
Efficient carbon dioxide separation with molecularly thin bilayer carbon membranes

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1. Supplementary methods

Materials

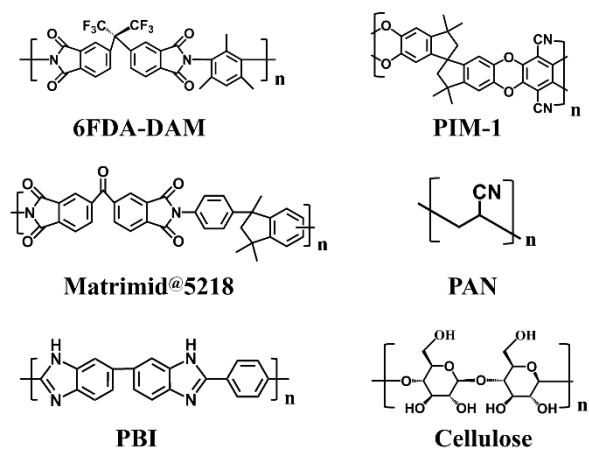
Cu foil (50 mm, 99.9%) was purchased from Strem. Si/SiO₂ wafer was bought from Ted Pella, and Si holey substrates were fabricated by photolithography. 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%) and 2,4,6-trimethyl-m-phenylenediamine (DAM, 99%) were purchased from Sigma-Aldrich and were purified by vacuum sublimation before polymerization. Acetic anhydride (C₄H₆O₃, 99.5%), Triethylamine ((C₂H₅)₃N, 99.5%) were purchased Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). 2,3,5,6-tetra-fluoroterephthalonitrile (TFTPN, 99%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, 97%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. Dichloromethane (DCM, 99%), N, N-dimethylformamide (DMF, 99%) and anhydrous potassium carbonate (K₂CO₃, 99.95%) were purchased Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Anhydrous methanol (99%) was purchased from Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China). Hydrochloric acid (HCl, 36.0-38.0%) was purchased from Rianlon Corporation (Tianjin, China). Polyimide (Matrimid® 5218), Polybenzimidazole (PBI), Polyacrylonitrile (PAN), and cellulose were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Chloroform, tetrahydrofuran, dichloromethane, dimethylacetamide, 1-ethyl-3-methylimidazolium acetate and Dimethyl sulfoxide (DMSO) and FeCl₃ were purchased from Shanghai Meryer Biochemical Technology Co., Ltd (Shanghai, China).

Synthesis

Synthesis of 6FDA-DAM polymers. The 6FDA-DAM polymer was synthesized using a step-growth polymerization method previously reported¹. Before the reaction, purified 6FDA and DAM were dried at 110 °C and 60 °C, respectively, in a vacuum oven for more than 24 h. 8.9244 g 6FDA (20 mmol) and 3.0104 g DAM (20 mmol) in a 200 mL bottle with 50 mL NMP. Reaction mixtures were stirred with a mechanical power stirrer under nitrogen purge at 0 °C for 24 h. Then the cyclization was achieved under nitrogen purge at room temperature for 24 h through the addition of 15 mL acetic anhydride (dehydrating agent) and 2 mL triethylamine (catalyst). The

polymer solution was precipitated with methanol and then washed three times by cold methanol and dried at 200 °C in vacuum oven for 24 h. The molecular weight was $M_w=293000$ g/mol and $M_n=118000$ g/mol, measured by gel permeation chromatography.

Synthesis of PIM-1 polymers. PIM-1 polymers were synthesized based on a reported low-temperature polymerization procedure². The monomer TTSBI was used after being purified through a recrystallization method from a methanol-dichloromethane solvent mixture, while TFTPn was used as received. All glassware was oven-dried before the polycondensation to ensure completely anhydrous conditions. A flask was charged with 5.1062 g (15 mmol) of TTSBI, 3.0014 g (15 mmol) of TFTPn, and 100 mL of anhydrous DMF. Under an argon environment and at a temperature of 65 °C, the mixture was vigorously stirred and formed a homogenous solution. Then 16.585 g K_2CO_3 was added to the solution with continuous stirring. The polymerization was kept for 72 h. Finally, the polymer was isolated by pouring the viscous mixture into water. The solid was then washed with 0.1 wt% HCl, water, and methanol. After drying at 120 °C for 12 h under vacuum, the product was solvated in chloroform to form a 5 wt% solution. Followed by full oscillation and standing, the PIM-1 solution was dripped into methanol, and PIM-1 polymers were reprecipitated. After filtration, the polymers were dried at 120 °C under vacuum for 24 h. Overall, the reaction yield was about 80%. The molecular weight was $M_w=221000$ g/mol and $M_n=50000$ g/mol, measured by gel permeation chromatography.



Scheme 1. Molecular structures of polymer precursors.

Computational details

MD simulation of CO₂/CH₄ separation

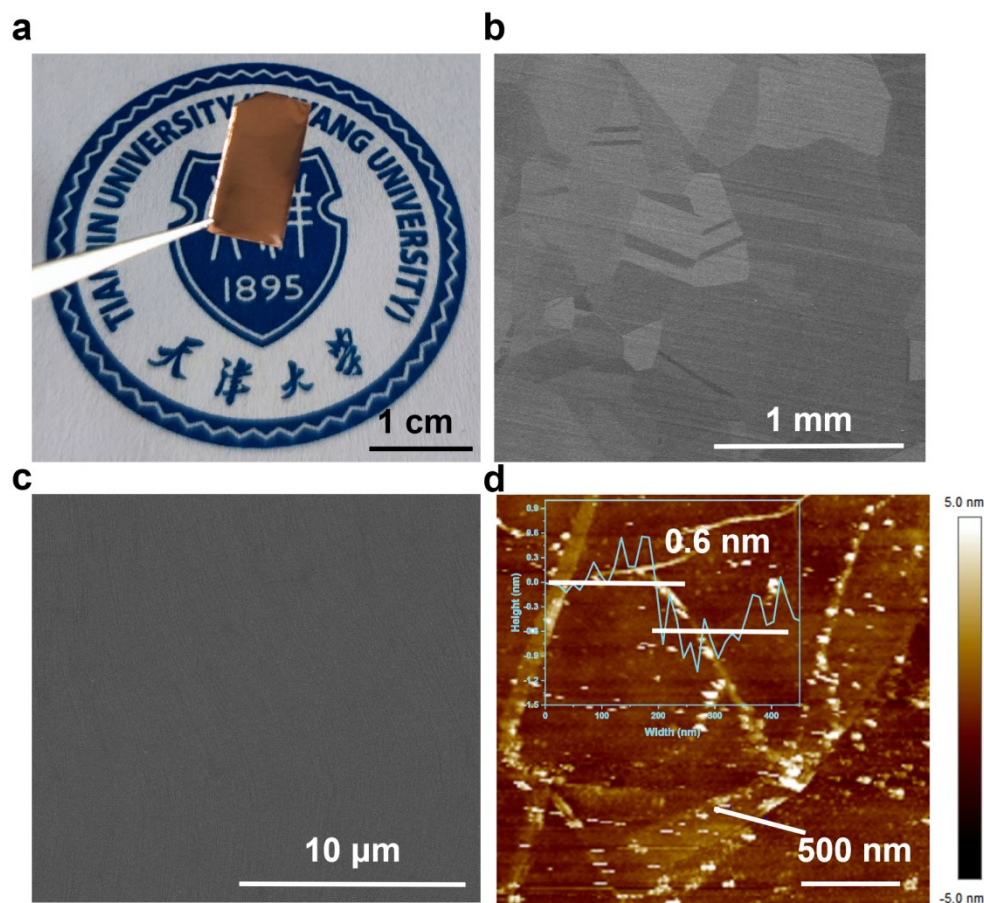
Classical molecular dynamics (MD) simulations were performed to further investigate the gas permeation behavior of the GAC membrane. The simulation system contained 2800 CH₄ molecules and 1200 CO₂ molecules initially positioned above the constructed membrane. An additional graphene sheet was placed at the top of the simulation box to confine the gas mixture and prevent molecular escape. To approximate an extended membrane surface, periodic boundary conditions were applied along the two in-plane directions of the membrane. All interatomic interactions were described using the Polymer Consistent Force Field (PCFF)³. For non-bonded interactions, the van der Waals contribution was described by the Lennard–Jones 9–6 potential with a cutoff radius of 10 Å. Partial atomic charges were assigned using the charge equilibration (QEq) method prior to the molecular dynamic simulations⁴. In the QEq scheme, the charge distribution is obtained by minimizing the electrostatic energy under the constraint of overall charge conservation, thereby equalizing the atomic chemical potentials according to element-specific electronegativity and hardness parameters. The resulting equilibrated charges were kept fixed during the subsequent simulations, while long-range electrostatic interactions were evaluated using the particle–particle particle–mesh (PPPM) method. The Lorentz-Berthelot mixing rule was adopted for the van der Waals interactions of different types of atoms. The detailed force field parameters for the GAC membrane, CO₂ and CH₄ were provided in Supplementary Tables 11-12. Before the simulations, energy minimization was conducted to obtain a locally stable configuration. The convergence tolerances for the system energy and atomic forces were set to 1.0×10^{-4} Kcal/mol and 1.0×10^{-4} Kcal/(mol·Å), respectively. Subsequently, MD simulations were conducted in the canonical ensemble (NVT) at 300 K for 10 ns with a timestep of 1.0 fs to evaluate the separation and permeation behavior of the CH₄/CO₂ mixture through the GAC membrane. During the simulations, a pressure of 1 bar was applied by exerting an external force to the upper graphene sheet. Meanwhile, the GAC membrane atoms were immobilized to prevent downward displacement of the membrane. Atomic trajectories were propagated according to Newton's equations of motion, which were integrated using the velocity-Verlet algorithm. All simulations

were carried out with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package⁵.

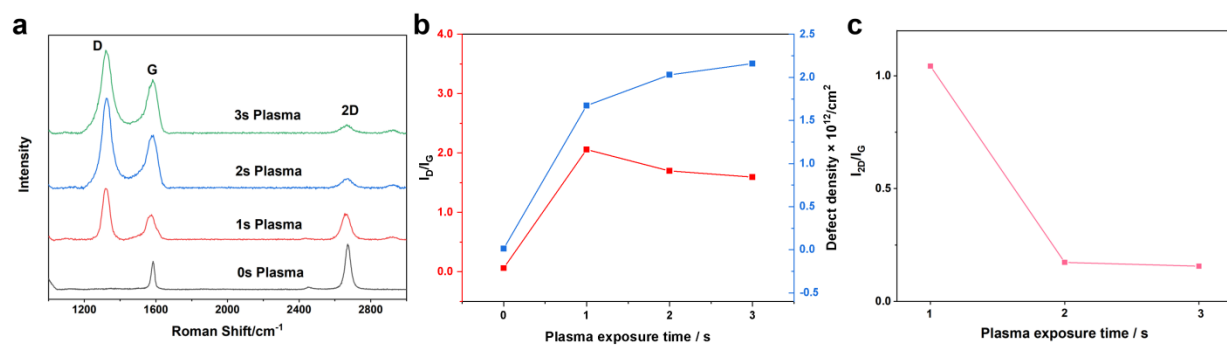
DFT calculation

All density functional theory calculations were performed using CP2K, version 2025.2. The Perdew–Burke–Ernzerhof generalized gradient approximation was adopted for the exchange–correlation functional, while long-range dispersion interactions were accounted for by Grimme’s D3 correction with Becke–Johnson damping^{6–8}. For the self-consistent electronic iterations, the convergence threshold was set to 1.0E-06. Structural relaxation was considered complete when the maximum atomic force and the maximum geometry displacement were below 4.5E-4 and 3E-3, respectively. These convergence settings were employed to obtain fully relaxed structures and stable electronic wavefunctions and total energies. Geometry optimizations were carried out using the DZVP-MOLOPT-SR-GTH basis set. To improve the accuracy of the calculated energies, subsequent single-point calculations were conducted with the larger TZV2P-MOLOPT-PBE-GTH basis set⁹. Independent Gradient Model based on Hirshfeld partitioning (IGMH) analyses were performed using Multiwfn version 2026.4.10, and the resulting interaction isosurfaces were rendered with VMD^{10–12}.

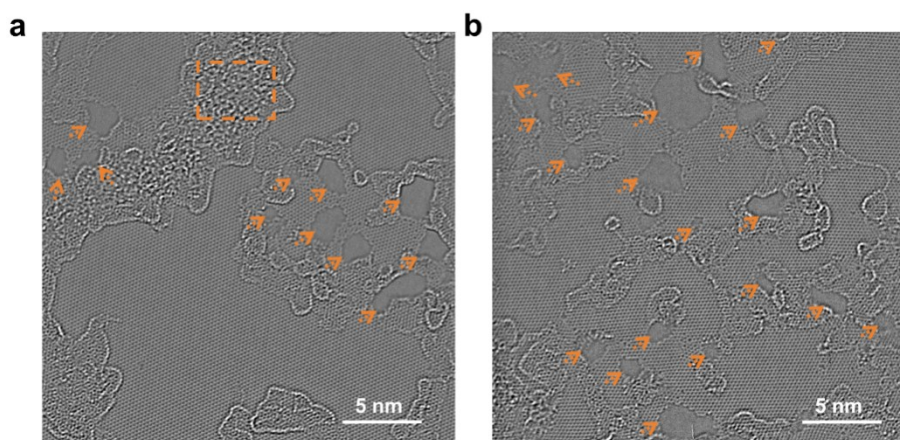
2. Supplementary figures



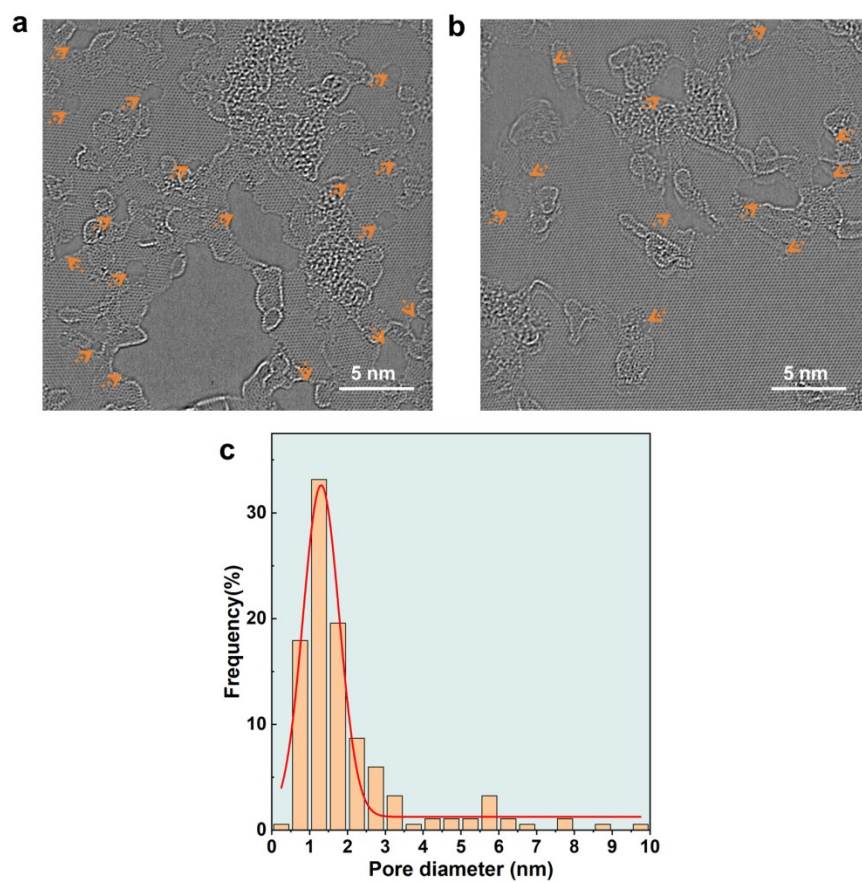
Supplementary Fig. 1 | Images of synthesized single layer graphene (SLG). **a**, Optical image of single layer graphene on copper foil. **b**, **c**, SEM images of single layer graphene on copper foil. **d**, AFM image of single layer graphene transferred onto silicon wafer.



