Electronic Supplementary Information

A facile synthesis of hierarchically porous graphene for high-performance lithium storage

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Synthesis of HPG and MG

1g of petroleum asphalt is added to 10ml of liquid aromatic petrochemical by-products and ultrasonically dispersed. The above mixture is ball-milled with 20g of NaCl: KCl (mass ratio 4.5:5.5) to obtain a homogeneous solid mixture. Next, the mixture was heated to 360 °C in a muffle furnace under air atmosphere and maintained for 4 h. Then the sample was heated to 700°C under Ar atmosphere and maintained for 2 h. The final sample, marked as HPG, was obtained after being washed and dried. For comparison, the MG was synthesized by the same procedure by using a Ar-flow instead of airflow when heated at 360 °C.

Characterization

The samples morphologies observation was performed on a field emission scanning electron microscope (FE-SEM, S-4800, HITACHI) and a transmission electron microscope (TEM, JEOL-2100F). The power X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer with Cu Kα radiation (D8 Advance, Bruker, λ =1.5418 Å). The Brunauer-Emmett-Teller (BET) measurements specific surface area was measured by using a Micromeritics ASAP 3020 system. The pore size distribution for each sample was calculated from the adsorption isotherm branch using the BJH method. XPS data were collected on a Kratos AXIS SUPRA(Shimadzu, Japan) X-ray photoelectron spectrometer operating in hybrid mode using monochromatic Al Kα X-rays (1486.7 eV). Raman analysis was performed using a Renishaw InVia Raman spectrometer under visible excitation at 633 nm.

Electrochemical measurements

The electrochemical properties of CR2025 button cells were assembled in a glove box filled with argon gas (H_2O < 0.1 ppm, O_2 < 0.1 ppm). The working electrodes were prepared by combining the synthesized active material (70 wt%), carbon black (20 wt%) and Polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2 pyrrolidone (NMP) and by grinding to form a homogeneous slurry. The resulting slurry was then coated on copper foil and dried in a vacuum oven at 120 °C for 12 h. Next, the obtained electrodes were rolled and stamped into 12 mm diameter electrode sheets with a loading mass of active material of 0.4 mg/cm^2. LIBs were assembled with lithium metal foil as a counter

electrode, 1 M $LiPF_6$ mixed in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) as electrolyte and polypropylene film as the septum.

Constant-current charge/discharge tests were performed using a Land CT2001A cell test system with potential windows of 0.005-3 V (vs. Li^+/Li). Cyclic voltammetry (CV) curves of LIBs were tested using CHI760D at scan rates of 0.2 mV s^{-1}. Electrochemical impedance spectra (EIS) were collected on an Autolab PGSTAT 302 N in the frequency range of 10^{-2}-10^5 Hz.

