Supporting Information

Demonstrating and Unraveling a Controlled Nanometer-Scale Expansion of the Vacancy Defects in Graphene by CO\textsubscript{2}

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1. Experimental procedures

1.1 Graphene synthesis procedure

Single-layer graphene (SLG) was synthesized by the low-pressure chemical vapor deposition (LPCVD) procedure developed by Li et al., on 25-μm-thick 99.8% purity Cu foil from Alfa Aesar. Briefly, a piece of Cu foil (2 × 5 cm²) was sonicated for 5 min in Acetone and subsequently for an additional 5 min in isopropyl alcohol (IPA). Then, it was blow-dried by N₂ and placed inside the 1-inch quartz CVD reactor. The Cu foil was treated at 1000 °C and 800 Torr in a CO₂ atmosphere for 30 min to remove the organic contaminations. Keeping the temperature at 1000 °C for the remaining of the process, the reactor was evacuated to 1 mTorr. Subsequently, 8 sccm of H₂ was introduced for 30 min, increasing the pressure to 80 mTorr, to anneal the Cu surface and reduce the surface oxides. Finally, 24 sccm of CH₄ was added for 30 min to synthesize the polycrystalline SLG film. While maintaining the H₂ flow, the CH₄ flow was cut off to stop the crystallization before further etching experiments were carried out.

1.2. CO₂ etching procedures

CO₂ etching was performed inside the mentioned CVD reactor system. To eliminate the effect of O₂ leak from the atmosphere to the reactor through the quartz tube connections with the gas inlet and the vacuum section, these areas were encapsulated by a pure N₂ gas environment (Figure S1). In addition, ultra clean gas filters from PerkinElmer were installed on the path of the ultra-pure CH₄ and CO₂ gases to further eliminate the effect of O₂ impurities. H₂ was produced on-site by NM-500 plus hydrogen generator and passed through the triple O₂, H₂O, and hydrocarbon ultra clean gas filter from PerkinElmer before entering the CVD system. CO₂ etching experiments were carried out based on the sample’s initial condition:

a) For freshly synthesized SLG sample that has been kept inside the reactor at H₂ atmosphere, the sample was heated to the desired etching temperature and maintained for 5 min to reach the equilibrium. Next, 500 mTorr CO₂ was introduced to the system via mass flow controller while maintaining the H₂ partial pressure of 300 mTorr. After the desired etching duration, CO₂ flow was cut off, and Cu foil was moved outside the heating zone to cool down the sample and stop the reaction quickly. The sample was taken out of the reactor when the entire system’s temperature reached below 30 °C.

b) For samples that were pretreated outside the CVD reactor, i.e., O₂-treated and O₃-treated, the system was evacuated to full vacuum and purged 4 times after the sample was placed inside the reactor. Then, it was heated to the desired etching temperature at 1 atm H₂ before performing the rest of the process as written in section a.

c) For the suspended SLG sample, a high density of nanopores were etched in a pristine SLG film suspended on the 1 μm holes of a holey silicon nitride (Si₃N₄) TEM grid using O₃.² Then, it was exposed to H₂ atmosphere at 900 °C for 1 h to remove adsorbed contaminations and O-containing functional groups from the lattice prior to the CO₂ expansion experiments.³ The nanopores present in the sample were thoroughly characterized using AC-HRTEM (221 pores from 22000 nm²). Using this nanoporous SLG (N-SLG) as a starting point, the pores were expanded by CO₂ by following the process written in section b. The N-SLG hosting the expanded pores were thoroughly characterized using AC-HRTEM (381 pores from 40000 nm²) without further treatments to eliminate any external factors.
1.3. O3-treatment of SLG on Cu procedure