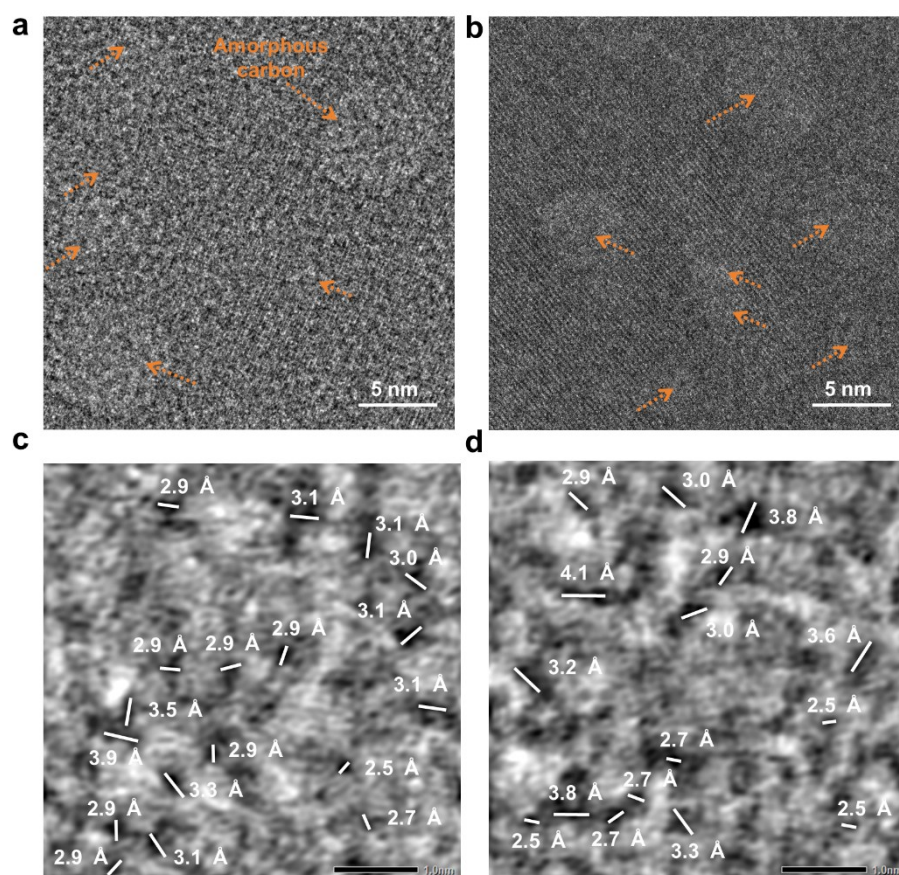
Supplementary Fig. 2 | Raman analysis of porous graphene. a, Raman spectra of oxygen plasma etching from 0 to 3 s. **b,** Changes in I_D/I_G and defect density with plasma etching time. **c,** Changes in I_{2D}/I_G with plasma etching time.



Supplementary Fig. 3 | AC-HRTEM images of single layer graphene after 2 s plasma etching (a, b). The arrows point to the nanopores, and the selected area is the contamination caused by paraffin-assisted wet-transfer. The experiment was repeated 15 times with the same results.



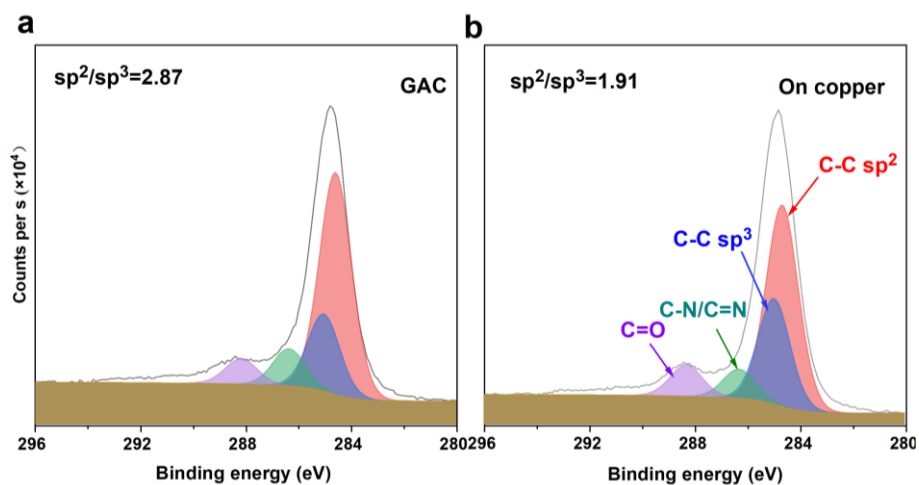
Supplementary Fig. 4 | AC-HRTEM images (a, b) and corresponding pore size distribution (c) of single layer graphene after 3 s plasma etching. The experiment was repeated 18 times with the same results.



Supplementary Fig. 5 | Structural characterization of pores in GAC film (500°C pyrolysis).

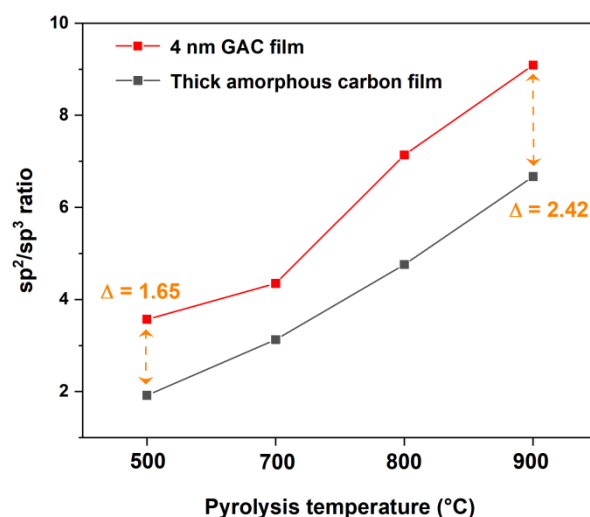
a, b, AC-HRTEM images of the GAC films, **c, d,** AC-STEM (Optimum Bright Field STEM) images of the GAC films.

The arrows in Supplementary Fig.5a-b show amorphous carbon masking the pores of graphene.



Supplementary Fig. 6 | XPS analysis of a 15 nm thick GAC film **(a)** and amorphous carbon film directly coated on copper **(b)**.

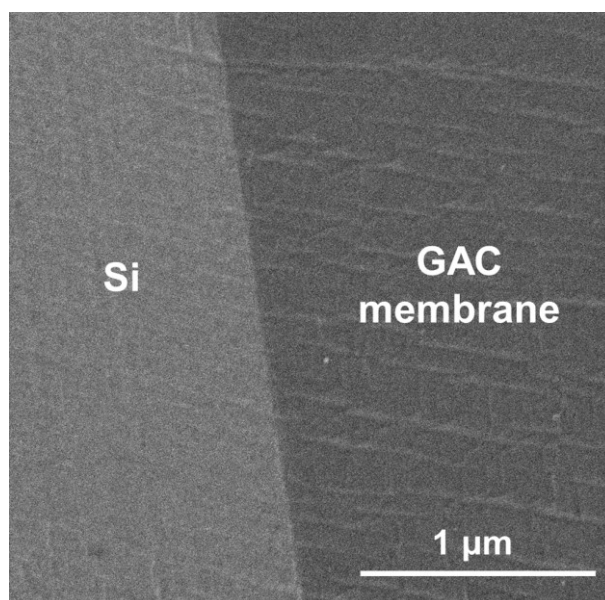
The detecting depth of XPS is about ~ 10 nm, thus, the graphene present in GAC films would contribute to the detected signal of sp^2 carbon. To eliminate this graphene-derived contribution, we prepared GAC films with a thickness greater than 10 nm.



Supplementary Fig. 7 | sp^2/sp^3 ratio evolution of both the GAC membrane and the pure amorphous carbon membrane as a function of pyrolysis temperature.

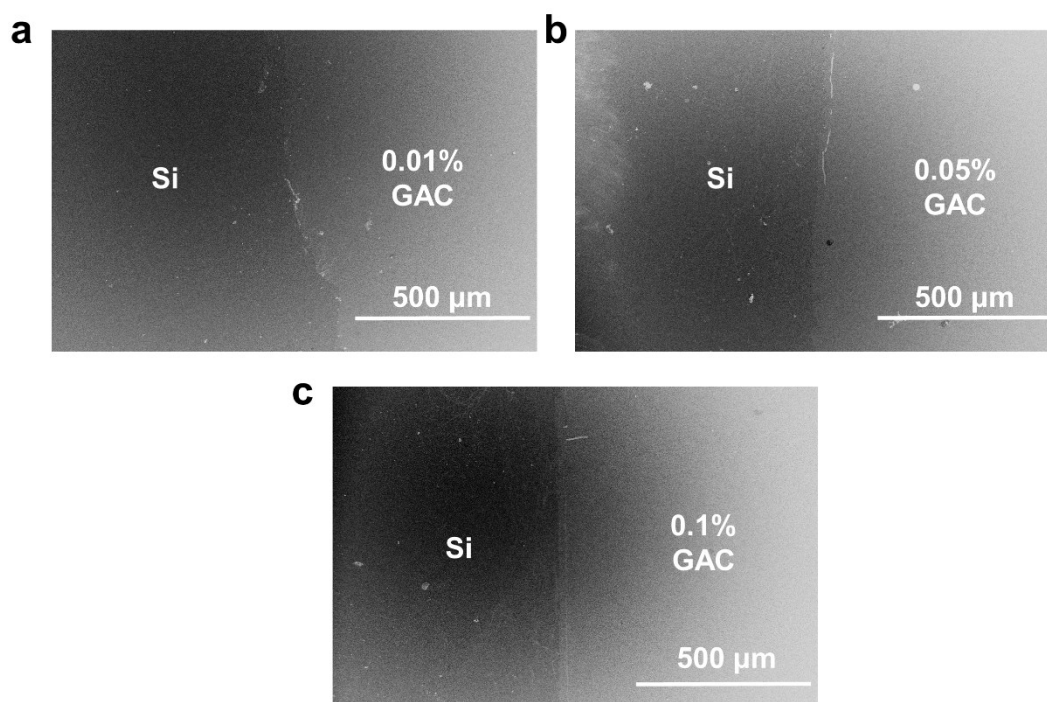
As the pyrolysis temperature increases from 500 °C to 900 °C, the sp^2/sp^3 ratio increases from 3.57 to 9.09, indicating progressive graphitization at higher temperatures. Importantly, these results correlate well with our AC-STEM (Fig. 1g-j) observations: higher pyrolysis temperatures not only increase the sp^2 fraction in the carbon network but also reduce the average pore size of the GAC membranes. This provides direct experimental evidence supporting the temperature-dependent mechanism of enhanced sp^2 formation and pore contraction.

To further clarify the role of the graphene layer in this temperature-dependent evolution, we also prepared thick amorphous carbon membranes ($\sim 35 \mu\text{m}$) without the graphene layer as a control. For the pure amorphous carbon membrane, the sp^2/sp^3 ratio also increases with pyrolysis temperature, from 1.92 to 6.67 as the temperature increases from 500 °C to 900 °C. Supplementary Fig.7 summarizes the sp^2/sp^3 ratio evolution of both the GAC membrane and the pure amorphous carbon membrane as a function of pyrolysis temperature. Compared with the pure amorphous carbon membrane, the GAC membrane consistently exhibits a higher sp^2/sp^3 ratio. Moreover, the difference in the sp^2/sp^3 ratio between the two membranes increases from 1.65 at 500 °C to 2.42 at 900 °C. This enlarged difference at higher temperature suggests that the graphene layer further promotes the graphitization of the adjacent polymer layer when the pyrolysis temperature increasing from 500 to 900 °C.

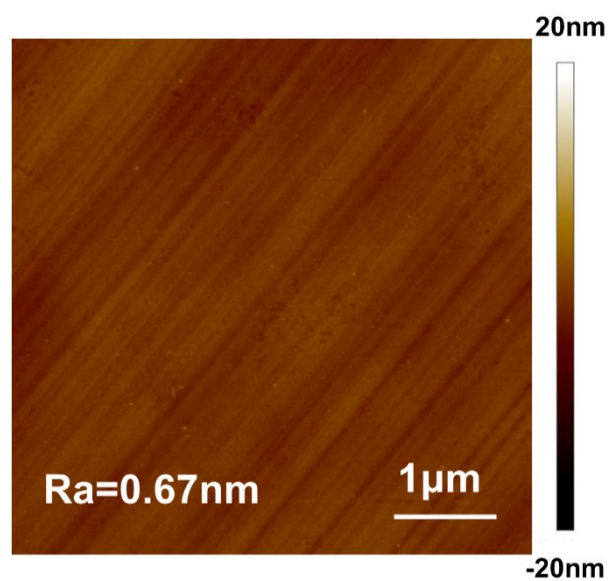


Supplementary Fig. 8 | SEM image of a 2nm GAC film.

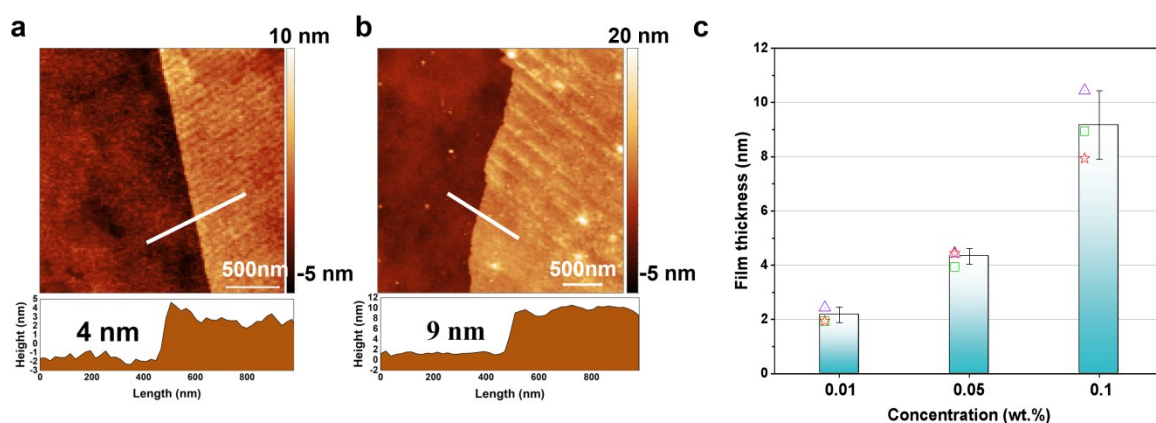
Cu substrates were etched in FeCl_3 (0.5 M). The resulting GAC films floating on the etchant surface were subsequently washed by HCl (0.1 M) and deionized water before being placed onto Si.



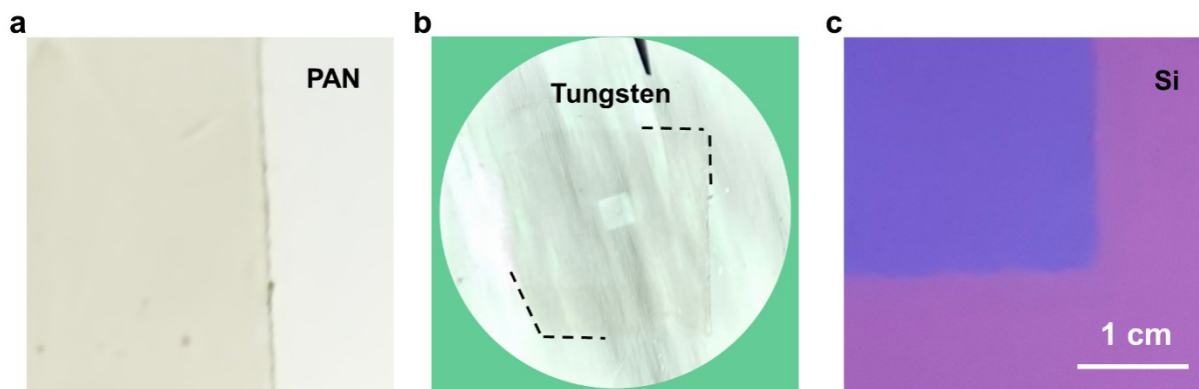
Supplementary Fig. 9 | SEM images of GAC films prepared with different concentrations of 6FDA-DAM precursors. a, 0.01 wt% 6FDA-DAM, b, 0.05 wt% 6FDA-DAM, c, 0.1 wt% 6FDA-DAM.



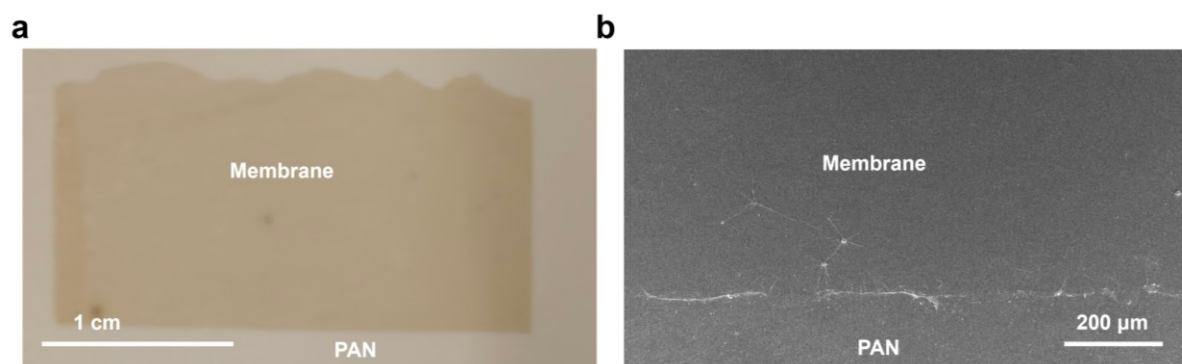
Supplementary Fig. 10 | AFM image of the GAC film. The root-mean-square roughness is 0.67nm.



