**3D Printing** 



# Laminated Object Manufacturing of 3D-Printed Laser-Induced Graphene Foams

Duy Xuan Luong, Ajay K. Subramanian, Gladys A. Lopez Silva, Jongwon Yoon, Savannah Cofer, Kaichun Yang, Peter Samora Owuor, Tuo Wang, Zhe Wang, Jun Lou, Pulickel M. Ajayan, and James M. Tour\*

Laser-induced graphene (LIG), a graphene structure synthesized by a onestep process through laser treatment of commercial polyimide (PI) film in an ambient atmosphere, has been shown to be a versatile material in applications ranging from energy storage to water treatment. However, the process as developed produces only a 2D product on the PI substrate. Here, a 3D LIG foam printing process is developed on the basis of laminated object manufacturing, a widely used additive-manufacturing technique. A subtractive laser-milling process to yield further refinements to the 3D structures is also developed and shown here. By combining both techniques, various 3D graphene objects are printed. The LIG foams show good electrical conductivity and mechanical strength, as well as viability in various energy storage and flexible electronic sensor applications.

Graphene, a 2D nanomaterial consisting of a monolayer of sp<sup>2</sup>hybridized carbon atoms, has attracted recent interest due to its unique materials properties, notably its high electrical and thermal conductivities and exceptional mechanical strength.<sup>[1–6]</sup> In order to pursue applications that require production of large objects of graphene, it is advantageous to integrate the properties of 2D graphene into macroscopic, 3D structures. Several different methods have been developed to produce 3D graphene macrostructures, often called graphene foams (GFs). The current fabrication process for GF can be categorized in one of two categories: 1) growth of graphene on a porous metal foam<sup>[7,8]</sup> and 2) printing and reduction of a graphene oxide (GO) dispersion.<sup>[9-11]</sup> A direct approach to GF that does not need metals or GO and that is not made from graphite using wet chemistry, is desirable. We have recently experimented with using powder-bed methods of additive manufacturing to create GFs, but these methods have shortcomings in that dissolution of the metal template is required.<sup>[8]</sup> Instead, laser-induced graphene (LIG), with its simple fabrication and exceptional electrical properties, serves as an excellent building block for macroscale graphene materials.<sup>[1,12-17]</sup> LIG and its sister material LIG fiber (LIGF),<sup>[18]</sup> a fibrous version of LIG, are made by irradiating commer-

cial polyimide (PI) film with a  $CO_2$  laser (10.6  $\mu$ m). The PI is converted to porous graphene film through this one-step laser photothermal process.<sup>[1,18]</sup> The laser can be computer controlled, allowing for complex geometries to be scribed.

In this study, we describe 3D GF synthesis using a modified, automated 3D-printing process based on laminated object manufacturing (LOM). In addition, by using a fiber laser, we are able to further refine the graphene foam into more complex 3D shapes. The study culminates in demonstrating the efficacy of the foam in flexible electronic sensors and as electrode material for Li ion capacitors.

D. X. Luong, G. A. Lopez Silva, Dr. J. Yoon, T. Wang, Z. Wang, Prof. J. M. Tour Department of Chemistry Rice University 6100 Main Street, Houston, TX 77005-1892, USA E-mail: tour@rice.edu D. X. Luong **Applied Physics Program Rice University** 6100 Main Street, Houston, TX 77005-1892, USA A. K. Subramanian, P. S. Owuor, Prof. J. Lou, Prof. P. M. Ajayan, Prof. J. M. Tour Department of Material Science and Nanoengineering Rice University 6100 Main Street, Houston, TX 77005-1892, USA The ORCID identification number(s) for the author(s) of this article

can be found under https://doi.org/10.1002/adma.201707416.

