A Hierarchical Carbon Derived from Sponge-Templated Activation of Graphene Oxide for High-Performance Supercapacitor Electrodes

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There has been an increasing demand for the development of electrochemical energy storage devices with high energy density and excellent rate performance. [1] Electrical double layer capacitors (EDLCs), also called supercapacitors (SCs), have attracted a worldwide attention owing to their long cycle lifetime and very high power density. [2–4] However, relatively low energy density (typically 3–5 Wh kg⁻¹) of commercially available carbon-based SCs has significantly restricted their applications in the primary power source. [4–6]

Graphene has attracted an extensive attention in energy storage applications regarding to its unique features of high surface area, flexibility, chemical stability, excellent electric and thermal conductivity. [1,7] Graphene platelets, however, especially those derived from graphene oxide (GO) tend to agglomerate during wet-chemistry processing and are therefore leading to lower surface areas than the theoretical value of 2630 m² g⁻¹. [8] Strategies have been developed to assemble graphene-based platelets to 3D structures in order to prevent the restacking of platelets for higher surface areas while maintaining the intrinsic conductivity of platelets. [9] For example, Su and co-workers demonstrated a 3D macroporous bubble graphene film, in which PMMA spheres serve as the hard templates. [10] Sun and co-workers realized a sponge-templated preparation of 3D graphene sheets (STGS) with a high electrosorptive capacity of 4.95 mg g⁻¹ for capacitive deionization. [11] Li et al. achieved a facile fabrication of 3D graphene networks for the decoration of silicon by employing polyurethane (PU) sponge as a template and GO as a building block. [12] Sun and co-workers prepared TiO₂-deposited reduced GO sheets using a porous PU sponge as template for photoelectrochemical oxidation of ethanol. [13] A recent study reported compressible all-solid-state SCs based on polyaniline–SWCNTs–sponge electrodes, in which sponge provides compressibility and polyaniline offers pseudocapacitance. [14]

As we can see, as a cost-effective template, sponge is able to act as an excellent support for the assembly of carbon nanostructures for SC electrodes. Sponge-templated graphene structures, however, have suffered from relatively low specific surface area (SSA) (STGS: 305 m² g⁻¹, for instance), which restricts the further improvement in the SC performance. On the other hand, most graphene-based assemblies with high SSAs have a low electrode density (typically <0.5 g cm⁻³), which leads to plenty of empty space in the electrode that will be flooded by electrolyte, thereby deteriorating the performance of the final devices. [15] Li and co-workers demonstrated chemically converted graphene hydrogel films with a high packing density of up to 1.33 g cm⁻³ and simultaneously prominent capacitive performances (209 F g⁻¹ and 261 F cm⁻³ in organic electrolytes). [16] The layer-like stacking of graphene platelets may deteriorate the power output due to the insufficient ion channels in the direction perpendicular to the layers.

Chemical activation is an effective method to create pores, e.g., in the preparation of activated carbons (ACs). [17] Among various chemical activation methods, KOH activation has been widely used to process graphene. [18,19] carbon nanotubes (CNTs), [20] pollens [21] and pomelo peels [22] to deliver porosity and thus to enhance SC performances. Our research group has previously reported the fabrication of a carbon named aMEGO by KOH activation of microwave expanded graphene oxide (MEGO), from which a specific capacitance of 166 F g⁻¹ in BMIMBF₄/AN electrolyte was achieved. [18] A direct mixture of GO suspension with KOH solution followed by drying and annealing could also lead to an activated graphene similar to aMEGO. [23] However, aMEGO also exhibits a relatively low electrode density (<0.35 g cm⁻³), which has largely reduced its volumetric performance. [24] Transforming low-density carbons to an assembly with a practically useful density yet with a relatively high porosity and high electrical conductivity is expected to practically useful SCs, especially when it is compatible to high-voltage organic electrolytes.

