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COMMUNICATION

High performance solid-state supercapacitors based on compressed graphene foam†

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Flexible and solid-state supercapacitors are made using compressed graphene foams as electrodes and highly conductive carbon nanotube films (CNTs) as current collectors. By using a 10 μm thick graphene electrodes we obtain a capacitance of 10 mF/cm^2 . The combination of graphene foam and CNT film leads to high performance devices.

The thriving market of information devices, such as mobile phones, touch pads, and wearable gadgets, is stimulating the demand for environment-friendly and durable energy storage devices. Moreover, the future electronics are expected to be flexible, which requires the integrated power supplier to be bendable. Flexible printed circuits,¹ which have a large variety of applications, are being intensively studied; Prototypes of smart phones with flexible displays have been released by some major companies.² Therefore, it is imperative to develop bendable and high-performance energy storage devices to replace the currently used rigid Li-ion batteries. Supercapacitors hold the potential to replace conventional batteries in the future. In addition to the well-known fast charge-discharge rate, supercapacitors have much longer cycle life and lower cost compared to Li-battery. Bulky supercapacitors based on activated carbon have been combined with batteries to improve the energy efficiency of electric vehicles. However, supercapacitors still lag behind conventional batteries in electrical energy storage capacity, creating the current bottleneck in technology. Nanomaterials could be the key to make thin and bendable supercapacitors with enough energy to power portable devices.

Two types of supercapacitors are currently being studied by researchers: pseudo-supercapacitors which rely on the redox process between electrodes and electrolyte,³ and electric double layer (EDL) supercapacitors which store charge through the physisorption of electrolyte ions onto porous carbon electrodes.⁴ The electrolyte can be either liquid or solid. Solid-state supercapacitors with polymer electrolyte are interesting in that the elaborate encapsulation is avoided and the device is suitable for space-saving design. For a liquid-based supercapacitor, usually a separator film between two electrodes is needed, adding thickness to the device. Today commercial supercapacitors are of the EDL type and the electrodes are based on porous activated carbon, normally made from coconut shell. In recent years several attempts to apply carbon nanomaterials in supercapacitors have been carried out. It was found that the performance of carbon-nanotube-based supercapacitors was not satisfactory.⁵ Graphene has been considered as an ideal candidate for supercapacitor electrodes since its discovery in 2004.⁶ Graphene has a theoretical specific surface area of 2630 m^2/g , which can give a calculated specific capacitance of 550 F/g .⁷ So far, various techniques to make graphene-based supercapacitors have been reported. Graphene prepared by chemical vapour deposition has high quality, but a low yield.⁸ Recently, researchers have been using reduced graphene oxide (rGO) as an alternative to make supercapacitors.⁹ GO is typically prepared by wet chemical methods with graphite powder as precursor. The highly resistive GO can be reduced by either solution method or by heating, increasing in this way its charge mobility, and converting the color from brown to black.

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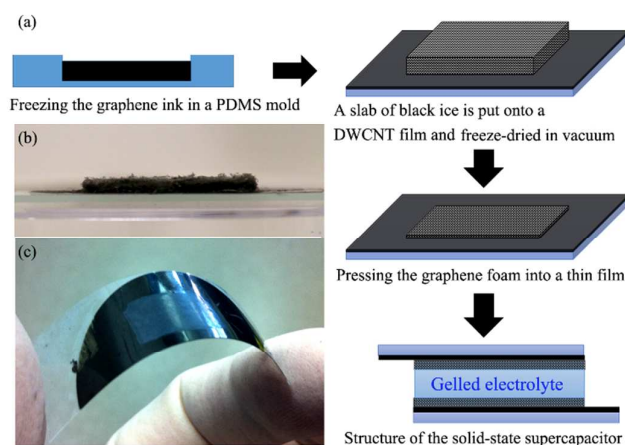


Fig.1 (a) Illustration of the process to produce a graphene foam. The sandwich structure of the device with compressed graphene foam is shown. (b) Side-view optical photograph of a graphene foam. (c) The graphene foam compressed against a DWCNT film. The good adhesion between the graphene film and DWCNT film is demonstrated by bending the plastic-based substrate.