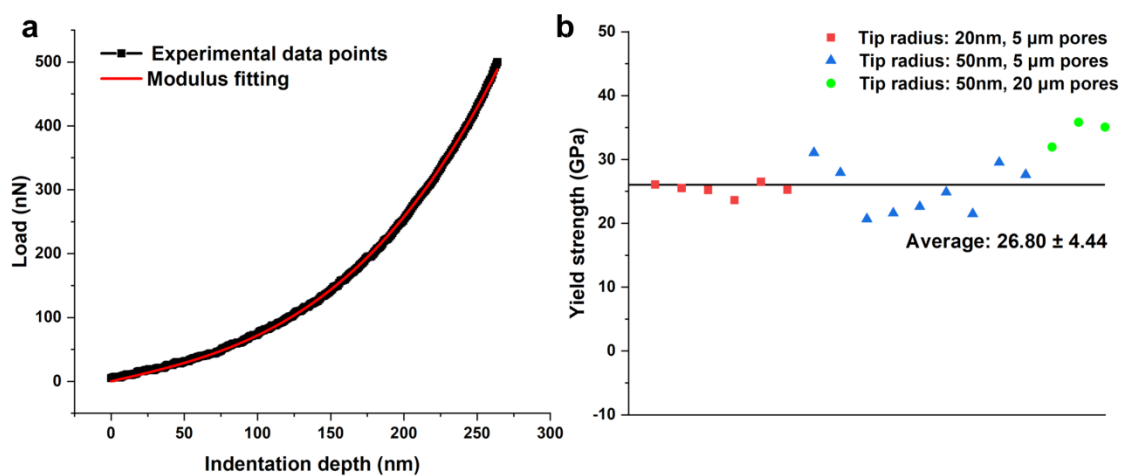
Supplementary Fig. 11 | AFM image of GAC films with different thickness (**a**, **b**), and the thickness of GAC film corresponding to different precursor concentrations (**c**). Data in **c** are presented as mean values $\pm$ SD. $n=3$ different membrane samples are measured independently for each data point.



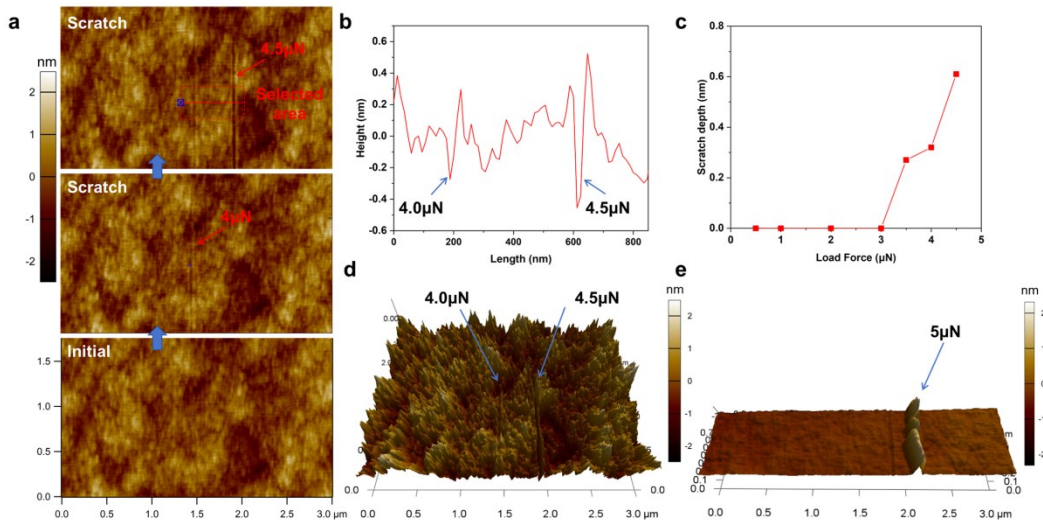
Supplementary Fig. 12 | Optical images of GAC films transferred onto various substrates. a, On PAN, **b,** On Tungsten, **c,** On Si wafer.



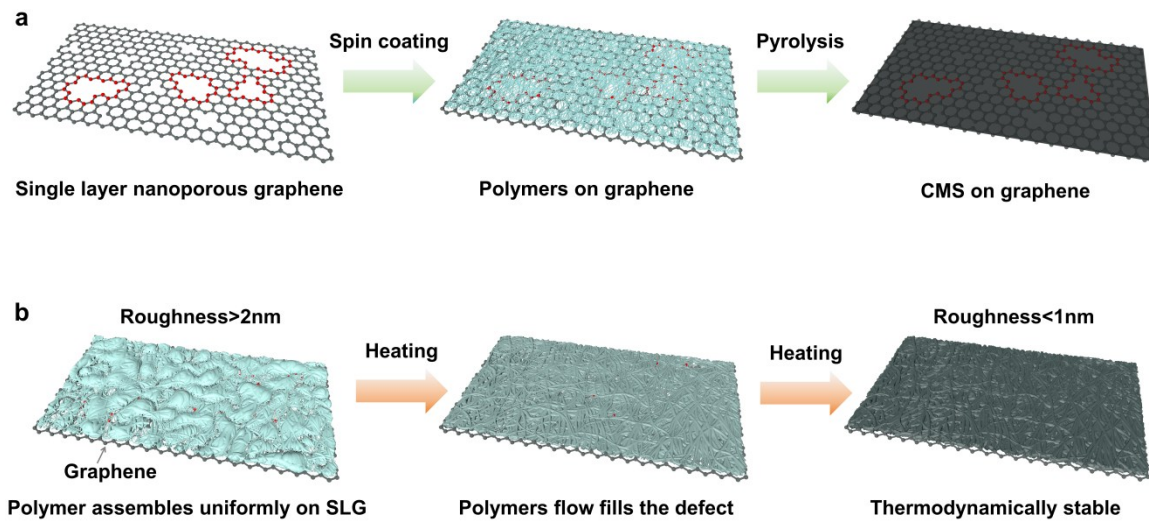
Supplementary Fig. 13 | Optical image (a) and SEM image (b) of GAC film after being bent on PAN.



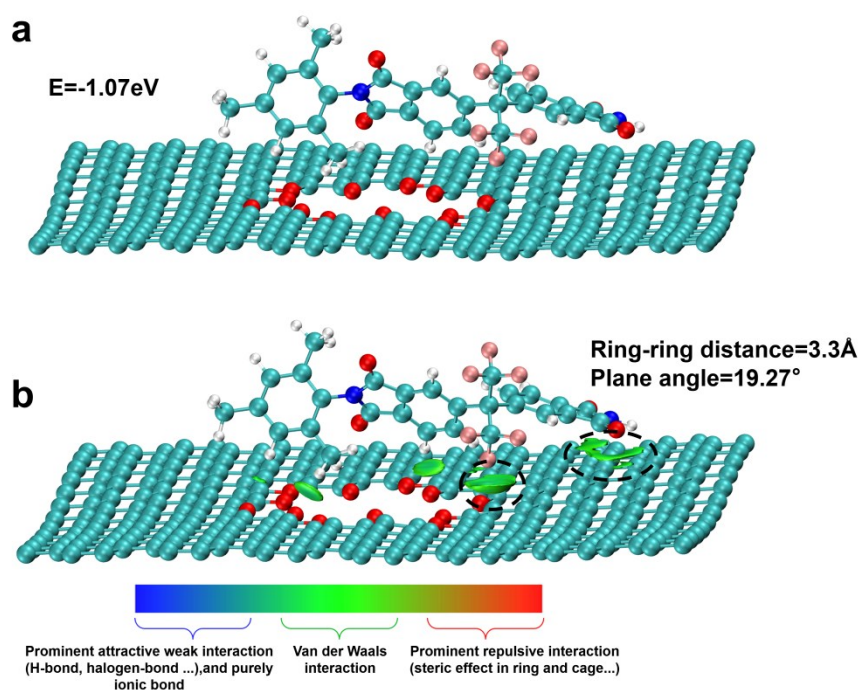
Supplementary Fig. 14 | **a**, Force-displacement curve and the fitting curve obtained from nanoindentation. **b**, Young's modulus at 18 points measured by two types of AFM probes.



Supplementary Fig. 15 | AFM-based nanoscratch tests. **a**, Scratched surface morphology at 4 μN and 4.5 μN load. **b**, Scratch cross-section profile of the area selected in Supplementary Fig.15a. **c**, Scratch depth as a function of load Force. **d**, 3D scratched surface morphology at 4 μN and 4.5 μN load. **e**, 3D scratched surface morphology at 5 μN load.



Supplementary Fig. 16 | **a**, Schematic diagram of the synthesis of GAC film. **b**, Schematic diagram of the morphological evolution of GAC film at different formation stages.



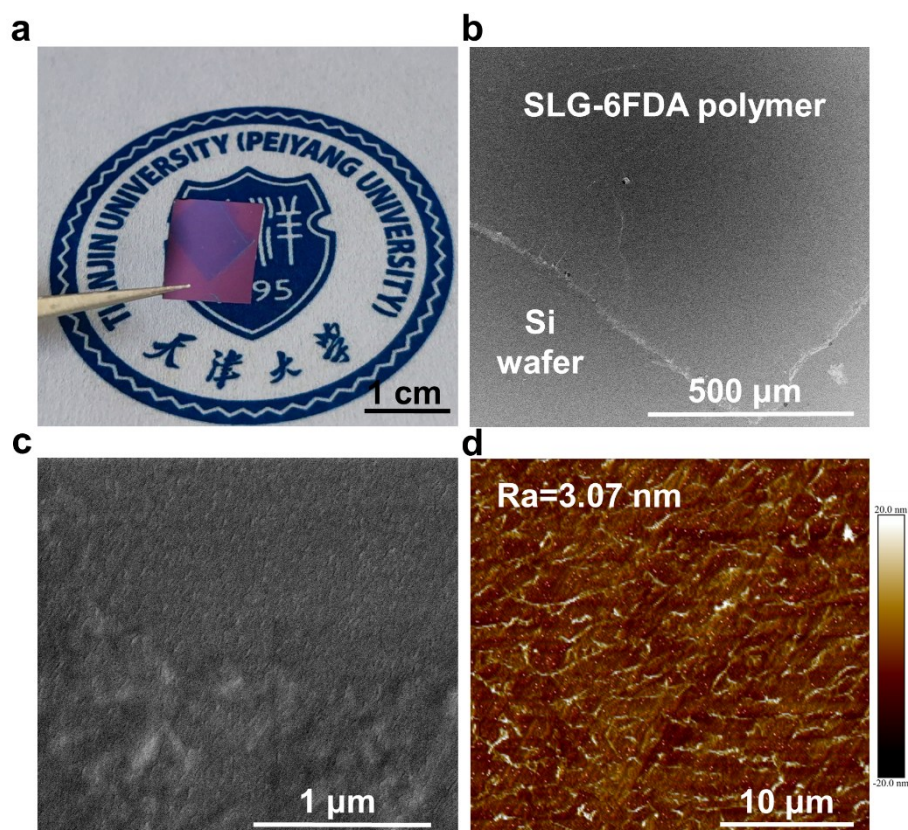
Supplementary Fig. 17 | DFT calculation. **a**, DFT structural optimization and binding energy calculation. **b**, Visualization of binding energy (IGMH).

To provide direct evidence for the interfacial interactions between graphene and the aromatic polyimide precursor, we performed density functional theory (DFT) calculations together with independent gradient model based on Hirshfeld partition (IGMH) analysis. As shown in Supplementary Fig.17a, the calculated interaction energy between the polymer precursor and graphene is -1.07 eV , indicating a strong interfacial interaction that can stabilize polymer adsorption on the graphene surface. The IGMH simulation results (Supplementary Fig.17b) identify five interaction regions, primarily belonging to π - π interactions or van der Waals interactions. Two key interaction sites stand out:

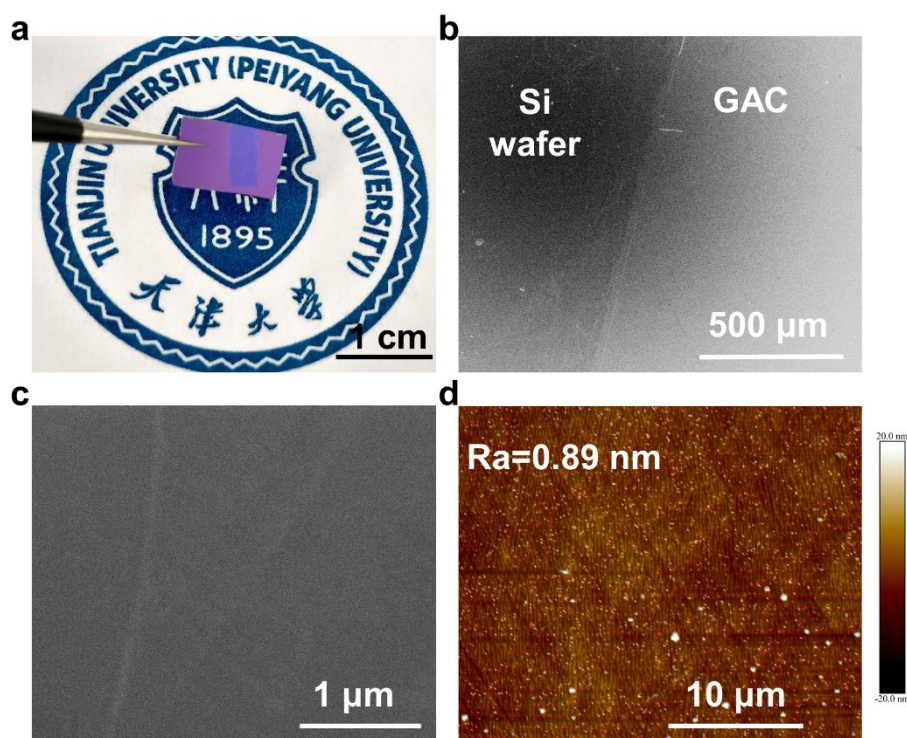
(i) π - π interactions between aromatic rings/N-containing five-membered rings in the polymer and the graphene basal plane: These interactions are characterized by a ring-to-ring distance of approximately $3.3 \text{ \AA}$ and a plane angle of 19.27° , which are consistent with typical π - π stacking configurations reported in aromatic carbon systems.

(ii) Interaction between the polymer $-\text{CF}_3$ groups and the graphene aromatic surface: The electron-rich π -system of graphene can engage in significant London dispersion forces with the electron-withdrawing $-\text{CF}_3$ moieties.

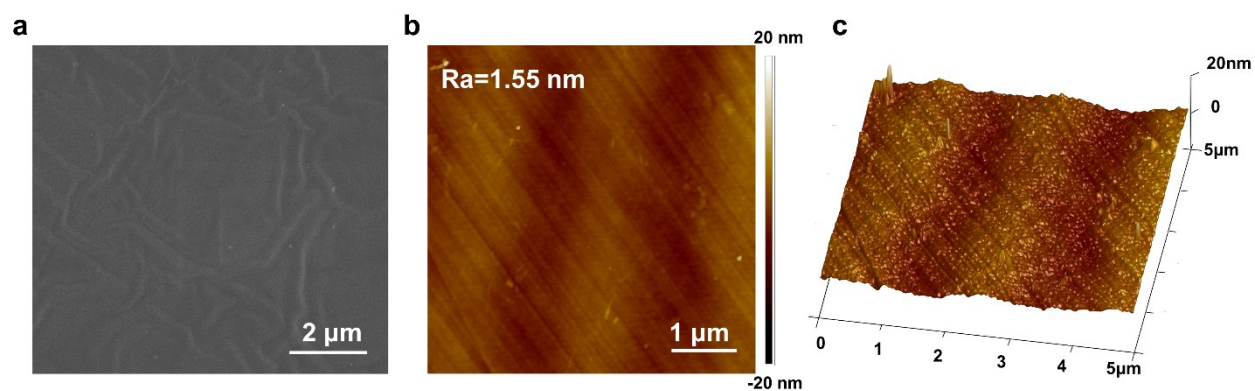
These interfacial interactions are expected to reduce the free energy barrier for heterogeneous nucleation, and promote preferential adsorption/orientation of polymer chains on graphene, thereby substantially increasing nucleation density and ultimately enabling the formation of ultrathin and compact membrane structures.



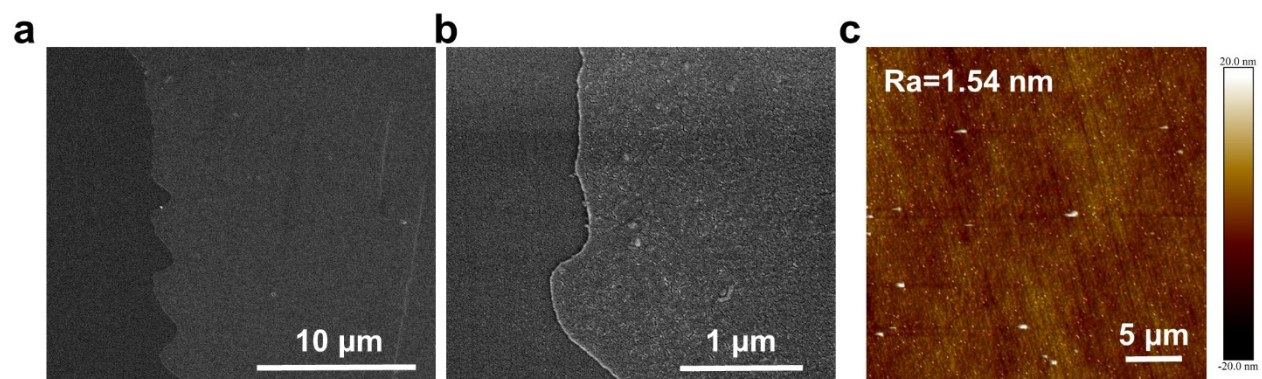
Supplementary Fig. 18 | Images of SLG-6FDA-DAM polymer bilayer film. Optical image (a), SEM images (b, c), and AFM image (d) of SLG-6FDA-DAM polymer bilayer film. The root-mean-square roughness is 3.07 nm.



