

Supplementary Information

On the thermal instability of hydrogen-substituted graphdiyne and its role in lithium-sulfur batteries

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Experimental Details

Materials

Triethynylbenzene, pyridine, copper (I) chloride, chloroform, ethanol, methanol, Lithium bis(trifluoromethane)sulfonimide (LiTFSI), lithium nitrate, dioxolane (DOL)/dimethoxyethane (DME) were all bought from Sigma-Aldridge. Sulfur was bought from Alfa Aesar. Carbon paper (Avcarb P50) was bought from the Graphite Store. High barrier graphene was bought from Carbonene. LiTFSI and lithium nitrate were dried in the glove box on a hot plate at 110°C for three days. DOL and DME were dried using 4 Å molecular sieves from Sigma-Aldrich.

Synthesis

HsGDY was obtained following a synthetic method previously reported. In a typical synthesis, 1,3,5-triethynylbenzene (30 mg, 0.2 mmol) and CuCl (6 mg, 0.06 mmol) were dissolved in pyridine (2 mL) in a glass vial. That vial was kept in a 40°C water bath for 72 h. The product was washed with pyridine, chloroform, methanol, and ethanol, three times each. The washed material was then stirred in water for 24 h to exchange the solvent inside and then the final HsGDY product was obtained by freeze-drying for 24 h.

S@ΔHsGDY was obtained by first mixing HsGDY and sulfur in a mass ratio of 1:9 using a mortar and pestle. Then the mixed powder was heated (5 °C /min) in a tube furnace under argon flow (20 mL/min) from ambient to 155 °C at 5 °C/min, and then held there for 12 h prior to cooling. The same method was used to make S@ΔGraphene, replacing HsGDY with graphene. S+HsGDY powder was prepared by mixing without the tube furnace heating step and the ratio of S and HsGDY was adjusted to match the final sulfur composition of the S@ΔHsGDY. ΔHsGDY was prepared without mixing with sulfur.

Characterization

Solid-state ¹³C MAS-NMR was collected on a Bruker AVIII-HD 300. A Renishaw Raman Spectrometer (488 nm laser excitation) was used for the Raman characterization. X-ray photoelectron spectroscopy was performed with a Thermo NEXSA G2 XPS. Peaks were corrected by first fitting the carbon peak and then shifting the right most peak to 284.5 eV. A Micrometrics Tristar II 3020

apparatus at 77 K was used for the nitrogen physisorption measurements. The samples were degassed under a 36 Torr vacuum at 40 °C for 12 h prior to the physisorption measurements. The measurement was performed across a P/P_0 range of 0.061 to 0.998. A Rigaku Miniflex Powder XRD was used for X-ray diffraction, Cary 5000 UV–Vis/NIR was used for the adsorption UV-Vis experiments. A Hitachi SU8010 and JEOL 100 CX-II were used for the scanning electron microscopy and transmission electron microscopy, respectively. Thermogravimetric analysis (TGA) was performed on Mettler Toledo TGA2. 1 mg of HsGDY was heated from 25° to 155 °C at a rate of 5°C/min, then the temperature was held at 155 °C for 12 h. The TGA experiments were conducted under argon flow at 20 mL/min.

Adsorption Test

In an argon filled glovebox, 0.7 mg of HsGDY and Δ HsGDY were each individually placed into 2 ml of 0.5 mM solution of Li_2S_8 in DMSO and left undisturbed for 3 days. The vials were then removed from the glovebox and the resulting solutions were then evaluated with UV-Vis analysis.

Electrochemistry

Electrochemical measurements were performed using CR2032 coin cells in an argon-filled glovebox. The half cells were assembled using slurry coated carbon paper as the cathode, a Li metal foil as the anode (10 mm diameter, 0.75 mm thick), a polypropylene separator (Celgard 2500) (12 mm diameter), and 40 μL of liquid electrolyte (1 M LiTFSI, 0.4 M LiNO_3 in DOL/DME (1:1 v)). The slurry consisted of 80% of the active material ($\text{S}@\Delta$ HsGDY, $\text{S}@\Delta$ Graphene or $\text{S}+\text{HsGDY}$), 10% carbon black and 10% PvDF in NMP ([.008 mL NMP]/[1 mg solid]) and was mixed using a Thinky Mixer AR-100 for 30 min. The slurry was cast using a Dr. Blade set to 30 μm on carbon paper and dried on a hot plate at 40°C for 12 hours in a fume hood. The assembled half cells were cycled between 1.8 and 2.8 V at 0.1C (167.5 mA/g S) using a LAND battery testing system. All cathodes had a sulfur mass loading of 1.9-2.1 mg/cm^2 .

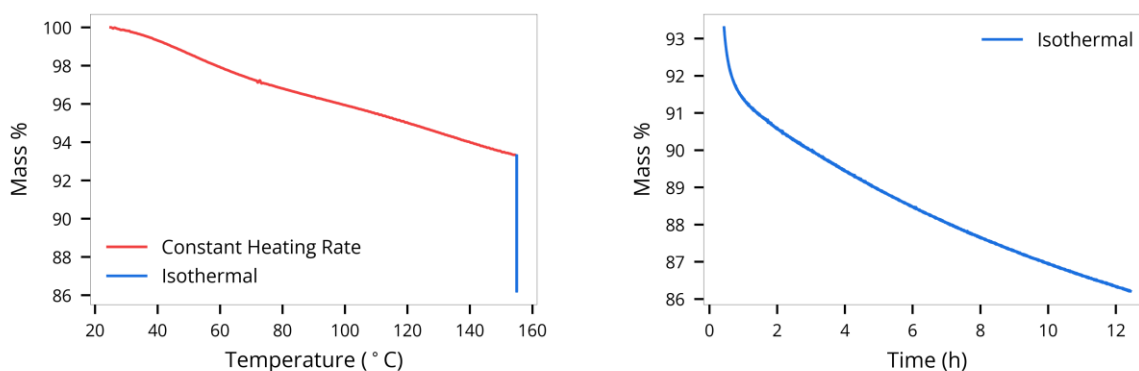


Figure S1. TGA for HsGDY, showing the full TGA data on the left and the isothermal portion (155 °C) on the right. The mass decreases from 25°C to 110°C because of the loss of water, and further decreases due to the degradation of HsGDY.