Figures

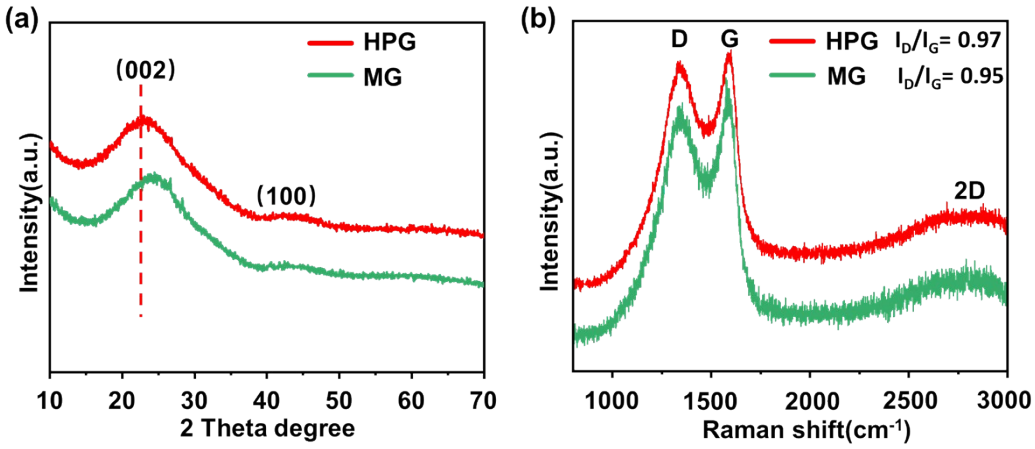

Fig. S1 a) XRD patterns and b) Raman spectra of HPG and MG

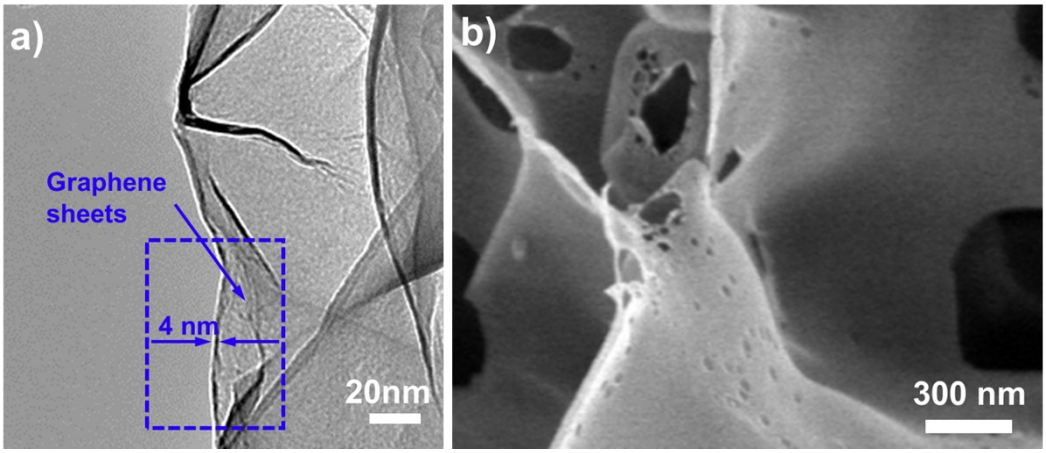

Fig. S2 a) TEM and b) SEM images of HPG.

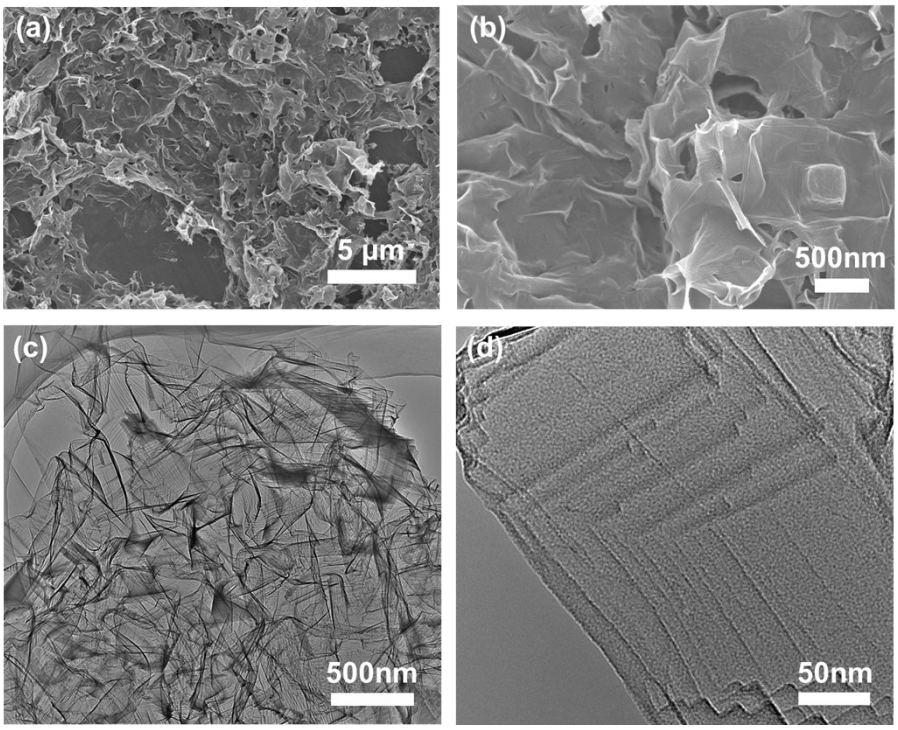

Fig. S3 a, b) SEM and c, d) TEM images of MG.

