Supercapacitors are increasingly in demand among energy storage devices. Due to their abundant porosity and low cost, activated carbons are the most promising electrode materials and have been commercialized in supercapacitors for many years. However, their low packing density leads to an unsatisfactory volumetric performance, which is a big obstacle for their practical use where a high volumetric energy density is necessary. Inspired by the dense structure of irregular pomegranate grains, a simple yet effective approach to pack activated carbons into a compact graphene network with graphene as the “peels” is reported here. The capillary shrinkage of the graphene network sharply reduces the voids between the activated carbon particles through the microcosmic rearrangement while retaining their inner porosity. As a result, the electrode density increases from 0.41 to 0.76 g cm\(^{-3}\). When used as additive-free electrodes for supercapacitors in an ionic liquid electrolyte, this porous yet dense electrode delivers a volumetric capacitance of up to 138 F cm\(^{-3}\), achieving high gravimetric and volumetric energy densities of 101 Wh kg\(^{-1}\) and 77 Wh L\(^{-1}\), respectively. Such a graphene-assisted densification strategy can be extended to the densification of other carbon or noncarbon particles for energy devices requiring a high volumetric performance.

Supercapacitors, which store energy by the adsorption of electrolyte ions on a porous electrode, have attracted widespread attention in the energy storage field. This is mainly due to their high power density and long life.[3–5] In recent years, volumetric performance has become more important for energy storage in a limited space, because it is the prior concern for many applications, typical examples being portable electronics such as mobile phones, wearable electronics, biosensors, and nanorobotics.[6–11] Activated carbons (ACs),[12–14] carbon nanotubes,[15] graphene,[16,17] or activated graphene,[18] and other porous carbon materials,[19,20] are potential candidates for supercapacitors mainly because of their large specific surface areas (SSAs) and acceptable electrical conductivity. Among the carbonaceous materials, ACs are the most commonly used owing to their abundant porosity and low cost, and thus have been already commercialized.[1,5,21] However, a high volumetric energy density \(E_v\) not only requires a high gravimetric capacitance \(C_g\), but also a high electrode density and a wide operation voltage \(E_v = \rho \times C_g \times (\Delta U)/2\).[9]

Recently, organic and ionic electrolytes were found to have a wide voltage window thanks to their high electrochemical stability.[22] However, the electrode density still remains low due to the existence of macropores and interparticle voids in the porous carbons,[23,24] which is a big obstacle for high volumetric performance. Mechanical compression is a simple and normally used method to increase the density by eliminating interparticle voids, however, it may cause collapse of the internal pores and reduce the accessible surface area and the number of conducting paths hence leading to a decreased performance.[10] So much effort has recently been made to increase the intrinsic densities of carbon materials with unimpeded ion transport channels by the dense assembly of graphene membranes, graphene monoliths, etc.[25–31] However, the high cost and complex synthesis still restrict their practical uses. Therefore, the densification of low cost commercial ACs offers a practical way to improve the volumetric performance of supercapacitors.

Pomegranates own an ideally densely packed structure of irregular particles (Figure 1a). In spite of inhomogeneous sizes
and shapes, pomegranate grains are packed in a compact way without voids. As a result, the internal space of its rind is fully exploited to store as much flesh as possible. Inspired by pomegranate, it is expected that the irregular AC particles can be highly dense-packed with minimal voids in a similar way. In this way, the more active materials are accommodated in a certain space, the higher energy is provided in a limited volume.

To realize the dense packing like pomegranate particles, AC particles as “pomegranate grains” demand for some kind of “peel” for package and a compression force to facilitate the densification. To make the AC particles into a compact integration, a “peel” is highly desired to wrap them in a compact way, which is supposed to be 1) sheet-like, 2) flexible, 3) strong, 4) electrically conductive, and 5) able to lap over each other as well.

