(47) Li, H. L.; Pang, S. P.; Wu, S.; Feng, X. L.; Müllen, K.; Bubeck, C. Layer-by-Layer Assembly and UV Photoreduction of Graphene-Polyoxometalate Composite Films for Electronics. *J. Am. Chem. Soc.* **2011**, *133*, 9423–9429.

(48) Zhang, Y. L.; Guo, L.; Xia, H.; Chen, Q. D.; Feng, J.; Sun, H. B. Photoreduction of Graphene Oxides: Methods, Properties, and Applications. *Adv. Opt. Mater.* **2014**, *2*, 10–28.

(49) Gengler, R. Y. N.; Badali, D. S.; Zhang, D. F.; Dimos, K.; Spyrou, K.; Gournis, D.; Miller, R. J. D. Revealing the Ultrafast Process Behind the Photoreduction of Graphene Oxide. *Nat. Commun.* **2013**, *4*, 2560.

(50) Zhang, Q.; Scrafford, K.; Li, M. T.; Cao, Z. Y.; Xia, Z. H.; Ajayan, P. M.; Wei, B. Q. Anomalous Capacitive Behaviors of Graphene Oxide Based Solid-State Supercapacitors. *Nano Lett.* **2014**, *14*, 1938–1943.

(51) Lin, J.; Zhang, C. G.; Yan, Z.; Zhu, Y.; Peng, Z. W.; Hauge, R. H.; Natelson, D.; Tour, J. M. 3-Dimensional Graphene Carbon Nanotube Carpet-Based Microsupercapacitors with High Electrochemical Performance. *Nano Lett.* **2013**, *13*, 72–78.

(52) Beidaghi, M.; Wang, C. L. Micro-Supercapacitors Based on Interdigital Electrodes of Reduced Graphene Oxide and Carbon Nanotube Composites with Ultra High Power Handling Performance. *Adv. Funct. Mater.* **2012**, *22*, 4501–4510.

(53) Li, H.; Pang, S.; Wu, S.; Feng, X.; Mullen, K.; Bubeck, C. Layerby-Layer Assembly and UV Photoreduction of Graphene-Polyoxometalate Composite Films for Electronics. *J. Am. Chem. Soc.* **2011**, *133*, 9423–9429.

(54) Cote, L. J.; Cruz-Silva, R.; Huang, J. Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite. J. Am. Chem. Soc. 2009, 131, 11027–11032.

(55) Huang, H.; Lei, C.; Luo, G.; Li, G.; Liang, X.; Tang, S.; Du, Y. UV-Assisted Reduction of Graphene Oxide on Ni Foam as High Performance Electrode for Supercapacitors. *Carbon* **2016**, *107*, 917–924.

(56) Zhang, H.; Lv, X. J.; Li, Y. M.; Wang, Y.; Li, J. H. P25-Graphene Composite as A High Performance Photocatalyst. *ACS Nano* **2010**, *4*, 380–386.

(57) Sun, X.; Xie, M.; Wang, G.; Sun, H.; Cavanagh, A. S.; Travis, J. J.; George, S. M.; Lian, J. Atomic Layer Deposition of TiO_2 on Graphene for Supercapacitors. *J. Electrochem. Soc.* **2012**, *159*, A364–A369.

(58) Wu, Z.-S.; Zhou, G. M.; Yin, L. C.; Ren, W. C.; Li, F.; Cheng, H. M. Graphene/Metal Oxide Composite Electrode Materials for Energy Storage. *Nano Energy* **2012**, *1*, 107–131.

(59) Wen, L.; Li, F.; Cheng, H.-M. Carbon Nanotubes and Graphene for Flexible Electrochemical Energy Storage: from Materials to Devices. *Adv. Mater.* **2016**, *28*, 4306–4337.

(60) El-Kady, M. F.; Strong, V.; Dubin, S.; Kaner, R. B. Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors. *Science* **2012**, 335, 1326–1330.