#### DOI: 10.1002/adma.201707416

S. Cofer

K. Yang

**Rice University** 

**Rice University** 

Prof. J. M. Tour

**Rice University** 

Department of Mechanical Engineering

6100 Main Street, Houston, TX 77005-1892, USA

6100 Main Street, Houston, TX 77005-1892, USA

Smalley-Curl Institute and the NanoCarbon Center

6100 Main Street, Houston, TX 77005-1892, USA

Department of Civil and Environmental Engineering







**Figure 1.** Manufacturing and processing of laser-induced GFs. a) Schematic of the LOM process. b) 3D "R" shape of the milled LIG foam. The height of the LIG foam is  $\approx$ 1 mm. c) Schematic of fiber laser milling process. d) 3D LIG foam printed by the combination of LOM and fiber laser milling.

As shown in Figure 1, 3D LIG foams are fabricated by preparing layers of LIG through the irradiation of PI film. The PI to LIG conversion has been covered in depth.<sup>[1]</sup> Figure 1a depicts the LOM process. First, layers of PI are irradiated so LIG is embedded into and upon a film of PI. One of the layers is used as a foundation or base for the GF. The layers are then coated with ethylene glycol (EG) and stacked on top of one another. EG acts as a binding agent, which is commonly used in LOM processes, due to its ease of wetting the LIG layer. Full wetting is achieved when using 0.75 mL cm<sup>-2</sup> of LIG. The EG serves as an adhesive through capillary forces between the layers. It also has a high boiling point and heat capacity, thereby protecting the LIG from the excessive heat during lasing. The sandwiched layers are then lased, fusing together the LIG sheets. The appropriate focus and laser average powers required are discussed in Figure S1 and Table S1 in the Supporting Information. This process is then repeated to build macroscale foams of LIG. After the process is complete to the desired height, the printed foam is dried in atmosphere at 200 °C to evaporate the remaining EG. Alternatively, the foam can be dried in vacuum at 600 °C to remove any excess polymer residue as well.

Although the LOM manufacturing technique is robust, the edges of printed LIG patterns have relatively poor resolution. This is likely due to the deformation of the wetted LIG foam when pressed against the next LIG layer. For high resolution printing, we found that fiber lasing could be employed to mill the bulk LIG. The fiber laser is commercially available with 1.06  $\mu$ m wavelength and peak power of 50 W. LIG has high absorption at 1.06 µm, resulting in the local heating and ablation of LIG. However, PI is transparent at 1.06 µm, so the applied laser neither destroys nor carbonizes the substrate. Thus, as shown in Figure 1b and Figure S2 in the Supporting Information, by tuning the output average power the fiber laser is used to mill the LIG structure to the desired thickness and shape. A schematic of this process is shown in Figure 1c. Using a fluence of 6 J cm<sup>-2</sup>, LIG is gradually thinned by multiple laser milling cycles. Interestingly, the Raman spectra show no difference between the original LIG and the thinned LIG. This indicates that the fiber laser only locally ablates the LIG while preserving its disordered graphene structure. After 5 cycles of milling, the PI base becomes visible, and after 10 cycles of milling, the LIG is completely ablated (Figure S2a, Supporting Information). The fiber laser has a diffraction limit 10× better than the 10.6 µm laser. However, in practice, LIG fabricated using the CO<sub>2</sub> laser process has a resolution of ~75 µm while the fiber laser has a resolution of 30 µm (Figure S2b, Supporting Information). This processing enables the formation of internal 3D geometries. Figure 1d demonstrates an example of a complex etched cube.

To demonstrate the potential for industrial manufacturing of 3D LIG, we built a homemade automation system that interfaces with the laser system where most of the parts were made on a plastics 3D printer (**Figure 2**). Figure 2a shows an image of the operating system, which consists of a sample platform attached to a linear stage and a *z*-axis driven stepper motor assembly, a roller to feed PI/LIG layers, and an Arduino control board attached to a stepper motor (Figure 2b). An automated run of the LOM machine is demonstrated in Video S1 in the Supporting Information. With this homemade automation, we are able to manufacture foams from 5 layers with height 4 mm (Figure S3, Supporting Information).