In this work, a 3D hierarchical carbon is prepared by combining sponge-templating with KOH activation of GO platelets. It is found that the sponge assemblies GO platelets around its backbone, while KOH suctioned inside the sponge creates a huge number of micropores in backbone during the thermal annealing, leading to a highly conductive yet highly porous carbon. Due to the shortened ion transport distance in the 3D hierarchical and inner porous structure, an excellent
electrochemical behavior with a high specific capacitance (of up to 401 F g\textsuperscript{-1} in aqueous electrolytes measured in three-electrode configuration, 207 F g\textsuperscript{-1} and 149 F cm\textsuperscript{-3} in organic electrolytes measured in two-electrode configuration) has been obtained, resulting in high energy density and high power density.

Preparation of the 3D hierarchical carbon (aPG-10) is briefly illustrated in the Figure 1a and a detailed experimental description is provided in Supporting Information. Typically, a piece of PU sponge was immersed into a homogeneous suspension named as GO-1-KOH-10 (1 mg mL\textsuperscript{-1} GO mixed with 10 mg mL\textsuperscript{-1} KOH) and repeatedly squeezed/released for a complete suction. Afterwards, the sponge was lifted out and dried to obtain a PU/GO/KOH mixture. The weight gains of sponge with bare KOH solution, bare GO suspension or mixed suspension have been recorded to verify the homogeneous suction of GO and KOH in the sponge, as shown in Table S1 in the Supporting Information. The dried PU/GO/KOH mixture was annealed at 900 °C for 2 h in argon flow and subjected to washing and drying, leading to a final sample named as aPG-10. PG-0, aPG-2, aPG-5, and aPG-20 were fabricated from the suspensions of GO-1 (1 mg mL\textsuperscript{-1} GO), GO-1-KOH-2 (1 mg mL\textsuperscript{-1} GO mixed with 2 mg mL\textsuperscript{-1} KOH), GO-1-KOH-5 (1 mg mL\textsuperscript{-1} GO mixed with 5 mg mL\textsuperscript{-1} KOH), GO-1-KOH-20 (1 mg mL\textsuperscript{-1} GO mixed with 20 mg mL\textsuperscript{-1} KOH), respectively, following the same process with that for aPG-10. In control experiments, pure PU sponges or dried mixture of PU/KOH solution (with a concentration of from 2 to 20 mg mL\textsuperscript{-1}) has been annealed with the same procedures, but no products could be obtained without the existence of GO platelets, indicating that sponge has been completely pyrolyzed during the annealing process. On the other hand, a certain amount of GO-1 or GO-1-KOH-10 suspension was directly dried without the existence of sponge at 60 °C and treated in the same process to obtain rGO or aGO-10 as references.

The morphology of as-prepared aPG-10 was examined by scanning electron microscopy (SEM). Figure 1b shows that aPG-10 owns a well-defined interconnected porous structure, similar to that of pure sponge without any processing as shown in Figure S1 in the Supporting Information. The dried PU/GO/KOH mixture was annealed at 900 °C for 2 h in argon flow and subjected to washing and drying, leading to a final sample named as aPG-10. PG-0, aPG-2, aPG-5, and aPG-20 were fabricated from the suspensions of GO-1 (1 mg mL\textsuperscript{-1} GO), GO-1-KOH-2 (1 mg mL\textsuperscript{-1} GO mixed with 2 mg mL\textsuperscript{-1} KOH), GO-1-KOH-5 (1 mg mL\textsuperscript{-1} GO mixed with 5 mg mL\textsuperscript{-1} KOH), GO-1-KOH-20 (1 mg mL\textsuperscript{-1} GO mixed with 20 mg mL\textsuperscript{-1} KOH), respectively, following the same process with that for aPG-10. In control experiments, pure PU sponges or dried mixture of PU/KOH solution (with a concentration of from 2 to 20 mg mL\textsuperscript{-1}) has been annealed with the same procedures, but no products could be obtained without the existence of GO platelets, indicating that sponge has been completely pyrolyzed during the annealing process. On the other hand, a certain amount of GO-1 or GO-1-KOH-10 suspension was directly dried without the existence of sponge at 60 °C and treated in the same process to obtain rGO or aGO-10 as references.

