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Porous asphalt/graphene composite for supercapacitors with high energy density at superior power density without added conducting materials<sup>†</sup>

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The promotion of electrode active materials with higher rate capabilities and lower cost has been a longstanding challenge in the field of supercapacitors. In this work, a novel composite of asphalt with graphene oxide is developed, and it is found that the introduction of a small amount of graphene oxide such as 1 wt% could increase conductivity up to ~400% and surface area up to ~114%. The composite materials without the addition of any conducting material demonstrate both high capacitance and cycling stability. In addition, their rate capability is well maintained from 0.5 A g<sup>-1</sup> to 100 A g<sup>-1</sup> with high capacitance retention (~88%). Furthermore, the optimized material, which is made mainly from the cheap waste material asphalt, demonstrates an excellent energy density (22.0 Wh kg<sup>-1</sup>) at an ultra-high power density (55.4 kW kg<sup>-1</sup>), which indicates its promising potential for industrial applications in green energy.

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### Introduction

Electrical double layer capacitors (EDLCs), in which the capacitance comes from the pure electrostatic charge accumulated at the electrode/electrolyte interface, have attracted much attention due to their ultra-high charge and discharge rates and extremely long cycle life.<sup>1-10</sup> Ultra-fast supercapacitors are desirable in military, civil and industrial fields, such as electromagnetic aircraft launch systems, battery steering devices, electromagnetic guns and laser devices.<sup>11</sup> However, the absence of suitable electrode carbon materials that can enhance both power density and energy density has limited the wider application of these energy devices. Supercapacitors with superior power density and high energy density require electrode materials that exhibit high specific capacity even at very high current density (high rate capability).

In the past few years, much effort has been devoted to optimizing the rate capability of active carbon materials for fast supercapacitors. Particularly, the design and synthesis of advanced carbon electrode materials of high specific surface areas (SSA) with proper porosities and high electrical conductivity are highly desirable due to their apparent structural advantages as follows: first, a high surface area guarantees sufficient contact area between the active sites and the electrolyte; second, a proper porosity structure with wellinterconnected pores (medium and large sized pores for enhancing rate capability<sup>12-17</sup>) provides the opportunity to optimize the rate capability of carbon materials as EDLC electrodes;<sup>4,5,14,18-20</sup> and third, the overall conductivity of the electrode material is believed to be beneficial for electron transport. In addition, low cost precursors and easy, cheap and scalable procedures are also necessary.<sup>12,18</sup> Nevertheless, the synthetic strategies for highly porous and conductive structures usually require expensive hard templates,<sup>15,21</sup> which have to be removed by additional treatments. Moreover, the template removal process involves hazardous chemical reactions. Furthermore, the raw materials used are expensive. Therefore, the preparation of highly porous and conductive structures combining simple methods with low cost precursors is highly desirable.

Graphene, due to its large specific surface area, mechanical flexibility, chemical stability and excellent conductivity,<sup>22</sup> has been introduced to address the above mentioned issues.<sup>15,20-24</sup> Asphalt, as a cheap and waste industrial material,<sup>23</sup> has been widely studied to prepare three dimensional hierarchically porous carbons (3DHPC) through the direct activation method for EDLC materials.<sup>24-28</sup> However, it remains a considerable challenge to simultaneously achieve high specific surface area with proper pore structure and high conductivity while retaining excellent rate capability. To address these issues, we develop an *in situ* solvothermal treatment with almost quantitative atomic yield and a facile chemical activation step using asphalt and graphene oxide (GO) as starting materials to prepare low cost, high specific surface area with proper porosity and highly

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conductive asphalt/graphene composite electrode materials for supercapacitors.