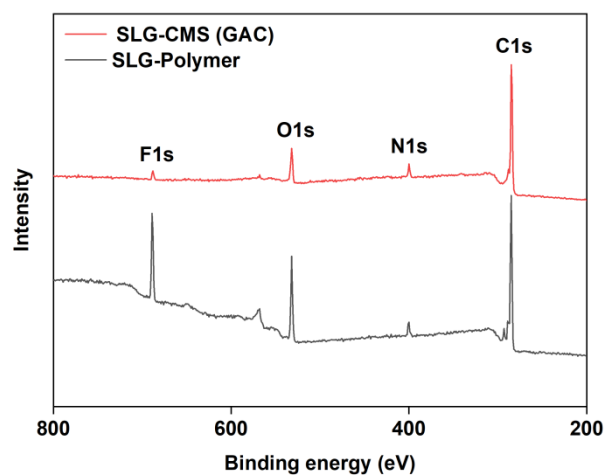
Supplementary Fig. 19 | Images of GAC film. Optical image (a), SEM images (b, c), and AFM image (d) of GAC film. The root-mean-square roughness is 0.89 nm.



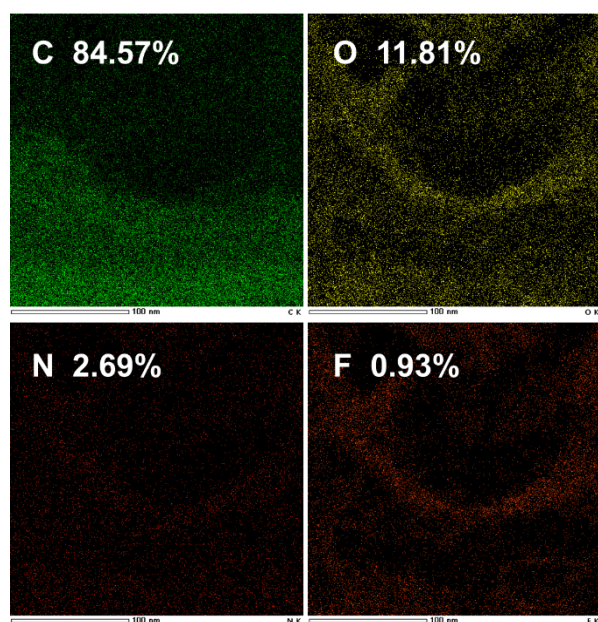
Supplementary Fig. 20 | SEM (a) and AFM (b, c) images of GAC film prepared by rapid heating (constant heating rate of 13.3 $^{\circ}\text{C}/\text{min}$).



Supplementary Fig. 21 | SEM images (a, b) and AFM image (c) of amorphous carbon films directly prepared on copper.

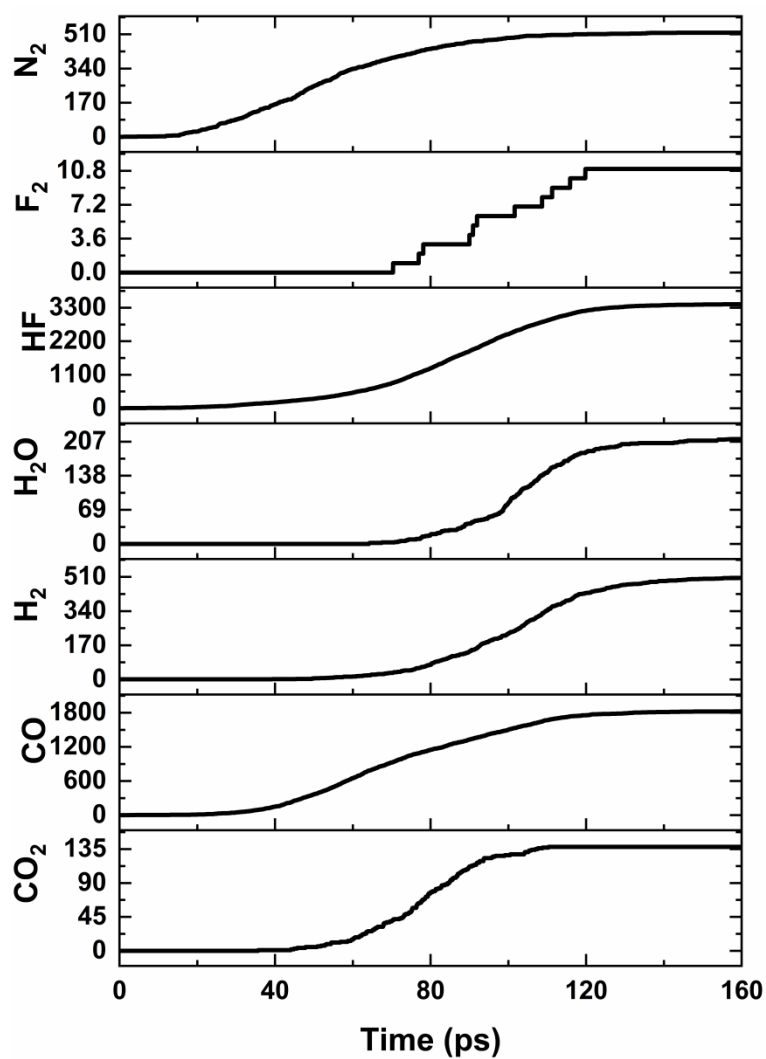


Supplementary Fig. 22 | XPS analysis of the SLG-6FDA-DAM polymer bilayer film and pyrolyzed GAC film. The changes in elemental content before and after pyrolysis are listed in Supplementary Table 2.



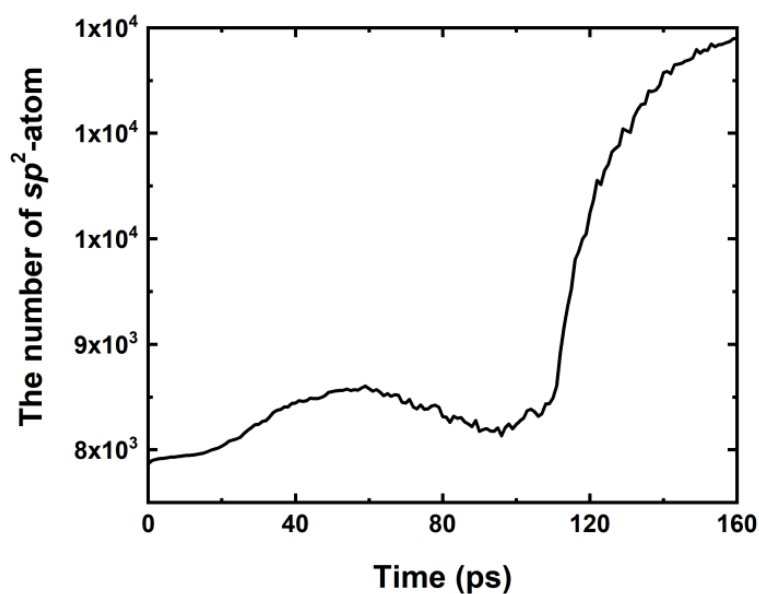
Supplementary Fig. 23 | EDS analysis of the GAC film.

The results of XPS and EDS indicate that the carbon content in GAC film is greater than 80% (Supplementary Figs.22 and 23, Supplementary Table 2), and the high carbon content is conducive to forming a more stable framework.



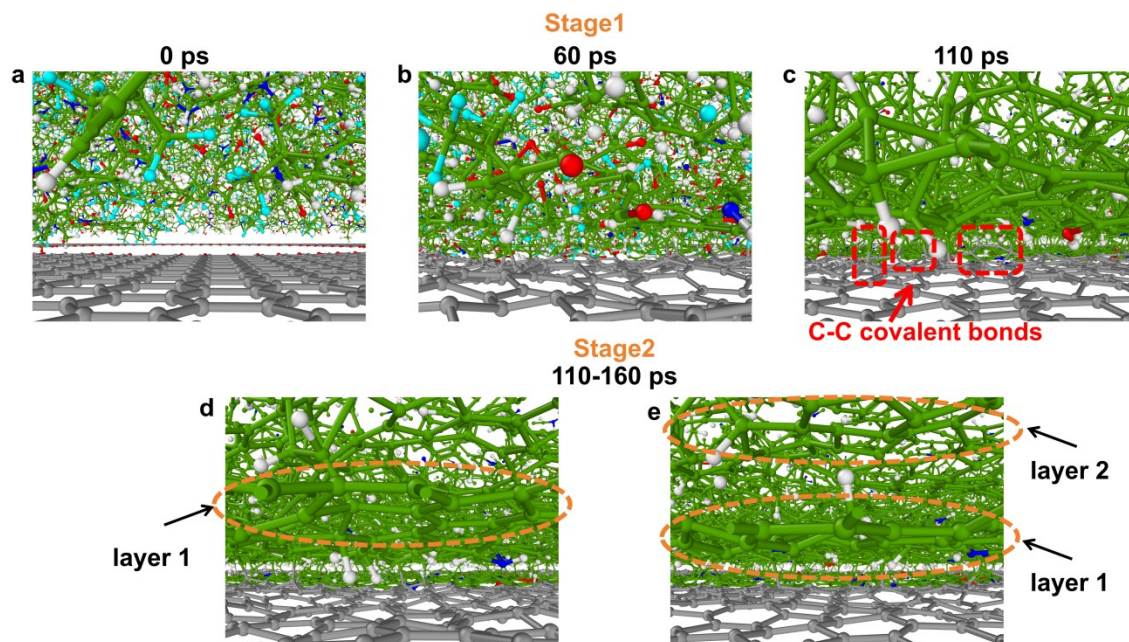
Supplementary Fig. 24 | Changes in the number of small molecules produced by pyrolysis over time.

Polymer chains undergo cleavage and aromatization during pyrolysis, converting into shorter rigid carbon chains while releasing small gases.



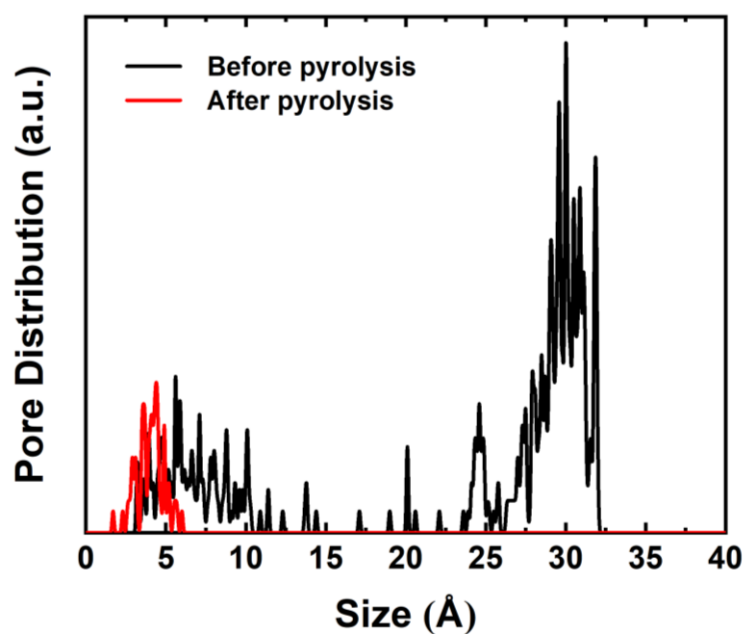
Supplementary Fig. 25 | Changes in the number of sp^2 carbons over time during pyrolysis.

This stage involves a slight increase in sp^2 carbon as heteroatom content decreases, followed by a transient decline in sp^2 carbon as extensive polymer decomposition takes place. Then, the graphene induces local graphitization, driving a rapid increase in sp^2 carbon.

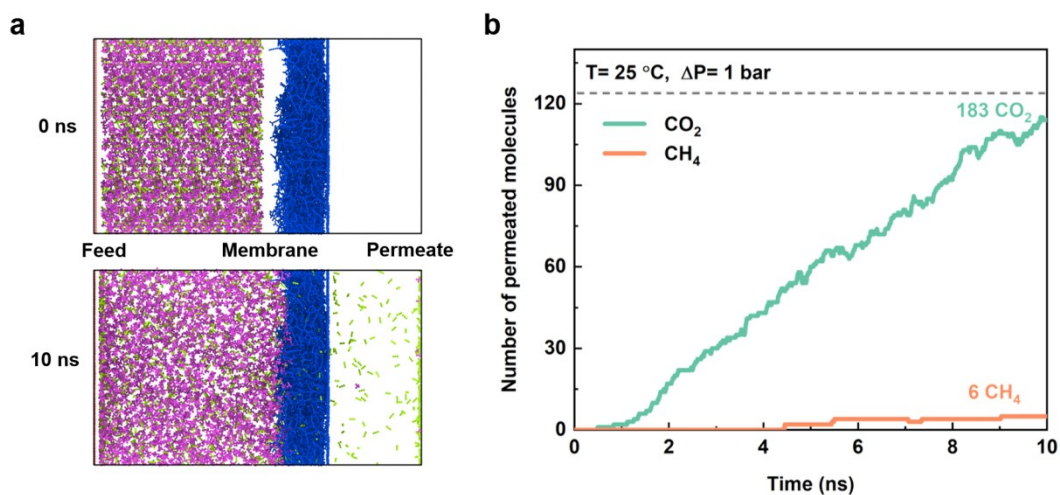


Supplementary Fig. 26 | Structural changes of GAC film during pyrolysis. C (green), N (dark blue), O (red), F (fluorescent blue), H (grey). This process demonstrates that the polymers gradually become ordered during pyrolysis, and the C-C covalent bonds are formed in situ between the polymer and graphene.

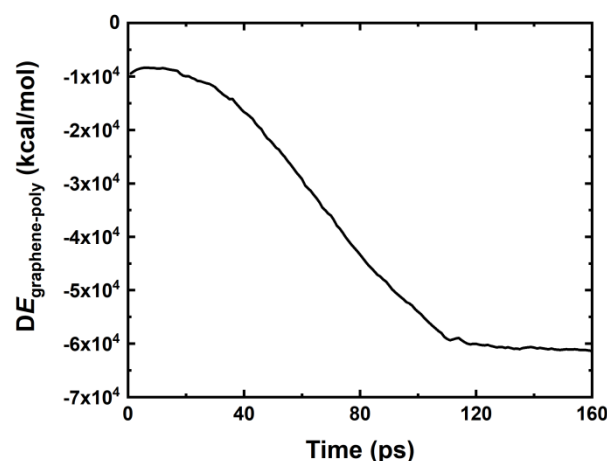
Initially, the polymer spin-coated on the graphene surface exhibits weak interfacial adhesion. Upon pyrolysis, it gradually integrates with the graphene, forming partial covalent bonds. The resulting amorphous carbon undergoes structural ordering and subsequently subdivides the non-selective pores of the graphene.



Supplementary Fig. 27 | Simulated pore size distribution of the SLG-6FDA-DAM polymer bilayer film and pyrolyzed GAC film.



Supplementary Fig. 28 | MD simulation of gas transport. **a**, Initial (0 ns) and final (10 ns) snapshots of CO₂ and CH₄ transport through the GAC membrane under 25°C and 1 bar. **b**, Number of permeated gases as a function of time under 25°C and 1 bar.

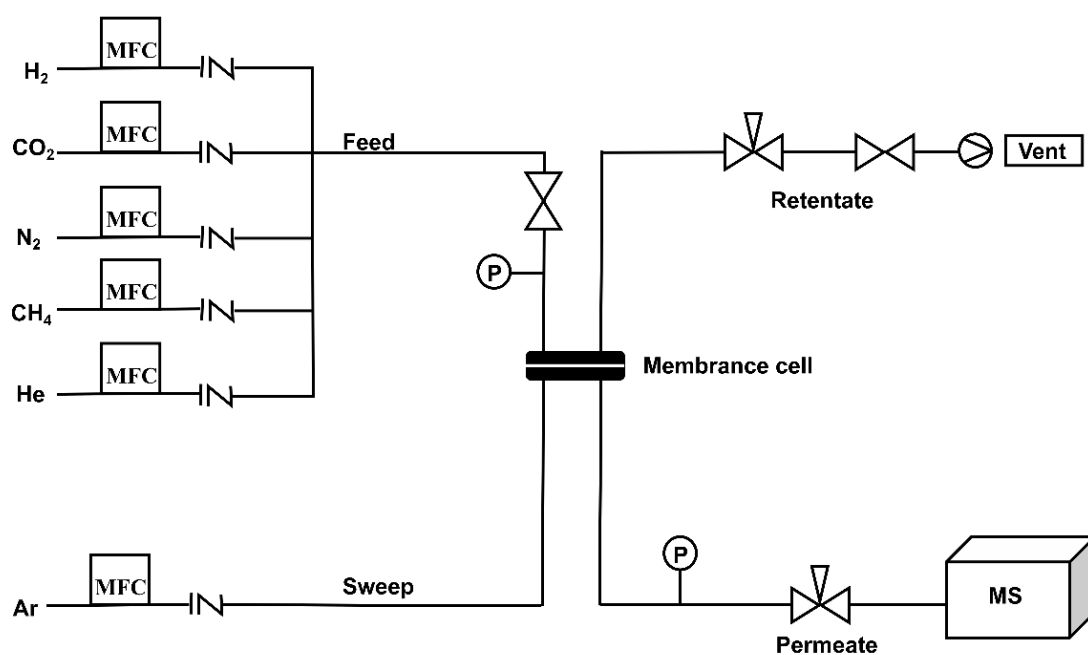


Supplementary Fig. 29 | The interaction energy between graphene and polymers varies with pyrolysis time.

