Supporting Information

A regular, compact but microporous packing structure: high-density graphene assemblies for high-volumetric-performance supercapacitors

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Sample preparation

Preparation of graphite oxide

Graphite oxide was prepared from natural graphite (Xinghe Co., Qingdao, China) according to a modified Hummers method: 120 mL 98 wt% H₂SO₄ was poured into a beaker containing a mixture of 5 g natural graphite and 2.5 g NaNO₃, and then the mixture was stirred in an ice bath for 30 min. 15g KMnO₄ was added slowly into the mixture, which was allowed to react for 2 h at a temperature no more than 20°C. Then, the temperature was risen to 35°C, and the reaction was performed for another 2 h. After that, the reactant mixture was poured slowly into 360 mL distilled water under violent stirring condition so as to control the temperature no more than 90°C, followed by further reaction at 75°C for 1 h. After the mixture was diluted to 1.5 L, 50 mL 30 wt% H₂O₂ was added to consume the remaining KMnO₄ and the produced MnO₂. The asobtained mixture was a bright yellow suspension. After filtered and washed with 5 wt% HCl and distilled water, the filter cake was dried in the air at 50°C for 24 h to obtain the graphite oxide.

Preparation of VrGO

1mg mL⁻¹ GO suspension was prepared by ultrasonic dispersion of graphite oxide in distilled water, and vitamin C (VC) was added into the GO suspension to bring the VC concentration to 0.02 mol L⁻¹. After heating at 90 °C for 1 h, the as-reduced GO suspension was filtered and washed with a large amount of distilled water. The final product, VrGO, was obtained by desiccation in the air at 75 °C for 24 h and mechanical milling.

Calculating the specific capacitance, energy density and power density on the basis of the electrochemical measurement results

From CV curves of a three-electrode system, the gravimetric capacitances were calculated according to the following equation:

$$C_{\rm g} = \frac{1}{2m \cdot \Delta E \cdot v} \left(\int i_{\rm a} dE + \int i_{\rm c} dE \right)$$

where C_{g} represents the gravimetric capacitance of a single electrode, *m* is the mass of the active material in the working electrode, *E* is the working electrode potential, ΔE is the potential window of the scan, *v* is the scan rate, i_{a} is the anodic current during the anodic scan, and i_{c} is the cathodic current during the cathodic scan.

From CV curves of a two-electrode system, the gravimetric capacitances were calculated according to the following equation:

$$C_{\rm g} = \frac{1}{m \cdot \Delta V \cdot v} \left(\int i_{\rm charge} dV + \int i_{\rm discharge} dV \right)$$

where C_{g} represents the gravimetric capacitance of a single electrode, *m* is the average mass of the active materials in the two electrodes, *V* is the voltage of the supercapacitor, ΔV is the voltage window of the scan, *v* is the scan rate, i_{charge} is the charging current during the charge scan, and $i_{discharge}$ is the discharging current during the discharge scan.

From galvanostatic charge/discharge measurements of a three-electrode system, the gravimetric capacitances were obtained from the acquired data using the following equation:

$$C_{\rm g} = \frac{i_{\rm discharge} \cdot \Delta t}{m \cdot \Delta E}$$

where C_{g} represents the gravimetric capacitance of a single electrode, $i_{discharge}$ is the constant discharging current during the discharge process, Δt is the discharge time, *m* is the mass of the active material in the working electrode, and ΔE is the discharge potential range.

From galvanostatic charge/discharge measurements of a two-electrode system, the gravimetric capacitances were obtained from the acquired data using the following equation:

$$C_{\rm g} = \frac{2i_{\rm discharge} \cdot \Delta t}{m \cdot \Delta V}$$

where C_{g} represents the gravimetric capacitance of a single electrode, $i_{discharge}$ is the constant discharging current during the discharge process, Δt is the discharge time, *m* is the average mass of the active materials in the two electrodes, and ΔV is the discharge voltage range.

From an EIS plot of a two-electrode system, the gravimetric capacitances at different frequencies were calculated according to the following equation:

$$C_{\rm g} = -\frac{1}{\pi f \cdot m \cdot Z''}$$

where C_{g} represents the gravimetric capacitance of a single electrode, f is the frequency of the sinusoidal signal, m is the average mass of the active materials in the two electrodes, and Z'' is the imaginary component of the complex impedance.