In this work, the composite materials demonstrate not only dimensional hierarchically porous structures with high SSA, but also high conductivity. The optimal material made from 1 wt% GO and asphalt exhibits an ultrahigh SSA ( $3500 \text{ m}^2 \text{ g}^{-1}$ ), excellent bulk conductivity (71 S m<sup>-1</sup>), and hierarchical pores (micro, meso-, and macro-pores), simultaneously. These combined excellent properties lay the foundation for superior super-capacitor performances without the addition of any conducting material in 1 M TEABF<sub>4</sub>/AN with a specific capacitance and energy density of 158 F g<sup>-1</sup> and 39.2 Wh kg<sup>-1</sup> at 1 A g<sup>-1</sup>, respectively. Moreover, it exhibits an excellent rate performance with high capacity retention (~88%) from 0.5 A g<sup>-1</sup> to 100 A g<sup>-1</sup>. Furthermore, this optimized sample shows excellent energy density (22.0 Wh kg<sup>-1</sup>) at an ultrahigh power density (55.4 kW kg<sup>-1</sup>).

### **Results and discussion**

# Preparation and characterization of asphalt/graphene composite materials

The preparation process for the asphalt/graphene composite materials (AnG) is shown in Fig. 1. The intermediate product HT-AnG (Fig. S1<sup>†</sup>) was first obtained through a solvothermal process and then mixed with 4 times its mass ratio of KOH to obtain the final AnG products, which showed the highest SSA based on our experimental results (Table S1 and Fig. S2<sup>†</sup>). The carbon yield of the solvent thermal reaction is about 60% and the activation yield is about 25% (carbon yields and carbon contribution from GO/asphalt of HT-AnG and AnG are shown in Table S2<sup>†</sup>). The high carbon yield and low cost of asphalt significantly decreases the cost of this composite material.

The structure and morphology of the final products AnG were analyzed *via* scanning electron microscopy (SEM). The introduction of graphene (reduced GO) led to obvious differences in the morphology of the products. As shown in Fig. 2a–c, A1G with the optimized GO ratio (1 wt%) shows a loosely stacked structure with many irregular micrometer-sized (macro-) pores or channels (Fig. 2b), which significantly differs from the rather firm/ solid structure derived from the pure asphalt carbon source (Fig. 2a). The particle size distributions of A1G at different cut sizes of 10%, 50% and 90% ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ , respectively) are shown in Fig. S3.† The  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  sizes are 8.8 µm, 29.7 µm and 57.9 µm, respectively, and the bulk density of A1G is 0.14 g cm<sup>-3</sup>. The product from the higher GO ratio (4 wt% in

Fig. 2c) has a tightly stacked layered structure. The macroporous voids with loosely stacked structure, as shown in the SEM image (Fig. 2b), are beneficial since during electrochemical testing they can serve as ion-buffering reservoirs. The transmission electron microscopy (TEM) images of A1G with different resolutions are shown in Fig. 2d-f. The mesoporous structure (~20 nm) in Fig. 2d and e implies a short distance for ion fast transport, and the interconnected structure indicates good electron conductivity. When a small amount of GO was added, the GO sheets blocked the stacking of the asphalt during the solvothermal reaction, and thus smaller active carbon particles were formed with more pores in the next activation step. The high-resolution TEM image (Fig. 2f) reveals that the microstructure of A1G has highly curved graphene-like domains, which indicates a threedimensional (3D) porous structure in the microscale (the HRTEM images of the other samples are provided in Fig. S4<sup>†</sup>).<sup>29</sup>

The mean width  $(L_a)$  of the graphitic domains was calculated for each specimen, which was proportional to the  $I_{\rm D}/I_{\rm G}$  ratio (Fig. S5<sup>†</sup>). The dimensional size of the optimized product A1G is estimated to be  $\sim$ 6.8 nm, which is much smaller than that of the products prepared from the pure asphalt source (8.1 nm) and A8G (10.9 nm) or reported pure GO (~11.9 nm) and commercial active carbon RP20 (10.7 nm).29 The X-ray diffraction (XRD) characterization (Fig. S6<sup>†</sup>) also suggests that our products have a much weaker and broader (002) peak, which indicates a more disturbed structure due to the presence of more randomly oriented aromatic carbon sheets in the amorphous carbon.<sup>30</sup> X-ray photoelectron spectroscopy (XPS) further indicates that most of the carbon atoms in A1G are sp<sup>2</sup> carbons (Fig. S7<sup>†</sup>), which is demonstrated by the strong peak at ~284.5 eV in the C<sub>1s</sub> XPS spectra.<sup>31</sup> Elemental analysis reveals that A1G contains 94.25 wt% C (Table S3†). Considering the low cost of asphalt and low content of GO and combined with its high SSA, high conductivity and characterized structure, A1G is attractive for practical application as an electrode in supercapacitors.

