

Electronic Supplementary Information

Graphdiyne aerogel architecture via a modified Hiyama coupling reaction for gas adsorption

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1 Experimental Section

1.1 Materials

Most chemicals, such as $\text{Cu}(\text{OAc})_2$, CuCl , pyridine, and N, N-dimethylformamide (DMF), were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. Hexakis-[(trimethylsilyl)]ethynylbenzene (HEB-TMS) was purchased from Jiangsu XFNANO Material Tech Co., Ltd. (Nanjing, China).

1.2 Methods

Preparation of GDY organogel: GDY organogel was prepared from HEB-TMS using a modified Hiyama coupling method. First, $\text{Cu}(\text{OAc})_2$ (18 mg, 0.1 mmol) was dissolved in pyridine (2 mL) in a glass vial under air and ultrasound for 3 min. Then, HEB-TMS (66 mg, 0.1 mmol) was added to the blue solution and ultrasound for another 3 min. The vial was sealed and put in the oven at 40 °C for 3 days without disturbance.

Solvent exchange: Typically, the obtained organogel was solvent exchanged two times sequentially with a large amount of pyridine, chloroform, ethanol, and water (every solvent exchange process takes 12 h).

Preparation of GDY aerogel: To prepare the GDY aerogel, a freeze dryer with a collector temperature of -90 °C and a vacuum of 0.015 mbar was used after the washed gel was flash-frozen by liquid nitrogen. A monolithic aerogel was obtained by freeze-drying for 3 days.

1.3 Characterization

NMR spectra were recorded on a Bruker AVANCE III-400 MHz NMR spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) with deuterated chloroform (CDCl_3) as solvent at room temperature. ^1H NMR chemical shifts were reported in ppm using tetramethylsilane (TMS, $\delta=0.00$ ppm) as the internal standard. ^{13}C NMR spectra were reported in ppm using solvent CDCl_3 ($\delta=77.2$ ppm) as an internal standard.

Scanning Electron Microscopy (SEM) images were collected on a Quattro

Environmental Scanning Electron Microscope operating at 5 kV. Samples were prepared by directly putting aerogels on the conductive tape.

Transmission Electron Microscopy (TEM) images were recorded using a FEI Tecnai F30 electron microscope operating at 300 kV. Samples were prepared for analysis by scattering in ethanol with ultrasonic power, dropping the dispersion on copper grids, and drying at room temperature.

Raman spectra were carried out on a Witec's alpha 300 apyron with an excitation laser wavelength of 532 nm.

X-ray photoelectron spectroscopy (XPS) was run on Kratos Axis Ultra DLD to evaluate the composition of materials.

Fourier Transform Infrared (FT-IR) spectra were performed on a Nicolet iS10 FTIR spectrometer with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory with a spectral range of 4000-600 cm^{-1} .

UV-visible spectra were acquired with GENESYS 10S UV-Vis spectrometer with a wavelength range from 200 to 1000 nm.

Gas Adsorption Measurement: H_2 and N_2 adsorption experiments were performed with ASAP 2420 (Micromeritics). CO_2 and CH_4 adsorption experiments were performed with ASAP 2050 (Micromeritics). Before the measurements, GDY aerogel samples were degassed at 80 °C for at least 20 hours on the Smart VacPrep system (Micromeritics).

Oil uptake measurement: Typically, a piece of aerogel was dropped into organic solvent or oil for 1 min. Then the weight gain (%) of aerogel was calculated by $W_g = 100 \cdot (w - w_0) / w_0$. Where w_0 and w represent the mass of aerogel before and after absorption, respectively.