The volumetric capacitances were calculated using the following equation:

$$C_{\rm v} = \rho \cdot C_{\rm g}$$

where C_v represents the volumetric capacitance of a single electrode, ρ is the density of the active material in the electrode, and C_g is the gravimetric capacitance of a single electrode,

The gravimetric and volumetric energy densities were calculated using the gravimetric capacitances obtained from the galvanostatic charge/discharge tests according to the following equation:

$$E_{g} = \frac{1}{8 \times 3.6} C_{g} \cdot \Delta V^{2}$$
$$E_{v} = \rho \cdot E_{g}$$

where E_{g} represents the gravimetric energy density against the mass of the active materials in the two electrodes, and E_{v} is the volumetric energy density against the volume of the active materials in the two electrodes.

The gravimetric and volumetric power densities were calculated according to the following equation:

$$P_{\rm g} = \frac{E_{\rm g}}{\Delta t}$$
$$P_{\rm v} = \rho \cdot P_{\rm g}$$

where P_{g} represents the gravimetric power density against the mass of the active materials in the two electrodes, Δt is the discharge time, and P_{v} is the volumetric power density against the volume of the active materials in the two electrodes. Full EDX spectrum of the KrGO film



Fig. S1 (a) Cross-sectional SEM image and (b) the corresponding full EDX spectrum of the KrGO film.



Distribution of the elements in the KrGO film

Fig. S2 (a) SEM image of the KrGO film and the corresponding EDX elemental mapping: (b) K, (c) C, (d) O.

Determination of densities

Determination of the density of the KrGO film

The KrGO-p paste was spread with an applicator onto an Al foil and dried in the air at 75° C for 12 h. After being peeled off from the Al foil, the obtained KrGO film was cut into a sheet with a size of 4×4 cm². The mass of the KrGO film was determined, and the thickness of the KrGO film was measured from the cross sectional SEM image of the film, and then the density of the film was further calculated.

The cross sectional SEM image of the KrGO film used to determine the thickness is presented in Figure S3. The thickness values at 20 positions of the KrGO film were measured using the software *Nanomeasure 1.2.5*, and the average of the 20 values was adopted as the thickness. The density of the KrGO film was determined to be 1.58 g cm⁻³.



Fig. S3 Cross sectional SEM image of the KrGO film used to determine the thickness.

Determination of the compression densities of the carbon powder materials

The carbon powder materials were mixed with PTFE according to a mass ratio of 95:5 with a proper amount of ethanol, and blended thoroughly, and then pressed into films. After dried under

vacuum at 75°C for 12 h, the carbon films were further punched into disks with a diameter of 14 mm, whose masses were determined. After the carbon disks were pressed under 10 MPa for 5 min, their thicknesses were measured. Based on the masses, surface areas and thicknesses of the carbon disks, the compression densities of the carbon powder materials were calculated and are listed in Table S1.

Table S1. Compression densities of several carbon powder mater	ials.
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Commlo	V-CO	VrCO	Cranhita	Thermally expanded	Acetylene	
Sample	Sample KIGO VIGO Graphile	graphene (TEG)	black	AC		
Density	1.52	1 17	2.07	0.21	0.26	0.59
$(g \text{ cm}^{-3})$	1.55	1.1/	2.07	0.51	0.30	0.38

Analyses of the pore structure characteristics and the corresponding calculation of densities for the carbon powder materials



Fig. S4 (a) N_2 adsorption/desorption isotherms and (b) the corresponding pore size distribution curves of the AC and KrGO powder materials.

Table S2. Pore structure parameters and the corresponding calculated densities of the carbon powder materials.

Commla	SSA_1^a	$V_{\text{Total-1}}^{a}$	SSA_2^{b}	V _{Total-2} ^b	$\rho_1{}^{\mathrm{c}}$	${\rho_2}^{ m d}$	ρ_3^{e}
Sample	$[m^2 g^{-1}]$	$[cm^{3} g^{-1}]$	$[m^2 g^{-1}]$	$[cm^{3}g^{-1}]$	$[g \text{ cm}^{-3}]$	$[g cm^{-3}]$	$[g \text{ cm}^{-3}]$
KrGO	449.48	0.131	7.82	0.012	1.53	1.58	1.95
VrGO	125.62	0.049	-	-	1.13	1.82	-
KrGO-300	278.3	0.084	-	-	1.61	1.71	-
Graphite	3.81	0.001	-	-	2.06	2	-
AC	-	-	1173.5	0.8875	0.52	-	0.72

^a SSA₁ and $V_{\text{Total-1}}$ are the specific surface area and pore volume of the micropores, which were obtained by DFT analyses of the CO₂ adsorption isotherm.