The morphology of as-prepared aPG-10 was examined by scanning electron microscopy (SEM). Figure 1b shows that aPG-10 owns a well-defined interconnected porous structure, similar to that of pure sponge without any processing as shown in Figure S1 in the Supporting Information. By zooming into inside the 3D structure (Figure 1c), the surface of the skeleton looks smooth while a large amount of honeycomb-like pores (about 0.9 μm in diameter, as shown in Figure S2 in the Supporting Information) are observed in the broken cross-section of skeleton, as shown in the inset of Figure 1c. The hierarchical structure can be observed more clearly with transmission electron microscopy (TEM). As can be seen from Figure 1d, the skeleton consists of plentiful pores which is covered with a thin membrane. The image with higher magnification (Figure 1e)
shows the amorphous feature of the carbon with micropores in the skeleton, similar to previous observations in ACs or activated graphene materials.\[6,18,21,25,26\] Such porous structure of aPG-10 has made it very fragile, leading to a low Young’s modulus of \(0.04\) MPa and a yield strength of \(0.005\) MPa, measured by a compression test.

Obviously aPG-10 has copied the macroporous structure of sponge while micropores and mesopores are introduced in KOH activation. To have the hint for the formation mechanism of the porous skeleton covered with a relatively smooth surface in aPG-10, elemental mapping was performed by energy dispersive spectrometer (EDS), as presented in Figure 2, to reveal the elemental distribution in the PU/GO/KOH dry mixture before annealing (activation) at \(900\) °C. Figure 2a shows the SEM image of the mixture, from which macroscopic pores with sizes similar to those in aPG-10 are observed, verifying that the 3D aPG-10 network is generated due to the sponge-templating. As shown in Figure 2b–d, the C element distributes on the whole surface of the skeleton in the sponge, where K signals could be hardly observed. Instead, abundant K has been found inside the backbone of the skeleton, as shown in Figure 2c. Such a distribution of K element may be explained by the existence of numerous pores in the backbone of the sponge, which may agglomerate more KOH by capillary force but block big GO platelets out of the skeleton during drying. The distribution of K element may be explained by the existence of abundant micropores in the aPG samples.\[18\] We attribute the improvement in the SSAs to the role of sponge-templating, which has prevented the aggregation of GO platelets\[13\] and the pyrolysis of sponge could also help the creation of pores. SSA increases with the content of KOH for aPG samples studied, while PG-0 exhibits a very low SSA of 17.8 m\(^2\) g\(^{-1}\). X-ray diffraction (XRD) is shown in Figure 3b. Two weak and broad peaks at about \(2\theta = 24^\circ\) and \(43^\circ\) are attributed to the (002) and (100) reflections of graphitic carbon layers, respectively. The high intensity in the low angle region results from the existence of abundant micropores in the aPG samples.\[18\] Peak width of (002) in aPG samples has been dramatically broadened by porous structure. By comparing the spectra of aPG-10 and aGO-10, we can see the sponge-templating might be more effective to interlayer-distance control as the spectrum of aGO-10 shows the most broadened (002) peak. The Raman spectra in Figure S7 in the Supporting Information further reveal the amorphous structure of aPG samples. The peaks observed at 1349 and 1590 cm\(^{-1}\) are the D(defects and disorder) and G(graphitic) bands of carbon materials respectively. All D/G intensity ratios of PG-0, aPG-2, aPG-5, aPG-10, and aGO-10 are about 1, indicating the similar level of amorphous carbon/defects in the samples.\[22\]
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Fourier transform infrared (FTIR) spectroscopy was applied to examine the functional groups in PU sponge, PG-0, aGO-10, and aPG-10, and check whether the PU sponge had been totally pyrolyzed by the annealing process. In the spectra shown in Figure 3c, the broad peak at 1620 cm\(^{-1}\) is attributed to the O–H vibrations of water absorbed on the surface of samples. Another broad band at about 1100 cm\(^{-1}\) stems from the C–O or C–N stretching vibration.[22] As can be seen, the spectrum of aPG-10 agrees well with that of aGO-10, totally contrary to that of PU sponge. The peaks observed from 650 to 1800 cm\(^{-1}\) in PU sponge disappear from aGO-10 and aPG-10, indicating the complete pyrolysis of the sponge in the activation process.[11,13] X-ray photoelectron spectroscopy (XPS) spectra are illustrated in Figure 3d and elemental compositions of these samples are shown in Table S2 in the Supporting Information, in which aPG-10 has a nitrogen content of 1.27 at%.