Table S1 Nitrogen adsorption-desorption measurements analysis data

Samples	**S_{BET}[a]** **$m^2\ g^{-1}$**	**V_t[b]** **$cm^3\ g^{-1}$**
HPG	397	0.99
MG	126	0.39

[a] BET specific surface area

[b] total pore volume from adsorption isotherms at a relative pressure P/P_0 of 0.99

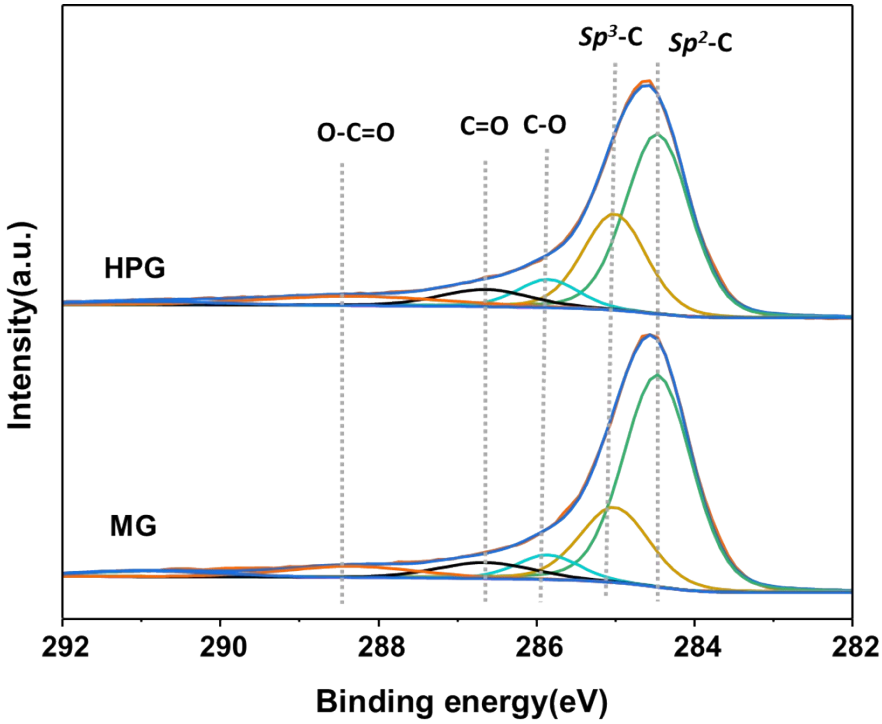

Fig. S4 C 1s XPS spectra of HPG and MG.

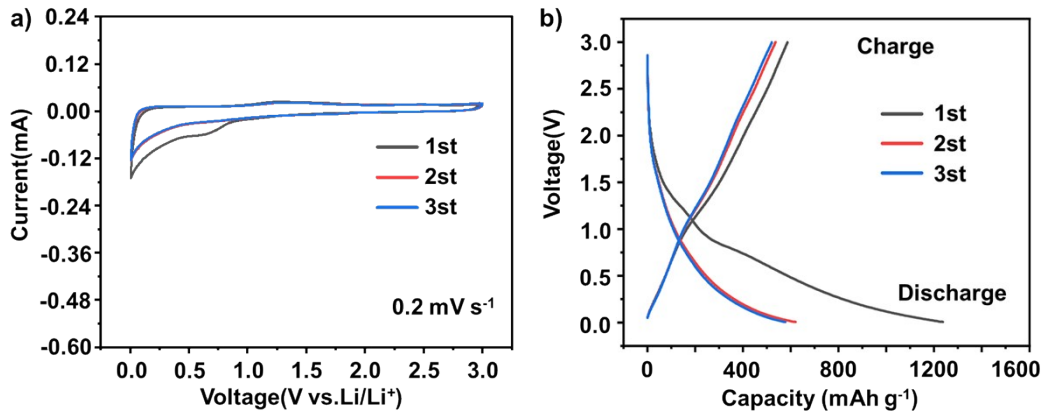

Fig. S5 a) CV curves of MG at a scan rate of 0.2 mV s^{-1} for LIBs. b) Galvanostatic charge and discharge profiles of MG electrode for LIBs cycled between 0.005 and 3 V (vs. Li/Li^+) at the current density of 100 mA g^{-1}.