To analyze the porosity of AnG,  $N_2$  adsorption–desorption isothermal analysis was performed. Unlike the commercial activated carbon, AnG exhibits typical type IV adsorption– desorption isotherms. The typical hysteresis loop (Fig. 3a) between the adsorption and desorption branches in this series of products is associated with capillary condensation, which indicates the existence of several mesopores in the products. The SSA of A1G was calculated to be as high as 3500 m<sup>2</sup> g<sup>-1</sup> using the Brunauer–Emmett–Teller (BET) model, which is the



Fig. 1 Schematic of the simple and green process for the preparation of the asphalt/graphene composite materials.



**Fig. 2** Scanning electron microscopy (SEM) images of the products from mixtures of asphalt and GO with different ratios (a–c): (a) A0G (no GO), (b) A1G (1 wt% GO) and (c) A4G (4 wt% GO). Low magnification (d and e) and (f) high-resolution transmission electron microscopy (TEM) images of the products from the mixture of asphalt and 1 wt% GO.

highest BET SSA among the AnG series products (Table 1) and is also higher than that of the product obtained from asphalt directly (asphalt V 4 KOH, 3077 m<sup>2</sup> g<sup>-1</sup>) without the solvent thermal process. This indicates that the solvent thermal process not only increases the atomic yield but also avoids some of the environmental release that occurs in the direct thermal treatment, which could also optimize the pore structure. In addition, A1G has the highest number of micropores and mesopores among the AnG series products (Fig. S8†). This may be due to the addition of GO and the hydrothermal process, which results in a much more porous structure. Additionally, this makes it much easier for GO to mix and react with KOH and leads to a much higher SSA than the direct active asphalt.

The BET SSA and conductivity of the AnG products obtained from the mixture of GO and asphalt with different ratios are plotted in Fig. 3b. There is a positive correlation between the GO mass percent and conductivity, which is related to the high conductivity of reduced/activated GO.<sup>18</sup> Moreover, the BET SSA achieves a peak value (3500 m<sup>2</sup> g<sup>-1</sup>) when the GO loading is 1 wt%.

As shown herein and in our earlier studies,<sup>29</sup> the addition of GO (which was converted to graphene during the activation process) to the composite causes the resulting material to

Table 1 Porosity properties of the AnG activated porous materials

Sample	BET SSA $(m^2 g^{-1})$	Conductivity (S $m^{-1}$ )
Asphalt V 4 KOH	3077	17
A0G	3246	18
A0.25G	3003	37
A0.5G	3153	45
A1G	3500	71
A2G	2912	128
A4G	2535	189
A8G	2166	263

exhibit high conductivity due to the high intrinsic conductivity of graphene. In addition, due to the excellent molecular-level dispersion at the very beginning and the nature of the two reaction steps, the added graphene sheets are distributed homogeneously in the whole carbon matrix and work as a conducting filler to enhance the overall conductivity. Only a small amount of filler is needed to achieve the required percolation and high conductivity. Furthermore, when a small amount of GO was added, the added graphene sheets from GO blocked the stacking of the AC precursor generated from the matrix carbon



Fig. 3 (a) N<sub>2</sub> adsorption-desorption isotherms of AnG and (b) specific surface area and conductivity of the samples prepared using different GO ratios.



**Fig. 4** (a) CV curves of A1G at different scan rates; (b) charge–discharge plots of A1G at different scan rates; (c) rate performance using samples prepared with different GO ratios as electrode materials and (d) life span of A1G at a current density of 1 A  $g^{-1}$  measured in 1 M TEABF<sub>4</sub>/AN electrolyte for the two-electrode devices.

sources and thus thinner and smaller AC particles were formed with more pores in the next activation step. When more GO is added, the chance of graphene sheet stacking from the added GO increases, which in turns has a negative effect on the SSA.