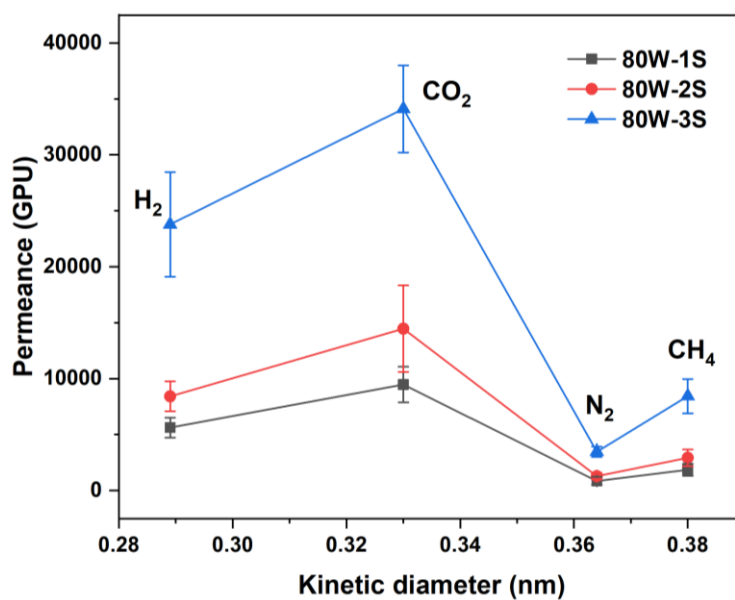
During the thermal treatment, the interaction between the polymer and graphene intensifies, eventually forming a strongly coupled sp^2 -hybridized interfaces.

The simulated evolution can be divided into two stages. In the first stage, defined as the interfacial reconstruction stage from 0 to 110 ps, polyimide chains near the graphene surface undergo rapid rearrangement, establishing stable π - π stacking and C-C covalent bonds with the graphene lattice (Supplementary Fig.26 a-c). This process enlarges the interfacial contact area and causes a sharp increase in the graphene-polymer interaction energy, which soon reaches a plateau (Supplementary Fig.29). During this period, the graphene surface promotes the sp^2 conversion of the adjacent polymer chains, forming an ordered sp^2 -hybridized planar layer at the interface (Supplementary Fig.25, 0–60 ps). Subsequently, from 60 to 110 ps, ongoing pyrolytic fragmentation and the release of gaseous by-products from the polymer matrix cause a slight drop in the overall sp^2 carbon fraction.

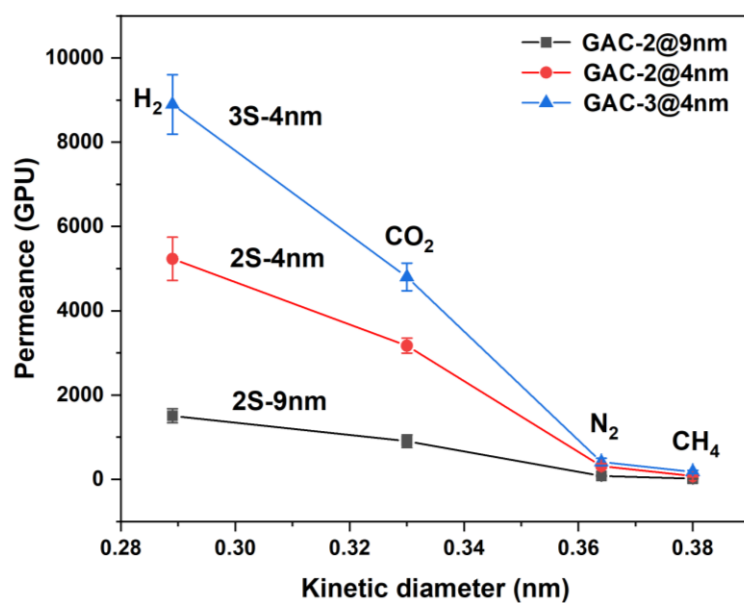
In the second stage, after approximately 110 ps, the interfacial structure becomes relatively stable, and the graphene-polymer interaction remains nearly constant. At this stage, the already formed ordered sp^2 carbon layer, anchored on graphene, serves as a template to induce graphitization and sp^2 conversion of the polymer layer immediately above it. This newly graphitized layer, in turn, promotes the ordering of the next adjacent layer, propagating the structural transformation in a layer-by-layer manner (Supplementary Fig.26 d-e). Consequently, the sp^2 carbon fraction rises markedly during this stage (Supplementary Fig.25, 110–160 ps), reflecting the successive formation of additional ordered carbon layers.



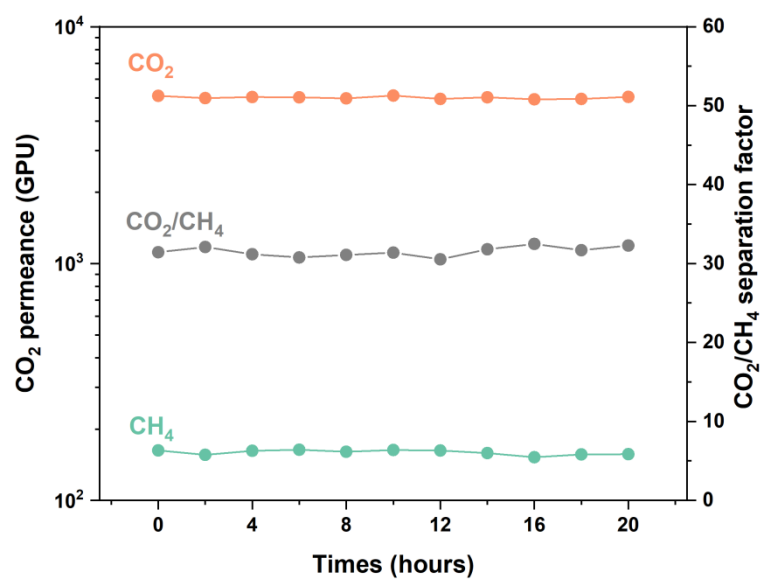
Supplementary Fig. 30 | Schematic diagram of gas separation performance testing device.



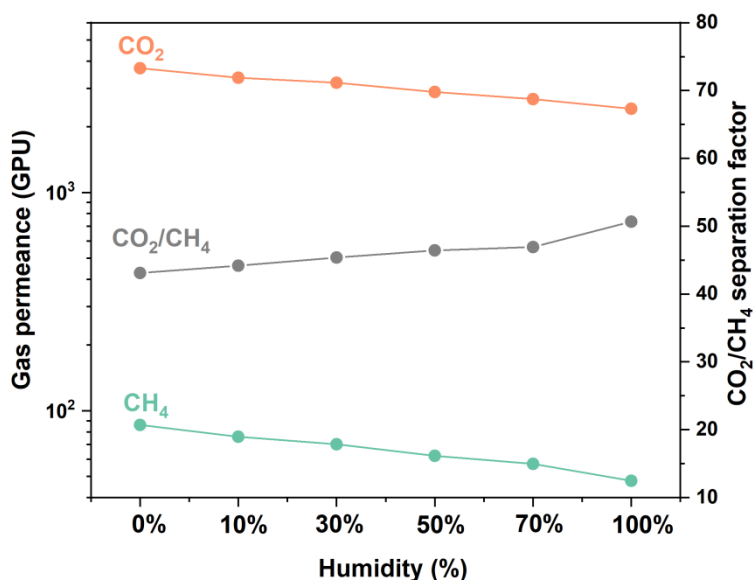
Supplementary Fig. 31 | Pure gas performance of SLG membranes under different plasma etching times. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



Supplementary Fig. 32 | Pure gas performance of GAC membranes with different plasma etching times and thicknesses. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



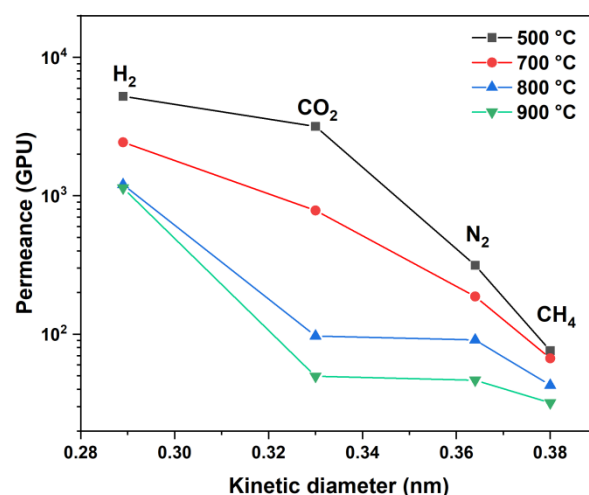
Supplementary Fig. 33 | CO₂/CH₄ mixed gas separation performance of the GAC-3@4 nm membrane.



Supplementary Fig. 34 | CO₂/CH₄ mixed-gas permeation measurements under controlled relative humidity (RH) conditions.

We performed CO₂/CH₄ mixed-gas permeation measurements under controlled relative humidity (RH) conditions ranging from 0% to 100%. The result indicates that increasing humidity leads to a gradual decrease in CO₂ permeance, while the CO₂/CH₄ selectivity slightly increases. This behavior can be attributed to competitive adsorption and partial pore blockage by water molecules: water molecules preferentially occupy some ultramicropores and decrease the effective pore size, reducing the CO₂ permeance. Meanwhile, the diffusion of the larger CH₄ molecules is more strongly hindered in the reduced pore size. As a result, the CO₂/CH₄ selectivity increases with increasing the humidity.

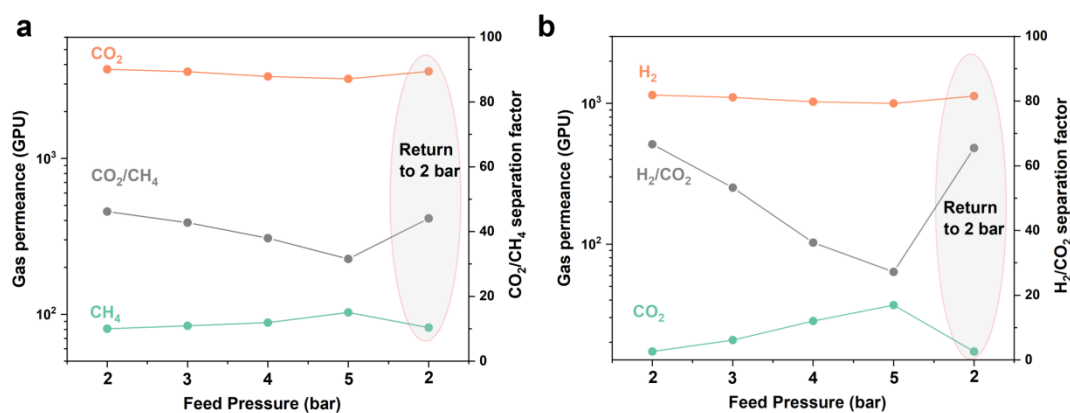
Notably, even at 100% RH, the GAC membranes maintain high CO₂ permeance (>2400 GPU) and excellent selectivity (>50), demonstrating robust performance under humid conditions relevant for practical CO₂ separation applications.



Supplementary Fig. 35 | Single gas measurements of 6FDA-DAM-derived GAC membrane at different pyrolysis temperatures under 25 °C and 2bar.

As shown in Supplementary Fig. 35, when the pyrolysis temperature is 500 °C, the membranes show a high CO₂/CH₄ selectivity of 47.7. This indicates that the effective ultramicropore size falls between the kinetic diameters of CO₂ (3.30 Å) and CH₄ (3.80 Å), allowing CO₂ to permeate while effectively blocking CH₄. This pore-size range is consistent with AC-STEM observations (Fig. 1g), which shows a distribution of 3.1–5.1 Å, with the majority of narrow pores residing within the discriminating window. Thus, at this stage the molecular cut-off lies between CO₂ and CH₄.

When the pyrolysis temperature increases to 700 °C, the CO₂/CH₄ selectivity decreases to 11.7, and the H₂/CO₂ selectivity remains low. This behavior suggests that the effective pores have shrunk but are still larger than the CO₂ kinetic diameter. When the pyrolysis temperature reaches 900 °C, the pore size further decreases (1.5–3.2 Å, Fig. 1j), shifting the molecular sieving cut-off from CO₂/CH₄ to H₂/CO₂. This trend is consistent with the AC-STEM imaging (Fig. 1g-j), which confirms that higher pyrolysis temperatures progressively reduce the ultramicropore size, enabling selective H₂ transport while blocking CO₂. In contrast, conventional 6FDA-based carbon molecular sieve membranes generally show enhanced CO₂/CH₄ selectivity with increasing pyrolysis temperature, but without a clear shift in the molecular cut-off^{13, 14}, highlighting the key role of graphene in regulating the pore size of the amorphous carbon layer.



Supplementary Fig. 36 | The the pressure resistance of GAC membrane. **a**, Pressure transformation test of 6FDA-DAM-derived GAC membrane at 25°C and CO₂/CH₄ (3/7 mixtures). **b**, Pressure transformation test of Matrimid-derived GAC membrane at 150°C and H₂/CO₂ (5:5 vol%).

We systematically evaluated the gas separation performance of two representative membranes, namely the 6FDA-DAM-derived GAC membrane (Supplementary Fig.36a) and the Matrimid-derived GAC membrane (Supplementary Fig.36b), under feed pressures ranging from 2 to 5 bar. The results reveal two contrasting trends: a decrease in the permeance of the faster gas and an increase in that of the slower gas, as explained below.

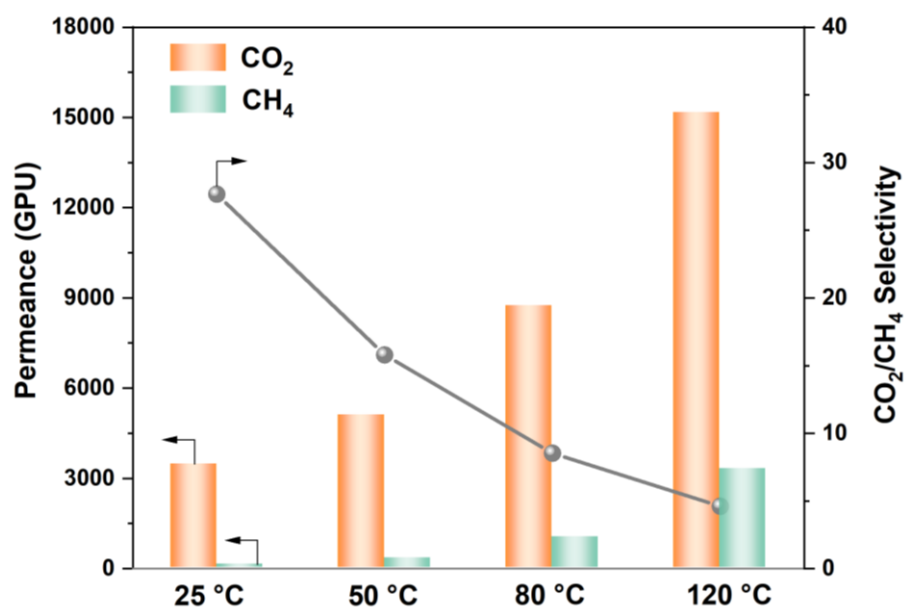
First, the increase in permeance of the slower gas (CH₄ or CO₂) could be attributed to the slight dilation of sub-nanopores in suspended ultrathin GAC membrane under pressure. As the feed pressure increases, slight dilation of a small fraction of sub-nanopores may occur. Such reversible dilation can reduce the activation barrier for the transport of larger and slower gas molecules, thereby decreasing their diffusion resistance and increasing their permeance. Although such effect also facilitates the transport of the smaller gas molecules (CO₂ or H₂), the smaller gas already exhibits a much higher permeance; therefore, the relative increase is less pronounced. In contrast, because the slower gas has a much lower permeance, even a small pressure-assisted enhancement can lead to an appreciable increase in the permeance.