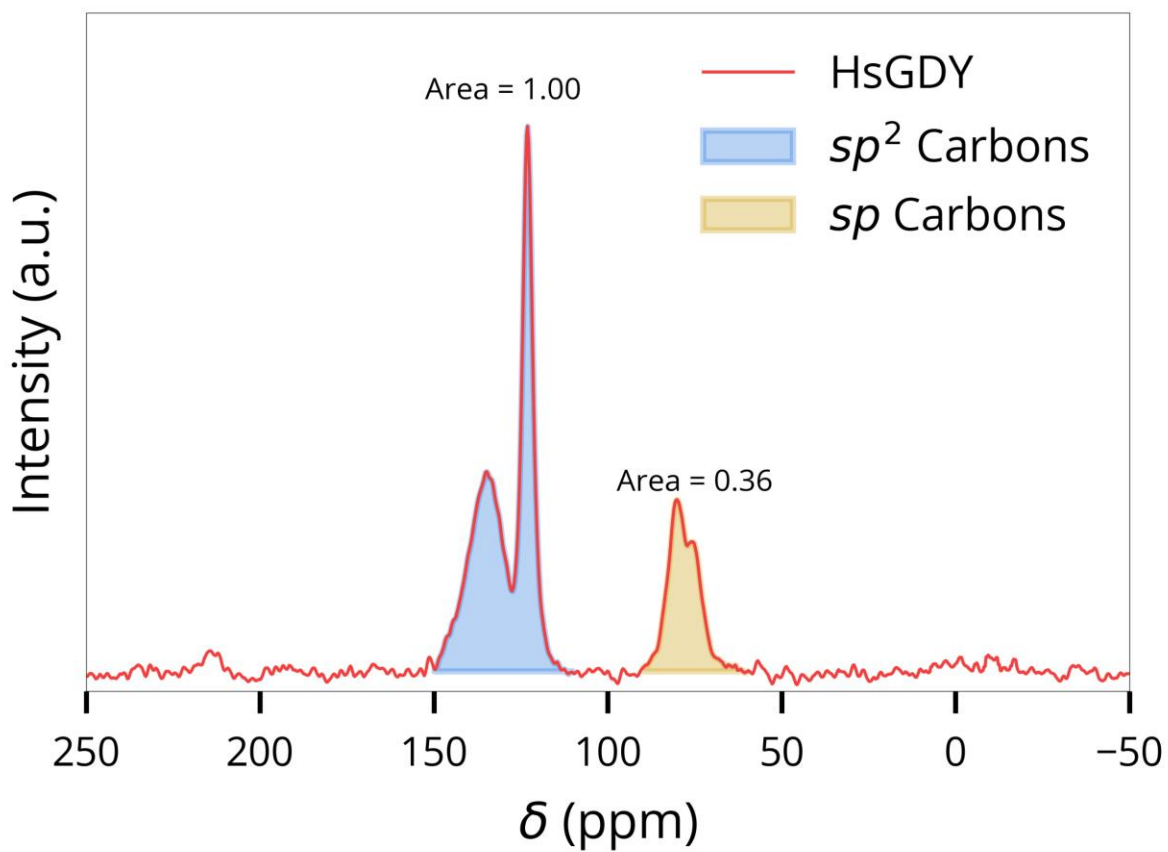


Figure S2. Fitting of HsGDY NMR Data to show that the $sp^2:sp$ ratio is about 3:1.

Comparison of High Resolution Carbon XPS of HsGDY and Heated HsGDY

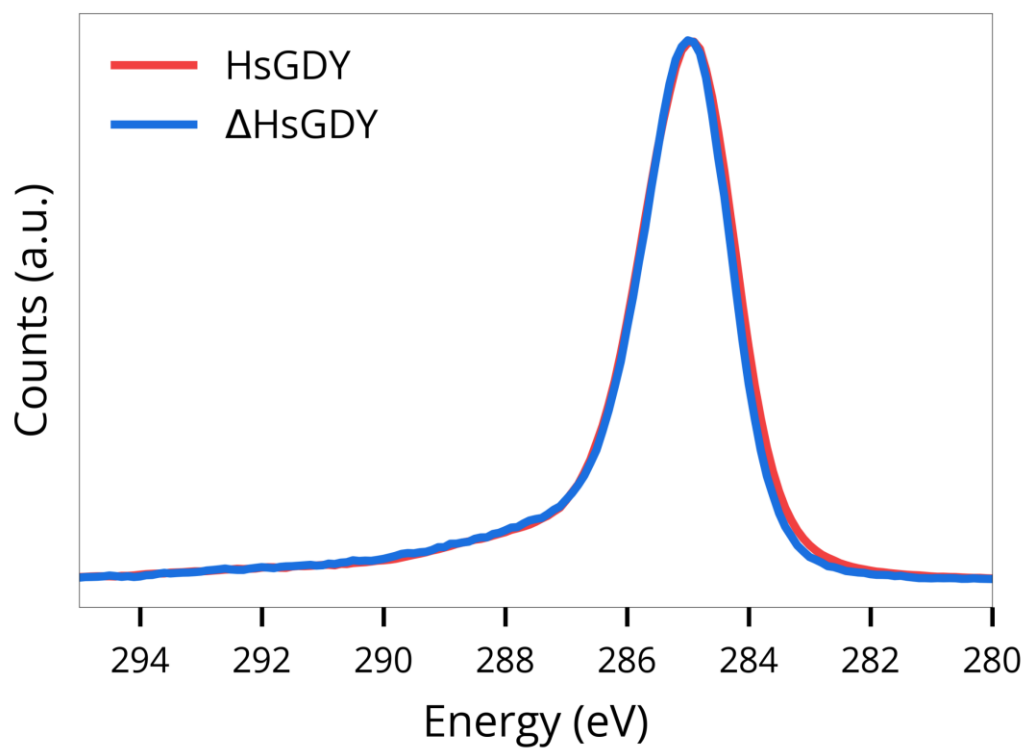


Figure S3. XPS Comparing both HsGDY and Δ HsGDY.