We can clearly see the existence of N in aPG-10 and PG-0, and the proportion of N decreases with the increase in KOH in the mixture before annealing. The N 1s spectra of aPG-10 have a nitrogen content of 1.27 at%.[11] The N 1s spectra of PG-0, aGO-10, and aPG-10 are shown in Figure S8 in the Supporting Information. Previous work reported that the conductivity and wettability of graphene sheets can be improved by nitrogen doping, leading to a considerable benefit to the application for SCs.[12] The performance of the aPG-10 as an electrode material for SCs was investigated using cycle voltammetry (CV) and galvanostatic charge–discharge (GCD).

Figure 3a,b show the performance of aPG-10 electrode coated on glassy carbon in a three-electrode configuration with 1.0 M H\(_2\)SO\(_4\) as electrolyte. The specific capacitance calculated from the discharge at a current density of 5 A g\(^{-1}\) is 401 F g\(^{-1}\), which remains 349 F g\(^{-1}\) at a current density of 100 A g\(^{-1}\). When aPG-10 was tested in 6.0 M KOH electrolyte, a specific capacitance of 227 F g\(^{-1}\) at 5 A g\(^{-1}\) was obtained in the three-electrode configuration, as shown in Figure S8 in the Supporting Information. Previous work reported that the conductivity and wettability of graphene sheets can be improved by nitrogen doping, leading to a considerable benefit to the application for SCs.[22,32] The N doping in aPG-10 should play such a role,[33] as proposed with a N-H redox mechanism in acidic condition.[34] Compared with porous carbon materials previously reported, aPG-10 is a very competitive electrode material in aqueous electrolytes, as shown in Table S4 in the Supporting Information. Notably, the specific capacitance and rate ability of aPG-10 shows a much lower value of 2.41 Ω sq\(^{-1}\), compared with rGO and aGO-10. Besides, the N atoms doped into carbon networks may enhance the wettability of electrode interface to electrolyte, and produce affluent faradic pseudocapacitance in aqueous electrolytes.[10]

The performance of the aPG-10 as an electrode material for SCs was investigated using cycle voltammetry (CV) and galvanostatic charge–discharge (GCD). Figure 4a,b show the performance of aPG-10 electrode coated on glassy carbon in a three-electrode configuration with 1.0 M H\(_2\)SO\(_4\) as electrolyte. The specific capacitance calculated from the discharge at a current density of 5 A g\(^{-1}\) is 401 F g\(^{-1}\), which remains 349 F g\(^{-1}\) at a current density of 100 A g\(^{-1}\). When aPG-10 was tested in 6.0 M KOH electrolyte, a specific capacitance of 227 F g\(^{-1}\) at 5 A g\(^{-1}\) was obtained in the three-electrode configuration, as shown in Figure S8 in the Supporting Information. Previous work reported that the conductivity and wettability of graphene sheets can be improved by nitrogen doping, leading to a considerable benefit to the application for SCs.[22,32] The N doping in aPG-10 should play such a role,[33] as proposed with a N-H redox mechanism in acidic condition.[34] Compared with porous carbon materials previously reported, aPG-10 is a very competitive electrode material in aqueous electrolytes, as shown in Table S4 in the Supporting Information. Notably, the specific capacitance and rate ability of aPG-10 shows a much lower value of 2.41 Ω sq\(^{-1}\), compared with rGO and aGO-10. Besides, the N atoms doped into carbon networks may enhance the wettability of electrode interface to electrolyte, and produce affluent faradic pseudocapacitance in aqueous electrolytes.[10]
Two-electrode symmetrical coin cells have also been assembled to evaluate aPG-10 in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), tetraethylammonium tetrafluoroborate (TEABF₄) electrolytes in acetonitrile (AN) or 6.0 M KOH aqueous electrolyte, by using the best-practice method.[35] Figure 4c demonstrates the CV curves for different scan rates from 50 to 150 mV s⁻¹ in 1.0 M BMIMPF₆/AN in a two-electrode configuration. d) Galvanostatic charge/discharge curves at constant currents of 0.5 and 1 A g⁻¹ in 1.0 M BMIMPF₆/AN. The inset shows the specific capacitance calculated at various current densities. e) Nyquist plot showing the imaginary part versus the real part of impedance in 1.0 M BMIMPF₆/AN. Inset magnifies the data in the high-frequency range. f) Ragone plots of aPG-10 electrode in 1.0 M BMIMPF₆/AN and 1.0 M TEABF₄/AN, compared with aMEGO,[18] asMEG-O,[6] PF16G-HA,[19] pre-FCG,[11] and post-FCG.[6]