Graphene would be an ideal candidate for such a peel due to its high strength and good conductivity, its flexibility to assemble into a 3D network and cling to the irregular particles, and more importantly, the shrinkage of the assembled graphene network caused by the capillary evaporation of water adsorbed inside it. As a proof of concept, we used commercial AC YP80 as a typical example to show the effectiveness of this densification strategy where a small amount of graphene is used and the self-shrinkage of the graphene “peel” exerts a force to densify the ACs inside. As expected, this densification results in a compact structure with a relatively high electrode density of $0.76 \text{ g cm}^{-3}$ that is much larger than the $0.41 \text{ g cm}^{-3}$ for pristine ACs. Besides, the AC and G work synergistically for a higher capacitance, with the former providing a porous structure for ions storage and avoiding G layer restacking, and the latter constructing a 3D conductive network and modifying the ion transport.

When used as an additive-free supercapacitor electrode in an ionic liquid electrolyte, the graphene-wrapped ACs show a gravimetric capacitance of $181 \text{ F g}^{-1}$ and a volumetric capacitance of up to $138 \text{ F cm}^{-3}$, resulting in high gravimetric and volumetric energy densities of $101 \text{ Wh kg}^{-1}$ and $77 \text{ Wh L}^{-1}$, respectively.

Figure 1a shows the AC densification strategy using the graphene “peel.” Typically, irregular AC particles were dispersed with amphiphilic graphene oxide (GO) sheets and then mixed with reductant L-ascorbic acid sodium salt (L-AASS) in a mixed solvent of water and ethanol. As the GO gradually reduced during the gelation process, the sheets overlapped to form an interconnected 3D network and modifying the ion transport. After shrinkage to form a hydrogel, it was densified by capillary evaporation-induced drying (CEID) on such a hydrogel results in an obvious volume shrinkage to produce a dense monolith. SEM images of b) the low-density YP80 powder and c) the low-density YP80/G composite foam after freeze drying, and d) the high-density YP80/G monolith after CEID.
evaporation-induced drying (CEID) to produce a compact AC/G composite. The densification strategy composed of three main steps shown in Figure 1a has following key points: 1) The self-assembly of G was clearly separated into two stages: gelation and shrinkage, which means that 3D network was firstly constructed before shrinkage. 2) The gelation time determines the graphene coating efficiency of AC, and we can make it up to 100% here even if a pretty small amount of graphene is used. The shrinkage associates with the reduction degree of GO and greatly influences the strength of hydrogel. 3) Compared to freeze drying which produces a foam-like structure that retains greater content, temperature, and reductant, and interaction between rGO sheets, such as concentration, are also important to adjust the gelation time (Figure S4, Supporting Information). In this work, the GO concentration of 1 mg mL$^{-1}$ with an L-AASS reductant concentration of 0.01 M at 80 °C for 16 h were chosen as the optimized condition to prepare theYP80/G composite. Shrinkage occurred in the solution as the number of oxygen-containing functional groups further decreased, causing stronger π−π interaction between the sheets and a continuous shrinkage of the network. The gel became smaller during the following 5 h shrinkage process but then remained its size because reduction had ended (Movie S1, Supporting Information). It was found that the solvent had a great influence on the shrinkage speed (Movies S2 and S3, Supporting Information). Shrinkage in the pure water was quite fast (50 min) whereas in the mixed solvent it took 5 h. The shrinkage speed is greatly influenced by the interaction between the rGO sheets and the solvent.$^{[14]}$ In the pure water, the rGO sheets have lower binding energy with the water molecules, which tend to be isolated from the water suspension. This favors the π−π interactions between sheets and hence results in a fast shrinkage. However, in the water/ethanol solvent, a stronger interaction between rGO and ethanol molecules actually restrains the crosslinking of rGO layers.

