Supporting Information

Multi-pulsed Millisecond Ozone Gasification for Predictable Tuning of Nucleation and Nucleation-decoupled Nanopore Expansion in Graphene for Carbon Capture

Kuang-Jung Hsu, Luis Francisco Villalobos, Shiqi Huang, Heng-Yu Chi, Mostapha Dakhchoune, Wan-Chi Lee, Guangwei He, Mounir Mensi, Kumar Varoon Agrawal

a Laboratory of Advanced Separations (LAS), École Polytechnique Fédérale de Lausanne (EPFL), Rue de l’Industrie 17, CH-1951 Sion, Switzerland
b Institut des Sciences et Ingénierie Chimiques, EPFL, Rue de l’Industrie 17, CH-1951 Sion, Switzerland

Supplementary Notes

Note S1. The mathematical model for the evolution of O₃ pressure in the MGR chamber.

The ozone concentration profile inside the MGR chamber was controlled by a millisecond leak valve (MLV) responsible for introducing O₃ and a needle valve which connects the chamber with the vacuum pump. Fine control over the pressure profile can be achieved by delivering the O₃ in the initially evacuated chamber in the form of pulses by opening and closing the MLV. The pressure profile in the chamber in this scenario is as a function of the opening time of the MLV ($\tau_o$), the time interval between two consecutive pulses ($\tau_i$), and the number of pulses ($F$). A mathematical model based on the transient mass transfer in the reactor was built to predict the pressure profile of ozone in the MGR:

The first pulse of MLV starts at $t = 0$ (opening of inlet MLV), and finishes at $t = \tau_o$ (inlet MLV is closed). Then, after the delay time ($\tau_i$), the second pulse of MLV starts (the time elapsed until the starts of the second pulse is $t = \tau_o + \tau_i$). The MLV is closed at the end of the second pulse at $t =$
The process is repeated for a predetermined number of pulses (F), following the same logic as above.

The pressure profile during each pulse (e.g., from time $0 < t < \tau_o$), where the O$_2$/O$_3$ mixture is introduced to the MGR by the MLV, can be calculated by equation S1 and S2.

\[
\left(\frac{dN}{dt}\right)_{in} = C_1 (P_{in} - P_r) \tag{S1}
\]

\[
P_{in} = P_{in0} - \Delta P \tag{S2}
\]

where $C_1$ is defined as the transport coefficient (or conductance) of the MLV, and $(\frac{dN}{dt})_{in}$ is the inward gas flow as a function of time. $P_{in}$ is the pressure of the ozone reservoir feeding the MGR. The initial pressure of the reservoir is $P_{in0}$ and it decreases $\Delta P$ after each MLV pulse. $P_r$ is the pressure of the MGR chamber and is zero initially.

The decrease in pressure in the MGR due to the outlet valve can be calculated using equation S3.

\[
\left(\frac{dN}{dt}\right)_{out} = C_2 P_r \tag{S3}
\]

where $C_2$ is defined as a transport coefficient (or conductance) of the outlet valve, and $(\frac{dN}{dt})_{out}$ is the gas flow pumped out of the MGR. The model assumes that the pressure achieved by the vacuum pump connected to the outlet side is 0 which is a reasonable assumption given the pressure next to the vacuum pump is only a few millitorrs whereas the pressure in the reactor is three to four orders of magnitude higher.
The mass balance on the MGR chamber is:

$$\frac{dN}{dt} = C_1 (P_{in} - P_r) - C_2 P_r$$  \hspace{1cm} (S4)

By rearranging the equation, the pressure change in the reactor can be calculated by:

$$\frac{dP}{dt} = \frac{RT}{V_r} (C_1 (P_{in} - P_r) - C_2 P_r)$$  \hspace{1cm} (S5)

where $V_r$ is the reactor volume (150 cm$^3$).

The equation S5 can be integrated to obtain an equation that describes the pressure rise in the MGR during a pulse of O$_3$:

$$P_r = P_{r, rise} = P_0 \exp\left(-\frac{RT(C_1 + C_2)}{V_r} t\right) + \frac{C_1}{C_1 + C_2} P_{in}\left[1 - \exp\left(-\frac{RT(C_1 + C_2)}{V_r} t\right)\right]$$  \hspace{1cm} (S6)

The increase in pressure of the reactor ($P_r$) during the pulses was referred as $P_{r, rise}$ in the equation S6 to differentiate it from the pressure decrease that occurs when the MLV is closed.

When inlet MLV is closed in between pulses (e.g., during time $\tau_0 < t < \tau_0 + \tau_i$), there is no O$_2$/O$_3$ mixture flowing into the MGR chamber, and the mixture gas inside the MGR is pumped out by the outlet MLV. The corresponding pressure profile for this step is described by equation S7 and S8.

$$\frac{dN}{dt} = -C_2 P_{r, rise}$$  \hspace{1cm} (S7)

$$\frac{dP_r}{dt} = -\frac{RT}{V_r} C_2 P_{r, rise}$$  \hspace{1cm} (S8)
By integrating equation S8, an equation to calculate the evolution of the pressure profile when the inlet MLV is closed (i.e., in between pulses and at the end of the process when the O$_3$ is purged from the system) can be obtained:

$$ P_r = P_{r,\text{rise}} \exp \left( \frac{R C_2}{V_r} (t - \tau_o) \right) $$  \hspace{1cm} (S9)

Equations S6 and S9 can be used to describe the evolution of the pressure during the first pulse and the first interval. They can then be used to describe the evolution of the pressure during the second pulse and the second interval using as initial conditions the pressure obtained from the first set of pulse and interval. Similarly, the mathematical model can for used to describe the pressure profile during any number of pulses.

