Supporting Information

Tunable Pore Size from Sub-Nanometer to a Few Nanometers in Large-Area Graphene Nanoporous Atomically Thin Membranes

Xiaobo Chen¹, Shengping zhang^{1,2,3,4}, Dandan Hou^{1,4}, Hongwei Duan^{1,2}, Bing Deng³, Zhiyang Zeng¹, Bingyao Liu^{2,3,4,5}, Luzhao Sun³, Ruiyang Song¹, Jinlong Du⁵, Peng Gao^{2,4,5,6,7} Hailin Peng^{3,4}, Zhongfan Liu^{3,4} and Luda Wang^{1,2,3,4*}

¹Institute of Microelectronics, School of Electronics Engineering and Computer Science, Peking University, Beijing, 100871, China.

²Academy for Advanced Interdisciplinary Studies, Peking University, Beijing,

100871, China.

³Center for Nanochemistry, Beijing Science and Engineering Center for Nanocarbons,

Beijing National Laboratory for Molecular Sciences, College of Chemistry and

Molecular Engineering, Peking University, Beijing, 100871, China.

⁴Beijing Graphene Institute, Beijing, 100095, China.

⁵Electron Microscopy Laboratory, School of Physics, Peking University, Beijing, 100871, China

⁶International Center for Quantum Materials, School of Physics, Peking University,

Beijing, 100871, China.

⁷Collaborative Innovation Center of Quantum Matter, Beijing, 100871, China.

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Supplementary section 1. Illustration of traditional method resulting in an uncontrollable pore size distribution



Figure S1. Illustration of fabrication steps in traditional method.

Supplementary section 2. Estimation of defect density using Raman calculation

The defect density of graphene was calculated using the ratio of the D peak (I_D) to G peak (I_G) , obtained from the Raman spectra. Two equations were applied to extract the estimated defect density of graphene depending on the different density regime. In low defect density regime, the average inter-defect distance (L_D) and the peak ratio can be described using the following equation^{1, 2}:

$$L_D(nm) = \sqrt{\frac{4.3 \times 10^3}{E_L^4 \times {}^{I_D} / {}_{I_G}}}$$
(1)

And the corresponding defect density is

$$n_D(cm^{-2}) = \frac{10^{1/2}}{\pi L_L^2}$$

(2)

E_L is the laser excitation energy in electron volts.

In high density regime, the I_D/I_G decreases as L_D decrease. And L_D is estimated using $L_D \propto \sqrt{I_D/I_G}$.



Figure S2. The corresponding average inter-defect distance of **Figure 2b Supplementary section 3. Estimation of defect density using ACTEM** The graphene specimens were directly transferred to TEM grid (SPI Au Quantifoil with

1.2-micron holey a-C film) to eliminate the potential contamination from the polymer.³ Prior to imaging, the specimens were firstly baked to further remove the surface contaminations. The ACTEM was operated at 60 keV to minimize the knock-off damage on graphene lattice by electrons.



Figure S3. Some of the HAADF images used to estimate the density of graphene NATMs. a) The single vacancy defect. b) The nanopore trapping a hetero-atom. (c) The area with no pore.



Figure S4. The TEM images of (a) pristine graphene (b) defect nucleated graphene. The possible defects were marked by red dotted circles.

Supplementary section 4. The simulation of oxygen plasma

2D-axial symmetry simulation using COMSOL was applied to qualitative study the screening effect of the Faraday cage in O₂ inductively coupled plasma etching. The simulated plasma chamber had a radius of 0.076 m with height of 0.165 m. Serval square coils at the edge of the chamber were built to stimulate the plasma. The coil power was 7 W and was consistent with the experimental condition. The aperture size of Faraday cage greatly reduced the electric field and electron density were studied. The Faraday cage greatly reduced the electric field near the substrate from about 10 V/m to less than 0.1 V/m and blocked the plasma into the cage (Figure S5). The injected ions were partly blocked by the Faraday cage and the collisions between plasma species inside the cage or between the species and the cage further decrease the energy of injected ions or atoms. As a result, Ion-bombardment of plasma was greatly reduced, while the neutral atomic oxygen or excited state molecular oxygen can still diffuse into the chamber and selectively etch the graphene.