^b SSA₂ and $V_{\text{Total-2}}$ are the specific surface area and pore volume of the pores larger than 0.7 nm, which were obtained by BET and BJH analyses of the N₂ adsorption isotherm.

 $^{c}\rho_{1}$ is the density determined by the compression method.

^d ρ_2 is the density calculated by the equation $\rho = \left\{ V_{Total} + \frac{1}{\rho_{Carbon}} \right\}^{-1}$ using $V_{Total} = V_{Total-1}$ and $\rho_{Carbon} = 2 \text{ g cm}^{-3}$.

^e ρ_3 is the density calculated by the equation $\rho = \left\{ V_{Total} + \frac{1}{\rho_{Carbon}} \right\}^{-1}$ using $V_{Total} = V_{Total-2}$ and $\rho_{Carbon} = 2 \text{ g cm}^{-3}$.

It can be observed that the values of SSA₂ and $V_{\text{Total-2}}$ of the KrGO are very low. This is because the BET analysis of the N₂ adsorption isotherm without the adsorbed data in the low relative pressure range cannot give the SSA of the "ultra-micropores" (pore width < 0.7 nm),² whereas the ultra-micropores are actually the dominating component of pores of the KrGO. Therefore, the values of SSA₂ and $V_{\text{Total-2}}$ of the KrGO only reflect the SSA and pore volume of the pores larger than 0.7 nm. In contrast, the values of SSA₁ and $V_{\text{Total-1}}$ of the KrGO are the SSA and pore volume of the micropores of the KrGO, nearly representing the SSA and pore volume of the total pores of the KrGO. And this interpretation also applies to the KrGO-300.

Therefore, it is not strange that the density value of the KrGO calculated by the equation $\rho = \left\{ V_{Total} + \frac{1}{\rho_{Carbon}} \right\}^{-1}$ using the pore volume of micropores (ρ_2 =1.58 g cm⁻³) is nearly the same as the value determined by the compression method (ρ_1 =1.53 g cm⁻³), and the reason should be that the KrGO has only micropores but no mesopores and macropores, and the compact and regular laminar-structure of the KrGO facilitates the elimination of interparticle spaces during compression process.

In contrast, the density value of the VrGO calculated by the equation $\rho = \left\{ V_{Total} + \frac{1}{\rho_{Carbon}} \right\}^{-1}$ using the pore volume of micropores (ρ_2 =1.82 g cm⁻³) is noticeably larger than the value determined by the compression method (ρ_1 =1.13 g cm⁻³), and the reason for this difference should be that the pore volume of mesopores and macropores of the VrGO is not included in the value of V_{Total} and

the considerable interparticle voids could not be eliminated during the compression process because of the protruding graphene sheet nature of the VrGO.

XPS analyses



Fig. S5 C1s XPS spectrum of the KrGO-300.

Table S3. Surface element contents and relative contents of the chemical bonds obtained from XPS spectra.

Samples	Carbon Oxygen		K Relative content of carbon bond				ds, %
The second se	(at.%)	(at.%)	(at.%)	$C=C(sp^2)$	$C-C(sp^3)$	C-0	O-C=O
GO	72.52	27.48	-	43.66	4.95	51.39	-
KrGO	79.39	20.31	0.3	52.54	11.13	21.95	14.38
KrGO-300	85.3	14.5	0.2	53.71	11.07	15.97	19.24

Electrochemical performances of the KrGO powder electrode in 1 mol L⁻¹



H₂SO₄ electrolyte in a three-electrode system

Fig. S6 Electrochemical performances of the KrGO powder electrode in 1 mol L^{-1} H₂SO₄ electrolyte using a three-electrode system configuration. (a) Relationship curves of the gravimetric capacitance and potential for the KrGO at different scan rates. (b) Gravimetric and volumetric capacitances of the KrGO as a function of the scan rate. (c) Galvanostatic charge/discharge curves of the KrGO at different current densities. (d) Gravimetric and volumetric capacitances of the KrGO as a function of the current densities.