$C_1$, $C_2$, and $\Delta P$ were extracted for our MGR by fitting the experimental data, which are shown in Table S1. When the opening time of the inlet MLV ($\tau_o$) is too long (e.g., $\tau_o = 0.1$), a new $C_1$ had to be extracted from experimental data because of the relatively large time delay for the O$_3$/O$_2$ mixture transferring from the reservoir to the MLV.
Note S2. Mathematical modeling of the etching kinetics

Nucleation and pore expansion in high ozone concentration

The ozone etching mechanism is proposed as below:

\[ \begin{align*}
\text{O}_3 (\text{g}) + \text{-C} & \leftrightarrow \text{-C-O}_3 \text{ (physisorbed)} \\
\text{-C-O}_3 \text{ (physisorbed)} & \leftrightarrow \text{-C-O (chemisorbed) + O}_2 \\
\text{-C-O (chemisorbed)} & \rightarrow \text{-C-O (cluster)} \\
\text{-C-O (cluster)} & \rightarrow \text{Vacancy + CO (g)}
\end{align*} \]

When an ozone molecule comes in contact with the graphene lattice, the first thing that occurs is that it physically adsorbs on the graphene surface. Then, it covalently bonds with the carbon lattice of graphene (chemisorption).\(^1\)–\(^4\) Epoxy groups are formed when an oxygen atom of the ozone molecule bonds with two carbon atoms of the graphene lattice.\(^1\) Epoxy groups diffuse to form energy-minimizing clusters which further evolve into ether chains, and subsequently, C-C bonds can be broken to form semiquinone groups.\(^4\)–\(^6\) This is driven by the fact that the strain present in clusters makes them relatively unstable.

A detailed analysis of the nucleation kinetics is reported in our previous work.\(^7\) Briefly, the adsorption and chemisorption can be considered to be in equilibrium, and the formation of vacancy defect is regarded as the rate-limiting step for pore nucleation. As a result, the expression of nucleation density is defined as equation S10.

\[ \frac{d\theta_v}{dt} = k_cHP \]  

(S10)
where \( \theta_v \) is the fractional occupancy of the nucleation sites for the nanopores, \( k_c \) is the effective rate constant of the reaction combining clustering and chemisorption, \( H \) is Henry’s coefficient for physisorption of ozone on graphene, and \( P \) is the ozone pressure.

The nucleation density between the time period \( t_0 \) and \( t_n \) can be calculated as follows:

\[
\theta_v = k_c H \int_{t_0}^{t_n} P \, dt
\]

\[(S11)\]

From our previous work\(^7\) where the experimental pore density was used to calculate \( k_c H \), we obtained \( k_c H \) as \( 3.2 \times 10^{-4} \) monolayer Torr\(^{-1}\) s\(^{-1}\) at 250 °C.

From equation S11, the nucleation sites are expected to increase proportionally to the ozone pressure at a given temperature. As a result, exposing graphene to a high ozone pressure for a short period of time is beneficial for obtaining a high nucleation density.

**Calculation of pore-size-distribution**

The pore expansion kinetics with respect to \( O_3 \) was recently fitted to be close to half-order.\(^7\) Hence, the total number of carbon atoms removed by pore expansion from N vacancy defects (\( dC \)) during an elemental time (\( dt \)) can be formulated as:

\[
\frac{dC}{dt} = k P^{0.5}
\]

\[(S12)\]

where \( k \) is the rate constant of pore expansion by \( O_3 \), and \( P \) is the ozone pressure in the MGR chamber. From our previous report,\(^7\) the \( k \) at 523 K is \( 4.6 \times 10^{12} \) atoms cm\(^{-2}\) s\(^{-1}\) Torr\(^{-0.5}\). Assuming that the reaction takes place from \( t_i \) to \( t_f \), then the total missing carbon atoms during this time interval is:

\[
C = \int_{t_i}^{t_f} k P^{0.5} \, dt
\]

\[(S13)\]
The PSD of the produced nanopores can be calculated by combining the pore nucleation and pore expansion kinetics. This way, the number of missing carbon atoms etched away from each pore in the \( t_i \) to \( t_j \) time interval can be calculated using equation S14.

\[
C_{\text{nucleation}}^{t_i-t_j} = \frac{\int_{t_i}^{t_j} kp^{0.5} dt}{k_c H \int_{t_0}^{t_i} P dt + k_c H \int_{t_i}^{t_j} P dt}
\] (S14)

The total number of the missing carbon atoms for nuclei generated in the time duration of \( t_{i-1} < t < t_i \) at the end of a particular etching period (\( t_j \)) can be calculated using equation S15. To obtain the final PSD, equation S15 is applied to each time interval and \( t_j \) is set as the final etching time.

\[
v_i^{t_j} = \sum_{m=i}^{j} \frac{\Delta C_m}{\Sigma_{k=1}^{m} N_k} = \frac{\Delta C_i}{N_1+N_2+\ldots+N_i} + \ldots + \frac{\Delta C_j}{N_1+N_2+\ldots+N_j}
\] (S15)

The PSD can be calculated for any given MGR condition following these steps: i) an equation for the pressure profile is defined using the mathematical model for ozone pressure; ii) the total etching time is divided into small time intervals (\( \Delta t \)), and for each \( \Delta t \), the newly formed pores and the number of missing carbon atoms are calculated using equations S11 and S13; iii) the total number of the missing carbon atoms for each nucleus is calculated by equation S15.