The 3D LIG foams were prepared from three increasing thicknesses of PI films. We produced different LIG foam structures from each thickness (Figure S4, Supporting Information). Scanning electron microscopy (SEM) micrographs confirm that with the thin PI (25.4 µm), the LIG product has a graphene, sheet-like structure, similar to previously studied 2D LIG (**Figure 3a**).<sup>[1]</sup> Using the thick PI (128 µm) results in LIGF dominating the morphology, indicated by the fibrous composition (Figure 3b).<sup>[18]</sup> LIG and LIGF foams have a low density of ~36 and 20 mg cm<sup>-3</sup> and porosity of 98% and 99%, respectively (Table S2, Supporting Information). The LIG sheets yield denser foam than the LIGF fibers (Table S2, Supporting Information). The intermediate thickness PI (50.8 µm) results in a hybrid LIG/LIGF formation, where there are short but fibrous







**Figure 2.** Laminated object manufacturing automation setup. a) 2D schematic of the automated 3D-printing setup. Inset: enlargement of the sample platform during the lasing process. b) Photograph of the automated 3D-printing setup. 1) The laser lases the first layer of LIG on 2) the sample platform, which is held in place by 3) the foam "finger"; the 4) Arduino controller board controls 5) the z-axis motor which is attached to 6) the linear stage to lower the sample platform; a series of 7) flipped LIG layers are rolled in by 8) the roller motor; tension of the LIG layer is generated by 9) weight at the end of the LIG layer strip. The base was made from wood and the remaining parts were 3D printed from plastic, aside from the activation motors and control board that were purchased.

products. Thus, tuning the thickness of the layered PI results in different morphologies and densities of foam. Using layered PI thicknesses of 25.4 and 50.8  $\mu$ m yielded homogeneous LIG and LIG/LIGF hybrid foam with seamless connection between layers (Figure S5 a,b, Supporting Information). LIGF foam fabricated with 128  $\mu$ m thick PI had a discernable LIGF forest layer (Figure S5c, Supporting Information). Each layer fuses together at the base and top of the LIGF forest.

To further confirm the graphene nature of the 3D-printed LIG and LIGF, transmission electron microscopy (TEM) and Raman spectroscopy are employed (Figure 3c–e). Sheet-like LIG and fibrous LIGF are observed, corresponding to the SEM observations. The Raman spectra show strong 2D peaks with high D/G ratios in both morphologies, indicating that the graphene contains defects. As confirmed by high resolution

TEM, the LIG is highly folded (Figure S6, Supporting Information). Finally, in Figure 3f, we used thermogravimetric analysis (TGA) to check the purity of the printed LIG. In air, LIG and LIGF are both oxidized. LIG is volatized from  $\approx$ 500 to  $\approx$ 800 °C, while LIGF is volatized from  $\approx$ 450 to  $\approx$ 700 °C. In argon, LIG is known to be stable to >900 °C.<sup>[1]</sup> This is confirmed by the flat TGA thermographs in both the LIG and LIGF. Notably, we see no sharp dip at  $\approx$ 200 or  $\approx$ 500 °C indicating that neither EG nor PI was present in the foam. X-ray photoelectron spectroscopy (XPS) showed a high content of N and O doping in 3D LIG and higher in 3D LIGF, likely from vaporized EG and degassed nitrogen during the PI carbonization (Figure S7, Supporting Information). LIG and LIGF foam have surface areas of 117 and 146 m<sup>2</sup> g<sup>-1</sup>, respectively, with pore size between 20 and 30 nm (Figure S8, Supporting Information).



Figure 3. Material characterization. a) SEM image of LIG foam. b) SEM image of LIGF foam. c) TEM image of LIG foam. d) TEM image of LIGF foam. e) Raman spectra of the LIG and LIGF foams. f) TGA of LIG and LIGF foams. Dashed line: TGA in air, solid line: TGA in Ar.