HsGDY High Resolution Carbon XPS

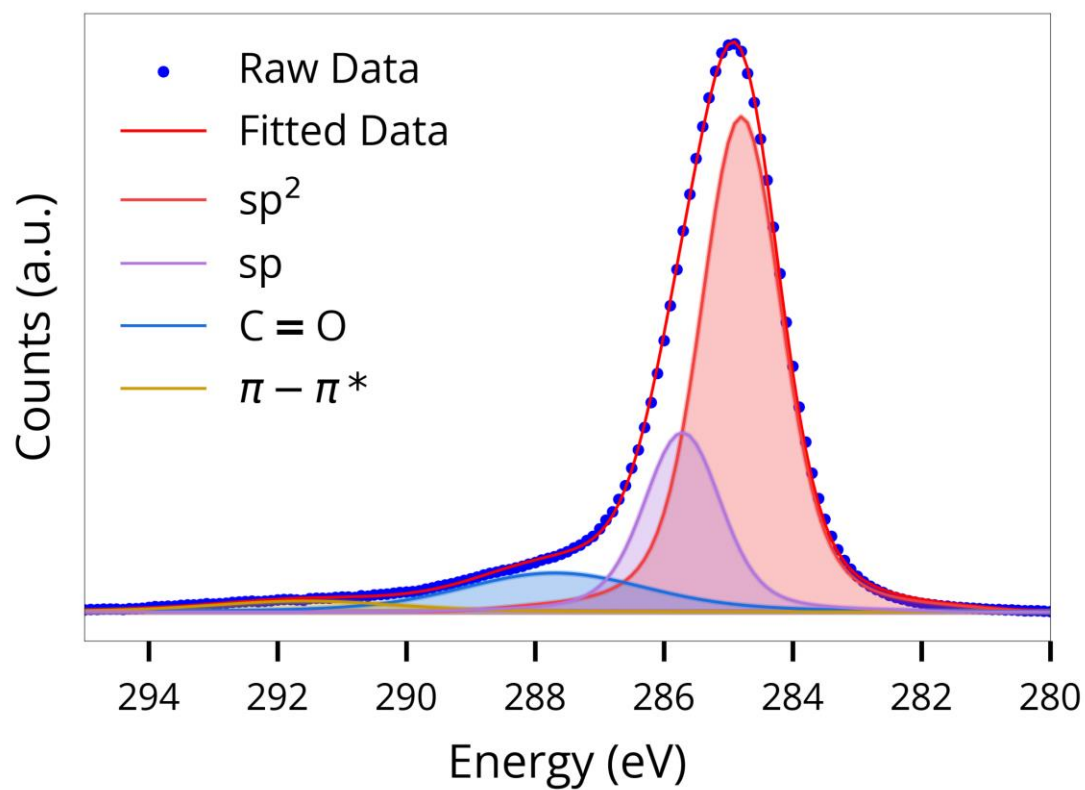


Figure S4. High-resolution XPS of the carbon peak of HsGDY and its fittings.

Δ HsGDY High Resolution Carbon XPS

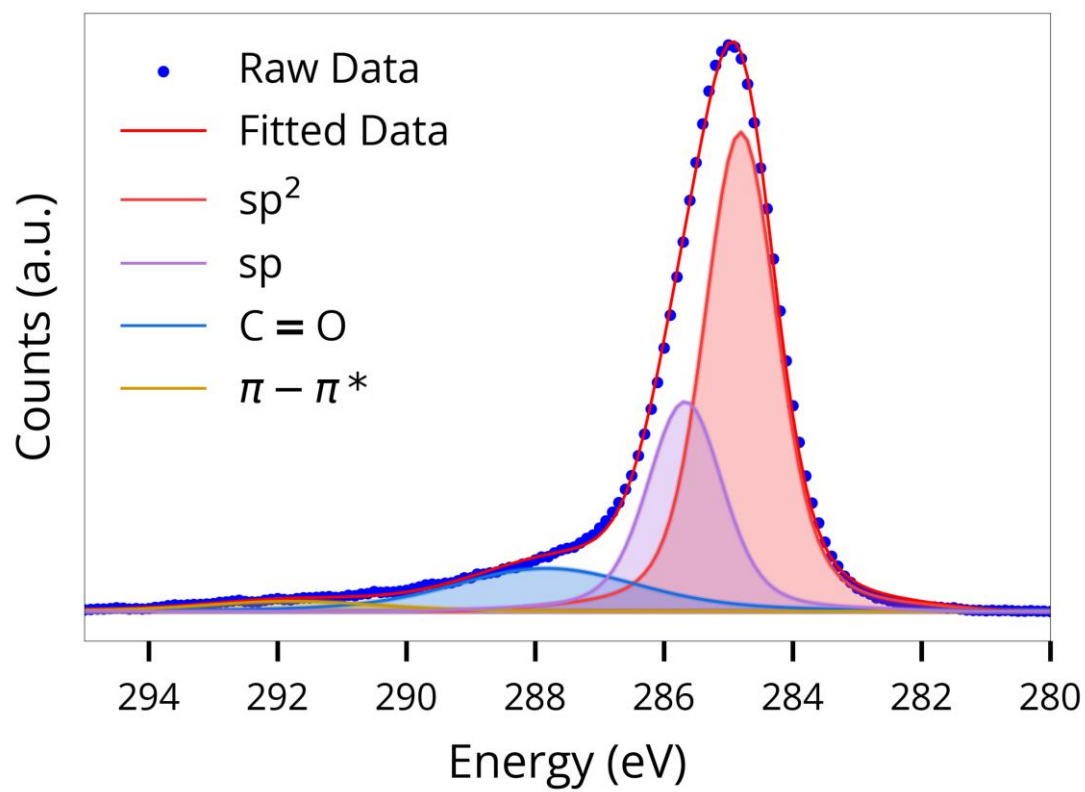


Figure S5. High-resolution XPS of the carbon peak of Δ HsGDY and its fittings.

