# Self-generating graphene and porous nanocarbon composites for capacitive energy storage

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# Supplementary information

# Experiments

# **Preparation of GO**

GO was synthesized from natural graphite by the modified Hummers method.  $H_2SO_4$  (92 mL) was added into a 1000 mL flask filled with graphite (2 g) and NaNO<sub>3</sub> (2 g) at room temperature. The flask was then cooled to 0 °C in an ice bath and agitated continuously for 4 h, followed by slow addition of KMnO<sub>4</sub> (12 g) and allowed to warm to room temperature. Next, the mixture was stirred mildly for 2 h before 184 mL de–ionized water was carefully added into it. After that, the mixture was moved into a water–bath of 98 °C and agitated for 15 min, followed by addition of 400 mL de–ionized water. Finally, sufficient  $H_2O_2$  was added prior to centrifugation and desiccation.

## **Preparation of HSG samples**

HSG samples were synthesized starting from the PVDF, the graphite oxide (GO) that was prepared by using Hummers method, and the KOH. Firstly, PVDF and GO with a mass ratio of 4:1 ~ 19:1 were mixed under hand grinding. The mixed powders were put into a nickel crucible and then added into solid state KOH. The weight ratio of KOH: (PVDF + GO) varies from 2:1 to 6:1. A medium temperature, 380 °C was chosen to melt the KOH but is not enough to react with carbon materials. During this process, the liquid phase of KOH is effective to homogenously disperse different substances. Besides, oxygen–containing groups in GO would be further reduced. With further increases temperature to 800 °C, the fluorine element of PVDF was ignition lost due to its high activation and the HSG samples with different morphologies were formed under tailor action of reduced GO hard template. For comparing, the preparation of activation carbon (AC02 and AC04) was also carried out without adding GO precursor.

## Morphological and structural characterizations

Field–emission SEM was carried out on Zeiss Sigma scan electron microscopes. EDX was carried out on a EDAX TEAM EDS. TEM and HRTEM were carried out on a JEOL JSM–2010 operating at an accelerating voltage of 200 kV. AFM images of HSG samples spin coated on a freshly cleaved mica surface were taken with a Nanoscope MultiMode SPM in tapping mode. Raman spectra were obtained on a RM2000 microscopic confocal Raman spectrometer employing a 514 nm laser beam. XRD of HSG samples was performed with a D8 Advance diffractometer with Cu radiation between 5° and 70° with a scan rate of 0.02°/step. XPS analysis was recorded on a PHI Quantera SXM<sup>TM</sup> (ULVAC–PHI. INC). Surface area measurement of dried HSG samples was performed with Micromeritics ASAP2020 surface area and pore size analyzer using nitrogen gas adsorption–desorption isotherm. TG-DSC measurement was performed on Netzsch STA 449 F3 Jupiter.

### **Preparation of supercapacitor electrodes**

HSG samples were used as electrode materials for symmetric supercapacitors and 2032 type coin cells were used. 85 wt% of the HSG samples, 7 wt% PTFE (Sigma Aldrich, 60 wt% dispersed in water and was further diluted to 10 wt% aqueous solution), and 8 wt % super C45 (Timcal) were firstly dispersed in isopropanol by supersonic dispersion. The obtained slurry was heated at 80 °C for removing excess isopropanol and then kneaded thoroughly and rolled down to ~120 µm thick films and pressed onto Al foil (Japan Capacitor Industrial CO., LTD.) with a thickness of 20 µm. After drying for 24 h at 120 °C, the films were then punched into 1.3 cm diameter electrodes. The electrode plates were further mechanically compacted at pressure of 10–38 MPa and punched into 1.1 cm diameter electrodes. TEABF<sub>4</sub> in 1 M PC, and ionic liquid (EMIMBF<sub>4</sub>, Sigma Aldrich, < 10 ppm H<sub>2</sub>O) were used as the electrolytes. 2032 type coin cells with organic and ionic liquid electrolytes were assembled in a dry glovebox (Labstar, Mbraun, Germany) in Ar with less than 1 ppm oxygen and H<sub>2</sub>O. For comparing, YP80F (Kuraray, Japan) electrodes were also prepared.