CEID played a vital role in the dense packing of ACs, since there was still a lot of empty space in the network after shrinkage in the solution, as shown in the scanning electron microscope (SEM) images of freeze-dried samples (Figure 1c). During CEID, solvent molecules were removed and the graphene network contracted as a result of capillary forces$^{[25]}$ and this forced the AC particles into a compact arrangement. Every “pocket” in the G network in which one or more AC particles settled shrank so that the flexible G clung to the surface of the irregular AC particles (Figure 1d and Figure S5a,b, Supporting Information). As a whole, the network formed a strong monolith with the smallest number of voids. Unlike the loose foam structure produced by freeze drying (Figure S5c, Supporting Information), this compact monolith had a smooth texture and appearance (low-magnification SEM images shown in Figure 1d). Despite the marked differences in apparent density, the samples dried by the two entirely different methods have similar SSAs and pore distributions (Figure S6a,b, Supporting Information), while XRD of the freeze-dried sample has a broader peak at around 24.4° (Figure S6c, Supporting Information), indicating a more disordered structure. As shown in Figure 2a, the composite materials were prepared by adjusting the mass ratio of YP80 and GO (details are listed in Table S1 of the Supporting Information). A cylindrical gel was formed even if a pretty small amount of G was chosen. Gelation time of GO (1 mg mL$^{-1}$) in the ethanol/water mixture (1.5 h, Movie S2, Supporting Information) is twice that in water (40 min, Movie S3, Supporting Information), due to the increased affinity of the mixed solvent. After AC was added, the gelation time increased even more (2.5 h, Movie S1, Supporting Information) because the AC particles between the graphene sheets increased the layer separation and hindered the gelation. Except for the solvent and packed materials, other factors involving the reduction of GO, like initial oxygen content, temperature, and reductant, and interaction between rGO sheets, such as concentration, are also important to adjust the gelation time (Figure S4, Supporting Information).
used to package the YP80 particles, yielding the sample with 96.7% YP80 in the final material. However, without sufficient G sheets to form a large network, the gel of this last sample had a deformed cylindrical shape with a thick bottom owing to particle deposition. As the YP80 content increases, N2 adsorption–desorption isotherms of the samples begin to show more YP80 features as shown in Figure 2b, with a hysteresis loop from G gradually disappearing while a plateau getting higher thanks to an increase in micropores. Note that the G sheets, whose diameters are hundreds of nanometers, have a great influence on the way the YP80 particles are stacked, but do not alter their pore structures (Figure 2c and Table S2, Supporting Information), so the calculated BET SSAs based on the mass ratios are close to the experimental values (Figure 2d). From the pore size distribution in Figure 2c, it is also found that there are a large number of micropores around 1 nm and small mesopores around 2 nm in the YP80/G, which are suitable for the storage of EMIMBF4 ions. Notably, there is a definite dependence of an electrode conductivity on the proportion of G, since G has a much better conductivity than YP80 (Figure 2e). Taking the 76.5% sample as an example, its conductivity is six times that of pristine YP80.

Figure 2f shows that an increase in the wt% of YP80 leads to an increase of SSA from 521 to 2165 m2 g−1, with a decrease in electrode density from 0.85 to 0.41 g cm−3. Obviously, a higher proportion of micropore-rich YP80 produces a higher SSA. However, a certain amount of G is needed to form a well-connected network to pack and compress AC particles to obtain a dense bulk material (Figure S7a,b, Supporting Information). If there is insufficient G, there are breaks in the G network (Figure S7c, Supporting Information) and this has a detrimental effect on the strength of the compression exerted by the graphene sheets to rearrange the AC particles, leading to a lower density. It is thus important to balance the SSA and density. Figure 2f shows that the SSA increases sharply as the AC content reaches 76.5 wt%. A higher AC content results in a moderate increase in surface area but a significant decrease in density. Therefore, 76.5% YP80/G is the optimized sample that can well balance SSA and electrode density, and it exhibits the highest volumetric capacitances of the composite electrodes with different YP80 mass loadings as expected (Figure S8, Supporting Information). At this point, the composite has a SSA of 1655 m2 g−1 and an electrode density of 0.76 g cm−3. The following parts for the discussion of YP80/G are all based on 76.5% YP80/G.