High Resolution Sulfur XPS

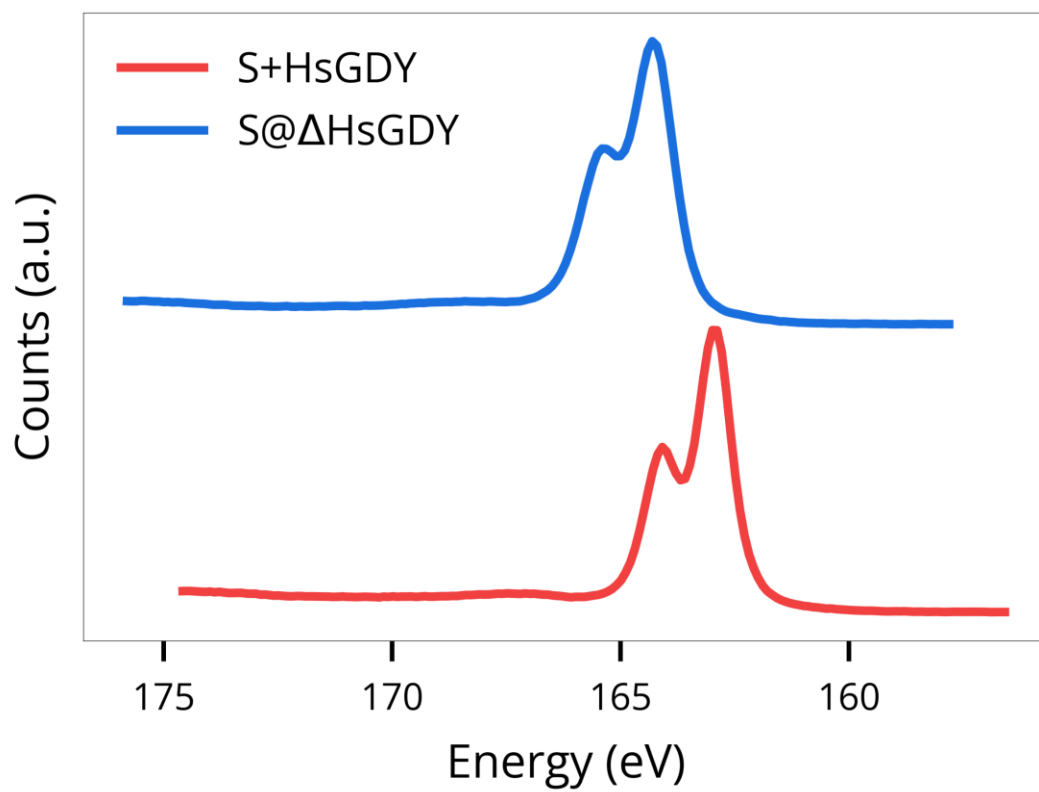


Figure S6. High-resolution XPS of the sulfur peaks of S+HsGDY and S@ Δ HsGDY.

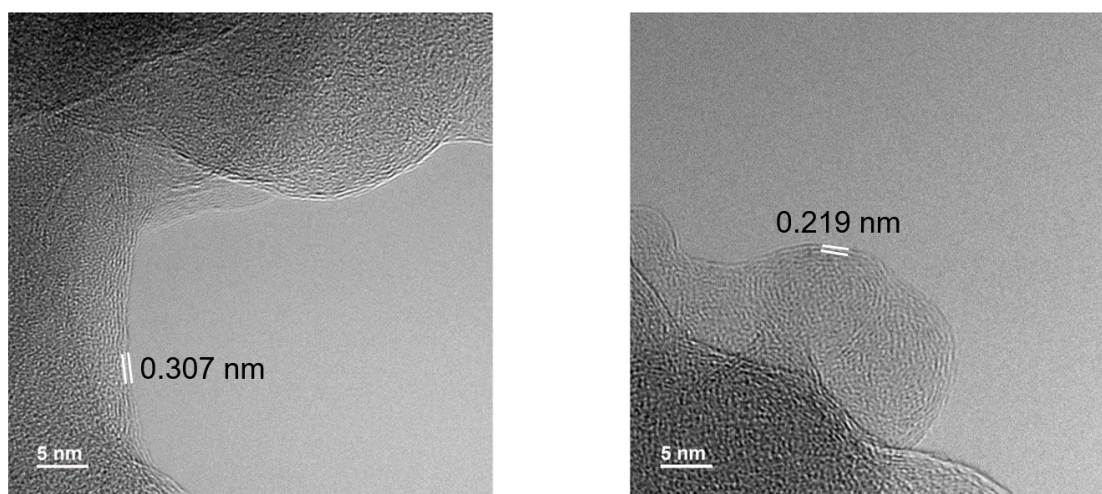


Figure S7. TEM of HsGDY (left) and Δ HsGDY (right).