#### **Electrochemical measurements**

CV curves and electrochemical impedance spectroscopy (EIS) were carried out using AutoLab PGSTAT302N equipment. CV curves were scanned at voltage ramp rates from 10 to 100 mVs<sup>-1</sup>. EIS was obtained in the frequency range from 100 kHz to 10 mHz with a  $\pm$ 10-mV voltage amplitude at open circuit voltage. Galvanostatic CD process and cycle–life test of supercapacitors was measured on an Arbin MSTAT4 multi–channel galvanostat/potentiostat instrument. Average *S<sub>C</sub>* was calculated from the second to forth galvanostatic CD processes using the following equation:

$$S_C = 4I\Delta t/UM \,(\mathrm{F/g}) \tag{1}$$

Where I,  $\Delta t$ , U and M are the applied current, the discharge time, the voltage window and the total mass of both electrodes, respectively.

The effective power density (P) and energy density (E) were calculated by using the following equations:

$$E = S_C U^2 / (2 \times 4 \times 3.6) \text{ (Wh/kg)}$$
 (2)

$$P = 3.6 \times E / t (kW/kg)$$
(3)

All of the values including the current densities were normalized with respect to the combined weight of both electrodes without including PTFE and Super C45.



Figure S1. TG-DSC curves for the precursor of G1p4K4-2 (named G1p4K4-2p, composed of graphite oxide, PVDF, and KOH), the composites of PVDF and KOH with weight ratio of 4:1, and pure PVDF powder. The sample temperature was increased at a rate of 10 °C min<sup>-1</sup>. A significant weight loss happens from 120 to 270 °C for containing KOH samples and corresponds to the loss of free and bound water because KOH is very easily to absorb the moisture, the reduction of graphite oxide. The slow rate of weight loss at temperature above ~700 °C results from activation process. The DSC analysis shows an abroad endothermic peak at about 170 °C resulting from the molten of PVDF. At 380 °C, the apparent endothermic peak mainly attributes to the molten of KOH and the carbonization of PVDF and maybe further completely reduces of graphite oxide. One apparent endothermic peak at ~700 °C in DSC curve originate from KOH react with the carbon materials. For G1p4K4-2p, an apparent exothermic peak at ~130 °C may mainly due to the reduction of graphite oxide.



Figure S2. FESEM of G1p9K6-4, three marked areas were used to EDX detection.



Figure S3. One typical EDX according to Figure S1 of G1p9K6-4.

Table S1. The atomic percentage of HSG samples. The data were calculated from arithmetic mean of three marked areas of EDX results.

Samples					
elements	G1p4K2-2	G1p4K4-2	G1p4K6-2	G1p9K6-4	G1p19K2-1
C K	95.1	96.0	96.6	97.3	95.6
O K	4.1	4.0	3.2	2.6	3.7
F K	0.4	0	0.2	0	0.1
K K	0.4	0	0	0.1	0.6



Figure S4. EDX mapping of the HSG samples. These images indicate that HSG samples have good uniformity. Here we only show the measured data for the sample of G1p4K4-2, the detailed information is not given for other samples.



Figure S5. Raman spectrum of the HSG samples. All the samples show one apparent G-band peak at ~1590 cm<sup>-1</sup> and a D-band peak at ~1350 cm<sup>-1</sup>. Besides, all the HSG samples present two peaks at higher wavelength with one locating at ~2685 cm<sup>-1</sup> and the other at ~2910 cm<sup>-1</sup>. The two peaks almost merge into one at ~2820 cm<sup>-1</sup> for the sample of AC04.



Figure S6. The measured data and fitted curves of Raman spectra for G1p4K4–2. G1p4K2–2a and G1p4K2–2b represents two batches for prove the repeatability. All other samples also carried out more characterizations, the same as G1p4K2–2.

The intensity of the D-band is inversely proportional to the effective crystallite size  $L_a$  in the direction of the graphite plane:

$$I_D / I_G = C(\lambda_L) / L_a \tag{4}$$

where  $I_D$  and  $I_G$  are the integrated intensities of the D and G bands, respectively,<sup>[1]</sup> and  $C(\lambda_L)$  is a wavelength dependent pre–factor and its value is 4.36 according to Matthews' work.<sup>[2]</sup> The average values of  $I_D/I_G$  for HSG samples are determined using the multi–peak fit (four Voigt functions for D, D', D'', and G bands, and the detailed fitting results are summarized in Table S3). All the fitted curves share a high R<sup>2</sup> value of > 0.998.