(61) Wu, Z.-S.; Liu, Z.; Parvez, K.; Feng, X.; Müllen, K. Ultrathin Printable Graphene Supercapacitors with AC Line-Filtering Performance. *Adv. Mater.* **2015**, *27*, 3669–3675.

(62) Zhang, S.; Pan, N. Supercapacitors Performance Evaluation. *Adv. Energy Mater.* **2015**, *8*, 1401401.

(63) Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. *Nat. Mater.* **2008**, *7*, 845–854.

(64) Zhu, Y. W.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W. W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; et al. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science* **2011**, *332*, 1537–1541.

(65) Pech, D.; Brunet, M.; Durou, H.; Huang, P.; Mochalin, V.; Gogotsi, Y.; Taberna, P.-L.; Simon, P. Ultrahigh-Power Micrometre-Sized Supercapacitors Based on Onion-Like Carbon. *Nat. Nanotechnol.* **2010**, *5*, 651–654.

(66) Aradilla, D.; Delaunay, M.; Sadki, S.; Gerard, J.-M.; Bidan, G. Vertically Aligned Graphene Nanosheets on Dilicon Using An Ionic Liquid Electrolyte: Towards High Performance On-Chip Micro-Supercapacitors. J. Mater. Chem. A 2015, 3, 19254–19262.

(67) Ma, Y.; Wang, M.; Kim, N.; Suhr, J.; Chae, H. A Flexible Supercapacitor Based on Vertically Oriented 'Graphene Forest' Electrodes. J. Mater. Chem. A **2015**, *3*, 21875–21881.

(68) Ben, H.; Julian, M.; Shuang, W.; Jung Bin, I.; Carlo, C.; Dimos, P.; Costas, P. G.; Roya, M. Highly Flexible, All Solid-State Micro-Supercapacitors from Vertically Aligned Carbon Nanotubes. *Nanotechnology* **2014**, *25*, 055401.

(69) Yu, D. S.; Goh, K.; Wang, H.; Wei, L.; Jiang, W. C.; Zhang, Q.; Dai, L. M.; Chen, Y. Scalable Synthesis of Hierarchically Structured Carbon Nanotube-Graphene Fibres for Capacitive Energy Storage. *Nat. Nanotechnol.* **2014**, *9*, 555–562.

(70) Meng, C.; Maeng, J.; John, S. W. M.; Irazoqui, P. P. Ultrasmall Integrated 3D Micro-Supercapacitors Solve Energy Storage for Miniature Devices. *Adv. Energy Mater.* **2014**, *3*, 1301269.

(71) Gogotsi, Y.; Simon, P. True Performance Metrics in Electrochemical Energy Storage. *Science* **2011**, 334, 917–918.

(72) Pech, D.; Brunet, M.; Taberna, P. L.; Simon, P.; Fabre, N.; Mesnilgrente, F.; Conedera, V.; Durou, H. Elaboration of A Microstructured Inkjet-Printed Carbon Electrochemical Capacitor. *J. Power Sources* **2010**, *195*, 1266–1269.

(73) Wu, Z. S.; Ren, W.; Gao, L.; Liu, B.; Jiang, C.; Cheng, H. M. Synthesis of High-Quality Graphene with A Pre-Determined Number of Layers. *Carbon* **2009**, *47*, 493–499.

(74) Wu, Z.-S.; Ren, W. C.; Gao, L. B.; Zhao, J. P.; Chen, Z. P.; Liu, B. L.; Tang, D. M.; Yu, B.; Jiang, C. B.; Cheng, H. M. Synthesis of Graphene Sheets with High Electrical Conductivity and Good Thermal Stability by Hydrogen Arc Discharge Exfoliation. *ACS Nano* **2009**, *3*, 411–417.

(75) Wu, Z. S.; Ren, W.; Wen, L.; Gao, L.; Zhao, J.; Chen, Z.; Zhou, G.; Li, F.; Cheng, H. M. Graphene Anchored with Co_3O_4 Nanoparticles as Anode of Lithium Ion Batteries with Enhanced Reversible Capacity and Cyclic Performance. *ACS Nano* **2010**, *4*, 3187–3194.