To investigate the in-plane conductivity of the 3D GFs, conductive silver paint is applied to both ends of an "I" shaped foam (Figure S9a, Supporting Information). The average inplane conductivity of the samples with the starting PI thicknesses of 50 and 125  $\mu$ m was 0.27  $\pm$  0.05 and 0.15  $\pm$  0.04 S cm<sup>-1</sup>, respectively (Figure S9b, Supporting Information). To investigate the Z-conductivity of the 3D GFs, conductive silver paint is applied to the top and bottom surfaces of the foam. The average Z-conductivity of the samples with the starting PI thicknesses of 50 and 125  $\mu$ m was 0.073  $\pm$  0.010 and 0.050  $\pm$  0.010 S cm<sup>-1</sup>, respectively (Figure S9c, Supporting Information). SEM is used to measure the foam thickness and to ensure no silver paint conductive pathway exists inside the foam (Figure S10, Supporting Information).

The mechanical behavior of both LIG and LIGF foams was characterized through dynamical mechanical analysis. Cylindrical samples of foams underwent compression testing in the vertical direction. Figure S11 in the Supporting Information depicts the stress–strain curves that show three distinct phases during loading. The first phase is linear-elastic, corresponding to elastic bending of foam walls and modulus of 40 and 25 kPa for LIG and LIGF, respectively. The second nonlinear phase corresponding to buckling of the cell wall (from  $\approx 20\%$  to  $\approx 40\%$  strain) is followed by another linear phase associated with a recoverable buckling with modulus of 300 and 120 kPa for LIG and LIGF, respectively.<sup>[19]</sup> Both LIG and LIGF show near-complete recovery after 50% strain. In addition, the GFs exhibit this behavior consistently over many cycles with no foam breakage, as shown by cyclic compression loading at 25% and 10% strain for LIG and LIGF, respectively (Figure S11c, Supporting Information).

The 3D LIG electronic and mechanical properties make it an attractive material for energy storage applications.<sup>[20]</sup> To demonstrate this, we tested 3D LIG as electrodes for Li-ion capacitors (LIC). This LIC has different architecture and function than the planar LIG micro-supercapacitors that were extensively studied in our previous work.<sup>[1,12,14,15,17,18]</sup> LICs have attracted the attention in the past years because they combine the best properties of Li-ion batteries and capacitors; they are composed of a Li-ion battery-type anode and a capacitor-type cathode which allows them to provide higher power densities than Li-ion batteries and higher energy densities than capacitors.<sup>[21–23]</sup> In this work, both cathode and anode were 100% composed of the 3D LIG foams. Because the foams are self-standing and present good electrical conductivity, use of a binder and current collectors are unnecessary. The electrodes were first characterized in half cells using Li foil as the reference and counter electrode. Their electrochemical performances are presented in Figure S12a-c in the Supporting Information where the anode was tested from 0.01 to 3 V and the cathode from 1 to 4.3 V. In the first three cycles, the anode achieved an average gravimetric capacity of 354 mAh g<sup>-1</sup>, close to the theoretical capacity of graphite (372 mAh g<sup>-1</sup>). Furthermore, as a cathode, the LIG foam achieved an average capacity of 83 mAh g<sup>-1</sup>, which is higher than the capacities of other carbon materials, such as activated carbon (30-70 mAh g<sup>-1</sup>).<sup>[21-23]</sup> A full LIC cell was assembled using an anode:cathode mass ratio of 1:5. Figure 4a shows the galvanostatic charge-discharge curves of



**Figure 4.** Energy and electronics applications. a) Galvanostatic charge–discharge curve of the 3D-LIG foam full LIC at different current densities and a voltage window of 0.01 to 4.3 V. b) Cycling stability of the 3D-LIG LIC. Energy densities >64 W h kg<sup>-1</sup> were achieved at low current densities (0.025). After the rate performance was attained, the 3D-LIG LIC was cycled at 0.1 A g<sup>-1</sup>. After 1000 cycles the capacity retention of 81% was found which indicated a good structural stability of the 3D-LIG foam and a reversible Li storage. c) Image of LIG/PDMS arterial pulse device. d) Arterial pulses waveform recorded by the stress sensor device. Inset: expanded view of a single pulse waveform.