El-Kady *et al* developed a laser-scribing method to thermally reduce the GO film, obtaining relatively high quality graphene with an incompact structure to make solid-state supercapacitors.¹⁰ The high electrical conduction of the rGO film makes it suitable both as supercapacitor electrode and as current collector. Though a specific capacitance of 5 mF/cm² was achieved, there is no much room for improvement, due to the limited of penetration depth of the laser-beam in a thick GO film. Yoon *et al* used a solution technique to make rGO sheets crumpled, thus when pasted to be supercapacitor electrodes the re-stacking behavior of graphene sheets is reduced and the capacitance is about 50 % increased.¹¹ This method is not suitable for making solid-electrolyte-based supercapacitors as the electrodes are too thick. The other way is to make graphene electrodes with a 3D structure, facilitating the infiltration of electrolyte.¹² In terms of device fabrication, the use of liquid electrolyte requires high-standard encapsulation and a separator between two electrodes which adds on the device thickness. Polymer electrolyte is suitable for making solid-state and thin supercapacitors if using a sandwich structure, for the thickness of electrolyte layer is less than 50 μm . Previously, we used electrochemically-exfoliated graphene to make solid-state supercapacitors: graphene films made by a vacuum filtration method are transferred onto highly conductive double-wall carbon nanotube (DWCNT) films, which act as current collectors.¹³

In this paper, we report the use of graphene foam and polymer electrolyte to make solid-state and high-performance supercapacitors.

The preparation of DWCNT films have been reported previously.¹³ Briefly, CNTs dispersed in chlorosulfonic acid were vacuum filtered onto a porous alumina membrane, followed by a chloroform wash to remove the acid. This produces a coagulation process through which CNTs stick to each other. The dried DWCNT film was transferred onto a polyethylene terephthalate (PET) plastic

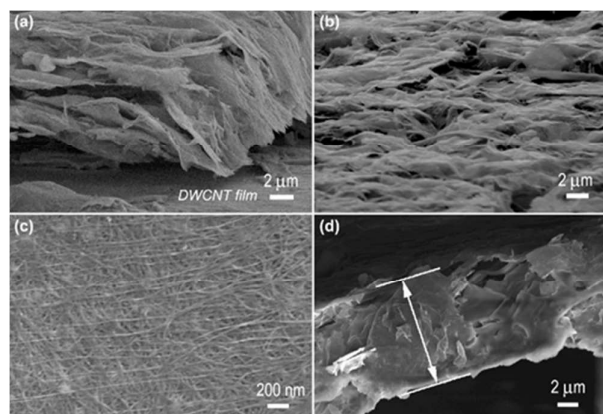


Fig.2 (a) FE-SEM images of the sample. (a) Side-view image of a compressed graphene foam. A tilted view image of the rough surface is shown in (b). (c) A plane-view image of the DWCNT film. (d) Cross-section of the compressed graphene foam, showing the thickness of $\sim 10 \mu\text{m}$.

substrate by dissolving the membrane with NaOH solution. The sheet resistance of the DWCNT film was measured to be 5 Ω/sq .

We produced graphene by a simple ultrasound-assisted electrochemical exfoliation method.¹⁴ To make a graphene foam, firstly the ink was prepared by dispersing graphene sheets into deionized water at concentration of 1.5 mg/ml. Figure 1a illustrates the process to make a graphene foam. First, the ink filled in a polydimethylsiloxane (PDMS) rubber mold was frozen into an ice slab. Second, this ice piece was transferred from the mold onto a PET-supported DWCNT film. Because the DWCNT film was not pre-cooled, the ice slab partially melted at the interface but was soon entirely frozen in the refrigerator, making the black ice stick to the substrate. After a vacuum freeze-drying process a graphene foam attached to the DWCNT film substrate was formed (Fig. 1b). Third, the foam was pressed at 520 MPa to make it into thin film form. This substrate was cut into rectangular shapes to make sandwich-structured supercapacitors as shown in Fig. 1a. It should be addressed that the compressed graphene foam was well attached to the substrate, and no visible cracks appear in the film when bent, as seen in Fig. 1c.

To make a device, polyvinyl alcohol (PVA) aqueous solution containing phosphoric acid was applied to the surfaces of two substrates with the graphene electrodes up. After drying for 5 h at room temperature in air, the two substrates were stacked together with the gelled electrolyte acting as binder. Typically the overlapped area of the two electrodes is 0.8 cm² and the thickness of electrolyte layer is about 20 μm .

Figure 2 shows the field-emission scanning electron microscopy (FE-SEM) images of carbon films used to make devices. The edge of the graphene film is shown in Fig. 2a. The tilted-view image in Fig. 2b shows the rough surface of the graphene film. From Figs. 2a and 2b it can be seen that graphene sheets in the electrode film are not tightly stacked. When the compressed foam is included into a device, voids among graphene sheets and pits in the rough