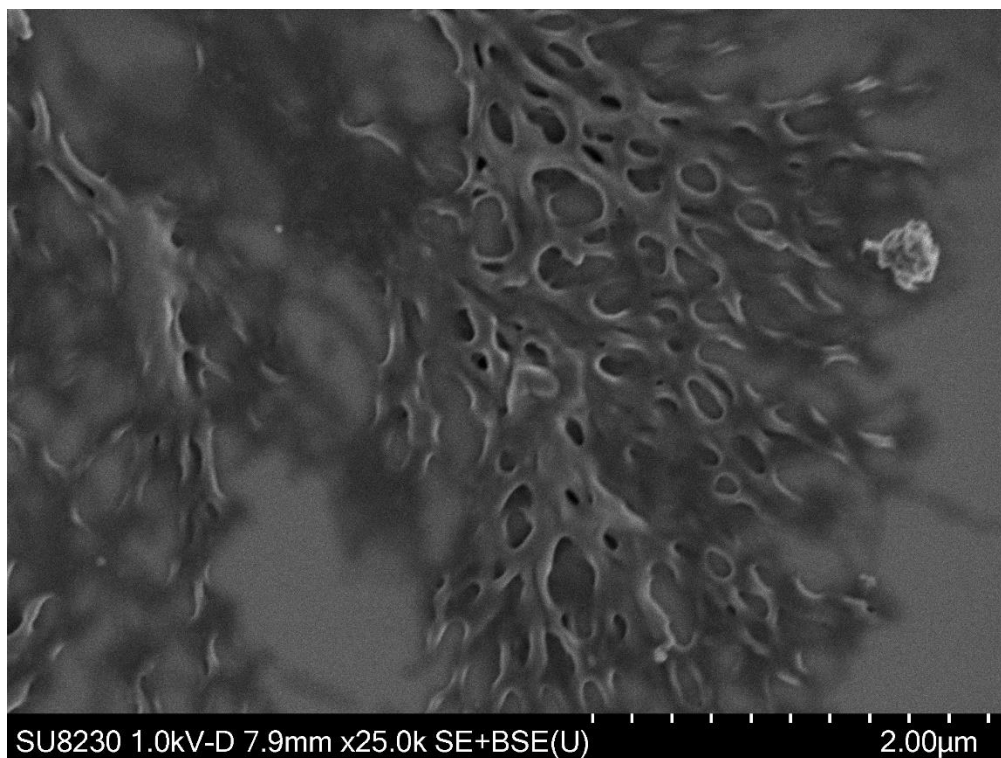
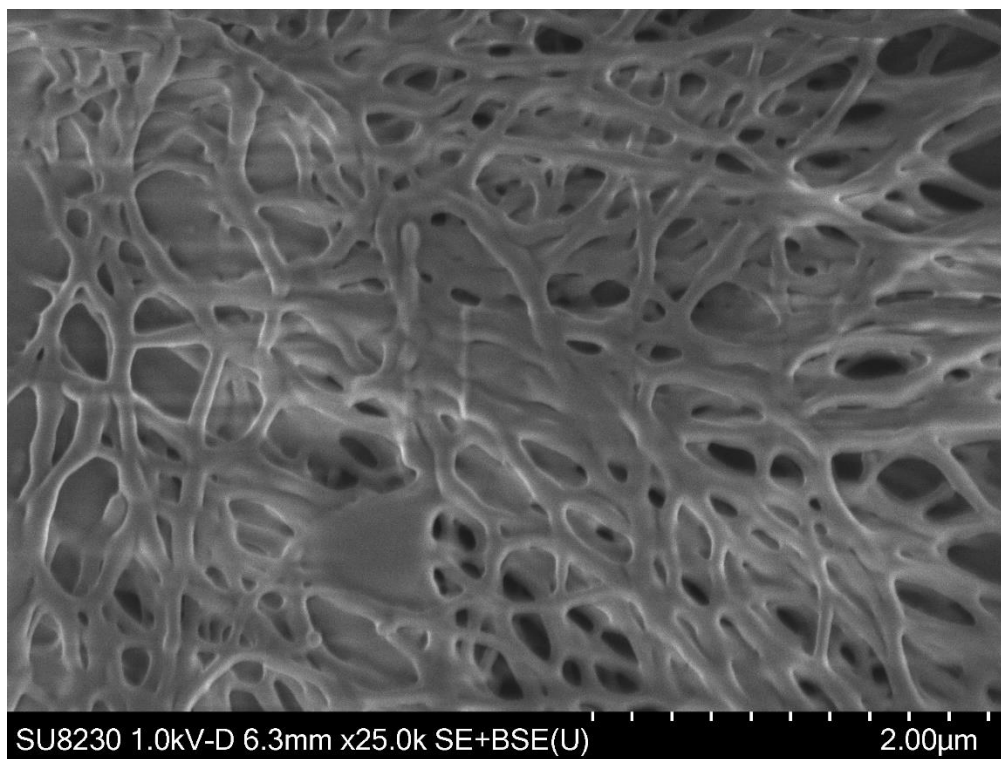


Figure S8. SEM of HsGDY (top) and Δ HsGDY (bottom). Both show a porous carbon morphology.

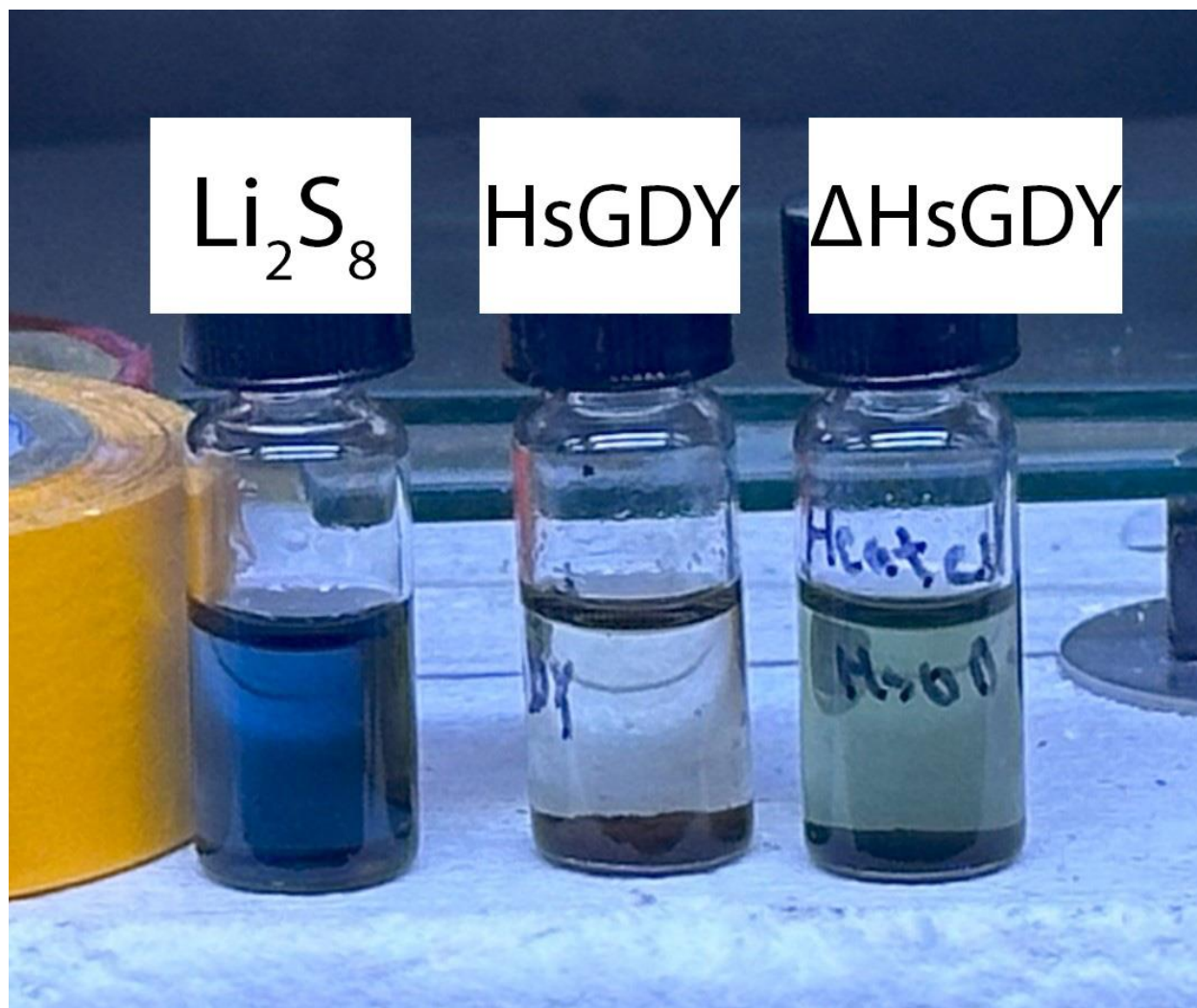


Figure S9. Adsorption test with Li_2S_8 in DMSO.