2 Supplementary Figures

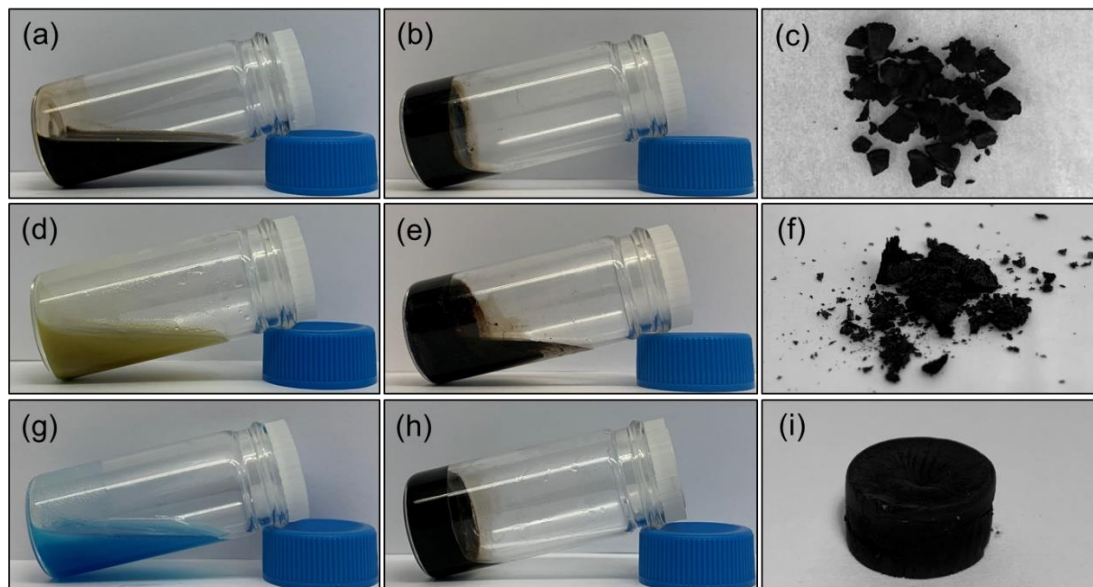


Figure S1. (a-b) The Eglinton coupling reaction used HEB as the monomer, $\text{Cu}(\text{OAc})_2$ as the catalyst and pyridine as the solvent at 40 °C for 3 days. (c) The corresponding product of b after freeze-drying. (d-e) The Hiyama coupling reaction used HEB-TMS as the monomer, CuCl as the catalyst, and DMF as the solvent at 60 °C for 3 days. (f) The corresponding product of e after freeze-drying. (g-h) The modified Hiyama coupling reaction used HEB-TMS as the monomer, $\text{Cu}(\text{OAc})_2$ as the catalyst, and pyridine as the solvent at 40 °C for 3 days. (i) The corresponding product of h after freeze-drying.

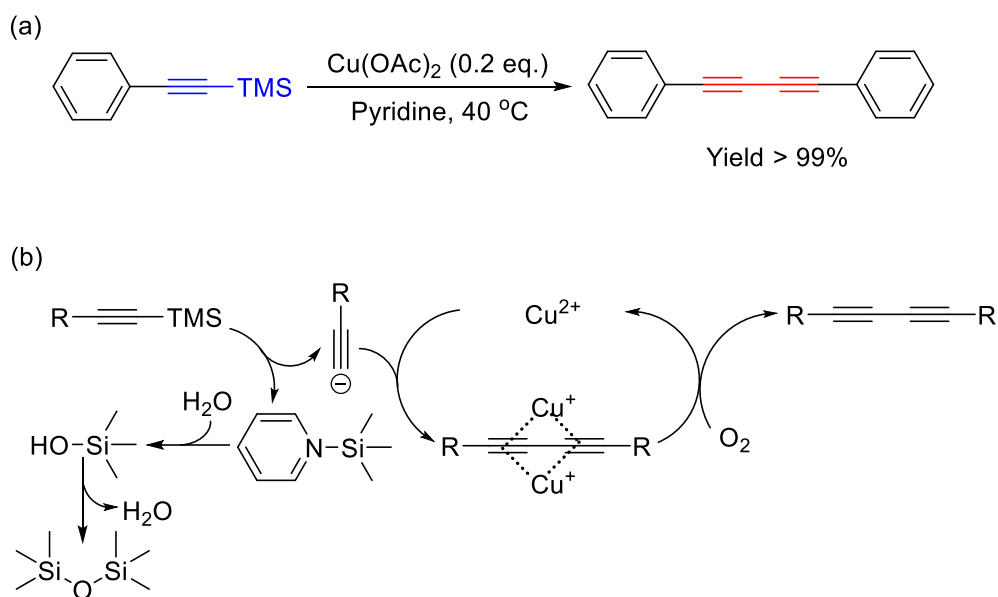


Figure S2. (a) A modified Hiyama coupling reaction was performed as the model reaction. (b) The proposed possible catalytic mechanism of the modified Hiyama coupling reaction.

Under pyridine/ $\text{Cu}(\text{OAc})_2$ system, the TMS group is eliminated (deprotection) and forms an alkynyl anion species. A reduction process then proceeds in the presence of the alkynyl anions species and Cu^{2+} to form binuclear-copper (I)-acetylide-intermediates.¹ Subsequently, these intermediates were dimerized oxidatively into a butadiyne product. The produced Cu^+ is further oxidized into Cu^{2+} in the presence of air for the next catalytic cycle. The byproduct, TMS- group, is captured by pyridine to generate trimethylsilyl pyridine and then converted into TMS-OH and eventually to TMS-O-TMS.²