This low percentage of GO added should decrease the cost of

producing A1G. The above studies demonstrate that the A1G

electrode not only exhibits much higher BET SSA than previ-

ously reported asphalt-based active carbon materials, but also

shows high conductivity even with a very small percentage of

GO precursor, which contributes to a higher ion accessible

surface area and more rapid ion transport in the unique hier-

archical porous network of A1G and thus greatly improves its

rate capability and capacitance retention at high charging/

# Electrochemical performance of optimized asphalt/graphene composite material (A1G)

Using the best recommended industry practice and method,<sup>32</sup> we fabricated and tested two-electrode symmetrical supercapacitor cells (SCs) using these materials as the electrode materials. It is important to note that no conducting material such as the generally used Super P is needed due to their excellent conductivity.<sup>29,33,34</sup> The areal mass loading of the composite material in one electrode was about 3–4 mg cm<sup>-2</sup> (100–120 µm in thickness). Typically, the cyclic voltammetry (CV) curves of A1G show rectangular shapes over a voltage scan range of 0 to 2.7 V and exhibit negligible small shape distortion (Fig. 4a), which indicate an ideal EDL effect for the tested SC and strong ion transport ability of the A1G composite.<sup>35</sup>



Fig. 5 (a) Gravimetric capacitance and capacitance retention of A1G and two previously reported low-cost carbon-based supercapacitor electrodes for comparison<sup>24,39</sup> and (b) gravimetric capacitance retention of A1G measured at different current densities. The gravimetric capacitances retention of some previously reported carbon-based supercapacitor electrodes are added for comparison.<sup>15,17,21,24,37,40-42</sup>

discharging rates.



Fig. 6 (a) Nyquist plots for the A1G and A0G-based SCs showing the imaginary part *versus* the real part of impedance. Inset provides the data at high frequency. Frequency response of the real capacitance (b) and imaginary capacitance (c) of the A1G-based SCs.

Fig. 4b shows the galvanostatic charge-discharge (GCD) curves of the A1G electrode at different current densities, which are symmetric and thus suggest excellent EDL capacitance properties. The normalized gravimetric capacitance values of A1G calculated from the galvanostatic charge-discharge (GCD) discharge curves are 158, 158, 157, 157 and 157 F  $g^{-1}$  at current densities of 0.5, 1, 2, 5 and 10 A  $g^{-1}$ , respectively. The powder density of A1G is  $\sim 0.35$  g cm<sup>-3</sup>, and thus the volumetric capacitance of A1G is calculated to be 55.3 F cm<sup>-3</sup> at 1 A g<sup>-1</sup>. A specific capacitance of 157 F  $g^{-1}$  at 10 A  $g^{-1}$  demonstrates a high rate capability of 99% capacitance retention upon a current increase to  $10 \text{ Ag}^{-1}$ , which is due to the effective rapid and short pathways for ionic and electronic transport provided by the sub-micrometer structure of A1G.<sup>13,15,16</sup> Furthermore, the capacitance values of A1G are much higher than those of the asphalt sample without solvent thermal treatment (144, 143, 143, 138 and 137 F  $\rm g^{-1}$  at a current density of 0.5, 1, 2, 5 and 10 A  $g^{-1}$ , respectively) and without GO after solvent thermal treatment (146, 148, 148, 144 and 141 F  $g^{-1}$  at a current density of 0.5, 1, 2, 5 and 10 A  $g^{-1}$ , respectively) (Fig. 4c and S9†). Although the high rate performance of pitch based electrodes is well demonstrated in previous literature,<sup>26,36-38</sup> the electrodes were mostly tested in aqueous electrolyte. Our electrodes are made without the addition of conductive carbon black and were tested in organic electrolyte, which exhibited a negligible capacitance decrease (less than 0.1% for A1G) from 0.5 A  $g^{-1}$  to 10 A  $g^{-1}$ . Since charge storage in A1G mainly occurs *via* a pure electric double layer process, the cycling performance of A1G was conducted at a current density of  $1 \text{ Ag}^{-1}$  for 8000 cycles in 1 M TEABF<sub>4</sub>/AN with high reversibility. As shown in Fig. 4d, the capacitance retention is 89% after 8000 cycles.