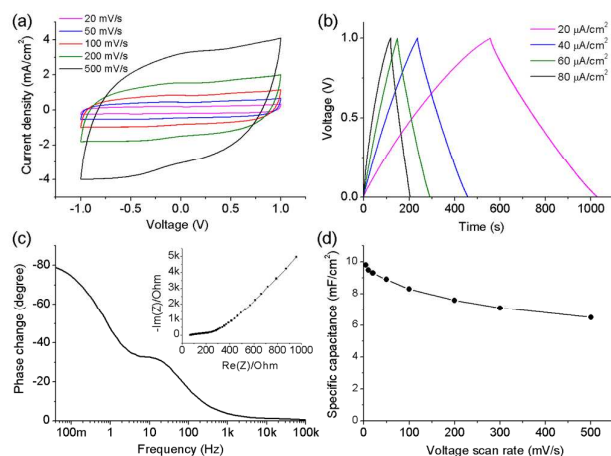


Fig. 3 (a) Current-Voltage curves of the device measured with different voltage scan rate. (b) Galvanostatic charge-discharge curves. (c) The relationship of phase angle change with frequency. (d) The relationship of specific capacitance, which are deduced from the CV curves, with the voltage scan rate.

surface are supposed to be filled with gelled electrolyte. The DWCNT film, which is about 200-nm-thick, has good contact with the graphene electrode and acts as the current collector. A typical SEM image in Fig. 2c shows the felt feature of the DWCNT film. In order to measure the thickness of the compressed graphene foam, we took cross-sectional images of a free-standing graphene film. The original thickness of the graphene foam was 1.5 mm. However it was squeezed to be 10 μm as can be seen in Fig. 2d.

Figure 3a shows the cyclical current-voltage (CV) curves of a typical device measured at different voltage scan rates and in the voltage range of -1.0 to 1.0 V. At low voltage scan rate the CV curves exhibit rectangular-like shape, indicating a good capacitance property. Figure 3b shows the galvanostatic charge-discharge (CD) curves of the device measured at different current densities. Both CV and CD curves can be used to calculate the capacitance of the device. Impedance spectroscopy analysis was carried out over a frequency range from 0.04 Hz to 1 MHz. Figure 3c shows the relationship of phase angle change with frequency. At low frequency a phase change of -78° is achieved. For our device the characteristic frequency f_0 for a phase angle of -45° , i.e. the point at which the resistive and capacitive impedances are equal is 1.2 Hz. For a supercapacitor with activated carbon electrode the value of f_0 is about 0.1 Hz.¹⁵ The inset in Fig. 3c shows the impedance spectrum, revealing that the series resistance of the device is about 60 Ω . We believe that most of the resistance is caused by the graphene electrode, as the DWCNT film is very conductive. Figure 3d shows the relationship of specific capacitance of the device against voltage scan rate, which is deduced from CV curves. For electrochemical supercapacitors a common phenomenon is that the capacitance decreases with increasing the voltage scan rate. The reason is that at lower voltage scan rate the ions from electrolyte have more time to diffuse into the electrode, thus the capacitance is higher. The maximum capacitance of our device with 10- μm -thick graphene electrode is around 10 mF/cm^2 . For the laser-scribed GO

film in Ref (9), the thickness of graphene layer is about 7.6 μm and the capacitance is 5 mF/cm^2 . Our graphene made by the electrochemical exfoliation method is actually few-layer graphene mostly composed of bilayer sheets.¹⁴ Though the electrochemical exfoliation method can produce graphene with high quality, it is difficult to obtain monolayer graphene.¹⁶ Considering that the ratio of surface area to weight plays an important role in specific

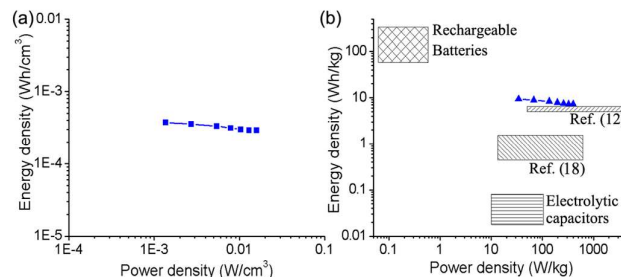


Fig. 4 Ragone plots showing the energy and power densities in (a) volume and (b) weight. For comparison the range of values for different devices in are shown.

capacitance, the capacitance would increase by reducing the percentage of thick graphene sheets.