Overall, the O\(_3\) pressure at a given time interval determines the number of missing carbon atoms leaving from each pore and the number of new pores created in that time interval. As the ozone pressure increases, the relative increment of pore nucleation is higher compared to the increment of total missing carbon atoms, leading to fewer missing carbon atoms leaving from each pore. On the contrary, dilute ozone conditions (\( P_{O3} < 1 \) torr) leads to a relatively higher increment of total
missing carbon atoms compared to the pore nucleation. In general, a sharp PSD is promoted by etching in a high ozone pressure environment.
Note S3. Modeling of pore expansion without nucleation

An etching model was built to describe pore expansion in low concentration ozone. It is based on the previously-described ozone etching kinetics but assumes that there are no newly formed pores during the etching process. The total number of missing carbon during the expansion process can be calculated from equation S13. And the number of missing carbon atoms etched per pore by the expansion process is calculated using equation S16:

\[
C_{\text{expansion}} = \int_{t_i}^{t_f} k P^{0.5} dt / N_{\text{sum}}
\]

(S16)

where \(C_{\text{expansion}}\) is the total number of missing carbon atoms per pore during an etching reaction taking place from \(t_i\) to \(t_f\), and \(N_{\text{sum}}\) is the total number of pre-existing pores in the sample.

The PSD of N-SLG after a high-pressure (nucleation and expansion) and low-pressure (expansion) ozone etching steps can be calculated by adding the total number of carbon atoms etched in each step for each pore.

\[
C_{\text{total}} = C_{\text{nucleation}} + C_{\text{expansion}}
\]

(S17)
Note S4. Analysis of the AC-HRTEM images

The number of missing carbon atoms of the vacancy defects was estimated using a graphical approach consisting of the following steps: i) the contour of the pore was manually drawn (Figure S4a); ii) the outline of the pore was overlapped on top of a pristine graphene lattice (in a random position) maintaining the same scale to match the AC-HRTEM image (Figure S4b); iii) all the carbon atoms that fell inside of the vacancy defect were deleted and ImageJ software was used to count the number of missing C atoms (only C atoms that were utterly removed were counted as missing C atoms). We note that this number of missing carbon atoms ($C_{\text{mismatch}}$) is an overestimation of the real number as the contour (edge of the nanopore) and the pristine lattice are not in a perfect match attributing to the lattice distortion present in the image (Figure S4c).

The error generated by the inherent mismatch between contour and digital graphene lattice of the proposed graphical approach is a function of the length of the contour line and geometric factors (such as the relative size of the dots representing the carbon atoms and the thickness of the contour line used, and the degree of mismatch between contour and digital lattice). To minimize the error, a correction factor ($C_{\text{correction}}$) that takes into account the number of carbon atoms that form the contour of the vacancy defect and geometric factors (to some degree) was developed.

\[ C_{\text{correction}} \propto G C_{\text{contour}} \]  \hspace{1cm} (S18)

where $C_{\text{contour}}$ is the number of carbon atoms that form the contour of the vacancy defect (Figure S4d) and can be extracted by measuring the length of the contour and dividing by the distance between carbon atoms in a graphene lattice (0.142 nm) and $G$ is a geometric correction factor.
The estimated number of missing carbon atoms \( (C_{\text{missing}}) \) was calculated using the following equation:

\[
C_{\text{missing}} = C_{\text{mismatch}} - G C_{\text{contour}}
\]  

(S19)

The geometric correction factor for our system was calculated by simulating 10 pores of a known structure \( (i.e., \text{known number of missing carbon atoms and number of carbon atoms in the contour}) \), analyzing them using the geometric approach, and minimizing the error between the real number of carbon missing atoms and \( C_{\text{missing}} \). The calculated geometric factor was 2.5. The calculated number of missing carbon atoms using the graphical approach for the P-22 shown in Figure S4 was 21 which corresponds to an error of 5% (Figure S4e).

The validity of the graphical approach was verified by analyzing four vacancy defects with three different mismatch angles each of them. The analyzed vacancy defects were P-6, P-13, P-22, and P-65 (containing 6, 13, 22, and 65 missing carbon atoms, respectively). The analysis done to P-22 is shown in Figure S5. The calculated number of missing carbon atoms by the graphical approach was in good agreement with the real number of missing carbon atoms (the observed errors were \( \leq 10\% \)).

An alternative approach to analyzing the vacancy defects is to precisely draw the graphene lattice around them and count the number of missing carbon atoms (Figure S4f). However, this type of analysis is time-consuming and is restricted to vacancy defects where the lattice is completely resolved around them.
Overall, the graphical approach is a powerful tool to meaningful calculate the PSD of nanoporous graphene samples. It allows the analysis of a vast number of pores because the lattice does not have to be resolved entirely around the pore.

**Note S5. PEI anchoring on N-SLG**

To prove covalent grafting of PEI on N-SLG, we carried out an additional experiment to anchor a monolayer of PEI on graphene. For this, we contacted N-SLG with PEI solution and washed off the excessive PEI solution. Briefly, a dilute PEI solution (10 mg/ml) was placed on the surface of ozone-gasified N-SLG, making sure that the solution does not dry off. After one hour, the PEI solution was rinsed off with water by placing N-SLG in a water bath overnight to remove the unreacted PEI. The resulting samples were characterized by XPS and HRTEM.