O3 etching was carried out in a homemade millisecond gasification reactor (MGR) setup.4 Briefly, as-synthesized SLG on the Cu foil was placed inside the MGR chamber, and the chamber was evacuated by a vacuum pump. A millisecond leak valve (MLV) was used to dose the gases and adjust the chamber pressure. First, the reactor was heated to the etching temperature (250 °C) with a H2 flow of 20 sccm. Next, H2 was cut off, and Ar was injected to purge the H2. Prior to exposure to O3, Ar was cut off to vacuum the chamber. The O3 etching step was controlled by a LabVIEW program that opens and closes the MLV to deliver the desired amount of O3/O2 mixture (100 ms of the opening time with 9% O3 on a molar basis) to the MGR chamber. Once the desired amount of O3 was delivered, Ar was introduced to purge the O3. Finally, the system was quickly cooled down to room temperature. The underlying Cu foil became oxidized with higher surface roughness after the O3 treatment. Prior to characterization and further CO2 expansion experiments, the sample was annealed at 900 °C in 1 atm H2 atmosphere for 3 h to reduce the copper oxide and to smoothen the underlying Cu surface to facilitate the STM characterization.

1.4. O2-plasma treatment procedure

O2-plasma treatment was done by a 13.56 MHz MTI EQ-PCE-3 plasma generator at 17 W. The chamber was fully evacuated and purged 3 times before fixing the flow of O2 to stabilize the system at 50 mTorr. Then, plasma was generated for the desired duration to introduce pores in the sample.

2. Characterization procedures

2.1. Scanning electron microscopy (SEM) characterization

Scanning electron microscopy (SEM) images were acquired by FEI Teneo at an operating voltage of 1-2 kV, an operating current of 13-25 pA, and a working distance of 4-7 mm. The in-column (T3) detector was utilized to image the expanded pores in SLG on Cu foil (the pore size is diameter of the biggest circle that can fit inside the pore), and the standard secondary-electron Everhart-Thornley detector was used to image the porous SLG sample after being oxidized in air. ImageJ software was used to analyze the pore size and density in each image.

2.2. Transmission electron microscopy (TEM) characterization

The SLG sample hosting the expanded pores was transferred onto an ultrathin carbon-coated TEM grid via the common wet transfer method.5 Briefly, 950 poly(methyl methacrylate) (PMMA) solution in anisole from Microchem was spin-coated on the SLG surface at 1000 and 2000 rpm for 1 min each. Then, it was heated at 70 °C for 30 min before etching the underlaying Cu foil by 0.5 M sodium persulfate (Na2SO4) solution. Next, the PMMA coated SLG was rinsed 3 times with deionized water (DIW) to remove the etching solution. Finally, the floating film was scooped on the ultrathin carbon-coated TEM grid and left to dry overnight. Before imaging the sample, it was placed in Acetone and isopropyl alcohol (IPA) to remove the PMMA layer. ImageJ software was used to analyze the pore size and density in each image. Bright-field and Dark-field TEM (BF-TEM and DF-TEM) images and selected area electron diffraction (SAED) patterns were obtained by FEI Tecnai G2 Spirit at the operating voltage of 120 kV.

2.3. Aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) characterization

As-synthesized SLG was transferred onto a TEM grid using a paraffin reinforcement layer. First, paraffin was melted by heating it to 80 °C and poured on top of the Cu-foil containing the freshly synthesized SLG. The paraffin was spin-coated at 1000 RPM for 30 s with the help of a hot-air gun to maintain the paraffin in liquid state during this process. Then, the Cu-foil was etched using a 1M FeCl3 solution, and the paraffin-reinforced SLG was washed in a HCl 1 M bath and a DIW bath. Next, the floating paraffin reinforced SLG was fished with a PELCO® Holey Silicon Nitride grid with 1 μm holes and dried at 45 °C for two days. Afterwards, the paraffin reinforcement layer was removed by immersing the grid for two hours in three consecutive heptane baths. Finally, the resulting grid with a free-standing SLG film covering > 70 % of its 1 μm holes was dried at room temperature for one day before introducing nanopores in it by O3 treatment, as mentioned in section 1.2.c.
AC-HRTEM was done with a double-corrected Titan Themis 60-300 (FEI) equipped with a Wein-type monochromator using an 80 keV incident electron beam to reduce the electron radiation damage. The electron beam was monochromated to reduce the effects of chromatic aberration, and a negative Cs of ~18–21 μm with a slight over-focus was used to give a “bright atom” contrast in the images. Typically, the lattice experienced a total dose of ~2 × 10^5 e⁻ Å⁻² during focusing and imaging. The images presented in the manuscript were obtained by integrating the first 5 to 10 frames (each frame corresponds to an exposure time of 200 ms and a dose of ~10^3 e⁻ Å⁻²) obtained during imaging of a particular area. When needed, the images were processed with a band-pass filter to make the lattice clearer. ImageJ software was used to analyze the pore size and density in each image.