# Rate capability, energy density and power density of optimized asphalt/graphene composite material (A1G)

A1G yields an excellent gravimetric capacitance of 149, 143 and 139 F g<sup>-1</sup> at high current density of 20, 50 and 100 A g<sup>-1</sup>, respectively, thus retaining ~88% of the capacitance when the current density increases by 200 times (from 0.5 A g<sup>-1</sup> to 100 A g<sup>-1</sup>). This A1G electrode also exhibits a higher gravimetric capacitance and capacitance retention compared with other two low cost electrodes (pitch-based and hemp-based carbonaceous materials in Fig. 5a). Moreover, to the best of our knowledge, the

gravimetric capacitance retention of A1G at a current density of 100 A  $g^{-1}$  is one of the highest values reported for carbon electrodes (Fig. 5b). This high electrochemical performance of asphalt/GO results from the addition of graphene (reduced GO). Graphene not only improves the conductivity but also adjusts the pore size and SSA of the composite, which affects its electrochemical performance, particularly the rate capability. Therefore, an appropriate amount of GO greatly improves the electrochemical performance of the composite. This higher capacity retention is desirable and particularly promising given the advantage of high cost efficiency.

The Nyquist plots of A0G and A1G illustrate vertical curves at low frequencies (Fig. 6a), which reflect the ideal capacitive behavior of the SCs. Compared to the A0G plot, the A1G plot exhibits a steeper slope and a shorter transition domain, which indicate a much smaller charge transfer resistance for electrolyte penetration into the pores and channels. More importantly, the real capacitance and imaginary capacitance plots as a function of frequency (Fig. 6b and c) show the effect of pore structures on the rate of ion transport.<sup>35</sup> The frequency at which the imaginary capacitance reaches its maximum value for the A1G based devices is 1.35 Hz. Specifically, the response time ( $\tau_o = 1/f_o$ ) for the A1G device is 0.74 s. This  $\tau_o$  value is considerably smaller than that for alginate-based porous carbon (2.4 s),<sup>35</sup>



Fig. 7 Ragone plot of the A1G and some previously reported asphalt/ pitch-based electrodes for supercapacitors.<sup>24,25,27,37,45</sup>

The results of our work are outstanding in organic electrolyte, even when compared with respect to graphene-based materials. Energy density and power density were further estimated based on SC measurements in TEABF<sub>4</sub>/AN electrolyte. The Ragone plots of A1G, calculated using the mass of the electrode materials, are exhibited and compared with state of the art materials in the literature in Fig. 7. A1G exhibits an energy density of 39.2 Wh kg<sup>-1</sup> (13.7 Wh L<sup>-1</sup>) at a power output of 360 W kg<sup>-1</sup> (126 W L<sup>-1</sup>), retaining 22.0 Wh kg<sup>-1</sup> (7.7 Wh L<sup>-1</sup>) at 55.4 kW kg<sup>-1</sup> (19.4 kW L<sup>-1</sup>). These values are much higher than those reported for asphalt-based active carbons, particularly those with high power density and energy density (Fig. 7 and Table S4<sup>†</sup>). We also estimated the packaged energy and power densities of A1G-based SCs on the basis of assuming  $\sim$ 30% mass percentage of carbon materials in the device.<sup>29</sup> The A1G-based device is estimated to have an energy density of  $\sim$ 6.6 Wh kg<sup>-1</sup> at a power output of 16.6 kW kg<sup>-1</sup>. It should be noted that supercapacitors with such high energy density at ultra-high rate are rarely reported, especially, with low cost materials.

#### Conclusion

A series of asphalt-based highly conductive asphalt-graphene composite porous carbon materials with enhanced electrochemical performances for supercapacitors were prepared via a simple method. The optimized sample with only 1% GO exhibits a high specific surface area (3500  $m^2 g^{-1}$ ) and conductivity (71 S  $m^{-1}$ ); moreover, it not only exhibits superior supercapacitor performances in 1 M TEABF<sub>4</sub>/AN with a specific capacitance and energy density of 158 F  $g^{-1}$  and 40 Wh  $kg^{-1}$ , respectively, but also shows excellent rate performance with high capacity retention ( $\sim$ 88%) from 0.5 A g<sup>-1</sup> to 100 A g<sup>-1</sup>. Furthermore, this optimized sample shows excellent energy density (22.0 Wh kg<sup>-1</sup>) and power density (55.4 kW kg<sup>-1</sup>) for asphalt based active carbon materials. Considering the low cost and abundance of the asphalt resource, this new electrode material is extremely promising for the development of advanced nanostructured functional carbon materials.