Figure S5. Simulation results of influence of Faraday cage. a) The distribution of electric field in whole simulated area without Faraday cage. b) Enlarged electric field near the substrate of a). c) The electron density near substrate without Faraday cage. d) The distribution of electric field in whole simulated area with Faraday cage. e) Enlarged electric field near the substrate of d). f) The electron density near substrate with Faraday cage. e) Enlarged electric field near the substrate of d). f) The electron density near substrate with Faraday cage.

Supplementary section 5. SEM data of graphene on PCTE.



Figure S6. SEM data of transferred graphene on PCTE. The hot-press method can offer a better contact between graphene and PCTE. As a result, not only the coverage of graphene on PCTE is increased, but also the PCTE can mimic the morphology of copper,

marked with white arrows in b).

Supplementary section 6. Discussion of merging of nanopores.

The merging of nanopores could be happened when two nanopores in graphene is closed to each other during pore growth. **Figure S7** shows the pore-merging during TEM imaging. The high-energy electrons (200 keV) could knock-off the carbon atoms at graphene edges and cause the growth of nanopores. Two nanopores could be found during the imaging (**Figure S7a**, marked using red dotted lines). **Figure S7b** is the same area of graphene after electron irradiation. The two nanopores were enlarged and finally merged into a bigger pore (marked using red dotted lines).



Figure S7. (a) TEM images of pore-enlarged graphene (b) TEM images of the same area after several seconds electron irradiation.

Supplementary section 7. Discussion of the increasing of I(D)/I(G) during oxygen plasma.

The estimation of defect density using $({}^{I_D}/{I_G})$ shown in manuscript was based on the local activation model that assumes the defects in graphene as point defects.² When the defect density is low, the equation can be approximated to

$$\frac{I_D}{I_G} = C_A \frac{r_A^2 - r_S^2}{r_A^2 - 2r_S^2} [e^{-\pi r_S^2/L_D^2} - e^{-\pi (r_A^2 - r_S^2)/L_D^2}] \cong C_A \frac{\pi (r_A^2 - r_S^2)}{L_D^2}$$

Where C_A is a parameter related to laser energy and is obtained by the fit of experimental data. Thus, the defect density can be calculated:

$$n_D(cm^{-2}) = \frac{10^{14}}{\pi L_D^2} = \frac{10^{14} \times E_L^4 \times \frac{I_D}{I_G}}{160 \times \pi^2 \times (r_A^2 - r_S^2)}$$

In this model, r_s was 1 nm and determines the radius of the structurally disorder area of the point defect. r_a was 3.1 nm and was defined as the radius of surrounding area that D band scattering could also happen, while still preserve its lattice structure (**Figure S8a**). The r_s value in this model was obtained through STM characterization. However, the r_s value was not universal and was related to defect structure. In our situation, when the nanopore was small, the enlargement was solely inside the r_s . At this stage, the r_s and r_a remains similar as before (**Figure S8b**). However, when the pore becoming comparable to the r_s , the oxygen plasma would start to etch at the edge of structurally

disorder area and causes the further expanding of it. As a result, both r_s and r_a would becoming larger (**Figure S8c**). This was the case for our two minutes sample. The pore radii of this sample were mainly between 0.33 nm (hydrated radius of K⁺) and ~0.5 nm (Stokes-Einstein molecular radius of Allura Red). Assuming the Raman relaxation length $l = r_A - r_s$ is constant for same laser energy and defect type, then the equation can be rewritten as

$$n_D(cm^{-2})) = \frac{10^{14} \times E_L^4 \times \frac{I_D}{I_G}}{160 \times \pi^2 \times (2r_s l + l^2)}$$

Thus, with the same defect density, an increased r_s would result in a higher I_D/I_G when nanopore becoming comparable to the defect size in the model.



Figure S8. The demonstration of (a) r_s and r_a with no nanopore (b) r_s and r_a remain almost same with small nanopore (c) r_s and r_a becoming larger for larger nanopore.

Supplementary References

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ASSOCIATED CONTENT

Corresponding Author

Luda Wang

Institute of microelectronics, School of Electronics Engineering and Computer Science,

Peking University, Beijing, 100871, China. E-mail: luda.wang@pku.edu.cn