Second, the decrease in permeance of the faster gas (CO₂ or H₂) at elevated pressure is mainly associated with adsorption saturation and competitive adsorption effects. (i) For the 6FDA-DAM-

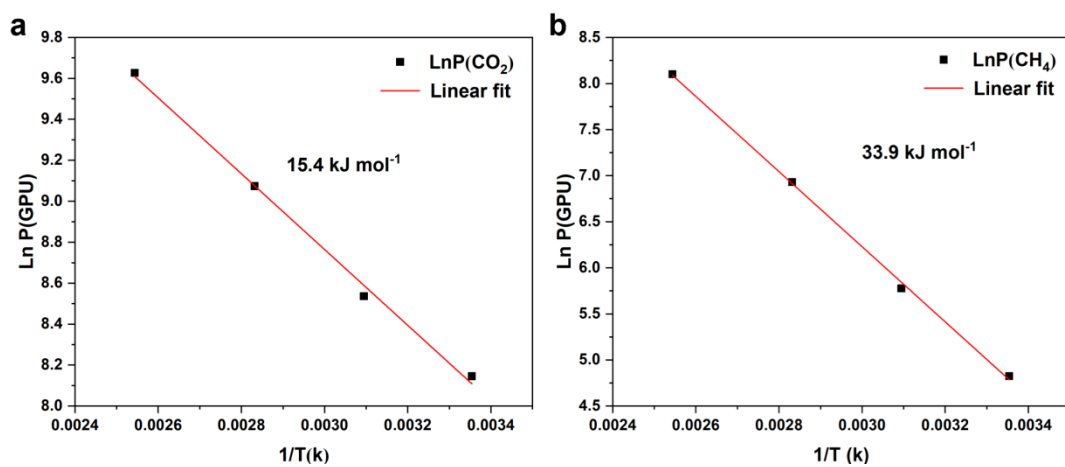
derived GAC membrane used for CO₂/CH₄ separation, CO₂ is preferentially adsorbed at low CO₂ partial pressure. Under these conditions, the CO₂-affinitive sites within the GAC membrane are not saturated, allowing most CO₂ molecules to be rapidly and selectively captured, which enhances the CO₂ permeance. In contrast, at high CO₂ partial pressure, the adsorption sites approach saturation, leading to a high fractional surface coverage on both the feed and permeate sides. This reduces the concentration gradient of adsorbed CO₂ across the membrane, thereby lowering the effective driving force for surface diffusion. Furthermore, the reduced availability of vacant adsorption sites within the micropores hinders the molecular jumping, which decreases the CO₂ diffusivity. Consequently, the CO₂ permeance slightly decreases with increasing feed pressure.

(ii) For the Matrimid-derived GAC membrane used for H₂/CO₂ separation, the decrease in H₂ permeance at higher pressure is also attributed to the aforementioned adsorption effects. In this specific case, CO₂ molecules, being more strongly adsorbing than H₂, can occupy a larger fraction of the adsorption sites, which restricts the passage of H₂. As a result, the H₂ permeance decreases with increasing pressure. It should be noted that such a pressure-dependent decline in permeance is a common characteristic observed in microporous molecular-sieving membranes.

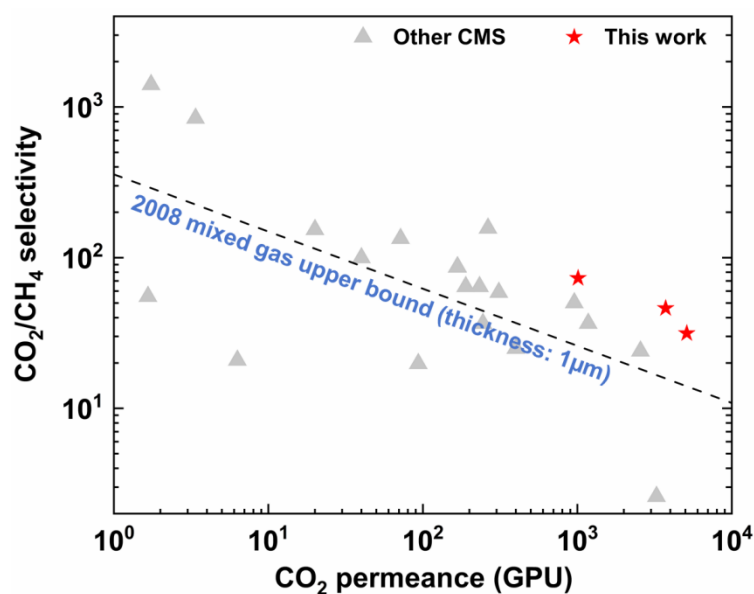
Notably, when the feed pressure is reduced back to 2 bar, the original membrane performance is fully recovered, indicating that the GAC membranes do not undergo permanent structural damage during pressure cycling. These results demonstrate that the GAC membranes can tolerate pressure fluctuations while maintaining their structural integrity. Nevertheless, despite the decrease in selectivity at 5 bar, the membrane still maintains appreciable separation performance, with CO₂/CH₄ selectivity remaining at 31.6 and H₂/CO₂ selectivity remaining at 27.2, respectively. Considering the extremely small selective-layer thickness (~4 nm), such reversible pressure tolerance is already remarkable. In contrast, many ultrathin membranes reported in the literature exhibit irreversible structural failure or permanent performance deterioration under elevated pressure conditions¹⁵⁻¹⁷.



Supplementary Fig. 37 | Performance of GAC membrane on CO₂/CH₄ mixture at different temperatures.

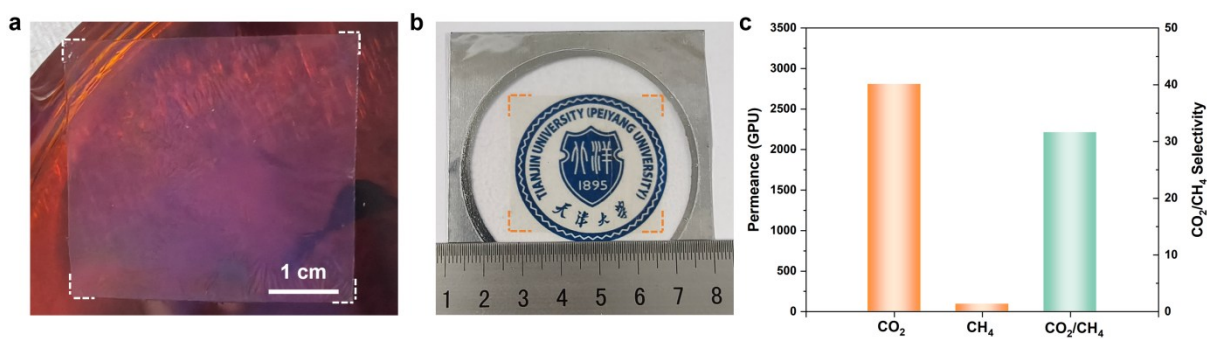


Supplementary Fig. 38 | Fitting curves of apparent activation energies of CO₂ (a) and CH₄ (b).

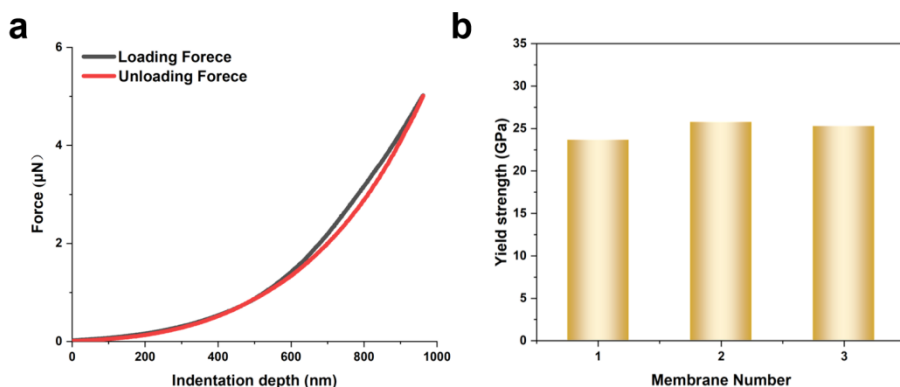


Supplementary Fig. 39 | Comparison of CO_2/CH_4 mixed gas separation performance between GAC membranes and traditional carbon molecular sieve membranes. Source data are supplied in Supplementary Table 5.

The thickness of GAC membranes is two to three orders of magnitude thinner than previously reported CMS membranes, leading to a record-breaking CO_2 permeance.



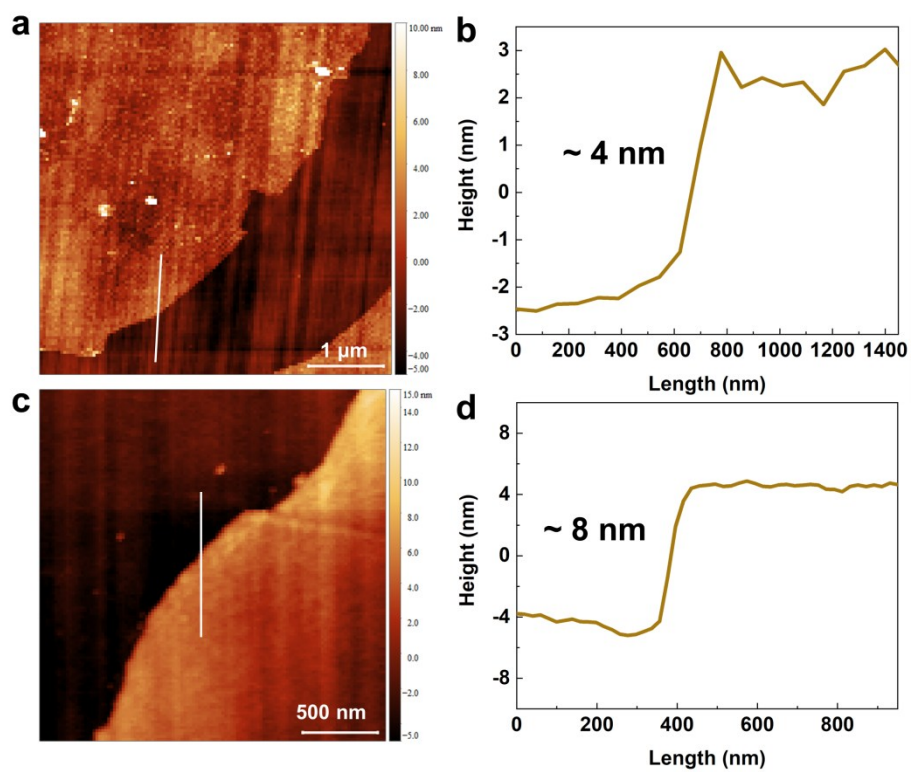
Supplementary Fig. 40 | Optical image and performance of the centimetre-scale GAC membrane. **a**, GAC membrane suspended on FeCl_3 solution. **b**, GAC membrane on AAO support. **c**, CO_2/CH_4 separation performance (3/7 mixtures) of the GAC membranes.



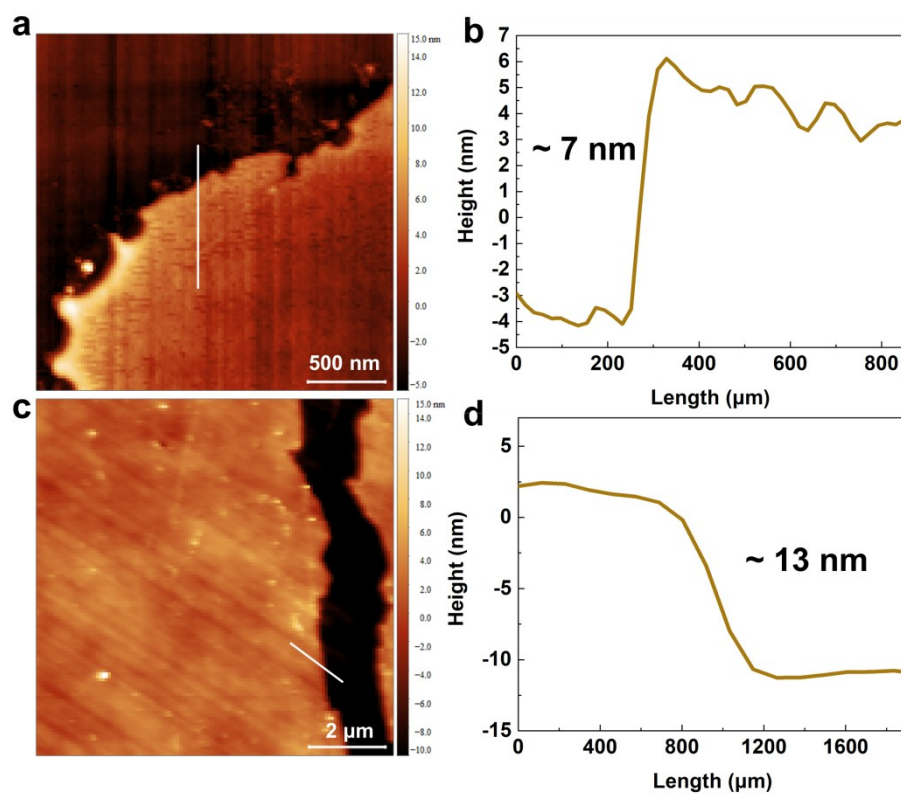
Supplementary Fig. 41 | AFM nanoindentation measurements of GAC membrane after gas separation operation. **a**, Force-displacement curve of the post-separation GAC membrane. **b**, Young's modulus of the post-separation GAC membrane.

To further verify the mechanical integrity of the GAC membrane after gas separation operation, we performed additional AFM nanoindentation measurements on membranes subjected to the same conditions used in the gas separation experiments. Specifically, the GAC membrane supported on porous silicon was placed in a membrane cell under a CO₂/CH₄ atmosphere at 25 °C and 2 bar for 24 h, consistent with the gas separation testing conditions.

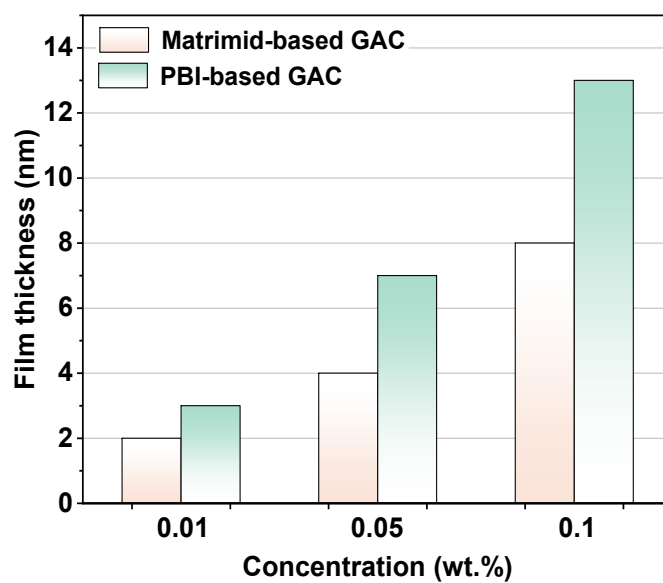
Fitting of the force-displacement curves in the suspended regions yields Young's modulus values of 25.78, 25.27, and 23.64 GPa for the three newly tested positions. These values remain within the range of our previously reported measurements (25.08 ± 5.98 GPa), confirming that the gas separation process did not induce mechanical degradation of the membrane.



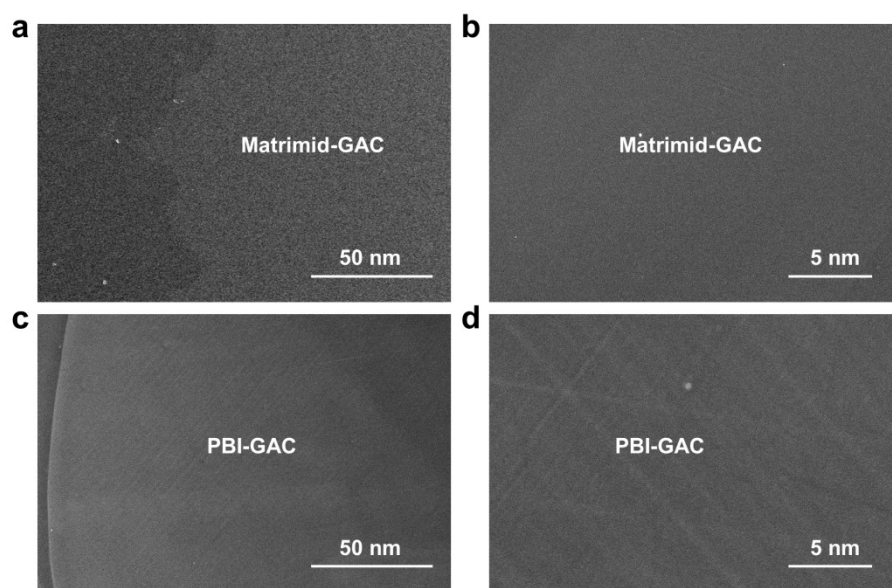
Supplementary Fig. 42 | AFM images of the GAC membranes prepared with different Matrimid® 5218 precursor concentrations. a, b, 0.05 wt%. c, d, 0.1 wt%.



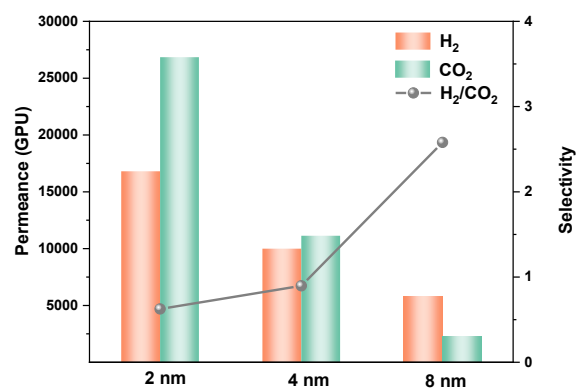
Supplementary Fig. 43 | AFM images of the GAC membranes prepared with different PBI precursor concentrations. a, b, 0.05 wt%. c, d, 0.1 wt%.



Supplementary Fig. 44 | Dependence of GAC membrane thickness on precursor concentration.