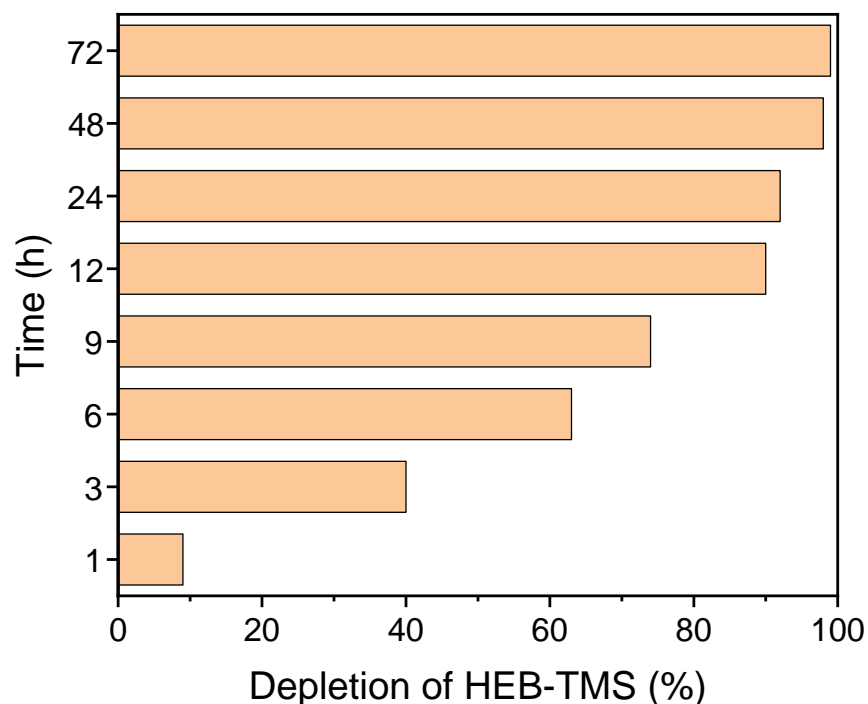


Figure S3. The depletion of monomer along with the reaction time. The depletion of monomer (%) was calculated by $D = 1 - M$, where M represents the residual amount of monomer (%) after the reaction. The residual amount of monomer was calculated by ^1H NMR spectra with mesitylene as the internal standard.

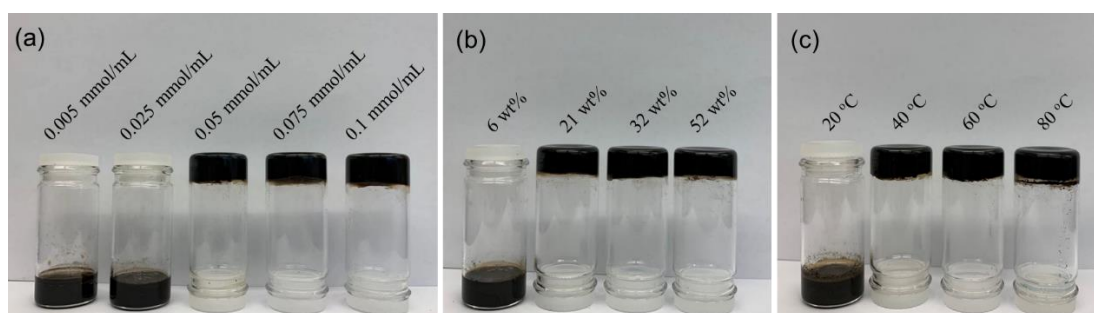


Figure S4. Photographs of GDY organogel prepared by varying (a) initial monomer concentrations, (b) catalyst amounts, and (c) reaction temperatures.