the LIC from 3D LIG foams at different current densities from 0.01 to 4.2 V, which exhibit good linear relation at larger current densities that can be translated into better power performance. Figure 4b shows that the LIC cell can support long-range cycling. After 970 cycles at 0.1 A g<sup>-1</sup>,  $\approx$ 70% energy density was retained. As shown in Figure S12d in the Supporting Information, at the selected current densities, the cell can deliver energy densities of up to 64 Wh kg<sup>-1</sup> and power densities up to 970 W kg<sup>-1</sup>; notably, these values are based on 100% the weight of both electrodes. The Coulombic efficiency of the first cycle was low, which can be attributed to the formation of the solid electrolyte interface layer. It increased and remained ≈100% during extended cycling, as seen in Figure S12 in the Supporting Information. This LIG based LIC has performance comparable among state of the art LICs where the electrodes are carbon based materials (Table S3, Supporting Information). The fabrication of the LIC is a proof of concept for the use of the 3D LIG foam as a substrate for electrodes since its mechanical and electrical properties allow the storage of charges on the surface as well as through intercalation of Li<sup>+</sup> ions. The simple fabrication method of 3D LIG foam allows future improvements in the energy density and rate performance by adding additional active sites such as nitrogen/ oxygen containing groups or metal oxides.<sup>[24-27]</sup>

The interconnected LIG network proves useful in graphene/ polymer composite applications, such as flexible electronic devices. To test the efficacy of LIG foams, LIG/polydimethylsiloxane (PDMS) composite devices were fabricated through simple infiltration. The infiltration of PDMS into LIG is aided by using vacuum to remove air trapped inside the LIG, resulting in a composite with little void space (Figure S13, Supporting Information). The conductivity of the composite does not differ from the conductivity of the free standing foam nor does the shape of the foam change after the infiltration, indicating the preservation of the graphene network. The LIG contributes to  $\approx 2\%$  of the weight of the composite but significantly increases the mechanical properties of PDMS, doubling the elastic modulus relative to LIG-free PDMS (Figure S14, Supporting Information). We further investigate the response in resistivity of the composite with applied stress. In Figure S15 in the Supporting Information, resistance of the composite increases as strain is applied with a gauge factor of  $\approx$ 3. Further optimization for the shape of the composite can yield a device with gauge factor of  $\approx$ 40. In the cyclic testing of the composite, the resting resistance remains relatively constant while the stretched resistance slightly increases over cycling due to breakage of the conductive paths (Figure S16, Supporting Information). The gauge factor of the composite increases over use, but it still retains full stretchability. We constructed a simple proof-of-concept arterial-pulse sensor from the LIG/PDMS composite as shown in Figure 4c. A 5 cm length thin strip of LIG/PDMS wrapped around the wrist (Figure 4d) shows the clear waveform of arterial pulses recorded from the device. The forward wave arises from the incoming blood flow and the reflected wave arises from the lower body with the dicrotic notch in between.<sup>[28]</sup> Further calibration can be done to extract the blood pressure from the pulse waveform amplitude.<sup>[29,30]</sup>

In conclusion, we have demonstrated a method of additive manufacturing for GFs using LIG and LIGF as fundamental building blocks. This method is simple; it does not require complicated chemical or physical processes, and it is potentially scalable for industrial production through easily modified, commercially available laser systems. Printed GFs have great potential in various applications.<sup>[31–36]</sup> While energy storage and electrical devices are presented in this work, other applications such as water treatment,<sup>[32,36–42]</sup> electrocatalysis,<sup>[31]</sup> or biological scaffolding<sup>[34]</sup> could be envisioned.