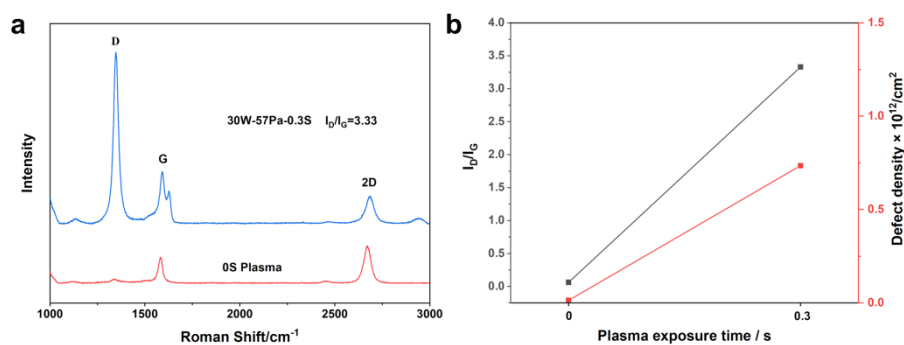


Supplementary Fig. 45| SEM images of GAC membranes prepared based on Matrimid® 5218 (**a**, **b**,) and PBI (**c**, **d**,) precursors.



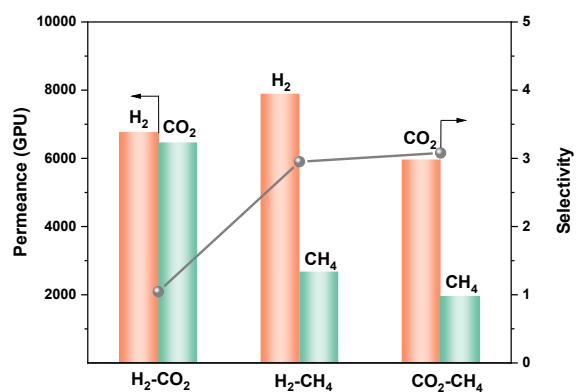
Supplementary Fig. 46 | H₂/CO₂ mixture gas performance of Matrimid-derived carbon membranes with different thicknesses.

The pristine amorphous carbon membranes (Matrimid-derived) directly coated on copper show no intrinsic H₂/CO₂ discrimination. This lack of selectivity persists even in conventional Matrimid-derived carbon molecular sieve membranes with micrometer-scale thicknesses.



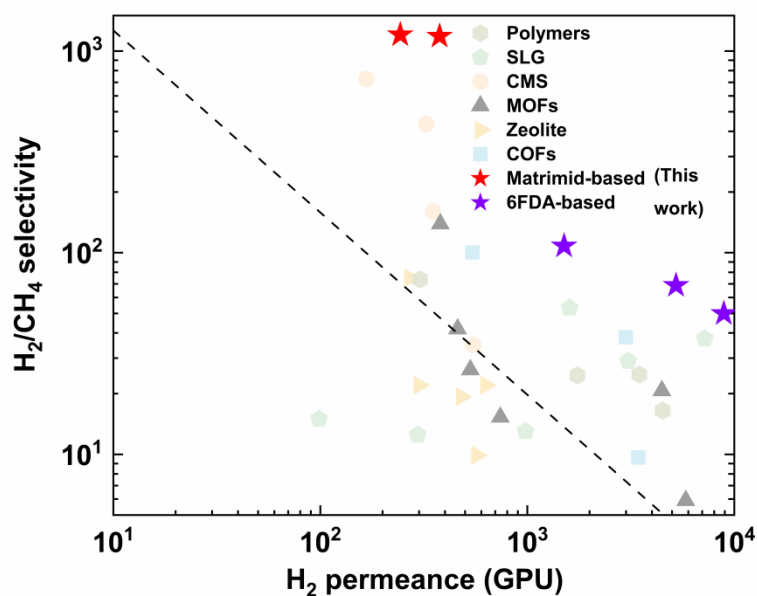
Supplementary Fig. 47 | Raman spectra **(a)** and defect density **(b)** of SLG under weak plasma etching conditions (etching time 0.3 S, power 30 W, pressure 57 Pa).

To engineer selectivity for H₂/CO₂ separation in the Matrimid-derived GAC membrane, we fabricated graphene with smaller pores by reducing the plasma treatment power and duration. However, this approach concurrently decreased the porosity of graphene, adversely affecting its permeance.

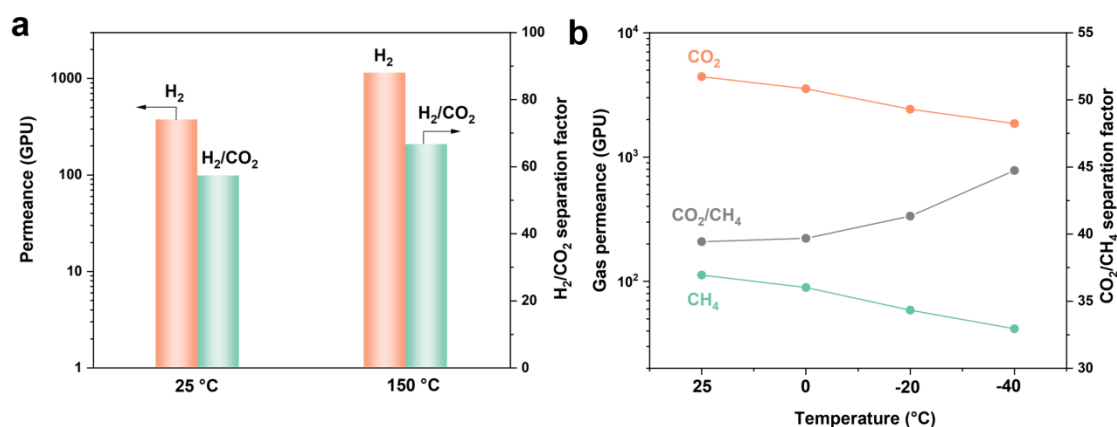


Supplementary Fig. 48 | Separation performance of SLG with different gas mixtures under weak plasma etching conditions (etching time 0.3 S, power 30 W, pressure 57 Pa).

Although graphene with smaller nanopores was engineered under weak plasma conditions, it remained non-selective for H₂/CO₂ separation on its own. However, the GAC membrane fabricated from this small-pore graphene and a Matrimid precursor exhibited remarkable H₂/CO₂ selectivity of 78.3 (Supplementary Table 7).



Supplementary Fig. 49 | Comparison of H_2/CH_4 separation performance of Matrimid- and 6FDA-based GAC membranes with state-of-the-art membranes. Source data are supplied in Supplementary Table 9.



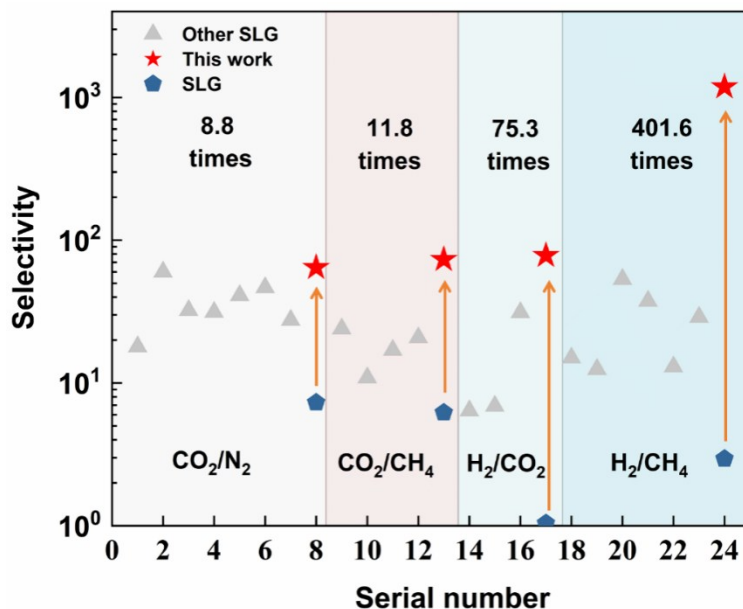
Supplementary Fig. 50 | Measurements with Temperature. **a**, Changes in H₂/CO₂ separation performance of Matrimid-derived GAC membrane at 25°C and 150°C. **b**, Changes in CO₂/CH₄ separation performance of 6FDA-DAM-derived GAC membrane from -40°C to 25°C.

We further investigated both the temperature-dependent CO₂/CH₄ separation behavior and the high-temperature H₂/CO₂ separation performance of the GAC membranes. With respect to temperature-dependence, elevating the operating temperature significantly enhances the H₂/CO₂ separation performance (Supplementary Fig.50a). Compared with the operation at 25 °C, operation at 150 °C increases the H₂ permeance by 205.8%, while the H₂/CO₂ selectivity increases by 16.5%.

This temperature-enhanced H₂/CO₂ separation behavior can be explained as follows: H₂ is weakly adsorbed and permeates primarily via activated transport mode. Increasing the temperature enables more H₂ molecules to overcome the diffusion barriers associated with the angstrom-scale pores, thereby substantially enhancing H₂ permeance. In contrast, CO₂ interacts more strongly with the pore surfaces, and its transport is governed by both adsorption and molecular diffusion within the channels. Although increasing the temperature promotes CO₂ diffusion, it simultaneously reduces CO₂ adsorption owing to the exothermic nature of physical adsorption. The resulting decrease in CO₂ adsorption within the pores partially offsets the enhancement in diffusivity. Consequently, at elevated temperature, the enhancement of H₂ permeance is more pronounced than that of CO₂.

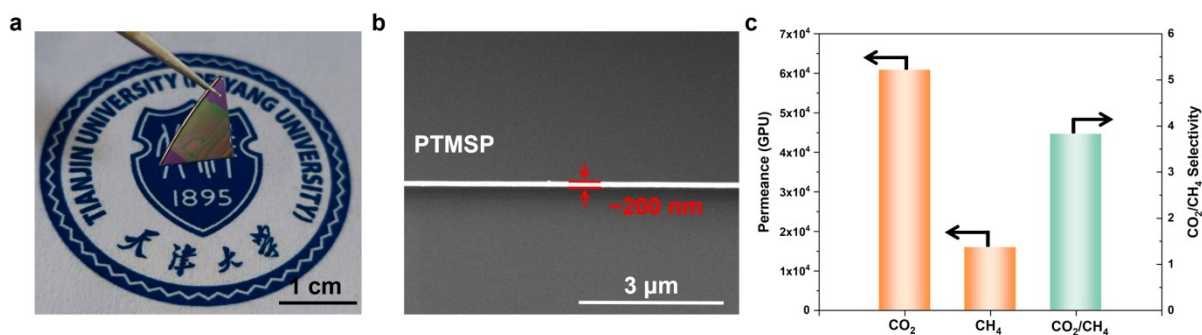
Moreover, we investigated the CO₂/CH₄ separation performance under low-temperature conditions from 25 °C to -40 °C at 2 bar (Supplementary Fig.50b). The results show that decreasing temperature gradually reduces CO₂ permeance while enhancing CO₂/CH₄ selectivity. Specifically,

the CO₂ permeance decreases from 4434.6 GPU at 25 °C to 1860.5 GPU at -40 °C, whereas the CO₂/CH₄ selectivity increases from 39.4 to 44.7 over the same temperature range. This trend is consistent with that of traditional carbon molecular sieve membranes¹. Specific reason is provided as follows. The observed transport behavior at low-temperature is consistent with the activated diffusion mechanism of ultramicroporous membranes. At reduced temperatures, gas diffusion within the sub-nanometer channels is kinetically hindered, resulting in a reduction in overall permeance. However, since the diffusivity of CH₄ exhibits a stronger temperature dependence than that of CO₂, the molecular sieving effect is amplified at low temperatures, ultimately leading to enhanced CO₂/CH₄ selectivity. In addition, lower temperature strengthens the preferential adsorption of CO₂ relative to CH₄, which may further contribute to the improved selectivity.



Supplementary Fig. 51 | Comparison of the selectivity among various GAC membranes and advanced nanoporous SLG membranes. Source data are supplied in Supplementary Table 10.

Compared to the previously reported monolayer porous graphene membranes, the GAC membrane demonstrates enhanced selectivity in the separation of various gas pairs. In addition, 6FDA-DAM-derived GAC membranes exhibit 8.8- and 11.8-fold increases in CO₂/N₂ and CO₂/CH₄ selectivity, respectively, while Matrimid-derived GAC membranes achieve remarkable 75.3- and 401.6-fold enhancements in H₂/CO₂ and H₂/CH₄ selectivity, respectively.



Supplementary Fig. 52 | Images and the CO₂/CH₄ mixed gas separation performance of PTMSP. Optical image (a) and cross-sectional SEM image (b) of PTMSP on silicon wafers, (c) CO₂/CH₄ mixed gas separation performance of PTMSP.

The PTMSP layer has a thickness of approximately 200 nm. Its CO₂ permeance is 60,860.0 GPU, and the corresponding CO₂/CH₄ selectivity is 3.8. Given its very high permeance, the transport resistance of the PTMSP layer is negligible in the overall membrane configuration.

3. Supplementary tables

Supplementary Table 1. Comparison between the Young's modulus and breaking strength of the GAC membrane and other membranes.

Membrane types	Membranes	Young's modulus (GPa)	Breaking Strength (MPa)	Ref.
Advanced ultrathin films	2DPA-1	12.7 ± 3.8	488	18
	TPC-CPF _{Cu(111)}	22.7	2130	19
	GNM/SWNT	9.7	380.6	20
6FDA-based copolyimide CMS	CMS-550 w/o pre-crosslinking	3.64 ± 0.25	-	21
	CMS-550 with pre- crosslinking	5.4 ± 0.23	-	
	CMS-675 with pre- crosslinking	7.61 ± 0.42	-	
	CMS-800 with pre- crosslinking	8.07 ± 0.28	-	
PBI CMS	PBI/CMS500	4.06	133.7	22
	PBI/CMS600	10	-	
	PBI-PPA0.30/CMS500	3.94	-	
	PBI-PPA0.30/CMS600	11.7	-	
	TADPS-IPA PBI	2.6	-	23
	Doped PANI/PBI (20/80)	2.06	30.19	24
	Celazole PBI	3.8	94	25
Microcrystalline cellulose CMS	Cellulose/CMS550	2.07 ± 0.25	-	26
	Cellulose/CMS700	5.69 ± 0.06	-	
	Cellulose/CMS850	7.53 ± 0.50	-	
Polymers	Polytetrafluoroethylene (PTFE)	0.4	-	27
	Polyethylene HDPE (high density)	0.8	15	
	ABS plastics	1.4-3.1	-	
	Polypropylene, PP	1.5-2	28-36	
	Polyethylene Terephthalate, PET	2-2.7	55	
	Nylon-6	2-4	45-90	
	Polyvinylchloride (PVC)	2.4-4.1	-	
	Polyamide	2.5	85	
	Polycarbonates	2.6	52-62	
Porous crystalline films	ZIF-8	3.44 ± 1.42	-	28
	ZIF-67	3.79 ± 1.83	-	
	HKUST-1	9.6 ± 1.1	-	29
	COF _{TAPB-DHTA} film	10.38	540	30
	COF-Tp-Azo _{sphere} thin-film	15.3	-	31
	Zn ₂ (NO ₂ BDC) ₂ (DABCO)⊃DMF	2.1	-	32
	IRMOF-1 (MOF-5)	2.7	-	33

	$\text{Cu}_3(\text{BTC})_2$	3.5 ± 2.5	-	²⁷
MXene	Pure MXene	3.52	22	³⁴
	MXene vacuum filtration	5.6	63	³⁵
	MXene Blade coating	20.6	570	³⁶
6FDA-derived GAC	GAC-2@ 4nm	26.80	9520	This work

Supplementary Table 2. XPS analysis of elemental content before and after pyrolysis.

Type	Atomic (%) Before pyrolysis	Atomic (%) After pyrolysis
C 1s	70.15	80.06
O 1s	11.41	12.68
N 1s	13.77	5.23
F 1s	4.67	2.03

Supplementary Table 3. CO₂/CH₄ mixed gas separation performance of 6FDA-derived GAC membranes with different thicknesses and plasma etching times.

Membranes	Thickness (nm)	Plasma etching time (s)	CO ₂ permeance (GPU)	CO ₂ permeability (Barrer)	CO ₂ /CH ₄ selectivity
GAC-2@2 nm	2	2	8725.11	17.45	15.36
	2	2	6710.07	13.22	17.39
	2	2	10840.32	21.68	13.45
GAC-2@4 nm	4	2	3729.81	14.92	46.18
	4	2	2600.93	10.40	51.38
	4	2	4750.23	19.00	40.93
	4	2	4434.59	17.74	39.44
	4	2	3437.34	13.75	45.77
	4	2	3616.76	14.47	44.09
GAC-2@9 nm	9	2	1010.33	9.09	73.19
	9	2	1440.77	12.97	59.63
	9	2	728.22	6.55	78.28
GAC-3@4 nm	4	3	5106.60	20.43	31.44
	4	3	8799.77	35.20	20.60
	4	3	5034.17	20.14	38.29

Supplementary Table 4. Comparison of the CO₂/CH₄ separation performance between the GAC membranes and the reported membranes in literature.