The monolithic form was maintained after the cylindrical wet gel experienced CEID at room temperature and annealing at 800 °C for an hour (Figure 3a). The bulk material has a remarkable mechanical strength, for a 76.5% YP80/G monolith with a diameter of around 0.85 cm can support 500 g. This confirms that graphene sheets that have excellent stiffness are able to overlap into a network with an outstanding mechanical performance. The tapping density of the material is calculated to be 0.53 g cm−3, which is twice that of YP80 (0.27 g cm−3). The SEM image in Figure 3a shows the compact packing structure of YP80 and close connection between the YP80 particles and the graphene sheets. In this composite, in addition to the primary role of packing the AC particles, the 3D graphene
An interfacial network provides conductive paths through the composite, and the sheets clinging to the surface of the AC particles. This face-to-face conductive contact effectively reduces the particle contact resistance, which is a major contributor to the resistance of aggregated carbon powders. In addition, the AC particles between the sheets prevent the graphene layers from restacking during electrode manufacture and electrochemical cycling, thus making more effective surface area available for charge storage. Inevitably, there are still some small cracks between the graphene sheets and the AC particles as seen in the SEM, but as the spaces in this dense composite structure, it will actually facilitate ion transport as an ion channel.

As an amorphous carbon, YP80 cannot form π–π interactions with graphene sheets and it only has small amounts of oxygen-containing functional group on its surface (3.8% as verified by TGA curve in Figure S9 and the XPS results in Table S3 of the Supporting Information). It is hard for YP80 to form covalent or hydrogen bonds with graphene sheets. Hence, there should be a physical combination between AC and graphene sheets, rather than chemical bonding.

From the X-ray diffraction (XRD) patterns in Figure 3b, a broad peak for YP80 at around 24.4° (002) indicates its amorphous nature and low degree of graphitization. In contrast, the more intense (002) peak in the G sample indicates higher graphitic ordering with an interlayer spacing of 3.45 Å. This peak is weaker in the composite because the stacking of graphene sheets is prevented by the presence of the YP80 particles. In Raman spectroscopy (Figure 3c), since YP80 is a microcrystalline carbon, an obvious G band, which represents sp²-hybridized carbon atoms, is present, while a stronger D band, attributed to disorder, indicates its long-range disordered structure, consistent with the XRD results. After compositing the two carbon materials the \( \frac{I_D}{I_G} \) value is slightly higher because the disorder degree of graphene increases due to the insertion of YP80 between sheets. In addition, since it is important to determine whether compressing the electrodes causes the collapse of pores,[10] \( \text{N}_2 \) adsorption–desorption isotherms were measured before and after the YP80 powder and YP80/G electrode were compressed (Figure 3d). Here, YP80/G electrode refers to the calendared electrode containing active materials (YP80/G) and additives after mechanical compression (10 MPa) onto the current collector. Similar to uncompressed samples (2165 and 1492 m² g⁻¹), the specific surface areas of the YP80 powder and YP80/G electrode are 2147 and 1435 m² g⁻¹ after compressing, respectively (Table S4, Supporting Information). And they exhibit almost the same pore size distribution as shown in Figure 3e. Different from flexible graphene, whose pores are either collapsed or compressed to a smaller size by this treatment, thus causing a significant increase in density,[31] the composite carbon retains its main porosity with a stable pore structure and surface area so its density increase caused by the pressure is greatly limited.
As shown in Figure 4, the electrochemical performances were performed in a symmetric two-electrode system in the ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄). For comparison, the YP80 and graphene mixed powder (YP80/G-P) with 76.5% YP80 was prepared without the above gelation process. As expected, the powder sample shows a low density of 0.51 g cm⁻³ due to the low density of graphene and YP80. In contrast, with the gelation process, YP80/G shows an obviously increased density of 0.76 g cm⁻³ (inset figure in Figure 4a). The thick restacked G layers in YP80/G-P led to a lower SSA (1497 cm² g⁻¹) than YP80/G. Besides, the thick restacked G layers in YP80/G-P is hard to be an efficient conductive additive due to their uneven distribution among the particles (Figure S10, Supporting Information), which is also unfavorable for the ion transport. Additive-free electrodes of YP80/G were prepared thanks to the excellent conductive networks formed by the graphene sheets. The specific capacitance of YP80/G, calculated from galvanostatic charge/discharge curves of cells charged at 4 V (Figure S11, Supporting Information), reaches 181 F g⁻¹ at 0.2 A g⁻¹, nearly comparable to YP80 (containing 10% conductive additive) and higher than that of YP80/G-P, 152 F g⁻¹ (Figure 4a). As the current density increases from 0.2 to 10 A g⁻¹, the YP80/G exhibits an excellent rate performance and retains 56.1% of its initial capacitance at 10 A g⁻¹ (102 F g⁻¹), much higher than that of YP80 (37.8%) and YP80/G-P (35.5%). Nyquist plots of the three samples (Figure 4b) show that they all have a more ideal capacitive behaviors because of the vertical curves in the low-frequency region.
According to the equivalent circuits, the YP80/G exhibits the lowest ohmic resistance (1.58 Ω) and charge transfer resistance (1.81 Ω) (Figure S12, Supporting Information). By contrast, the resistance in an ionic liquid electrolyte is higher than that in an organic electrolyte (Figure S13, Supporting Information) due to a higher viscosity, lower conductivity and larger ion size of ionic liquid, and YP80/G shows a high specific capacitance of 138 F g\(^{-1}\) at 10 A g\(^{-1}\) in 1 m EMIMBF\(_3/\)AN. However, the neat ionic liquid electrolyte has the advantage of high-voltage stability, resulting in a higher energy density.\(^{[21,22]}\)