Table S2. Comparisons of electrochemical performance of different graphene materials as anodes for LIBs

Sample	BET surface (m^2 g^{-1})	Cycling capacity (mAh g^{-1}) at current densities (A g^{-1}) Initial	End	Cycle Number	References
HPG	**397**	**5/407.5**	**5/543.9**	**700**	**This work**
3DMGS	503	5/227.4	5/260	1100	*Electrochim. Acta*, 2021, **390,** 138839
3D IH-rGO	59.81	5/320	5/460	1000	*Chem. Eng. J.*, 2020, **394,** 124956
FG	454.7	5/460	5/412	1000	*Chem. Eng. J.*, 2020, **392,** 123668
rGO@NDC	52.8	3.72/200	3.72/222.8	1200	*Electrochim. Acta*, 2019, **309**, 228
3DGPM	-	2/180	2/249	500	*Surf. Coat. Technol.*, 2019, **360**, 232
PGS	186	2/150	2/142	1200	*J. Energy Chem.*, 2021, **55**, 62
N-MCN	900	2/510	2/604	600	*ACS Appl. Mater. Inter.*, 2016, **8**, 11720
N-rGO	-	1.6/330	1.6/346	500	*Appl. Surf. Sci.*, 2019, **485**, 529
HMNG	768	1.488/710	1.488/723	500	*Nat. Commun.*, 2019, **10**, 1474
RGO	276	1.488/500	1.488/ 400	300	*J. Mater. Chem. A*, 2017, **5**, 23228
N-3D GFs	281.42	1/450	1/691	500	*J. Power Sources*, 2015, **293**, 799
NTLP	245	1/430	1/501	1000	*J. Solid State Chem.*, 2021, **294**, 121859

TAGnPs	-	1/100	1/154	1000	*Nano Energy*, 2019, **62**, 419
carbon/rGO	327	1/565	1/377	1000	*J. Mater. Chem. A*, 2016, **4**, 1423
3D-ECG	126.25	1/580	1/499.6	1000	*Adv. Funct. Mater.*, 2020, **30**, 1904645
GO-2DM	27.18	1/200	1/215	1000	*Electrochim. Acta*, 2021, **380**, 138114

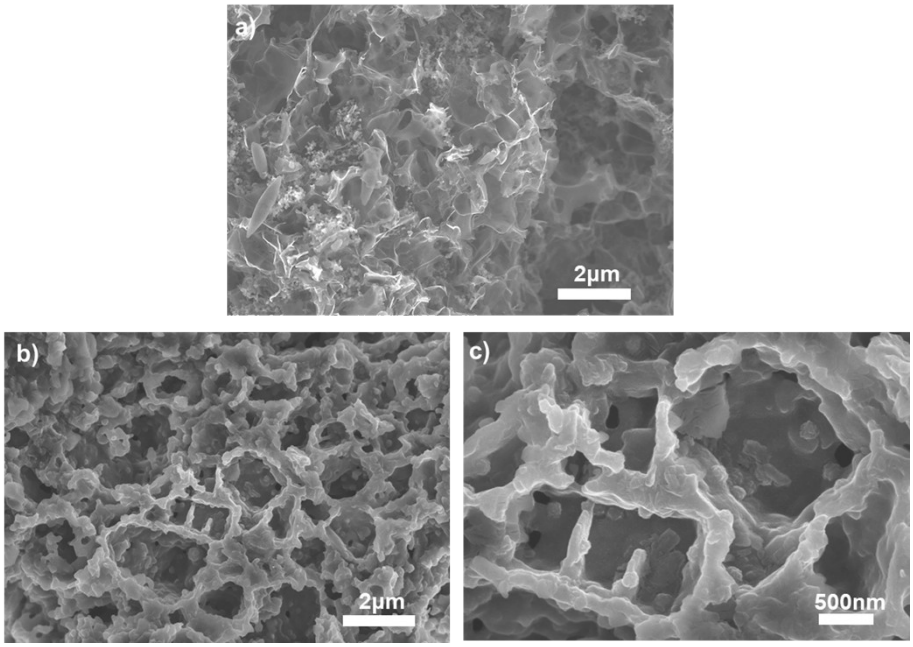

Fig. S6 SEM images of the HPG electrodes a) before and b, c) after cycles.