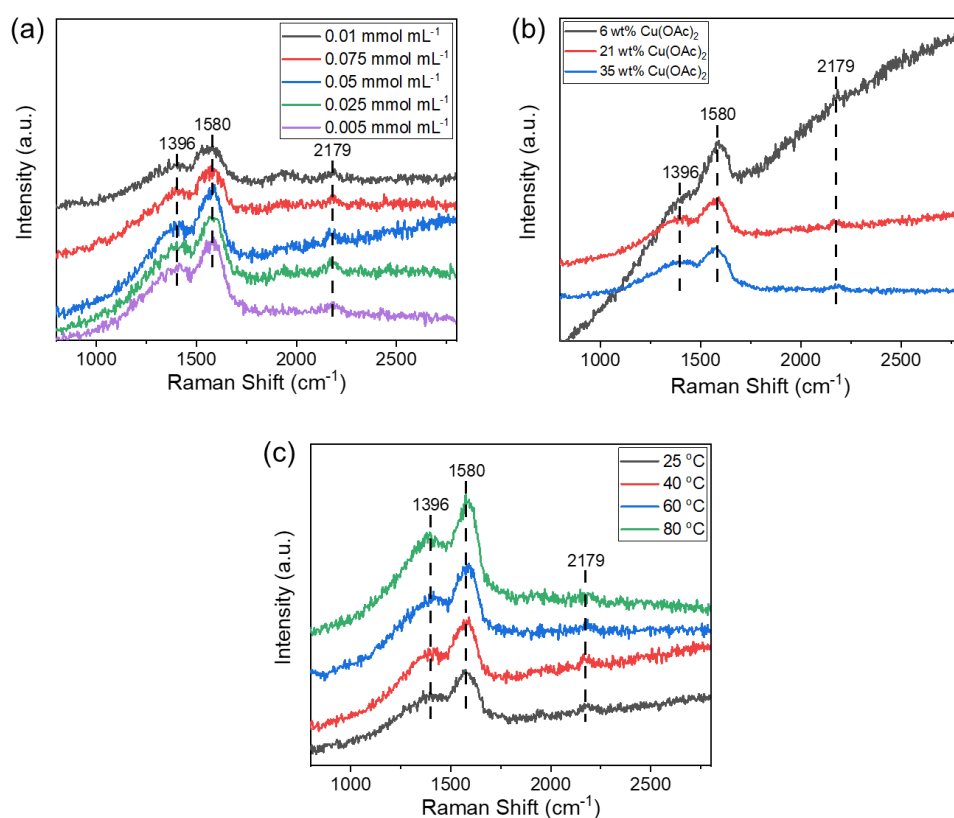


Figure S5. The Raman spectra of GDY aerogels collected with (a) different monomer concentrations, (b) different catalyst amounts, and (c) different reaction temperatures.

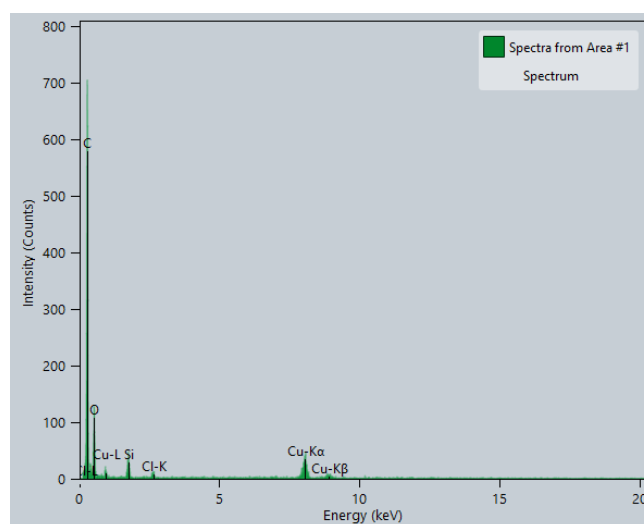


Figure S6. EDS spectra of GDY aerogels on Cu grid.

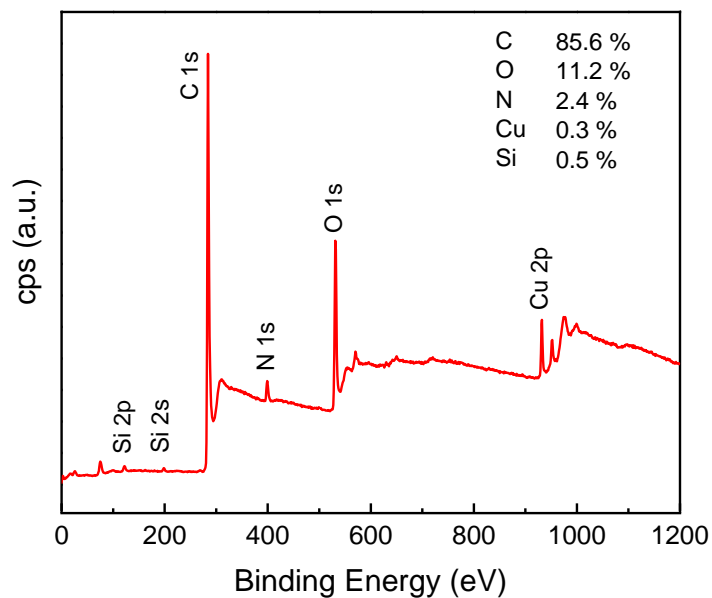


Figure S7. XPS survey spectrum of GDY aerogel.