#### Material preparation

First, graphene oxide (GO) was synthesized from natural flake graphite (average particle diameter of 170  $\mu$ m, 99.95% purity, Qingdao Huarun Graphite Co., Ltd.) *via* a modified Hummers' method. It was then centrifuged (12 000 rpm, 30 min) 5 times to replace the solvent with ethanol (99.5%), and finally a GO alcogel was prepared with a concentration of 5–8 mg mL<sup>-1</sup>. Then the GO was diluted with ethanol (99.5%) to obtain different concentration alcohol gels. Furthermore, 10 g of asphalt (styrene-butadiene rubber modified petroleum asphalt) was dispersed in 100 mL THF to obtain a viscous solution. Then, 100 mL of this viscous solution (100 mg mL<sup>-1</sup>) was slowly dropped into 200 mL GO alcogel with a certain concentration during intense agitation. After 2 h, the mixed liquid was poured

into a 100 mL Teflon-lined stainless steel autoclave and kept 180 °C for 14 h. The resulting cylindrical product was washed and dried under vacuum at 120 °C for 24 h to obtain the intermediate product. Then, this intermediate product (2 g) was mixed with KOH (8 g) and placed in a horizontal tube furnace, and heated to 900 °C for 1 h at a heating rate of 5 °C min<sup>-1</sup> under an Ar atmosphere. After cooling to room temperature, the obtained product was thoroughly washed with 0.1 M HCl and distilled water until the pH value was 7. The final product was obtained after drying under vacuum at 120 °C for 24 h. The weight ratio of GO/asphalt final products was 0.25%, 0.5%, 1%, 2%, 4% and 8%, which were denoted as A0.25G, A0.5G, A1G, A2G, A4G and A8G (AnG for the series of final products and the intermediate products were denoted as HT-AnG), respectively. Asphalt was using a similar method for comparison, and the product was named A0G.

#### Characterization

The experimental carbon yields from asphalt or GO only are 58.0% and 70.0%, respectively, in the solvothermal process. Thus, we could use this to further calculate the theoretical carbon yield of HT-AnG according the equation HT-AnG = $58.0\% \times 100/(100 + n) + 70.0\% \times n/(100 + n)$ , where *n* is the ratio if asphalt used is treated as 100. Similarly, the carbon contribution from GO and asphalt could be obtained using the equations 58.0%  $\times$  100/(100 + n) and 70.0%  $\times$  n/(100 + n), respectively. For the activation step, the carbon yield of HT-A0G and HT-GO are 25.8% and 49.6%, respectively, which was obtained by only using asphalt or GO in the activation reaction. Then we further calculated the carbon contribution of AnG from GO and asphalt using the carbon contribution from GO (HT-AnG × 49.6% and carbon contribution from asphalt (HT-AnG)  $\times$  25.8%, respectively. Transmission electron microscopy (TEM) was performed using a JEOL TEM-2100 electron microscope operated at 200 kV. The morphology of AnG was observed via scanning electron microscopy (Nova Nano SEM 230 operated at 10.0 kV). The particle size distribution was measured using a Malvern Mastersizer 3000 laser diffraction instrument (Malvern Instruments). Powder X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max-2500 diffractometer with Cu Kα radiation. Nitrogen adsorption-desorption analysis was conducted at 77 K on a Micromeritics ASAP 2020 apparatus. Surface area was calculated using the BET method based on adsorption data in the relative pressure  $(P/P_0)$  range of 0.05 to 0.3. The pore size distribution (PSD) was analyzed using the NL-DFT method with a slit pore model from the nitrogen adsorption data. Raman spectra were obtained using a LabRAM HR Raman spectrometer with laser excitation at 514.5 nm. Lorentzian fitting was carried out to obtain the positions and widths of the D and G bands in the Raman spectra. According to the Raman spectra, the size of the graphene domains  $L_a$  (nm) can be estimated using the equation  $L_{\rm a} = (2.4 \times 10^{-10})$  $\lambda^4 (I_{\rm D}/I_{\rm G})^{-1}$ , where,  $\lambda$  is the laser energy in nanometers, and  $I_{\rm D}$ and IG are the intensities of the D and G bands, respectively. The electrical conductivity of the products was tested using the following method: the products were mixed with 1 wt%