Ex situ Raman of Cathodes at different Potentials

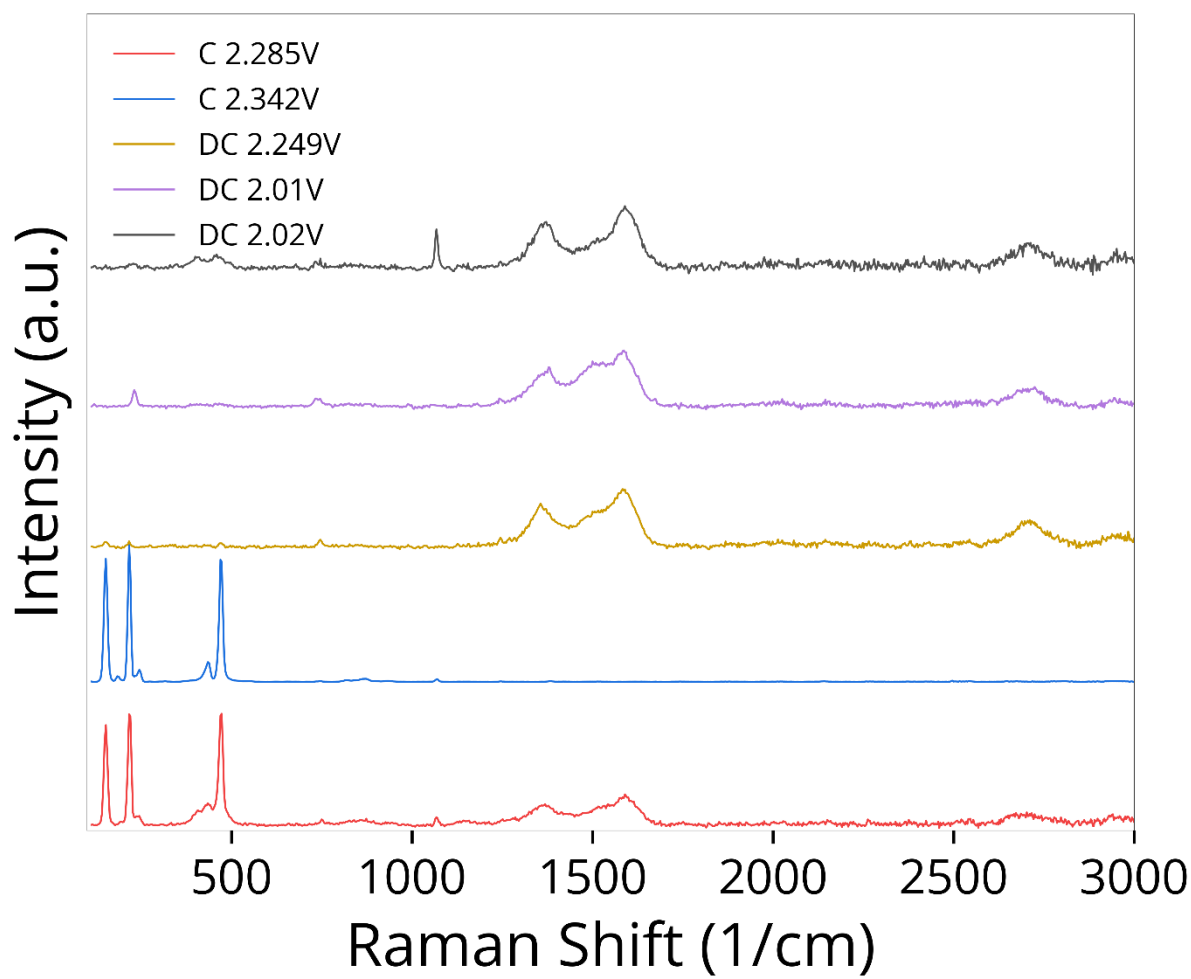


Figure S10. Raman of ex-situ S@ Δ HsGDY cathodes. C represents charge and DC represents discharge. For example, “C 2.285V” means that the cathode was harvested at 2.285 V in the charge phase. No alkyne bond peak (~ 2300 $1/\text{cm}$) is present for any of the cathode samples.