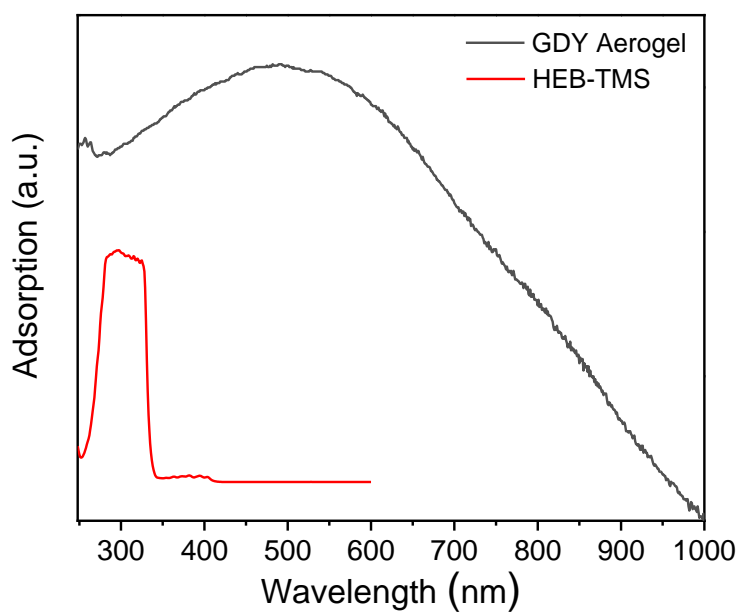


Figure S8. UV-vis spectra of HEB-TMS monomer and as-grown GDY aerogel.

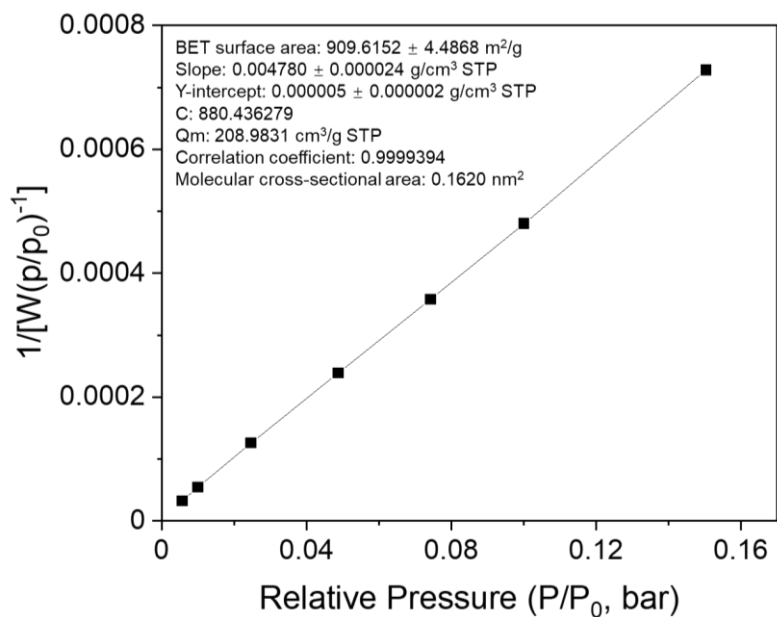


Figure S9. BET plot of GDY aerogel calculated from N₂ adsorption isotherm at 77K.



Figure S10. Photographs of GDY aerogel monolith (left) and GDY xerogel monolith (right). The GDY xerogel was obtained by open-atmosphere drying. The volume of GDY aerogel is 2.035 cm^3 (1.8 cm of diameter and 0.8 cm of height), while the volume of GDY xerogel is 0.039 cm^3 (0.5 cm of diameter and 0.2 cm of height).