## **Experimental Section**

Fabrication and Characterization of Laser-Induced Graphene Foams: Laser induction was conducted on PI film substrates using a 75 W 10.6  $\mu$ m CO<sub>2</sub> laser and 50 W 1.06 µm fiber laser in Universal Laser System's XLS10MWH platform operating in pulse width modulation. The pulse separation (or image density) was fixed at 50 µm (or 500 pulses per inch; the commercial laser setting; 1 in. = 2.54 cm); the laser scanning speed was fixed at 15 cm s<sup>-1</sup> for CO<sub>2</sub> laser and 60 cm s<sup>-1</sup> for fiber laser. Laser average power was changed by tuning the duty cycle. The resultant GFs were characterized through SEM with a JEOL 6500F SEM at 5 kV with working distance of 10 mm. TEM images were taken with a JEOL 2100F field emission gun transmission electron microscope at 200 kV. Raman spectra were collected with a Renishaw Raman microscope using a 514 nm laser with a power of 5 mW. XPS data were collected with a PHI Quantera SXM Scanning X-ray Microprobe with a base pressure of  $5 \times 10^{-9}$  Torr. Survey spectra were recorded using 0.5 eV step sizes with a pass energy of 140 eV. Elemental spectra were recorded using 0.1 eV step sizes with a pass energy of 26 eV. All of the XPS spectra were corrected using the C1s peaks (284.5 eV) as reference. TGA readings were measured with Q-600 Simultaneous TGA/ differential scanning calorimetry (DSC) at a ramping rate of 10 °C min<sup>-1</sup> The surface area of LIG was measured with a Ouantachrome autosorb-3b BET surface analyzer. Mechanical Compression Testing was done through the Q800 Dynamical Mechanical Analyzer from TA Instruments. The standard sample testing size was larger than the thicknesses of the fabricated LIG/LIGF foams, and therefore compression testing was conducted in only the layering direction in this study. Data from the compression test in the transverse direction, where the sample was not sufficiently sized, was not reliable enough to draw any conclusion. Electrical conductivity was measured through B1500A Semiconductor Device Analyzer from Agilent Technologies.

Application Testing: LIC fabrication: The electrochemical characterizations of LIG electrodes as LICs were made using 2032 coin cells for the half-cells (Li foil used as reference and counter electrode). The cells were tested using an MTI Battery Analyzer. Electrodes were prepared from 3D LIG foams, without the use of binders or current collectors. Celgard 2400 membranes were used as separators and 1.0 м  $LiPF_6$  in a mixture 50/50, v/v of ethylene carbonate:diethyl carbonate as the electrolyte. The half-cells were tested between 1 and 4.3 V for the cathode and 0.01 and 3 V for the anode. All of the cells were assembled in a Ar-filled glovebox with  $\mathsf{O}_2$  and  $\mathsf{H}_2\mathsf{O}$  content below 2 ppm. For full cell fabrication, half-cells were assembled and cycled five times before being combined in a full device. The 3D LIG anode was assembled in its lithiated state and the cathode in the unlithiated state; the mass ratio used was anode:cathode 1:5. The full LIC was tested between 0.01 and 4.2 V at different current densities. To infiltrate the LIG with PDMS for composite devices, a SYLGARD 184 SILICONE ELASTOMER KIT was mixed at the appropriate component ratios. The uncured mixture was poured on the foam, and then both were put inside a vacuum desiccator. Air bubbles rapidly rose out of the GF as the polymer infiltrated the GF. After 30 min the composite was removed from the desiccator, the excessive PDMS was drained, and the treated GF was cured in air at 80 °C overnight.