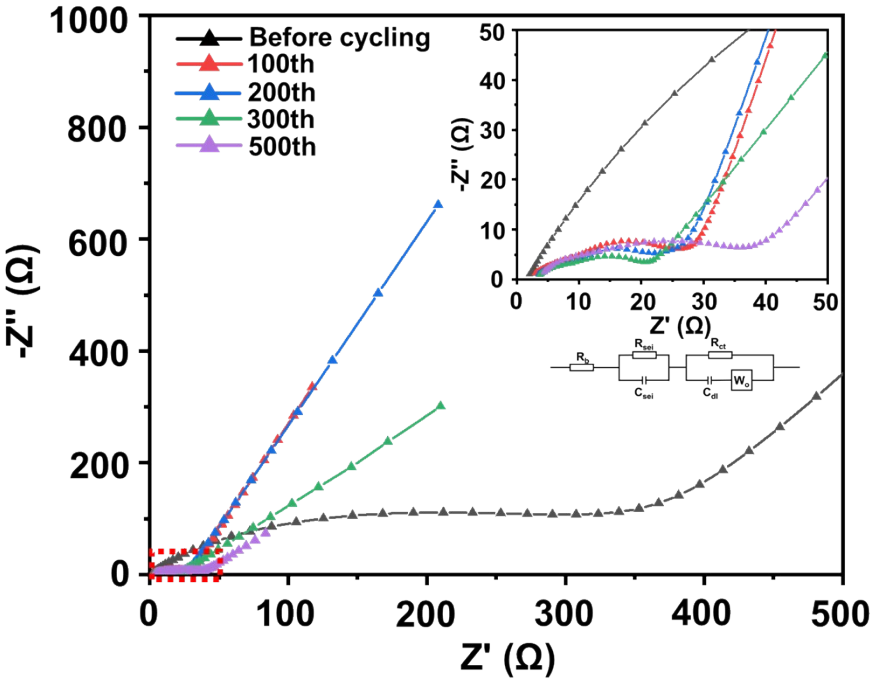

Fig.S7 Nyquist plots of HPG electrode at different cycles.

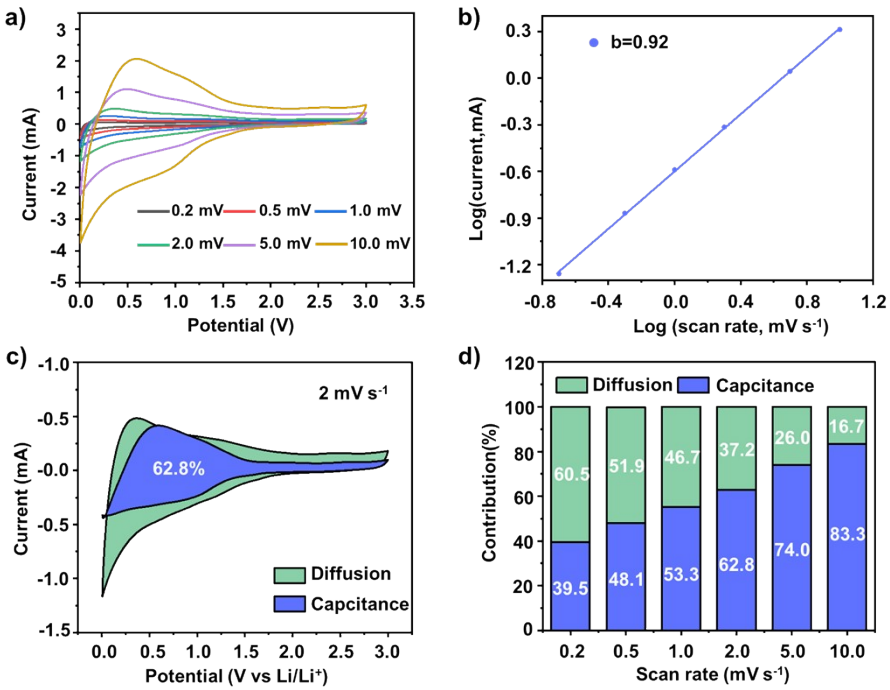

Fig.S8 a) CV curves of HPG as LIBs anode at different scan rates. b) relationship between logarithm current vs. logarithm scan rate. c) The shape of the blue region is a capacitive contribution to total capacity at 2.0 mV s^{-1}. d) The contribution percentage of capacitance capacities at different scan rates.