The XPS spectrum of N-SLG before treatment to PEI (control sample, Figure S17a, b) was used as a reference. As a result of oxygen functionalization from O$_3$ etching, the C1s peak had a shoulder at $\sim$286 eV (C-O, from epoxy and ether groups, 14.5%, Table S15), and there was no N1s peak. In sharp contrast, N-SLG treated with PEI had a strong N1s peak confirming the anchoring of PEI on graphene (Figure S17d). The shoulders in C1s are also significantly altered (Figure S17c, Table S16). The primary, second, and tertiary amine groups in N1s peak are listed in Table S17. The increased intensity of peak at $\sim$286 eV in the C1s peak can be attributed to the C-N bonding from PEI grafting on graphene by ring-opening chemistry of C-O groups, as well as the intrinsic C-N bonds in PEI.

**Note S6. Quantification of amine functionalization**

To quantify the number of available sites in graphene for amine functionalization, we used ethylenediamine (EDA) as a simple probe molecule. Briefly, the surface of the N-SLG was covered
by an EDA film (a similar experiment to that used for PEI functionalization). The excessive EDA was rinsed off with water by soaking N-SLG in a water bath overnight. The resulting sample was characterized by XPS (Figure S19).

EDA is a linear molecule terminated with two primary amine groups at its two ends (Figure S20). After the functionalization with N-SLG, the grafted amine group should turn from primary to secondary amine. As a result, the percentage of the secondary amine group gives the information of the number of carbon atoms grafted with EDA molecules.

From the XPS data of EDA treated N-SLG, there is a clear N1s peak (Figure S19, Table S18). This peak indicates that nitrogen constitutes 14.6% of all atoms (Table S19). Here, the secondary amine constitutes 10.5%, while the primary amine accounts for 4.1%. Given that EDA does not have secondary amine, the secondary amine (10.6% sites) observed here is a clear indication of the extent of functionalization. We note that the amount of secondary amine is comparable to the amount of C-O (14.5%) in N-SLG before functionalization (Table S15), indicating that the oxygen functional group (C-O) gives way to amine functionalization, likely by the ring-opening chemistry.
Figure S1. Photograph (a) and schematic (b) of the MGR equipped with a millisecond leak valve (MLV) to deliver the O$_3$. (c) The illustration of pressure profile in MGR during the reaction. From i to ii the MLV valve was closed (i.e., interval time between pulses), and from ii to iii the MLV was opened (i.e., pulse). The number of blue points shows the number of pulses. The area under the pressure-time curve, A, is proportional to the pore density.
Figure S2. Simulated (black curve) and recorded (red curve) pressure profiles in the MGR chamber. The following conditions were used for each experiment: (a) $\tau_o = 10$ ms, $\tau_i = 500$ ms, and $F = 15$; (b) $\tau_o = 10$ ms, $\tau_i = 100$ ms, and $F = 15$; and (c) $\tau_o = 100$ ms, $\tau_i = 100$ ms, and $F = 15$. 
Figure S3. Simulated pressure profile and PSD for various conditions. (a) Pressure profiles, and (d) PSD for a $\tau_o$ of 5 ms, 10 ms, and 100 ms with a fixed $\tau_i = 100$ ms, and $F = 15$; (b) Pressure profiles, and (e) PSD for a $\tau_i$ of 100 ms, 500 ms, and 1000 ms with fixed $\tau_o = 10$ ms, and $F = 15$; (c) Pressure profiles, and (f) PSD for a $F$ of 1, 6, and 15 with fixed $\tau_o = 100$ ms, and $\tau_i = 100$. 
Figure S4. Graphical approach to efficiently analyze the number of missing carbon atoms of vacancy defects in AC-HRTEM images. Refer to supplementary Note S4 for more details.
**Figure S5.** Vacancy defect with 22 missing carbon atoms analyzed using the graphical approach. The validity of the graphical approach was verified by comparing the calculated number of missing carbon atoms in a P-22 defect, assuming different mismatch angles between the contour of the vacancy defect and the graphene lattice.
Figure S6. SEM image of the cross-section of a PTMSP film deposited on a silicon wafer.
Figure S7. XPS of as-synthesized SLG (a), and N-SLG fabricated using the “high” pressure profile (b). c) XPS of N-SLG fabricated using controlled expansion of specimen in (b). The expansion was carried out using the following parameters ($\tau_o = 5$ ms and $\tau_i = 350$ ms, $F = 120$).
Figure S8. Simulated and experimental pressure profiles in the MGR when a low concentration of ozone was used to controllably expand the nanopores. The $\tau_o$ and $\tau_i$ were 5 and 350 ms, respectively for all cases. The number of openings (F) were (a) 10, (b) 15, (c) 20, and (d) 40.
Figure S9. AC-HRTEM images of N-SLG fabricated using the “intermediate” pressure profile and expanded using 20 pulses (low concentration of ozone, $\tau_0 = 5$ ms and $\tau_i = 350$ ms). All scale bars are 2 nm.
Figure S10. AC-HRTEM images of N-SLG fabricated using the “intermediate” pressure profile and expanded using 40 pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms). All scale bars are 2 nm.
Figure S11. Comparison of the AC-HRTEM images of N-SLG fabricated using the “intermediate” pressure profile as a starting point (a) with those prepared by expansion with low-pressure ozone using 20 pulses (b) and 40 pulses (c). The expansion parameters were: $\tau_o = 5$ ms and $\tau_i = 350$ ms. d) AC-HRTEM image demonstrating two nanopores that coalesced together during the pore expansion process. All scale bars are 2 nm.
Figure S12. Model predicted PSD when the N-SLG fabricated using the “intermediate” pressure profile was expanded using (a) 20 pulses, and (b) 40 pulses with a low concentration of ozone. In both cases, $\tau_o = 5$ ms and $\tau_i = 350$ ms.
Figure S13. The predicted PSD considering both nucleation and expansion during the expansion step for the N-SLG fabricated using the “intermediate” pressure profile and expanded using a low concentration of ozone ($\tau_o = 5$ ms, $\tau_i = 350$ ms, $F = 40$).
Figure S14. Evolution of gas transport as a function of the controlled pore expansion. (a) CO$_2$ permeance and CO$_2$/N$_2$ separation factor; (b) H$_2$, CO$_2$, N$_2$, and CH$_4$ single gas permeation results. PTMSP refers to a standalone PTMSP membrane without graphene. 0 – 40 pulses referred to the N-SLG membrane fabricated using the “intermediate” pressure profile and expanded using 0 - 40 pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms).
**Figure S15.** AC-HRTEM images of the N-SLG fabricated using the “intermediate” pressure profile. Some vacancy defects are close enough to potentially merge during the expansion process. The dashed line in panel (b) shows two of such pores. All scale bars are 2 nm.
Figure S16. Schematic of the gas permeation setup.
Figure S17. The XPS spectra from N-SLG (a, b) and N-SLG treated with PEI followed by water washing (c, d). a-c) C1s spectra. b-d) N1s spectra.
Figure S18. HRTEM images and corresponding fast Fourier transform (FFT) from PEI-treated N-SLG. (a) and (b) are acquired from the top side of the film. (c) and (d) are acquired after flipping the TEM grid upside down, i.e., imaging from the graphene side of the film.
Figure S19. The XPS spectrum of (a) C1s and (b) N1s of EDA-functionalized N-SLG