Bulk YP80/G material has an obvious advantage regarding to volumetric capacitances benefiting from excellent gravimetric capacitance and high electrode density among all samples. As shown in Figure 4c and Figure S14 (Supporting Information), YP80/G has the highest volumetric capacitance of 138 F cm\(^{-3}\) at 0.2 A g\(^{-1}\), much higher than that of YP80 (78 F cm\(^{-3}\)), YP80/G-P (75 F cm\(^{-3}\)), YP80/G foam (60 F cm\(^{-3}\)), and G (75 F cm\(^{-3}\)). Such volumetric capacitance advantage is also demonstrated in organic and aqueous electrolytes (Figures S15 and S16, Supporting Information). The Figure 4d exhibits the cyclic stability of YP80/G, YP80/G-P, and YP80. YP80/G retains 91% of its initial capacitance and keeps a stable surface morphology (Figure S17, Supporting Information) after 5000 cycles at a current density of 2 A g\(^{-1}\).

Since the porous AC forms the majority of the composite structure, its high SSA ensures a high gravimetric performance. At the same time, the more efficient packing of the AC particles produced by the graphene sheets and capillarity forces, maximizes the volumetric performance of the composite. The Ragone plots in Figure 4e shows that supercapacitors with YP80/G electrodes, which have an excellent gravimetric energy density of up to 101 Wh kg\(^{-1}\) (Figure S18a, Supporting Information), contribute to an increase in maximum volumetric energy density from 42 to 77 Wh L\(^{-1}\) compared to YP80 electrodes. Due to a superior balance of porosity and density, the YP80/G composite shows the highest volumetric energy density and power density among the samples (Figure S18, Supporting Information). Besides, the tight contact between graphene sheets and ACs particles enables an excellent conductive network and the high-efficiency ion transport channels, which are two key factors in helping the compact supercapacitors maintain their rate performance. For further comparison, the YP80/G has a volumetric energy density of 43 Wh L\(^{-1}\) at a power of 7.6 kW L\(^{-1}\), while the YP80 exhibits 15 Wh L\(^{-1}\) at a power of 4.1 kW L\(^{-1}\). And the gravimetric and volumetric values both outperform carbon-based materials existing in previously reported electrode materials (Figure 4f and Table S5, Supporting Information). Moreover, the dense structure ensures that there is sufficient but not redundant space for the electrolyte inside the electrode materials, which greatly promotes the utilization of the electrolyte and reduces the weight and volume fraction of the non-electrochemically active components, thus improving the gravimetric and volumetric energy densities of the final device.\(^{[6]}\) Moreover, such a densification strategy can be also extended to other porous yet low-density activated carbons (Figure S19, Supporting Information), which has great potential in terms of a high volumetric energy density.