polytetrafluoroethylene (PTFE, DuPont) as a binder, and homogenized in an agate mortar. Then they were rolled into  $\sim 100 \ \mu\text{m}$  thick sheets, and cut into 3 cm  $\times$  1 cm sheets to obtain resistance (*R*). The conductivity of the film was calculated using the formula  $\lambda = L/(R \times W \times d)$ , where,  $\lambda$  is the electrical conductivity of the sample; and *L*, *W* and *d* are the length, width and thickness of the sheet, respectively.

#### Device fabrication and electrochemical characterization

All the supercapacitor structure devices for the material performance study in this work were evaluated using a twoelectrode industry level device following the method recommended for best industry practice to obtain reliable performance data as much as possible. To fabricate the EDLC type electrode, AnG powder was mixed directly with 10% polytetrafluoroethylene (PTFE, DuPont) (due to the excellent conductivity of AnG, there was no need to use Super P as conductive additive), and rolled into thin sheets (100-120 µm), then punched into 1.2 cm diameter electrodes and hot pressed onto aluminum foil with a conducting carbon coating. 1 M tetraethylammonium tetrafluoroborate in AN (TEABF<sub>4</sub>/AN, BASF) was used as electrolyte. Charge/discharge measurements were performed using battery test systems (LAND CT2001A model; Arbin, Multi-Stations, Multi-Electrodes PST/GST) in the voltage window range of 0 to 2.7 V at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectral measurements were recorded using an Autolab system (Metrohm). CV tests were carried out at a scan rate of  $50 \text{ mV s}^{-1}$ , 100 mV s<sup>-1</sup>, 200 mV s<sup>-1</sup> and 500 mV s<sup>-1</sup> in the potential range of 0 to 2.7 V. EIS measurements were carried out at an AC amplitude of 10 mV in the range of 100 kHz to 10 mHz.

Galvanostatic charge–discharge measurements on the symmetric supercapacitors were carried out at various current densities with voltage windows specific to the materials using a battery test system (LAND CT2001A model, Wuhan LAND Electronics Ltd and Multi-Stations, Multi-Electrodes PST/GST, Arbin). The specific capacitance  $C_{\rm s}$  (F g<sup>-1</sup>) of A1G in the symmetric supercapacitor was calculated according to the equation:

$$C_{\rm s} = \frac{4I}{m\,{\rm d}V/{\rm d}t}\tag{1}$$

where *I* is the constant current (A), *m* (g) is the total active material mass of the two electrodes, and dV/dt (V s<sup>-1</sup>) is the slope obtained by fitting a straight line to the discharge curve of the symmetric supercapacitor.

The real capacitance C' and imaginary capacitance C'' were calculated from the frequency response analysis using the equations:

$$C' = \frac{Z''}{2\pi f Z^2} \tag{2}$$

$$C'' = \frac{Z'}{2\pi f Z^2} \tag{3}$$

where, f is the frequency in Hz and Z' and Z'' are the real part and imaginary part of the impedance Z, respectively. The energy density values E (Wh kg<sup>-1</sup>) of symmetric supercapacitors were obtained using the following equation:

$$E = C_{\rm s} V^2 / 8 \tag{4}$$

where, V(V) is the discharge voltage.

The (average) power density values P (W kg<sup>-1</sup>) of the symmetric supercapacitors were calculated according to the following equation:

$$P = E/\Delta t \tag{5}$$

where,  $\Delta t$  is the discharge time.

## Conflicts of interest

There are no conflicts to declare.

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