2.4. Scanning tunneling microscopy (STM) characterization

STM was carried out by the Createc low-temperature scanning tunneling microscope (LT-STM) at 4.7 K. Before imaging, the sample was annealed at 873 K for 60 min inside the STM chamber to desorb the surface contaminations. The O₂- and O₃-treated SLG samples were measured at 0.2 V bias and 0.5 nA current, and the highly oriented pyrolytic graphite (HOPG) sample was measured at 0.15 V bias and 0.5 nA current. The image tilt was reduced by flattening in Gwyddion software.

2.5. Raman spectroscopy characterization

Raman spectroscopy was carried out using a Reinshow inVia™ confocal spectroscope equipped with a 457 nm excitation laser and a 100x objective. The laser spot size was ~500 nm, and the lateral step for each point in the map was set to 500 nm resulting in a mapping resolution of ~500 nm. The laser power was kept below 1 mW to reduce the localized heating led damages to graphene. Based on the mapped area, 36 to 500 spectra were recorded for different samples. The 2D peak intensity and I_D/I_G and I_2D/I_G ratios were calculated after background subtraction and curve fitting the 2D, G, and D peaks in MATLAB.

2.6. X-ray photoelectron spectroscopy (XPS) characterization

The X-ray photoelectron spectroscopy (XPS) analysis was conducted on the Cu foil using the monochromated Ka line of an aluminum X-ray source (1486.6 eV) with the analyzer set at pass energy of 20 eV. The samples were electrically grounded to the XPS sample stage. Shirley’s background was used for the peak fitting. The components of the Cu2p were fitted with symmetric line shapes. The following binding energies were used for the Cu2p fitting: Cu2p₁/₂: ~933; Cu2p₃/₂: ~953 eV.

2.7 Size distribution of expanded pores

Size distribution of the expanded pores was determined by analyzing the SEM images of the non-oxidized samples of graphene on Cu foil for the smaller pores, and the optical images of graphene transferred to SiO₂/Si substrate for the larger pores.
3. Additional Figures

Figure S1. Schematic of the CVD system used for graphene synthesis and CO\textsubscript{2} treatment

Figure S2. Raman spectroscopy analysis of the synthesized pristine SLG.
Figure S3. (a) SEM image of the SiOx particles on the graphene covered Cu surface, and (b) their corresponding EDX spectra revealing the nature of the particles.

Figure S4. (a and b) Raman spectroscopy mapping of the SLG hosting expanded pores after transferring onto a SiO2/Si substrate.

Figure S5. SEM images of the expanded pores in SLG on Cu foil at 900 °C for (a) 15 min and (b) 60 min. (c) Optical image of the expanded pores in SLG on Cu foil at 900 °C for 150 min after transfer onto a SiO2/Si substrate.
Figure S6. SEM images of expanded pores in SLG by 500 mTorr CO\textsubscript{2} on Cu foil at (a) 1000 °C, (b) 950 °C, (c) 900 °C, (d) 850 °C, and (e) 800 °C.

Figure S7. Schematic of etching of zigzag edge of graphene lattice by CO\textsubscript{2}.

Figure S8. (a) BF-TEM image of SLG hosting expanded pores at 950 °C and (b) the false-colored DF-TEM image of the same area displaying the location of pores (dark areas) with respect to the three different graphene grain orientations. White arrows and yellow arrows point out the pores inside the graphene grain and at the graphene grain boundary, respectively. (c-I) SAED pattern and (c-II, c-III, and c-IV) the corresponding DF-TEM images of the selected diffraction spot differentiated by the matching frame colors.
Figure S9. AC-HRTEM images of the initial O₃-treated SLG before exposure to CO₂.

Figure S10. AC-HRTEM images of the O₃-treated SLG sample shown in Figure S9 after exposure to 500 mTorr CO₂ at 800 °C for 3 min.