Figure S20. The structure of ethylenediamine with two terminated primary amine
Table S1. MLV conductance and the pressure drop in the O$_3$ reservoir after each pulse used for the mathematical model.

| $\tau_0$ (s) | $C_1$ (mol s$^{-1}$ Pa$^{-1}$) | $C_2$ (mol s$^{-1}$ Pa$^{-1}$) | $\Delta P$ (Pa) |
|--------------|-----------------------------|-----------------------------|----------------|
| 0.1          | $5.7 \times 10^{-8}$       | $1.5 \times 10^{-7}$       | 23000          |
| 0.01         | $1.3 \times 10^{-7}$       | $1.5 \times 10^{-7}$       | 8000           |
| 0.005        | $3.8 \times 10^{-8}$       | $1.5 \times 10^{-7}$       | 1000           |

Table S2. Comparison between the total pore density and the density of CO$_2$ permeable pores present in each sample.

|                  | Pore density (cm$^{-2}$) | CO$_2$ permeable pores (%) | Pore density (cm$^{-2}$) |
|------------------|--------------------------|----------------------------|--------------------------|
| Control          | $1.8 \times 10^{12}$     | 10.5                       | $1.9 \times 10^{11}$     |
| “Low”            | $7.2 \times 10^{12}$     | 25.0                       | $1.8 \times 10^{12}$     |
| “Intermediate”   | $5.3 \times 10^{12}$     | 7.2                        | $3.8 \times 10^{11}$     |
| “High”           | $1.3 \times 10^{13}$     | 2.2                        | $2.9 \times 10^{11}$     |
Table S3. Mixed gas permeation results for N-SLG/PTMSP membranes (CO$_2$ concentration of 20 mol%, $T = 30 \, ^\circ$C, feed pressure = 2 bar).

|               | CO$_2$ Permeance (GPU) | N$_2$ Permeance (GPU) | CO$_2$/N$_2$ Separation factor |
|---------------|------------------------|-----------------------|-------------------------------|
| Control       | 4870 ± 1600            | 330 ± 120             | 15.0 ± 0.5                    |
| “Low”         | 25530 ± 2350           | 2040 ± 90             | 12.5 ± 1.7                    |
| “Intermediate”| 3170 ± 730             | 170 ± 30              | 18.6 ± 0.8                    |
| “High”        | 4400 ± 2070            | 140 ± 100             | 33.4 ± 7.9                    |

Table S4. Single gas permeation results for N-SLG/PTMSP membranes ($T = 30 \, ^\circ$C, feed pressure = 2 bar).

|               | CO$_2$ Permeance (GPU) | N$_2$ Permeance (GPU) | CH$_4$ Permeance (GPU) | CO$_2$/CH$_4$ Ideal Selectivity | CO$_2$/N$_2$ Ideal Selectivity |
|---------------|------------------------|-----------------------|------------------------|---------------------------------|-------------------------------|
| Control       | 4280 ± 1280            | 350 ± 120             | 810 ± 180              | 5.2 ± 0.4                       | 12.2 ± 0.4                    |
| “Low”         | 22470 ± 170            | 2940 ± 2130           | 3540 ± 2050            | 4.8 ± 0.3                       | 13.2 ± 3.6                    |
| “Intermediate”| 2290 ± 950             | 120 ± 70              | 330 ± 130              | 7.0 ± 1.5                       | 19.1 ± 2.4                    |
| “High”        | 4370 ± 200             | 150 ± 100             | 530 ± 390              | 9.5 ± 3.2                       | 32.0 ± 8.3                    |
Table S5. Simulated number of missing carbon atoms, PSD, and pore density considering (i) only expansion, and (ii) both nucleation and expansion during the dilute ozone etching step.