# **Supporting Information**

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





www.advmat.de

### Acknowledgements

D.X.L. and A.K.S. contributed equally to this work. This work was supported by the Air Force Office of Scientific Research (FA9550-14-1-0111). D.X.L. thanks the Vietnam Education Foundation for support. Rice University gratefully acknowledges the support of Universal Laser Systems, and for their generously providing the XLS10MWH laser system with Multiwave Hybrid technology that was used for this research. Mr. J. Hillman of Universal Laser Systems kindly provided regular helpful advice. The measurement of the arterial blood pulse in this work did not meet the definition of human subject research at Rice University, therefore no IRB protocol approval was needed.

# **Conflict of Interest**

Rice University owns intellectual property rights to the LIG process and materials. Those rights are being licensed to a company in which J.M.T. might become a shareholder, though not an officer, director, or employee. All potential conflicts of interest are managed through regular disclosure to and oversight by the Rice University Office of Sponsored Programs and Research Compliance.

### **Keywords**

3D printing, flexible electronics, graphene foams, laser-induced graphene, Li-ion capacitors

Received: December 19, 2017 Revised: March 21, 2018 Published online:

- J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, J. M. Tour, *Nat. Commun.* 2014, *5*, 5714.
- [2] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, *Nano Lett.* 2008, *8*, 902.
- [3] C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 2008, 321, 385.
- [4] A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183.
- [5] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, *81*, 109.
- [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] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H.-M. Cheng, Nat. Mater. 2011, 10, 424.
- [8] J. Sha, C. Gao, S.-K. Lee, Y. Li, N. Zhao, J. M. Tour, ACS Nano 2016, 10, 1411.
- [9] C. Zhu, T. Y.-J. Han, E. B. Duoss, A. M. Golobic, J. D. Kuntz, C. M. Spadaccini, M. A. Worsley, *Nat. Commun.* **2015**, *6*, 6962.
- [10] Y. Xu, K. Sheng, C. Li, G. Shi, ACS Nano 2010, 4, 4324.
- [11] E. García-Tuñon, S. Barg, J. Franco, R. Bell, S. Eslava, E. D'Elia, R. C. Maher, F. Guitian, E. Saiz, *Adv. Mater.* **2015**, *27*, 1688.
- [12] Z. Peng, J. Lin, R. Ye, E. L. G. Samuel, J. M. Tour, ACS Appl. Mater. Interfaces 2015, 7, 3414.
- [13] R. Ye, Z. Peng, T. Wang, Y. Xu, J. Zhang, Y. Li, L. G. Nilewski, J. Lin, J. M. Tour, ACS Nano 2015, 9, 9244.