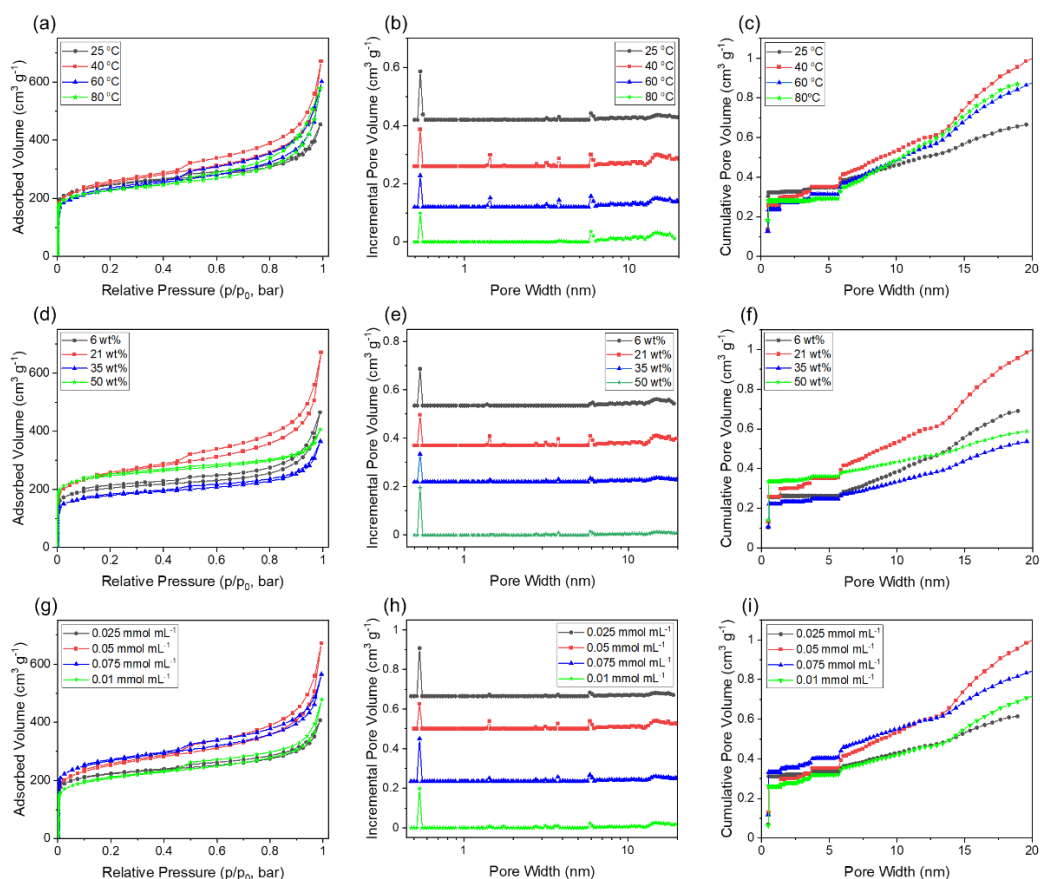


Figure S11. The N_2 adsorption-desorption isotherms, incremental pore size distribution curves, and cumulative pore size distribution curves of GDY aerogels collected from different reaction temperatures (a-c), catalyst amounts (d-f) and monomer concentrations (g-i).

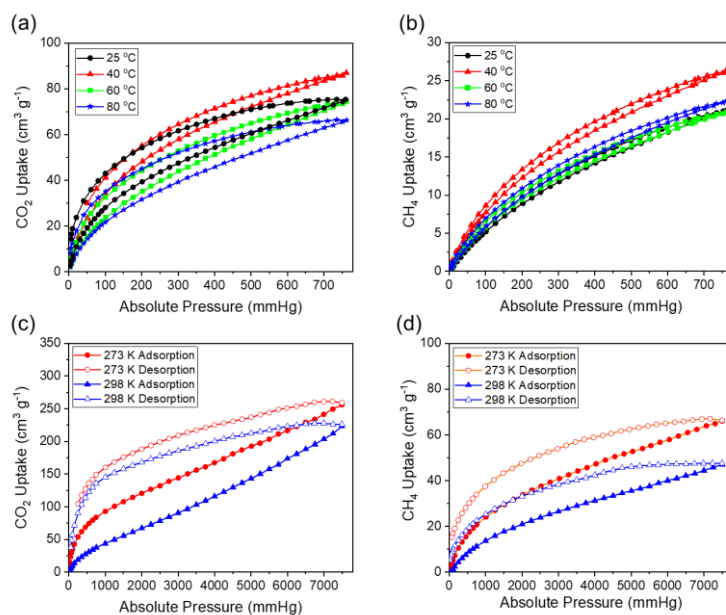


Figure S12. (a-b) The CO₂ and CH₄ adsorption-desorption isothermals of GDY aerogels obtained at different reaction temperatures. (c-d) Extended pressure adsorption-desorption isotherms of CO₂ and CH₄ on GDY aerogels at different test temperatures.

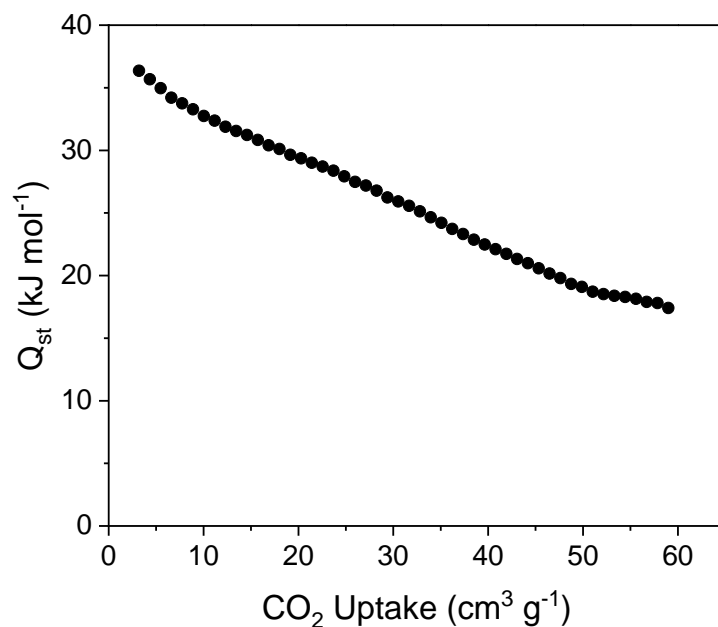


Figure S13. Isosteric heats of adsorption (Q_{st}) for CO₂, calculated using the Clausius-Clapeyron equation.