We propose a general densification strategy for packing AC particles in a dense graphene monolith, inspired by the dense structure of pomegranate where irregular grains are compactly packed in the peel. The flexible graphene network package compressed by capillary forces achieve a compact arrangement of the particles and make the AC powder materials into dense bulk materials, while the porous texture of the ACs is well retained. By balancing the porosity and density of the AC/G, the optimized composite increases the electrode density to 1.9 times that of pure AC and achieves a high volumetric energy density of 77 Wh L\(^{-1}\). This densification strategy has great potential for use with other porous yet low-density granular carbon materials besides ACs for the production of high volumetric energy storage devices, not limited to supercapacitors. Furthermore, to our best knowledge, as the first densification strategy reported for commercial ACs, this method is simple and easily scalable, promising to accelerate the development of industrial supercapacitors with higher volumetric energy densities.

**Supporting Information**

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

**Acknowledgements**

P.L., H.L., and D.L.H. contributed equally to this work. The authors appreciate the supports from the National Science Fund for Distinguished Young Scholars of China (No. 51525204), National Natural Science Foundation of China (No. 51702229), Guangdong Natural Science Funds for Distinguished Young Scholars (No. 2017B030306006), Guangdong Special Support Program (No. 2017TQ04C664), Shenzhen Basic Research Project (Nos. JCYJ20150529164918734 and JCYJ20170412171630020).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

activated carbons, capillary shrinkage, compact graphene network, supercapacitors, volumetric performance

---

Received: December 28, 2018
Revised: April 2, 2019
Published online: May 8, 2019

---

[1] P. Simon, Y. Gogotsi, Nat. Mater. 2008, 7, 845.
[2] P. Simon, Y. Gogotsi, B. Dunn, Science 2014, 343, 1210.
[3] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, Nat. Mater. 2015, 14, 271.
[4] M. R. Lukatskaya, B. Dunn, Y. Gogotsi, Nat. Commun. 2016, 7, 12647.
[5] F. Wang, X. Wu, X. Yuan, Z. Liu, Y. Zhang, L. Fu, Y. Zhu, Q. Zhou, Y. Wu, W. Huang, Chem. Soc. Rev. 2017, 46, 6816.
[6] Y. Gogotsi, P. Simon, Science 2011, 334, 917.
[7] C. Zhang, W. Lv, Y. Tao, Q.-H. Yang, *Energy Environ. Sci.* 2015, 8, 1390.

[8] M. Beidaghi, Y. Gogotsi, *Energy Environ. Sci.* 2014, 7, 867.

[9] H. Li, Y. Tao, X. Zheng, J. Luo, F. Kang, H.-M. Cheng, Q.-H. Yang, *Energy Environ. Sci.* 2016, 9, 3135.

[10] C. Liu, X. Yan, F. Hu, G. Gao, G. Wu, X. Yang, *Adv. Mater.* 2018, 30, 1705713.

[11] X. Yang, C. Cheng, Y. Wang, L. Qiu, D. Li, *Science* 2013, 341, 534.