High Resolution Carbon XPS for ex situ cathodes

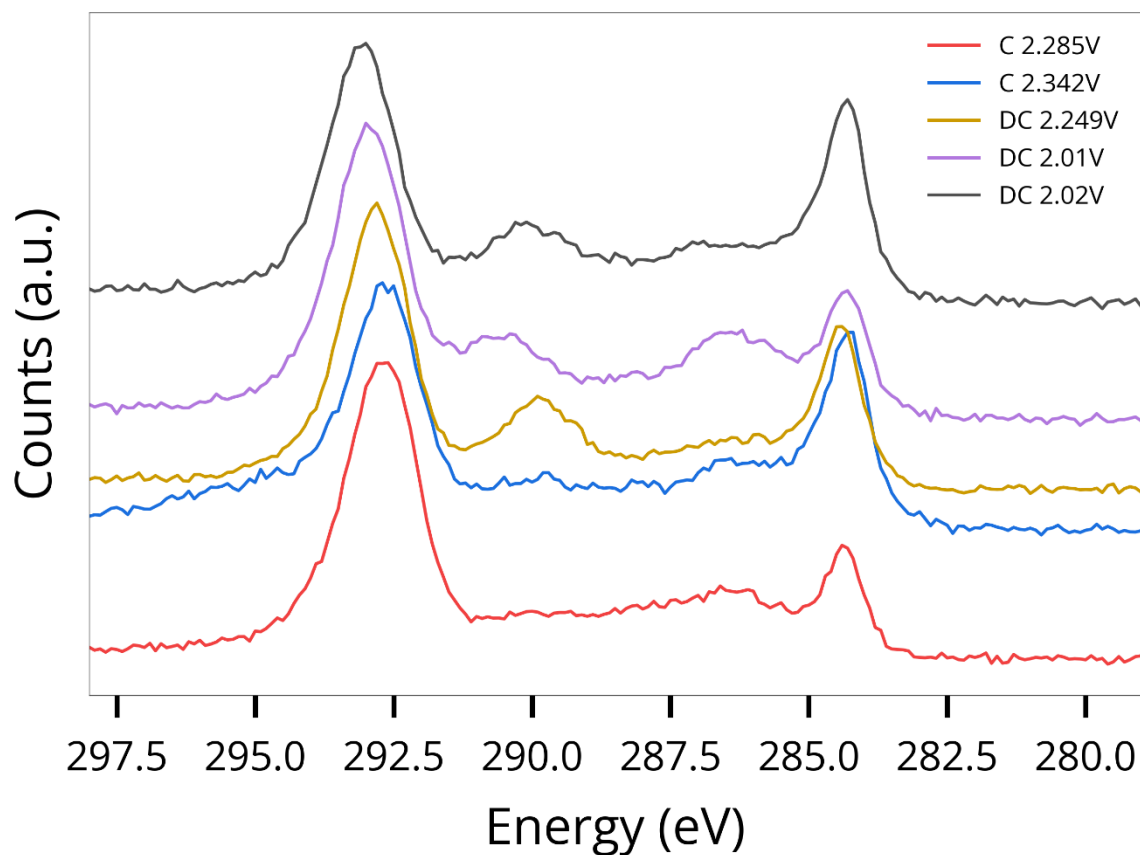


Figure S11. High-resolution XPS of the carbon peaks of ex-situ S@ Δ HsGDY cathodes. The carbon peaks centered around 284 eV are not changing by a noticeable amount. The carbon peaks around 293 eV are associated with LiTFSI, so the change is not due to HsGDY.

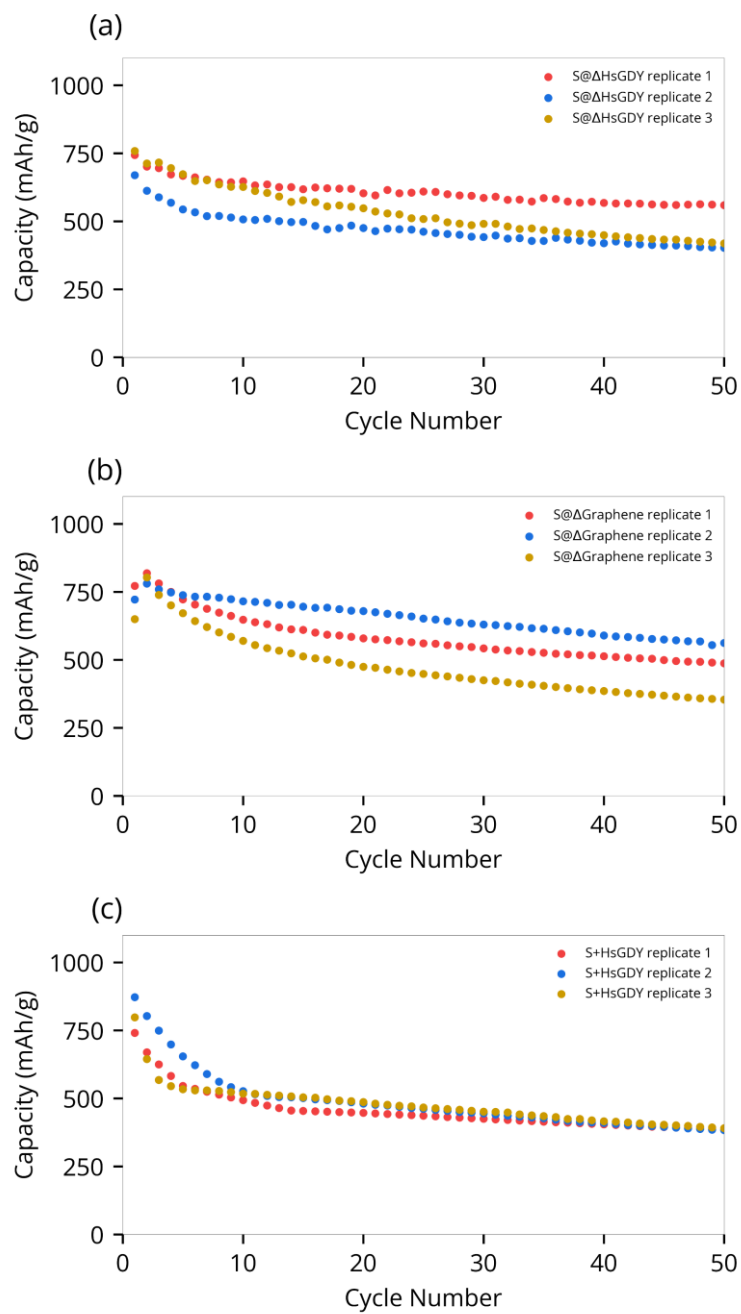


Figure S12. All coin cell data.

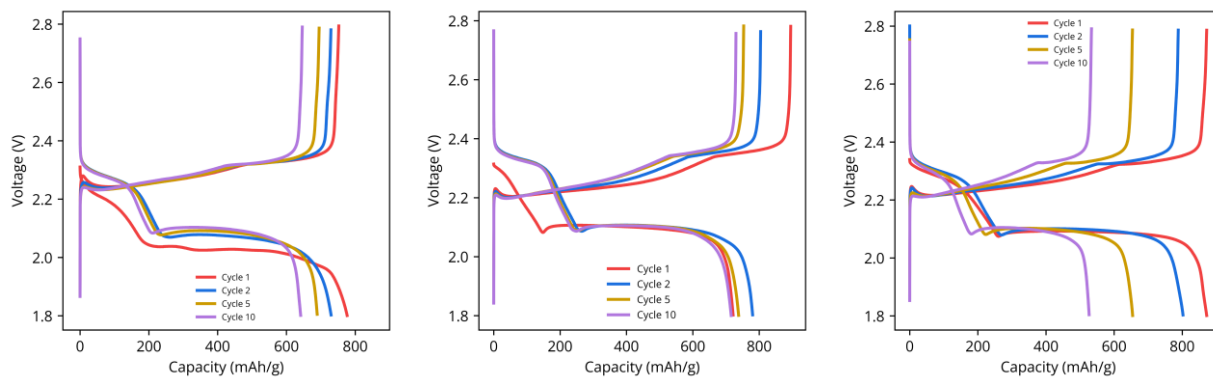


Figure S13. Voltage profiles of S@ Δ HsGDY (left), S@ Δ Graphene (middle), and S+HsGDY (right).