|                                | Only expansion | Both nucleation and expansion |
|--------------------------------|----------------|------------------------------|
| Percentage of newly nucleated nanopores | -              | 23%  
(corresponding to 1 to 7 missing carbon atoms) |
| Pore density (cm$^{-2}$)       | $6.7 \times 10^{12}$ | $8.7 \times 10^{12}$ |
**Table S6.** CO$_2$/N$_2$ and CO$_2$/CH$_4$ mixed gas permeation results for N-SLG/PTMSP membranes before and after expanding the nanopores using a dilute ozone etching step (CO$_2$ concentration of 20 mol%, $T = 30\, ^\circ C$, feed pressure = 2 bar). The control sample is the N-SLG fabricated using the “intermediate” pressure profile. The expansion was done by exposing the control N-SLG to a number of O$_3$ pulses (low concentration of ozone, $\tau_e = 5$ ms and $\tau_i = 350$ ms). Data for a standalone PTMSP membranes are added for reference.

| Pulses | CO$_2$ Permeance (GPU) | N$_2$ Permeance (GPU) | CO$_2$/N$_2$ Separation Factor |
|--------|------------------------|------------------------|-------------------------------|
| 0 (control) | 3170 ± 730 | 170 ± 31 | 18.6 ± 0.8 |
| 10 | 3700 ± 420 | 210 ± 17 | 18.0 ± 0.5 |
| 15 | 4680 ± 610 | 350 ± 18 | 13.5 ± 1.0 |
| 20 | 8080 ± 790 | 670 ± 194 | 12.4 ± 2.4 |
| 40 | 14350 ± 3380 | 1320 ± 238 | 10.8 ± 0.6 |
| PTMSP | 33290 ± 7140 | 3130 ± 760 | 10.7 ± 0.3 |

| Pulses | CO$_2$ Permeance (GPU) | CH$_4$ Permeance (GPU) | CO$_2$/CH$_4$ Separation Factor |
|--------|------------------------|------------------------|-------------------------------|
| 0 (control) | 3300 ± 870 | 580 ± 360 | 6.4 ± 1.8 |
| 10 | 3540 ± 230 | 470 ± 120 | 6.8 ± 1.5 |
| 15 | 4520 ± 830 | 670 ± 120 | 6.8 ± 0.0 |
| 20 | 7120 ± 1700 | 1360 ± 420 | 5.3 ± 0.4 |
| 40 | 14060 ± 4340 | 2400 ± 660 | 5.8 ± 0.2 |
| PTMSP | 32840 ± 5690 | 6980 ± 1850 | 4.8 ± 0.5 |
Table S7. Single gas permeation results for N-SLG/PTMSP membranes before and after expanding the nanopores using a dilute ozone etching step (T = 30 ºC, Feed P = 2 bar). The control sample is the N-SLG fabricated using the “intermediate” pressure profile. The expansion was done by exposing the control N-SLG to a number of O₃ pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms). Data for a standalone PTMSP membranes are added for reference.

| Pulses  | H₂ Permeance (GPU) | CO₂ Permeance (GPU) | N₂ Permeance (GPU) | CH₄ Permeance (GPU) |
|---------|--------------------|---------------------|--------------------|--------------------|
| 0 (control) | 1940 ± 3 | 2290 ± 950 | 120 ± 70 | 330 ± 130 |
| 10      | 2880 ± 500 | 3700 ± 420 | 220 ± 50 | 490 ± 90 |
| 15      | 2860 ± 3 | 5650 ± 220 | 410 ± 50 | 870 ± 0 |
| 20      | 5230 ± 640 | 8080 ± 790 | 720 ± 120 | 1110 ± 900 |
| 40      | 12810 ± 4940 | 16170 ± 6310 | 1480 ± 350 | 2580 ± 770 |
| PTMSP   | 23840 ± 16950 | 30340 ± 6140 | 3360 ± 830 | 7490 ± 1680 |
Table S8. CO₂ permeance, CO₂/N₂ and CO₂/CH₄ ideal selectivity of the expanded for N-SLG/PTMSP membranes before and after expanding the nanopores using a dilute ozone etching step (T = 30 °C, feed pressure = 2 bar). The control sample is the N-SLG fabricated using the “intermediate” pressure profile. The expansion was done by exposing the control N-SLG to a number of O₃ pulses (low concentration of ozone, τ₀ = 5 ms and τᵢ = 350 ms). Data for a standalone PTMSP membranes are added for reference.

| Pulses | CO₂ Permeance (GPU) | CO₂/N₂ Idea Selectivity | CO₂/CH₄ Idea Selectivity |
|--------|---------------------|--------------------------|--------------------------|
| 0 (control) | 2290 ± 950          | 19.1 ± 2.4               | 7.0 ± 1.5                |
| 10     | 3700 ± 420          | 18.0 ± 0.9               | 7.8 ± 1.4                |
| 15     | 5650 ± 220          | 13.4 ± 0.5               | 6.8 ± 0.0                |
| 20     | 8080 ± 790          | 12.4 ± 1.0               | 5.3 ± 0.4                |
| 40     | 16170 ± 6310        | 11.0 ± 2.4               | 5.8 ± 0.2                |
| PTMSP  | 30340 ± 6140        | 9.1 ± 0.4                | 4.0 ± 0.1                |
Table S9. AC-HRTEM-based and model-based pore densities for the N-SLG membranes fabricated using the “intermediate” pressure profile before and after expanding the pores using 20 and 40 pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms). Here, the model used only considers pore expansion (no nucleation). The model does not capture pore coalescence.