Membranes		CO ₂ permeance (GPU)	CO ₂ /CH ₄ selectivity	Reference
SLG	PIM/NG-1s	960	24	37
	M4-PEI-6s	5540	10.9	38
	N-SLG	2620	17	39
	AF-reinforced PNG-M6	625	20.83	40
Other 2D materials	LDH	150	33	41
	GO	105	16	42
	B-GO(50)	650	75	
	GO-PEGDA500	175.5	69.5	43
	GO/IL	37	39	44
	MBP-75	350	15.3	45
MOFs	PDA/UIO-66	1115	28.9	46
	BIO-MOF-1	3254	2.6	47
	ZIF-8	47.34	12.9	48
	ZIF-69	296	4.6	49
	ZIF-90	37.6	4.7	50
	MIL-160/CAU-10-F	716	78	51
CMS	Carbon/ carbon mixed-matrix	0.82	3570	52
		1.74	1410	

	(CCMM) hollow fiber	3.38	842	
	PPO layer coated on PI derived CMS layer	264	157	53
	ULT CMS-6F0.5	2560	24	54
COFs	ACOF-1	29.55	86.3	55
	NCOFM	506.1	35.5	56
		185.8	61.7	
	DhaTG _{Asp}	228	65	57
MMMs	GO-DA-Cys	21.68	82	58
	PIM-1/CuBDC-ns	407.3	15.6	59
	QAPSF/sβ-CD	10.8	39	60
Polymers	TOL-PUU	1433.8	7.8	61
	PVA-PDA(0.5)/PES	17	43.2	62
	Pebax/PEG	93	23	63
6FDA-derived GAC	GAC-2@ 9nm	1010.33	73.19	This work
	GAC-2@ 4nm	3729.81	46.18	
	GAC-3@ 4nm	5106.60	31.44	

Supplementary Table 5. Comparison of the CO₂/CH₄ separation performance between the GAC membranes and the traditional carbon molecular sieve membrane.

Membranes	CO₂ permeance (GPU)	CO₂/CH₄ selectivity	Reference
CMS derived from Matrimid[®]	40	100	64
CMS derived from PMDA-ODA	93.4	19.8	65
CMS derived from PEI (Ultem 1000)/PVP	1.66	55.33	66
CMS derived from PIM-1	20	153.8	67
CMS derived from P84[®]	0.276	38.9	68
CMS derived from Matrimid[®]	6.3	20.86	69
CMS derived from Sheath/core Matrimid[®]/Matrimid[®] composite	1177	36.7	54
CMS derived from PI-LPSQ20	956	50.2	70
CMS derived from 6FDA:BPDA-DAM	400	25	71
CMS-675 derived from dip coated on P84[®]/P84[®] composite	310	58.8	72
CMS-800 derived from dip coated on P84[®]/P84[®] core	166.7	86.5	
CMS derived from 6FDADAM/Matrimid[®] at 800 °C	167.9	86.9	73
CMS derived from 6FDADAM/Matrimid[®] at 675 °C	232.5	64.3	
CMS derived from 6FDA:BPDA-DAM /(Matrimid[®]+SiO₂) at 675 °C	244.6	36.6	74
CMS derived from Matrimid[®]/(Matrimid[®]+SiO₂) CMS at 550 °C	189.5	64.3	

CMS derived from Matrimid[®]/(Matrimid[®]+SiO₂) CMS at 675 °C	71.7	134.2	
ULT CMS-6F0.5	2546	24.1	54
Carbon/ carbon mixed-matrix (CCMM) hollow fiber	0.82	3570	52
	1.74	1410	
	3.38	842	
PPO layer coated on PI derived CMS layer	264	157	53
6FDA-derived GAC	1010.33	73.19	This work
	3729.81	46.18	
	5106.60	31.44	

Supplementary Table 6. Comparison of the CO₂/N₂ separation performance between the GAC membranes and the reported membranes in literature.

Membranes		CO ₂ permeance (GPU)	CO ₂ /N ₂ selectivity	Reference
SLG	PG/MRF/PES	8792	18	75
	IL/NPG	1542	32.3	76
	PNG-3	5700	31.4	77
	M1-PEI-4s	980	41.1	38
	Polymer-functionalized NSLG	2060	46.7	78
	N-SLG (MGR at 250 °C)	2600	27.6	39
Other 2D materials	MoS ₂ SILM	47.88	131.42	79
	WS ₂ SILM	47.3	153.21	80
	M SILM	80	87	81
	BN SMILM	20.3	90	82
MOFs	ZIF-69	308.8	6.3	49
	PDA/UIO-66	1115	51.6	46
	ZIF-8	22	52	83
	ZIF-8@CA	24.2	168.8	84
	CAU-1	4000	22.8	85
CMS	PPO layer coated on PI derived CMS layer	264	156	53
		342	86	

	PIM-CMS	1206	47	86
COFs	NCOFM	1068.2	35.4	56
		558.7	69.5	
		370.7	79.8	
MMMs	MAPDA/PIM-1	157.2	23.9	87
	TPB-DMTP-COF/PIM-1	457	20.2	88
	(M(2+)CTFs)/PI	15.6	37	89
	COF-TpPa-1/PIM-1	64.4	17.7	90
	ZIF-7/Pebax [®] 1657	291	97	91
	UiO-66-NH ₂ /PGMA-co-POEM	488	31.9	92
	ZIF-8-d-MK	152	78	93
	ZIF-8@NENP-NH ₂	301	91	94
	polyMOF/PIM-1	3577	21.5	95
	PAP/IL/ZIF-8	1017	33	96
Polymers	Pebax	287	34	91
	PAN-PDMS	1200	53	97
	PVAm/PSf	483	65	98
	Pebax/P1	916	33	99
6FDA-derived GAC	GAC-2@ 9nm	931.21	64.38	This work
	GAC-2@ 4nm	3848.46	41.12	
	GAC-3@ 4nm	4457.80	26.79	

Supplementary Table 7. H₂/CO₂ and H₂/CH₄ mixed gas separation performance of GAC membranes with different thicknesses, plasma etching conditions and precursor.

Membranes	Thickness (nm)	Plasma etching power and time	H₂ permeance (GPU)	H₂/CO₂ selectivity	H₂/CH₄ selectivity
Matrimid® 5218-derived GAC	2	30W-0.3S	523.23	26.35	73.79
	4	30W-0.3S	377.10	46.33	1184.63
	8	30W-0.3S	243.47	78.30	1203.64
PBI-derived GAC	13	80W-3S	1497.86	23.22	-

Supplementary Table 8. Comparison of the H₂/CO₂ separation performance between the GAC membranes and the reported membranes in literature.

Membranes		H ₂ permeance (GPU)	H ₂ /CO ₂ selectivity	Reference
SLG	Ozone-treated graphene	98.5	6.4	100
	M5 (ozone-etched)	328.4	6.9	101
CMS	SPPO derived CMS hollow fiber	60.5	56	102
	PI derived CMS hollow fiber	100	60	103
	Resorcinol-formaldehyde resin derived CMS	150	22.3	104
	Polyfurfuryl alcohol derived CMS	529	16	105
	MSC CMS	1977	8	106
	poly(imide siloxane) derived CMS	2520	5	107
	6FDA/BPDA-DAM	4.7	80	108
	CHFM-850	148.2	83.9	26
	CHFM-550	446.8	11.1	
Zeolite	HKUST-1	6332.1	6.84	109
	CAU-1	322.6	12.34	110
COFs	COF-LZU1-ACOF-1	731.8	24.2	111
	TpEBr@TpPa-SO ₃ Na	2566	22.6	112

MOFs	ZIF-8	471.9	4.6	113
	NH ₂ -MIL-53(Al)	5928.9	30.9	114
	ZIF-7	238.9	6.7	115
	ZIF-7	27.1	8.4	116
Polymers	PIM-EA-TB	42.1	1.09	117
	mPBO	5.1	6.2	118
	PHBOA (8:2)	1	8	119
	Polybenzimidazole (PBI)	3.2	20	120
	Pure PBI	1.8	8.6	121
GAC	Matrimid® 5218- derived GAC	243.47	78.30	This work
		377.10	46.33	
		523.23	26.35	
	PBI-derived GAC	1497.86	23.22	

Supplementary Table 9. Comparison of the H₂/CH₄ separation performance between the GAC membranes and the reported membranes in literature.

Membranes		H ₂ permeance (GPU)	H ₂ /CH ₄ selectivity	Reference
SLG	Ozone-treated graphene	98.5	15	100
	M5 (ozone-etched)	295.5	12.5	101
	AF-reinforced PNG-M6	1600	53.33	40
	PBA/graphene	7200	37.5	122
	α -AH (membrane #2)	979	13	123
	Graphene-150 °C, O ₃ (2 cycles)	3071	29	124
CMS	TiN4-3 supported CMS	167	726	125
	Steam activation CMS	548	35	126
	PPO/PVP blend CMS	350	160	127
	Composite supported alumina-CMS	324	435	128
COFs	LA- α -CD-in-TpPa-1	2995	38.1	129
	COF-LZU1	3432.8	9.65	111
	COF-LZU1-ACOF-1	543.3	100.2	
MOFs	ZIF-8/GO	380	139	130
	ZIF-90	740	15.3	131
	Cu ₃ (BTC) ₂	5830	5.9	132
	ZIF-67	460	41.9	133

	JUC-150	530	26.3	134
	NH ₂ -MIL-53(Al)	4470	20.7	115
Zeolite	AIPO-18	300	22	135
	FAU	570	9.9	136
	SSZ-13	630	22	137
	DDR	270	75	138
	LTA	480	19.3	139
Polymers	CC3	4509.5	16.5	140
	P33DT-ThC4	302.9	73.6	141
	Vertically aligned TFB-BD	3477.9	24.9	142
GAC	6FDA-derived GAC	8897.44	49.92	This work
		5232.73	68.81	
		1506.54	107.90	
	Matrimid® 5218- derived GAC	377.10	1184.63	
		243.47	1203.64	

Supplementary Table 10. Comparison of the gas separation selectivity between the GAC membranes and single layer porous graphene membrane.

Gas mixture	Serial number	Membranes	Selectivity	Reference
CO₂/N₂	1	PG/MRF/PES	18	75
	2	Pyridinic-N-substituted porous graphene	53.3	143
	3	IL/NPG	32.3	76
	4	PNG-3	31.4	77
	5	M1-PEI-4s	41.1	38
	6	Polymer-functionalized NSLG	46.7	78
	7	SLG (MGR at 250 °C)	27.6	39
	8	6FDA-derived GAC	64.38	This work
CO₂/CH₄	9	PIM/NG-1s	24	37
	10	M4-PEI-6s	10.9	38
	11	N-SLG	17	39
	12	AF-reinforced PNG-M6	20.83	40
	13	6FDA-derived GAC	73.19	This work
H₂/CO₂	14	Ozone-treated graphene	6.4	100
	15	M5 (ozone-etched)	6.9	101
	16	M-3 100 nm Au	31.26	144
	17	Matrimid® 5218-derived GAC	78.30	This work
H₂/CH₄	18	Ozone-treated graphene	15	100

	19	M5 (ozone-etched)	12.5	101
	20	AF-reinforced PNG-M6	53.33	40
	21	PBA/graphene	37.5	122
	22	α -AH (membrane #2)	13	123
	23	Graphene- 150 °C, O ₃ (2 cycles)	29	124
	24	Matrimid® 5218-derived GAC	1203.64	This work

Supplementary Table 11. Lennard-Jones parameters for the CO₂ and CH₄.

Site	ϵ (kcal/mol)	σ (Å)	q (e)
CH ₄ -H	0.02	2.995	0.053
CH ₄ -C	0.054	4.01	-0.212
CO ₂ -C	0.064	4.01	0.24
CO ₂ -O	0.06	3.535	-0.12

Supplementary Table 12. Lennard-Jones parameters for atoms in GAC membrane.

Atom type	Element	ε (kcal/mol)	σ (Å)	Chemical role
cp	C	0.064	4.01	aromatic C
c	C	0.054	4.01	sp ³ C (CH ₃ /CF ₃ /bridge)
c_1	C	0.12	3.81	carbonyl C (imide)
o_1	O	0.267	3.3	carbonyl O (imide)
n	N	0.106	4.07	imide N
f	F	0.0598	3.2	fluorine (CF ₃)
h	H	0.02	2.995	H (aromatic or methyl)

4. Supplementary notes

Supplementary Note 1. Analysis of the defect-density based on the Raman data.

The evolution of the defect-density in graphene with the plasma exposure time can be divided into two stages: low-defect-density stage and high-defect-density stage. In the low-defect-density stage, the I_D/I_G increases with plasma exposure time due to that the breathing of six-atom ring in graphene lattice is activated by the presence of defects. In the high-defect-density stage, the I_D/I_G decreases with exposure time, attributing to the fact that the porosity of nanoporous graphene is increased with the time, reducing the number of ordered six-atom rings. In the low-defect-density stage, the average distance between defects, L_d , can be calculated according to the following equation^{145, 146}:

$$L_d^2(nm^2) = (1.8 \pm 0.5) \times 10^{-9} \lambda^4 \left(\frac{I_D}{I_G}\right)^{-1} \quad (S1)$$

where λ is the Raman excitation wavelength (532 nm in this study).

In the high-defect-density stage, the L_d can be calculated according to the following correlation equation:

$$\frac{I_D}{I_G} = D(\lambda) \times L_d^2 \quad (S2)$$

where $D(\lambda)$ can be obtained by imposing continuity between the two stages ($\sim 0.1082 \text{ nm}^{-2}$ in our study).

We can roughly estimate the defect density (number of defects per unit area), n_D , according to the following equation:

$$n_D^2(cm^{-2}) = 10^{14} / (\pi L_d^2) \quad (S3)$$

In our case, at the etching power of 80W, the etching time range of 1-3 seconds is within the high-defect-density stage. At the etching power of 30W, the etching time of 0.3 seconds is within the low-defect-density stage. Thus, the defect density of as-synthesized graphene and 0.3 s (30W) plasma graphene can be calculated according to the equation S1 and S3, while the defect density of 1-3 s (80W) plasma graphene can be calculated according to the equation S2 and S3.

Supplementary Note 2. Force curve analysis based on nanoindentation.

The force-displacement behavior of GAC membranes can be approximated as¹⁴⁷:

$$F = \sigma_0^{2D} (\pi a) \left(\frac{\delta}{a}\right) + E^{2D} (q^3 a) \left(\frac{\delta}{a}\right)^3 \quad (\text{S4})$$

where F is applied force, δ is the deflection at the center point, σ_0^{2D} is the pretension in the film, n is Poisson's ratio [taken here as 0.165, the Poisson's ratio for graphite in the basal plane], and $q = 1/(1.05 - 0.15n - 0.16n^2) = 1.02$ is a dimensionless constant.

In this work, a represents the pore radius of the porous silicon wafer, which is 2.5 nm. The curve fitted based on the force-displacement data is shown in Supplementary Fig.13a. The calculated $E^{2D} = 100.3 \pm 23.9 \text{ N m}^{-1}$.

Young's modulus can be calculated according to the following equation:

$$E = E^{2D} / t \quad (\text{S5})$$

where t is the membrane thickness. In this work, $t = 4 \text{ nm}$.

Supplementary Note 3. AFM-based nanoscratch tests.

We performed AFM-based nanoscratch tests to further evaluate the mechanical robustness of the ultrathin GAC membrane (~4 nm thick). The results demonstrate that no obvious scratch track could be observed under loads below 3.5 μN , indicating excellent resistance against the local mechanical stress. By contrast, previously reported monolayer h-BN, monolayer MoS_2 and monolayer graphene exhibited partial scratch damage at loads of 0.8 μN , 1.5 μN and 3.0 μN , respectively¹⁴⁸, highlighting the superior mechanical robustness of the GAC membrane.

As shown in Supplementary Fig.15a–d, when the applied load increases to 3.5, 4.0, and 4.5 μN , the corresponding scratch depths were only 0.27, 0.32, and 0.61 nm, respectively, all smaller than the total membrane thickness (~4 nm). As shown in Supplementary Fig.15e, when the load is increased to ≥ 5 μN , the scratch morphology transitions from a well-defined groove to severe material pile-up (>20 nm in height), indicating that the GAC membrane is plastically deformed but remains intact without fracture. These observations indicate that the membrane can largely maintain its structural integrity even under concentrated local mechanical stress.

The scratch hardness is a good indicator to evaluate the relative scratch resistance, which is widely used to compare the scratch resistance of different kinds of materials^{149, 150}. In the case of using a Berkovich indenter, the scratch hardness can be calculated by the following equation¹⁵¹:

$$H_S = \frac{F_N}{A} = 2.31 \frac{F_N}{d^2} \quad (\text{S6})$$

where F_N is the maximum normal force applied on the indenter during the nano-scratch test, A is the area of the residual scratch groove, and d is the residual width of the scratch.

Based on the test results under a 4 μN load (scratch depth of 0.32nm), the scratch hardness is estimated to be approximately 7.42 GPa, which is comparable to that of four layer graphene (scratch hardness of approximately 5-7 GPa at a scratch depth of 0.32nm) and significantly higher than that of previously reported graphene-based nanocomposites (0.3 GPa)^{152, 153}.

These AFM scratch-test results provide direct evidence that the GAC membrane possesses exceptional resistance to local mechanical stress, which strongly supports its applicability in practical and sustainable separation processes.

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