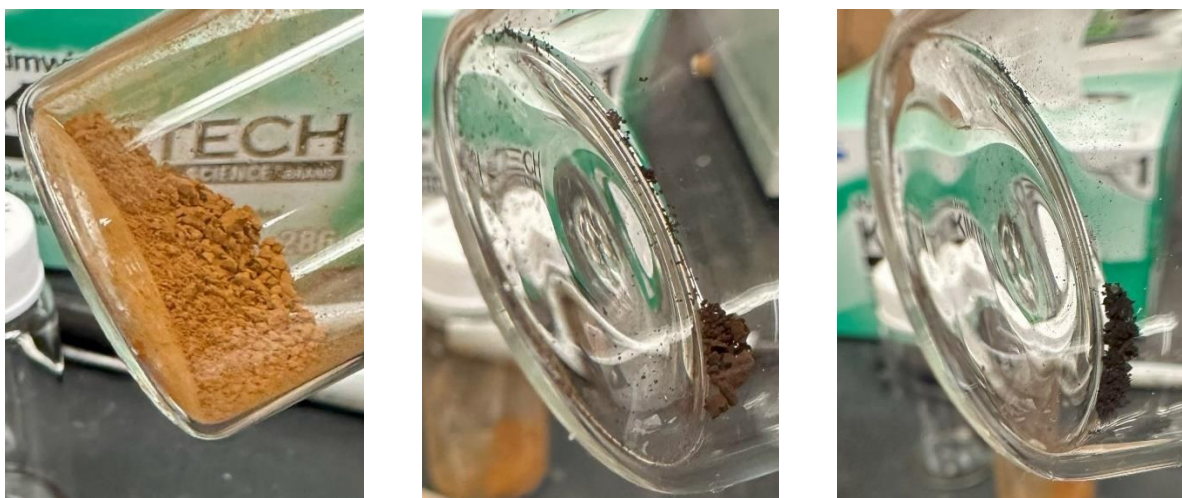


Figure S14. Digital photographs of HsGDY, Δ HsGDY and S@ Δ HsGDY from left to right.

Cathodes	Material: Loading (mg cm ⁻²)	Initial discharge capacity@rate	Capacity retention (%)	Electrolyte	ref
S@HsGDY	S:~2	750 mAh/g@0.1C	80% after 50 cycles	LiTFSI in DOL and DME w/ LiNO ₃	This work
S-HPC and S-LPC	S:1.2	1339 mAh/g@0.2C	93% after 300 cycles	LiTFSI in DOL and DME w/ LiNO ₃	1
Graphene nanoplatelets-nanosulfur (GNS) /w CNT	S: ~2	1000 mAh/g @0.12C	75% after 100 cycles	LiTFSI in DOL and DME w/ LiNO ₃	2
Sulfur nafion graphdiyne (S@Nafion@GDY)	S: 1.5	850 mAh/g @0.5C	100% after 800 cycles	LiTFSI in DOL and DME w/ LiNO ₃	3
1,3,6,8-Tetrasiliclyl Acetylene Pyrene (TSAP) Polypyrene Acetylene (GPOF) Porous Organic Framework	S: 1-1.5	925 mAh/g @0.2C	100% after 250 cycles	LiPF ₆ in EC and DEC	4
Hydrogen substituted graphyne (HsGY) (1,3,5 triphenylbenzene monomer [TDB] monomer	S: 1.2-1.4	881 mAh/g @2C	63% after 200 cycles	LiTFSI in DOL and DME w/ LiNO ₃	5

SGDY (hexaethynylbenzene monomer)	S: 1	836 mAh/g @0.5C	100% after 100 cycles	LiPF6 in EC and DMC	6
Sulfur-polyacrylonitrile (S-PAN)	N/A	850 mAh/g @0.2 mA/cm ²	75% after 50 cycles	LiPF6 in EC and DEC	7
Sulfur-polyacrylonitrile (S-PAN)	S-PAN: 0.85	1300 mAh/g @0.2C	73% after 1000 cycles	LiPF6 in EC and DEC	8
Tellurium-sulfur-polyacrylonitrile (TeS-PAN)	Te&S: 1- 2	1167 mAh/g @0.6C	70% after 600 cycles	Both (as above)	9
Sulfur-Polyaniline (SPANI)	S: 1.2	640 mAh/g @1C	90% after 500 cycles	LiPF6 in EC and DEC	10
Sulfur doped graphdiyne (2,3,4,5-tetraethynylthiophene monomer)	S-GDY: 0.24	1678 mAh/h @0.06C	55% after 50 cycles	LiPF6 in EC and DMC	11
benzyl disulfide (BDS) (S source) with GDY	na	390 mAh/g @1.19C	99% after 1000 cycles	LiPF6 in EC and DMC	12
Tetrathiafulvalene-graphdiyne (TTF-GDY)	TTF-GDY: 2	530 mAh/g @0.3C	100% after 200 cycles	LiPF6 in EC and DEC	13
Graphdiyne-Molybdenum disulfide (GDY-MoS ₂)	NA	1463 mAh/g @0.03C	100% after 100 cycles	NA	14
CNT-S coated with GDY (1,3,5 triethynylbenzene (TEB) monomer) mixed Graphite	S: 1.2	1000 mAh/g @1C	55.5% after 500 cycles	LiTFSI in DOL and DME w/ LiNO ₃	15
Pd-conjugated microporous polymer (Pd-CMP)	S: 1.2	1295 mAh/g @0.3C	71% after 200 cycles	LiTFSI in DOL and DME w/ LiNO ₃	16
Nanosulfur, graphene and poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (SGP)	S: 2	1008 mAh/g @1C	80% after 500 cycles	LiTFSI in DOL and DME w/ LiNO ₃	17
Li ₂ S-graphene	Li ₂ S: 2	1150 mAh/g @0.1C	66% after 200 cycles	LiTFSI in DOL and 1,1,2,2- tetrafluoro-3- (1,1,2,2- tetrafluoroethoxy)	18
Li ₂ S/N,P-C	Li ₂ S: 1.2	670 mAh/g @0.7C	72% after 300 cycles	LiTFSI in DOL and DME w/ LiNO ₃	19

Table S1 Comparison of Cathodes from Literature

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