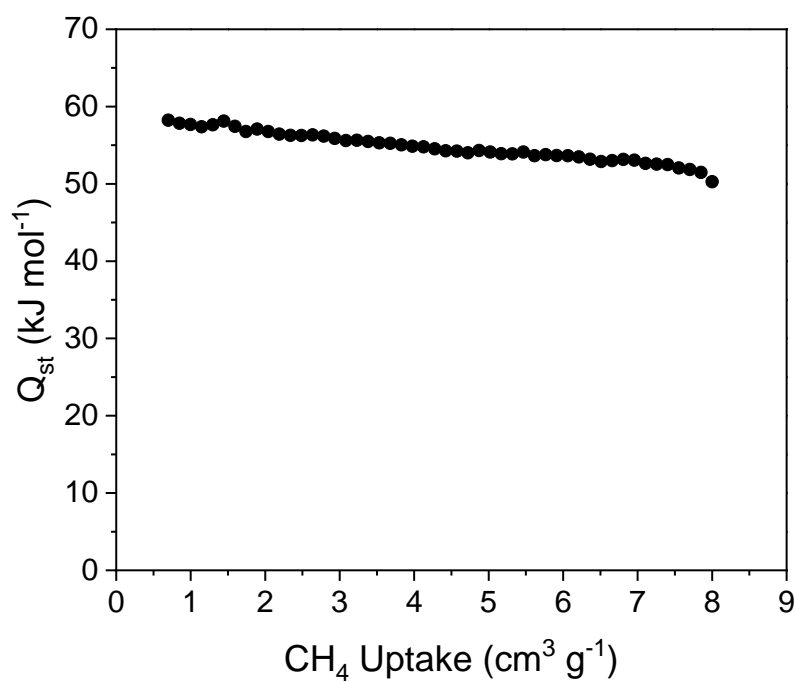


Figure S14. Isosteric heats of adsorption (Q_{st}) for CH_4 , calculated using the Clausius-Clapeyron equation.

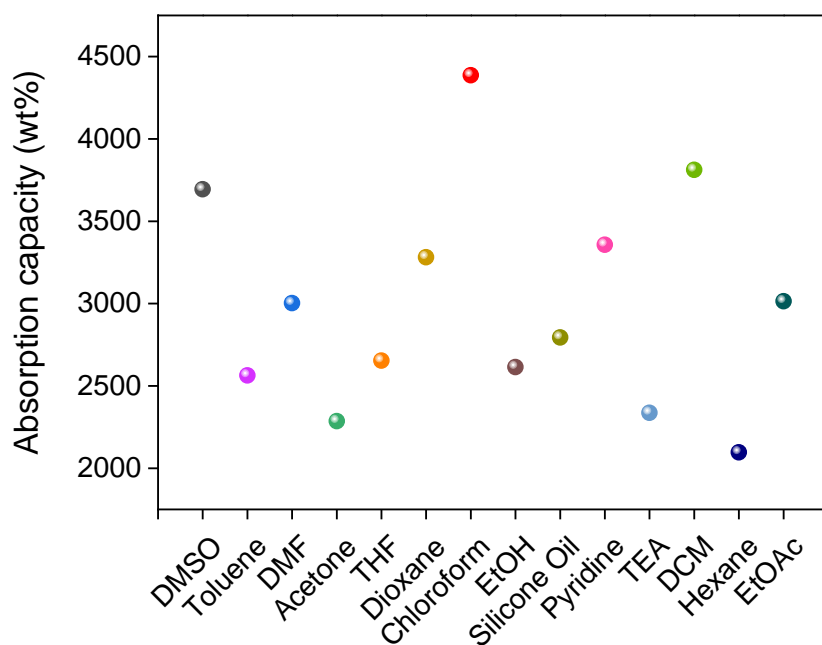


Figure S15. Mass-based adsorption capacity of the GDY aerogel.

Table S1. Summary of BET surface area of GDY materials and GDY analogues.