Samples	G-band / cm <sup>-1</sup>	D-band / cm <sup>-1</sup>	$I_D / I_G$	$L_a / nm$
G1p4K2-2	1595±3	1351±3	3.37±0.01	1.29±0.01
G1p4K4-2	1596±1	1344	2.30±0.14	1.90±0.11
G1p4K6-2	1593±1	1345±4	1.54±0.12	2.83±0.14
G1p9K4-1	1592±1	1354±1	2.39±0.17	1.82±0.13
G1p9K4-2	1589±3	1342±3	2.44±0.06	1.79±0.05
G1p9K4-4	1587±2	1348±4	1.55±0.01	2.81±0.01
G1p9K6-4	1596	1351	1.83±0.09	2.38±0.11
G1p19K2-1	1596±3	1351±1	2.45±0.05	1.78±0.03
G1p19K4-2	1593±5	1345±4	2.25±0.07	1.94±0.05
AC04	1605±1	1362	2.83±0.09	1.54±0.05

Table S2. The concrete band positions, the relative strength and the crystal size of Raman parameters for HSG samples.



Figure S7. XPS survey curves of HSG samples. There are three peaks assigned to C1s, O1s, and O KLL from low to high binding energy, and no apparent other peak are detected using survey method.



Figure S8. The measured and fitted C1s spectra of G1p4K4-2, G1p4K6-2, G1p9K6-4, and G1p19K2-1 samples.

Samples					
elements	G1p4K2-2	G1p4K4-2	G1p4K6-2	G1p9K6-4	G1p19K2-1
СК	93.7	95.2	95.1	96.1	94.3
O K	5.9	4.6	4.7	3.9	5.2
F K	0.4	0.2	0.2	0	0.5
K K	0	0	0	0	0

Table S3. The atomic percentage of HSG samples determined by XPS measurements

	BET SSA $(m^2 r^{-1})$	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	BJH adsorption	Average
Samples			volume of pores (cm <sup>3</sup>	pore size
	(III <sup>-</sup> g <sup>-</sup> )		$g^{-1}$ )	(nm)
G1p4K2-2	1101	0.65	0.27	2.4
G1p4K4-2	2585	1.70	1.70	2.6
G1p4K6-2	2030	1.63	1.73	3.2
G1p9K2-1	896	0.48	0.15	2.1
G1p9K2-2	1136	0.61	0.24	2.2
G1p9K4-2	2309	1.42	1.23	2.5
G1p9K4-4	2061	1.48	1.33	2.9
G1p9K6-1	2218	1.65	1.71	3.0
G1p9K6-4	2684	2.05	2.18	3.1
G1p19K2-1	970	0.60	0.27	2.5
G1p19K4-2	2724	1.65	1.51	2.4
AC02	842	0.52	0.23	2.5
AC04	2294	1.45	1.36	2.5
YP80F	2223	1.19	0.85	2.1

Table S4. Values of SSA, PSD, and pore volume acquired from  $N_2$  gas sorption isotherms for HSG samples and the YP80F.



Figure S9. The EIS plots of HSG samples in 1 M PC + TEABF<sub>4</sub> (a) and EMIMBF<sub>4</sub> (b) electrolytes. The inner are the enlarged figures at high frequency. G1p4K4–2, G1p4K6–2, and G1p9K6–4 electrodes have the internal resistance of  $\sim$ 3.5 and  $\sim$ 5  $\Omega$  in PC + TEABF<sub>4</sub> and EMIMBF<sub>4</sub> electrolytes, respectively.



Figure S10. The volumetric capacitances of HSG samples in 1 M PC + TEABF<sub>4</sub> (a) and EMIMBF<sub>4</sub> (b) electrolytes. G1p4K4–2, G1p4K6–2, and G1p9K6–4 electrodes have package densities of  $0.50 \pm 0.01$ ,  $0.76 \pm 0.02$ , and  $0.65 \pm 0.03$  g cm<sup>-3</sup> including PTFE binder and Super C45 conducting agent. For comparing, YP80F supercapcitors with a package density of  $0.60 \pm 0.02$  g cm<sup>-3</sup> was also shown. (c) The volumetric capacitance of these samples depends on the voltage at a scan rate of 20 mV s<sup>-1</sup> in IL electrolyte. It should be noted that the polarization phenomenon of YP80F at high voltage of > 3.3 V is more apparent than that of HSG samples.

# References

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