[12] E. Frackowiak, F. Beguin, *Carbon* 2001, 39, 937.

[13] M. Sevilla, R. Mokaya, *Energy Environ. Sci.* 2014, 7, 1250.

[14] L. Yu, L. Hu, B. Anasori, Y.-T. Liu, Q. Zhu, P. Zhang, Y. Gogotsi, B. Xu, *ACS Energy Lett.* 2018, 3, 1597.

[15] H. Pan, J. Li, Y. Feng, *Nanoscale Res. Lett.* 2010, 5, 654.

[16] W. Lv, Z. Li, Y. Deng, Q.-H. Yang, F. Kang, *Energy Storage Mater.* 2016, 2, 107.

[17] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nano Lett.* 2008, 8, 3498.

[18] Y. Zhu, S. Murali, M. D. Stoller, K. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, *Science* 2011, 332, 1537.

[19] L. L. Zhang, X. S. Zhao, *Chem. Soc. Rev.* 2009, 38, 2520.

[20] T. Lin, I.-W. Chen, F. Liu, C. Yang, H. Bi, F. Xu, F. Huang, *Science* 2015, 350, 1508.

[21] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, *Adv. Mater.* 2014, 26, 2219.

[22] P. J. Hall, M. Mirzaeian, S. I. Fletcher, F. B. Sillars, A. J. Rennie, G. O. Shitta-Bey, G. Wilson, A. Cruden, R. Carter, *Energy Environ. Sci.* 2010, 3, 1238.

[23] F. Xu, Z. Tang, S. Huang, L. Chen, Y. Liang, W. Mai, H. Zhong, R. Fu, D. Wu, *Nat. Commun.* 2015, 6, 7221.

[24] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* 2012, 335, 1326.

[25] Y. Tao, X. Xie, W. Lv, D.-M. Tang, D. Kong, Z. Huang, H. Nishihara, T. Ishii, B. Li, D. Golberg, *Sci. Rep.* 2013, 3, 2975.

[26] S. Wu, Y. Zhu, *Sci. China Mater.* 2017, 60, 25.

[27] Y. Yoon, K. Lee, S. Kwon, S. Seo, H. Yoo, S. Kim, Y. Shin, Y. Park, D. Kim, J.-Y. Choi, *ACS Nano* 2014, 8, 4580.

[28] Y. Bu, T. Sun, Y. Cai, L. Du, O. Zhuo, L. Yang, Q. Wu, X. Wang, Z. Hu, *Adv. Mater.* 2017, 29, 1700470.

[29] D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura, S. Iijima, *Nat. Mater.* 2006, 5, 987.

[30] Y. Zhou, M. Ghaffari, M. Lin, E. M. Parsons, Y. Liu, B. L. Wardle, Q. Zhang, *Electrochim. Acta* 2013, 111, 608.

[31] S. Murali, N. Quarles, L. L. Zhang, J. R. Potts, Z. Tan, Y. Lu, Y. Zhu, R. S. Ruoff, *Nano Energy* 2013, 2, 764.

[32] W. Lv, C. Zhang, Z. Li, Q. H. Yang, *J. Phys. Chem. Lett.* 2015, 6, 658.

[33] Y. Xu, K. Sheng, C. Li, G. Shi, *ACS Nano* 2010, 4, 4324.

[34] C. Luo, W. Lv, C. Qi, L. Zhong, Z. Z. Pan, J. Li, F. Kang, Q. H. Yang, *Adv. Mater.* 2018, 1805075.

[35] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.-L. Taberna, *Science* 2006, 313, 1760.

[36] C. Largeot, C. Portet, J. Chmiola, P.-L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* 2008, 130, 2730.

[37] A. Pandolfo, A. Hollenkamp, *J. Power Sources* 2006, 157, 11.

[38] A. Pandolfo, G. Wilson, T. Huynh, A. Hollenkamp, *Fuel Cells* 2010, 10, 856.