The energy and power densities of the device, obtained from the galvanostatic CD curves, are given in Fig. 4. Our device is designed to be thin and flat. One reason that we squeeze the graphene foam into thin film form is to make the thinnest-possible device. Therefore, to evaluate the device performance, power and energy densities in volume should be considered. In Fig. 4a, the energy density of our device is in the scale of 10^{-4} Wh/cm^3 and the power density is in the range of 10^{-3} - 10^{-2} W/cm^3 . As a comparison, the energy density of Li-ion thin film battery reported in literature is in the range of 10^{-4} - 10^{-3} Wh/cm^3 .¹⁷ For the supercapacitor based on laser-scribed graphene and with PVA- H_3PO_4 gelled electrolyte, the energy density is in the scale of 10^{-5} Wh/cm^3 .¹⁰ The energy and power densities in weight are commonly used to evaluate supercapacitors with liquid electrolyte. Normally the thickness of such devices is not an important issue. Using the areal density (0.08 mg/cm^2) of the compressed graphene foam, the energy and power densities of our device are deduced and shown in Fig. 4b. For the device with graphene hydrogel foam as electrode,¹² the rGO foam was compressed against a gold foil and the thickness was ~ 120 μm . The energy and power densities of that device with gelled electrolyte are included in the narrow rectangular in the Ragone plot. Wang *et al* coated porous graphene onto carbon cloth and made solid-state supercapacitors,¹⁸ of which the region for energy and power densities are given in Fig. 4b. In our device the 3D structure of compressed graphene foam makes gelled electrolyte fully infiltrated into the electrode, favoring the energy density. Moreover, no reduction process is required for these exfoliated graphene sheets. This approach of using compressed graphene foams as supercapacitor electrodes could be further improved by incorporating CNTs to prevent restacking of graphene sheets.¹⁹

In summary, we have made solid-state and bendable supercapacitors with compressed graphene foams as

electrodes and highly-conductive DWCNT films as current collectors. The 10 μm graphene electrode is infiltrated by gelled electrolyte and exhibits high specific capacitance, of the order of 10 mF/cm^2 . The device shows high volumetric energy density comparable to that of Li-ion thin film battery. Moreover, our high quality graphene sheets, prepared by a simple electrochemical exfoliation method, produce a 3D-structure well attached to the DWCNT film. Energy density around 10 Wh/Kg is achieved from the device.

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- 1 W. Wong, A. Salleo, *Flexible electronics: Materials and applications*, Springer, Germany, 2009.
- 2 <http://edition.cnn.com/2013/10/08/tech/mobile/lg-flexible-display/index.html>
- 3 M. Zhi, C. Xiang, J. Li, M. Li, and N. Wu, *Nanoscale*, 2013, **3**, 72.
- 4 F. Béguin, V. Presser, A. Balducci, and E. Frackowiak, *Adv. Mater.* 2014, **26**, 2219.
- 5 K. H. An, W. S. Kim, Y. S. Park, Y. C. Choi, S. M. Lee, D. C. Chung, D. J. Bae, S. C. Lim, and Y. H. Lee, *Adv. Mater.*, 2001, **13**, 497; S. Hu, R. Rajamani, and X. Yu, *Appl. Phys. Lett.*, 2012, **100**, 104103; H. Lin, L. Li, J. Ren, Z. Cai, L. Qiu, Z. Yang, and H. Peng, *Sci. Rep.* 2013, **3**, 1353.
- 6 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, 2004, **306**, 666.
- 7 <http://en.wikipedia.org/wiki/User:Elcap/Supercapacitor>
- 8 Y. Zhang, L. Zhang, and C. Zhou, *Acc. Chem. Res.* 2013, **46**, 2329.
- 9 L. L. Zhang, R. Zhou, and X. S. Zhao, *J. Mater. Chem.* 2010, **20**, 5983; Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, and Y. Chen, *J. Phys. Chem. C* 2009, **113**, 13103; C. Liu, Z. Yu, D. Neff, A. Zhamu, and B. Z. Jang, *Nano Lett.* 2010, **10**, 4863; B. Zhao, P. Liu, Y. Jiang, D. Pan, H. Tao, J. Song, T. Fang, and W. Xu, *J. Power Sources*, 2012, **198**, 423.
- 10 M. F. El-Kady, V. Strong, S. Dubin, and R. B. Kaner, *Science*, 2012, **335**, 1326.
- 11 Y. Yoon, K. Lee, C. Baik, H. Yoo, M. Min, Y. Park, S. M. Lee, and H. Lee, *Adv. Mater.*, 2013, **25**, 4437.
- 12 Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, and X. Duan, *ACS Nano*, 2013, **7**, 4042.
- 13 M. Notarianni, J. Liu, F. Mirri, M. Pasquali, and N. Motta, *Nanotechnology*, 2014, **25**, 435405.
- 14 J. Liu, M. Notarianni, G. Will, V. T. Tiong, H. Wang, and N. Motta, *Langmuir*, 2013, **29**, 13307.
- 15 J. R. Miller, R. A. Outlaw, B. C. Holloway, *Science*, 2010, **329**, 1637.
- 16 C. Y. Su, A. Y. Lu, Y. Xu, F. R. Chen, A. N. Khlobystov, and L. J. Li, *ACS Nano*, 2011, **5**, 2332.
- 17 D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, and P. Simon, *Nat. Nanotech.*, 2010, **5**, 651.

- 18 S. Wang, B. Pei, X. Zhao, R. A. W. Dryfe, *Nano Energy*, 2013, **2**, 530.
- 19 L. Jiang, L. Sheng, C. Long, Z. Fan, *Nano Energy*, 2015, **11**, 471.