It can be observed from Figure S6a that the quasi-reversible redox peaks also appear on the CV curves of the KrGO powder electrode at the same potential range as on the CV curves of the KrGO film electrode, indicating the existence of the Faradaic reactions of the oxygen-containing groups on the graphene layers.³

Although the loading density (6~8 mg cm⁻²) is significantly enlarged compared with the KrGO film electrode (0.15~0.2 mg cm⁻²), a high gravimetric capacitance of 270 F g⁻¹ and a high volumetric capacitance of 413 F cm⁻³ are achieved at a scan rate of 1 mV s⁻¹. At the same time, a high gravimetric capacitance of 259 F g⁻¹ and a high volumetric capacitance of 397 F cm⁻³ are realized at a current density of 0.48 A g⁻¹.

Furthermore, with an active material loading density close to that of commercial supercapaictor electrodes, the KrGO powder electrode exhibits an excellent high-rate capability.

EIS plots of the carbon powder electrodes in 1 mol L⁻¹ H₂SO₄ electrolyte in two-electrode systems



Fig. S7 (a) Nyquist plots and (b) the corresponding frequency response curves of gravimetric capacitance for the KrGO, VrGO and AC powder electrodes in 1 mol L^{-1} H₂SO₄ electrolyte in two-electrode systems.

Electrochemical impedance spectroscopy (EIS) tests were conducted using a CHI660E workstation (Chenhua, Shanghai, China). The EIS tests were performed at open circuit conditions using sinusoidal signals with a frequency range of $10^5 \sim 0.01$ Hz and an amplitude of 10 mV.

EIS plots of the KrGO-300 powder electrode in 1 mol L⁻¹ H₂SO₄ electrolyte in



a two-electrode system

Fig. S8 (a) Nyquist plots and (b) the corresponding frequency response curves of gravimetric capacitance for the KrGO-300 powder electrode in 1 mol L^{-1} H₂SO₄ electrolyte in a two-electrode system.

Electrochemical impedance spectroscopy (EIS) tests were conducted using a CHI660E workstation (Chenhua, Shanghai, China). The EIS tests were performed at open circuit conditions using sinusoidal signals with a frequency range of $10^5 \sim 0.01$ Hz and an amplitude of 10 mV.

Comparison of the gravimetric and volumetric capacitances in aqueous electrolytes of the KrGO with previously reported carbon materials

Table S4. Comparison of the gravimetric and volumetric capacitances in aqueous electrolytes of different carbon materials.

Matariala	Materials	Density	C_{g}	$C_{\rm V}$	Electrolyt-	Test devis-	Def
Materials	form	[g cm ⁻³]	[F g ⁻¹]	[F cm ⁻³]	Electrolyte	l est device	KeI.
KrGO	film	1.58	322	508	$1 M H_2 SO_4$	Three-electrode	This work
K CO		1.50	270	413	$1 M H_2 SO_4$	Three-electrode	This work
KrGO	powder	1.53	205	314	$1 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	Two-electrode	This work
ALG-C	powder	0.91	198	180	$1 M H_2 SO_4$	Two-electrode	4
TiC-CDC	powder	0.74	190	140	$1 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	Two-electrode	5
СМ	slice	1.17	292	342	$2M H_2 SO_4$	Two-electrode	6
LN600	powder	0.79	264	208	$1 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	Two-electrode	7
EM-CCG	film	1.33	192	256	$1 M H_2 SO_4$	Two-electrode	8
СХАη-30	powder	0.66	251	166	1 M H ₂ SO ₄	Three-electrode	9
MCNT	powder	-	249	-	$1 \text{ M H}_2 \text{SO}_4$	Three-electrode	10
Z-900	powder	0.93	214	200	0.5 M H ₂ SO ₄	Three-electrode	11
C800	powder	0.50	188	94	$1 \text{ M H}_2 \text{SO}_4$	Two-electrode	12
Y-AN	powder	0.74	340	250	1 M H ₂ SO ₄	Three-electrode	13
COU-2	powder	0.86	184	159	$1 \text{ M H}_2\text{SO}$	Three-electrode	14
HPGM	slice	1.58	260	410	6M KOH	Three-electrode	15
			238	376		Two-electrode	
FGN-300	powder	1.03	456	470	6M KOH	Three-electrode	16
PVF700C	powder	0.826	264	218	6M KOH	Three-electrode	17
OMC/Ni/CNTs-5	powder	-	338	-	6M KOH	Three-electrode	18

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