Figure 4. a) Cyclic voltammetry curves for scan rates of from 50 to 500 mV s⁻¹ in 1.0 M H₂SO₄ measured in a three-electrode configuration. b) Galvanostatic charge/discharge curves under different constant currents in 1.0 M H₂SO₄. The inset shows the rate ability with increased mass loading on glassy carbon electrode. c) Cyclic voltammetry curves for different scan rates from 50 to 150 mV s⁻¹ in 1.0 M BMIMPF₆/AN in a two-electrode configuration. d) Galvanostatic charge/discharge curves at constant currents of 0.5 and 1 A g⁻¹ in 1.0 M BMIMPF₆/AN. The inset shows the specific capacitance calculated at various current densities. e) Nyquist plot showing the imaginary part versus the real part of impedance in 1.0 M BMIMPF₆/AN. Inset magnifies the data in the high-frequency range. f) Ragone plots of aPG-10 electrode in 1.0 M BMIMPF₆/AN and 1.0 M TEABF₄/AN, compared with aMEGO,[18] asMEG-O,[6] PF16G-HA,[19] pre-FCG,[11] and post-FCG.[6]
reached in aPG-10 among all samples. Figure 4e shows the Nyquist plot obtained from electrochemical impedance spectroscopy (EIS) in the frequency range of 0.01 Hz to 100 kHz, and a magnified view of the curve in the high-frequency region in the inset. From the plots, we can see that aPG-10 demonstrates a nearly ideal capacitive behavior with a vertical slope at the low-frequency region and an ionic resistance of as small as 3.16 Ω. The cycling test shows that the electrode has a retention of 93% in capacitance in BMIMPF_6/AN at 10 A g\(^{-1}\) after 4000 times of charging/discharging.

The energy storage performance of symmetric SCs assembled with aPG-10 as the electrode is shown in the Figure 4f, by comparing with previous works based on aMEGO\[^{[18]}\] with BMIMBF_4/AN and TEABF_4/AN electrolyte, asMEG-O\[^{[6]}\] with EMIMTFSI/AN electrolyte, PF16G-HA\[^{[26]}\] with TEABF_4/AN electrolyte, Pre-FCG\[^{[31]}\] and Post-FCG\[^{[31]}\] with TEABF_4/AN electrolyte. Benefiting from the high specific capacitance of up to 207 F g\(^{-1}\) (in BMIMBF_4/AN at a current density of 0.5 A g\(^{-1}\)) and an operating voltage of 3.5 V, aPG-10 exhibits a high energy density of \(\approx 89 \text{Wh kg}^{-1}\) (\(\approx 64 \text{Wh L}^{-1}\)) at a power density of \(\approx 99 \text{kw kg}^{-1}\) (\(\approx 71 \text{kw L}^{-1}\)), and a high power density of \(\approx 512 \text{kw kg}^{-1}\) (\(\approx 369 \text{kw L}^{-1}\)) at an energy density of \(\approx 36.54 \text{Wh kg}^{-1}\) (\(\approx 26 \text{Wh L}^{-1}\)). The overall performance of aPG-10 is comparable and even superior to those previously reported porous carbon materials, as summarized in Table S5 in the Supporting Information. In addition, the areal capacitance of aPG-10 is calculated to be 15.53 μF cm\(^{-2}\) previously reported porous carbon materials, as summarized in Table S5 in the Supporting Information.

**Supporting Information**

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

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