| Sample                        | Pore density (cm$^{-2}$) | AC-HRTEM | Simulated |
|-------------------------------|--------------------------|----------|-----------|
| Initial condition (IC #1)     | “Intermediate” PSD       | $5.7 \times 10^{12}$ | $5.3 \times 10^{12}$ |
| IC #1 + Short expansion:      | 20 pulses                | $3.2 \times 10^{12}$ | $5.3 \times 10^{12}$ |
| IC #1 + Long expansion:       | 40 pulses                | $2.6 \times 10^{12}$ | $5.3 \times 10^{12}$ |
Table S10. Mixed gas permeation results (CO₂ concentration of 20 mol%, T = 30 °C, feed pressure = 2 bar) for the polymer-functionalized N-SLG made using an expanded “intermediate” N-SLG (4 membranes tested) and an expanded “high” N-SLG (3 membranes tested). The expanded “intermediate” N-SLG is the N-SLG fabricated using the “intermediate” pressure profile and expanded using 40 O3 pulses (low concentration of ozone, τ₀ = 5 ms and τ₁ = 350 ms). The expanded “high” N-SLG is the N-SLG fabricated using the “high” pressure profile and expanded using 120 O3 pulses (low concentration of ozone, τ₀ = 5 ms and τ₁ = 350 ms).

|                          | CO₂ Permeance (GPU) | CH₄ Permeance (GPU) | CO₂/CH₄ separation factor | CO₂ Permeance (GPU) | N₂ Permeance (GPU) | CO₂/N₂ separation factor |
|--------------------------|---------------------|---------------------|--------------------------|---------------------|---------------------|--------------------------|
| Polymer-functionalized N-|                     |                     |                          |                     |                     |                          |
| SLG membranes (Expanded  | 5280                | 570                 | 9.2                      | 5160                | 190                 | 27.1                     |
| “intermediate”)          | 2970                | 280                 | 10.7                     | 2990                | 70                  | 43.6                     |
|                          | 4280                | 420                 | 10.3                     | 4110                | 150                 | 28.1                     |
|                          | 2180                | 180                 | 11.9                     | 2060                | 44                  | 46.7                     |
| Polymer-functionalized N-|                     |                     |                          |                     |                     |                          |
| SLG membranes (Expanded  | 8880                | 960                 | 9.2                      | 8710                | 390                 | 23.0                     |
| “high”)                  | 7541                | 810                 | 9.3                      | 7280                | 330                 | 22.2                     |
|                          | 9160                | 930                 | 9.9                      | 8730                | 261                 | 33.4                     |
**Table S11.** Single gas permeation results (T = 30 °C, feed pressure = 2 bar) for polymer-functionalized N-SLG made using an expanded “intermediate” N-SLG (4 membranes tested) and an expanded “high” N-SLG (3 membranes tested). The expanded “intermediate” N-SLG is the N-SLG fabricated using the “intermediate” pressure profile and expanded using 40 O$_3$ pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms). The expanded “high” N-SLG is the N-SLG fabricated using the “high” pressure profile and expanded using 120 O$_3$ pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms).

|                      | CO$_2$ Permeance (GPU) | CO$_2$/N$_2$ ideal selectivity | CO$_2$/CH$_4$ ideal selectivity |
|----------------------|------------------------|-------------------------------|-------------------------------|
| Polymer-functionalized N-SLG membranes (Expanded “intermediate”) | 5010                   | 25.9                          | 8.4                           |
|                      | 2670                   | 42.6                          | 9.8                           |
|                      | 3900                   | 27.7                          | 9.5                           |
|                      | 2060                   | 39.7                          | 11.7                          |
| Polymer-functionalized N-SLG membranes (Expanded “High”) | 8330                   | 23.0                          | 9.2                           |
|                      | 6850                   | 20.7                          | 8.5                           |
|                      | 8550                   | 24.6                          | 9.0                           |
Table S12. Mixed gas permeation results for membrane before and after the polymer functionalization (CO$_2$ percentage of 20 mol%, T = 30 ºC, feed pressure = 2 bar). The expanded “intermediate” N-SLG is the N-SLG fabricated using the “intermediate” pressure profile and expanded using 40 O$_3$ pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms). The expanded “high” N-SLG is the N-SLG fabricated using the “high” pressure profile and expanded using 120 O$_3$ pulses (low concentration of ozone, $\tau_o = 5$ ms and $\tau_i = 350$ ms).

| Membrane       | Pore density (cm$^{-2}$) | CO$_2$ Permeance (GPU) | CO$_2$/N$_2$ | CO$_2$/CH$_4$ | CO$_2$ Permeance (GPU) | CO$_2$/N$_2$ | CO$_2$/CH$_4$ |
|----------------|-------------------------|------------------------|--------------|--------------|------------------------|--------------|--------------|
| Expanded “intermediate” | $5.3 \times 10^{12}$ | 3580±1350              | 36.4±10.2    | 10.5±1.1     | 14350±3380            | 10.8±0.6    | 5.8±0.2      |
| Expanded “high”   | $1.3 \times 10^{13}$ | 8240±830               | 26.2±6.2     | 9.5±0.4      | 17230±440             | 11.6±0.3    | 5.1±0.7      |
Table S13. CO$_2$/N$_2$ mixture separation performance comparison between the N-SLG membranes presented in this work and state-of-the-art membranes.