Materials	BET surface area (m² g⁻¹)	Reference
GDY aerogel	1155	This work
GDY/G	390	[3]
The pristine GDY powder	120	[3]
Nanochain	1150	[4]
Nanoribbon	186	[4]
3D Framework	766	[4]
HGDY	207	[5]
MeGDY	559	[5]
CNGDY	636	[5]
BGDY	725	[6]
PR-GDY	408	[7]
NSFLGDY-900	431	[8]
HsGDY	667	[9]
HsGDY	2184	[10]
3D GDY powder	369	[11]
P-GDY	918	[12]
HK@GDY/CMC-B	945	[13]
TGDY	758	[14]
TA-BGY	300	[15]
F-GDY	422	[16]
HsGY	1453	[17]

Table S2. Oil/organic solvent uptake capacity and density of various carbon-based adsorbents.

Materials	Density (mg cm ⁻³)	Absorbate	Capacity (g g ⁻¹)	Reference
GDY aerogel	12	DMSO, Toluene, DMF, Acetone, THF, Dioxane, Chloroform, Ethanol, Triethylamine, Pyridine, DCM, Hexane, Ethyl acetate, Silicon oil.	22-44	This work
Activated carbon	-	Benzene, Toluene.	<1	[18]
Graphene aerogel	12~18	DMF, Ethanol, Toluene, Hexane, Cyclohexane, Chlorobenzene, Phenixin, Pump oil, Vegetable oil, Paraffin oil, Kerosene.	15-60	[19]
PVA/CNTs aerogels	27~82	DMF, Chloroform, THF, Acetonitrile, Acetone, Hexane, Toluene, Bean oil.	10-52	[20]
Lignin/Agarose/PVA carbon aerogels	52	THF, Toluene, Oleic acid, DCM, Chloroform, Hexane, Vacuum pump oil, Liquid paraffin.	20-40	[21]
Polydopamine/chitosan/rGO aerogel	80	Ethanol, Gasoline, Acetone, Diesel, Hexane, Toluene.	10-21	[22]
PTEB aerogel	30	Triethylamine, n-Butylamine, Cyclohexane, Ethanol, Acetone, Toluene, Pyridine, DMSO, Nitrobenzene, Chloroform, Bromobenzene, Phenoxin, Pump oil, Bean oil, Motor oil.	13-53	[23]
HCMPs	-	Kerosene, Ethyl acetate, DCM, Nitrobenzene, Toluene, Benzene, Bromobenzene, Aniline, Xylene, Trimethylbenzene,	1-16	[24]

Table S3. Summary of CO₂ and CH₄ adsorption data of various materials.

Materials	BET surface area (m ² g ⁻¹)	CO ₂ uptake (mmol g ⁻¹)	CH ₄ uptake (mmol g ⁻¹)	Reference
HCPs				
BINOL network 4	1015	3.96	-	[25]
1,3,5-tripheylbenzene-based HCP	1059	3.61	-	[26]
HCP-1	1646	3.01	-	[27]
HCP-2	1684	3.3	-	[27]
HCP-3	1531	3.24	-	[27]
HCP-4	1642	3.92	-	[27]
COFs				
COF-1	750	2.32	-	[28]
COF-5	1670	1.34	-	[28]
COF-6	750	3.84	-	[28]
COF-8	1350	1.43	-	[28]
COF-10	1760	1.21	0.35	[28]
COF-102	3620	1.56	0.63	[28]
COF-103	3530	1.7	-	[28]
CMPs				
CMP-0	1018	2.1	-	[29]
CMP-1	837	2.05	-	[29]
CMP-3	522	2.18	-	[29]
CMP-5	512	1.11	-	[29]
TCMP-0	963	2.38	-	[29]
TCMP-3	691	2.25	-	[29]
TCMP-5	494	1.22	-	[29]
TNCMP-2	995	2.62	-	[29]
NCMP-2	900	2.1	-	[29]
PTEB aerogel	1701	3.47	0.913	[23]
Tet-1	3160	2.55	-	[30]
Tet-2	1102	1.96	-	[30]

Tet-3	3180	2.66	-	[30]
Tet-4	1917	3.03	-	[30]
CTFs				
CTF-0	2011	4.22	-	[31]
CTF-1	746	2.47	-	[32]
FCTF-1	662	4.67	-	[32]
CTF-P6	1152	3.36	-	[33]
CTF-P6M	947	4.17	-	[33]
PCTF-1	2235	3.25	1.05	[34]
PCTF-2	784	1.85	0.67	[34]
PCTF-3	641	2.17	0.76	[34]
PCTF-4	1090	2.31	0.9	[34]
PCTF-5	1183	2.59	0.91	[34]
PCTF-7	613	2.18	0.65	[34]
PAFs				
PAF-1	5600	2.05	0.8	[35]
PAF-3	2932	3.48	1.21	[36]
PAF-4	2246	2.4	0.8	[36]
Cages				
Cage 1	23	1.27	0.55	[37]
Cage 2	533	3	1.13	[37]
Cage 3	624	2.47	1.53	[37]
Cage 5	1333	3.07	-	[38]

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