- [14] Z. Peng, R. Ye, J. A. Mann, D. Zakhidov, Y. Li, P. R. Smalley, J. Lin, J. M. Tour, ACS Nano 2015, 9, 5868.
- [15] L. Li, J. Zhang, Z. Peng, Y. Li, C. Gao, Y. Ji, R. Ye, N. D. Kim, Q. Zhong, Y. Yang, H. Fei, G. Ruan, J. M. Tour, *Adv. Mater.* **2016**, *28*, 838.
- [16] M. K. Smith, D. X. Luong, T. L. Bougher, K. Kalaitzidou, J. M. Tour, B. A. Cola, Appl. Phys. Lett. 2016, 109, 253107.
- Y. Li, D. X. Luong, J. Zhang, Y. R. Tarkunde, C. Kittrell, F. Sargunaraj,
  Y. Ji, C. J. Arnusch, J. M. Tour, *Adv. Mater.* 2017, *29*, 1700496.
- [18] L. X. Duy, Z. Peng, Y. Li, J. Zhang, Y. Ji, J. M. Tour, Carbon 2018, 126, 472.
- [19] Z. Qin, G. S. Jung, M. J. Kang, M. J. Buehler, Sci. Adv. 2017, 3, e1601536.
- [20] C. Zhu, T. Liu, F. Qian, W. Chen, S. Chandrasekaran, B. Yao, Y. Song, E. B. Duoss, J. D. Kuntz, C. M. Spadaccini, M. A. Worsley, Y. Li, *Nano Today* **2017**, *15*, 107.
- [21] H. Wang, Y. Zhang, H. Ang, Y. Zhang, H. T. Tan, Y. Zhang, Y. Guo, J. B. Franklin, X. L. Wu, M. Srinivasan, H. J. Fan, Q. Yan, *Adv. Funct. Mater.* **2016**, *26*, 3082.
- [22] Y. Ma, H. Chang, M. Zhang, Y. Chen, Adv. Mater. 2015, 27, 5296.
- [23] A. Du Pasquier, I. Plitz, S. Menocal, G. Amatucci, J. Power Sources 2003, 115, 171.
- [24] S. Xin, Y. You, S. Wang, H.-C. Gao, Y.-X. Yin, Y.-G. Guo, ACS Energy Lett. 2017, 2, 1385.
- [25] S. W. Bokhari, A. H. Siddique, H. Pan, Y. Li, M. Imtiaz, Z. Chen, S. M. Zhu, D. Zhang, RSC Adv. 2017, 7, 18926.
- [26] M. Yang, Z. Zhou, Adv. Sci. 2017, 4, 1600408.
- [27] C. Liu, B. B. Koyyalamudi, L. Li, S. Emani, C. Wang, L. L. Shaw, *Carbon* 2016, 109, 163.
- [28] W. W. Nichols, Am. J. Hypertens. 2005, 18, 3S.
- [29] C. S. Boland, U. Khan, G. Ryan, S. Barwich, R. Charifou, A. Harvey, C. Backes, Z. Li, M. S. Ferreira, M. E. Möbius, R. J. Young, J. N. Coleman, *Science* **2016**, *354*, 1257.
- [30] T. Yang, X. Jiang, Y. Zhong, X. Zhao, S. Lin, J. Li, X. Li, J. Xu, Z. Li, H. Zhu, ACS Sensors 2017, 2, 967.
- [31] Z.-S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, J. Am. Chem. Soc. 2012, 134, 9082.
- [32] W. Wang, Z. Wang, J. Liu, Z. Zhang, L. Sun, Sci. Rep. 2017, 7, 43755.
- [33] F. Yavari, Z. Chen, A. V. Thomas, W. Ren, H.-M. Cheng, N. Koratkar, Sci. Rep. 2011, 1, 166.
- [34] N. Li, Q. Zhang, S. Gao, Q. Song, R. Huang, L. Wang, L. Liu, J. Dai, M. Tang, G. Cheng, *Sci. Rep.* **2013**, *3*, 1604.
- [35] Y. Zhang, Y. Huang, T. Zhang, H. Chang, P. Xiao, H. Chen, Z. Huang, Y. Chen, Adv. Mater. 2015, 27, 2049.
- [36] Z. Sui, Q. Meng, X. Zhang, R. Ma, B. Cao, J. Mater. Chem. 2012, 22, 8767.
- [37] R. Tjandra, W. Liu, L. Lim, A. Yu, Carbon 2018, 129, 152.
- [38] C.-T. Hsieh, D.-Y. Tzou, Y.-C. Chen, D.-K. Huang, Mater. Chem. Phys. 2015, 164, 230.
- [39] S. Li, X. Wang, J. Power Sources 2015, 282, 394.
- [40] J. J. Ren, L. W. Su, X. Qin, M. Yang, J. P. Wei, Z. Zhou, P. W. Shen, J. Power Sources 2014, 264, 108.
- [41] W. Liu, J. Li, K. Feng, A. Sy, Y. Liu, L. Lim, G. Lui, R. Tjandra, L. Rasenthiram, G. Chiu, A. Yu, ACS Appl. Mater. Interfaces 2016, 8, 25941.
- [42] W. Ahn, D. U. Lee, G. Li, K. Feng, X. Wang, A. Yu, G. Lui, Z. Chen, ACS Appl. Mater. Interfaces 2016, 8, 25297.