| Membrane type                      | Membrane Nomenclature                       | CO$_2$ permeance (GPU) | CO$_2$/N$_2$ selectivity | Reference |
|------------------------------------|--------------------------------------------|------------------------|--------------------------|-----------|
| Commercial membrane                | Cellulose acetate                          | 110                    | 30                       | [11]      |
|                                    | Polaris®                                   | 1000                   | 50                       | [11]      |
| Graphene oxide (GO)                | GO with PEGBA                              | 186                    | 59                       | [12]      |
|                                    | GO with ionic-liquid                       | 37                     | 130                      | [13]      |
|                                    | GO                                         | 103                    | 18                       | [14]      |
| Facilitated transport membranes    | Borate in GO                               | 650                    | 57                       | [15]      |
|                                    | Piperazine in GO                           | 1020                   | 680                      | [16]      |
|                                    | Enzymatic solution                         | 2600                   | 788                      | [17]      |
|                                    | Polyvinylamine                             | 1827                   | 500                      | [18]      |
| Mixed matrix membranes             | UiO-66-NH$_2$ in PEBAX®                    | 338                    | 57                       | [19]      |
|                                    | ZIF-8 in PEBAX®                           | 345                    | 32                       | [20]      |
|                                    | GO in thermally-reduced (TR) polymer       | 1784                   | 18*                      | [21]      |
|                                    | Carbon nanotubes in cellulose acetate      | 742                    | 40.2                     | [22]      |
|                                    | ZIF-8 in Ultem®                            | 26                     | 36                       | [23]      |
|                                    | Ionic liquid in graphene                   | 4000                   | 20                       | [24]      |
| Polymeric membranes                | PEG/PDMS                                   | 1210                   | 22                       | [25]      |
|                                    | PEG/NH$_2$-MIL-53                          | 2600                   | 14                       | [26]      |
|                                    | DAmPEG-TMC                                  | 1310                   | 33                       | [27]      |
|                                    | Pebax2533/PEG-b-PPFPA                      | 3330                   | 22*                      | [28]      |
|                                    | TR polymer                                 | 1938                   | 13*                      | [29]      |
| Hybrid membrane                    | Poly(ionic liquids)                        | 132                    | 27                       | [30]      |
|                                    | Metal-induced ordered microporous polymers (MMPs) | 3000               | 78                       | [31]      |
| Polymer-functionalized N-SLG       | Polymer-functionalized N-SLG membranes (Expanded “intermediate”) | 5164 | 27 |
|                                    |                                            | 2985                   | 44                       | This work |
|                                    |                                            | 4111                   | 28                       |           |
|                                    |                                            | 2065                   | 47                       |           |
|                                    | Polymer-functionalized N-SLG membranes (Expanded “high”) | 8714 | 23 |
|                                    |                                            | 7277                   | 22                       |           |
|                                    |                                            | 8730                   | 33                       |           |

* Indicate the ideal selectivity.
Table S14. Single gas permeation results (T = 30 ºC, feed pressure = 2 bar) for the cm²-scale membranes prepared using polymer-functionalized N-SLG membranes (Expanded “high”).

|          | CO₂ Permeance (GPU) | CO₂/N₂ ideal selectivity | CO₂/CH₄ ideal selectivity |
|----------|---------------------|--------------------------|---------------------------|
| M1       | 2660                | 18.0                     | 7.5                       |
| M2       | 3390                | 17.7                     | 7.0                       |
| M3       | 2090                | 26.8                     | 11.5                      |

Table S15. The binding energy and percentage of each component in C1s spectrum of ozone-treated N-SLG.

| Component       | Binding Energy (eV) | (%)  |
|-----------------|---------------------|------|
| C-C sp²         | 284.6               | 59.9 |
| C-C sp³         | 285.0               | 11.5 |
| C-O             | 286.2               | 14.5 |
| C=O             | 288.7               | 10.7 |
| O=C=O           | 289.5               | 3.5  |

Table S16. The binding energy and percentage of each component in C1s spectrum of PEI-functionalized N-SLG.

| Component       | Binding Energy (eV) | (%)  |
|-----------------|---------------------|------|
| C-C sp²         | 284.4               | 51.9 |
| C-C sp³         | 285.0               | 11.8 |
| C-N + C-O       | 285.8               | 26.3 |
| C=O             | 288.0               | 7.6  |
| O-C=O           | 289.0               | 2.3  |

Table S17. The percentage of the C-N bonds extracted from the N1s peak of N-SLG treated with PEI.

| Component in N1s (%) | Primary amine in N1s (%) | Secondary amine in N1s (%) | Tertiary amine in N1s (%) |
|----------------------|--------------------------|-----------------------------|---------------------------|
|                      | 69.0                     | 27.8                        | 3.2                       |
Table S18. The binding energy and percentage of each component in C1s and N1s spectra of EDA-functionalized N-SLG.

|     | C1s            | Binding Energy (eV) | (%)  |
|-----|----------------|---------------------|------|
|     | C-C sp²        | 284.5               | 34.9 |
|     | C-C sp³        | 285.0               | 22.6 |
|     | C-N            | 285.9               | 29.3 |
|     | C-O            | 286.3               | 5.5  |
|     | C=O            | 288.2               | 7.8  |

|     | N1s            | Binding Energy (eV) | (%)  |
|-----|----------------|---------------------|------|
|     | C-N (primary amine) | 400.3               | 27.7 |
|     | C-N (secondary amine) | 399.5               | 72.3 |

Table S19. The percentage of primary and secondary amine in N1s, and C1s in XPS spectrum.

| Primary amine (N1s) (%) | Secondary amine (N1s) (%) | C1s (%) |
|-------------------------|----------------------------|--------|
| 4.0                     | 10.6                       | 85.4   |
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