Figure S11. AC-HRTEM images of the O₃-treated SLG sample shown in Figure S10 after exposure to 500 mTorr CO₂ at 800 °C for 3 min.
Figure S12. STM images of a typical O$_2$-induced pore in SLG on Cu foil (a) before and (b) after exposure to 500 mTorr CO$_2$ at 800 °C for 3 min.

Figure S13. STM images of the 2s O$_2$-plasma treated HOPG after exposure to 500 mTorr CO$_2$ at 800 °C for 3 min.
4. Additional Notes

Note S1: Shape of the expanded pores

Analysis of the SEM images of the expanded pores in CVD graphene on Cu foil revealed that all expanded pores were faceted. Being faceted or not depends on the initial structure of the pore before exposure to CO₂. In our study, etching was originated from the intrinsic defects and resulted in faceted expanded pores, validating the conclusion of the previous reports on graphite and other carbon substrates, and expanding it to graphene. Two explanations have been suggested for a similar observation in reaction of CO₂ with graphite: steric hindrance and etching mechanism. The first argument suggests that the pore’s initial structure determines the shape of the expanded pore.⁷,⁸ In case of a pore constructed from a few missing atoms, resembling graphene intrinsic defects⁹, the dimension of the pore is smaller than the collision diameter of the etching gas molecules in the early stages of the expansion. Hence, the corner atoms have a lower probability of interaction with CO₂ due to steric hindrance. In case of a larger circular pore, no such restriction is present, and CO₂ can access all edge atoms. The second argument is based on the proposed mechanism of carbon gasification by CO₂. After physical adsorption of the CO₂ molecule on the defective site, simultaneous chemical adsorption and breakage of the first C=O bond occur. This step is widely known as dissociative chemisorption and is believed to be the rate-limiting step. A DFT study by Zhu et al. argues that dissociative chemisorption of CO₂ can only occur on two consecutive edge sites, thus preventing the reaction of corner atoms with CO₂.¹⁰ Figure S15 visualizes the evolution of pore expansion for several relevant initial pore structures.

Figure S14. Schematic of the evolution of pore expansion based on its initial structure for single vacancy, double vacancy, triple vacancy, slit-shaped, and 5-atom missing pores. The red dotted lines show the carbon atoms being etched in each step.
Note S2: Effect of Cu crystallographic grain orientation on CO2 etching of SLG

Surveying a large area, ~ 2 mm², of expanded pores in CVD graphene resting on the Cu foil revealed that mean pore size and density of the expanded pores do not depend on the Cu grain orientation (Figure S14).

Figure S15. A typical SEM image of pore size and pore density distributions in CVD graphene on several Cu grains.

Note S3: Non-oxidative interaction of CO2 and SLG on Cu foil

X-ray photoelectron spectroscopy (XPS) analysis of the Cu foil exposed to 1000 °C for 1 h demonstrated that CO2 does not oxidize the Cu substrate (Figure S16), making pore expansion by CO2 a suitable method to etch graphene where Cu substrate needs to remain active and/or smooth for further processing (e.g., utilizing the catalytic property of exposed Cu substrate) or characterization (e.g., STM analysis). In contrast, O2 and O3 rapidly oxidize the Cu foil at elevated temperatures, increasing its surface roughness and reducing its catalytic activity due to the formation of a copper oxide layer on the surface of the Cu foil.4,11 Moreover, Yang et al., utilizing XPS, demonstrated that amount of C=O groups does not change after exposing graphene to CO2 at 1000 °C, and thus it does not oxidize graphene either.12

Figure S16. XPS Cu2p profiles from Cu foil (a) before and (b) after exposure to CO2 at 1000 °C for 1 h.
Note S4: DF-TEM analysis

DF-TEM is a powerful tool for identifying vacancy defects in graphene and mapping graphene grains. Graphene is a crystalline material that scatters the electrons at defined angles (diffracted beams). However, areas without graphene (i.e., expanded vacancy defects) do not. Creating a dark-field TEM image from graphene’s diffracted beams highlight graphene grains with a bright contrast while vacancy defects appear with dark contrast. Additionally, the relative orientation of the different graphene grains can also be determined if only the diffraction spots for specific orientations are used to create the DF-TEM image (instead of using all the graphene’s diffraction spots). In this case, only the graphene grains of the selected orientations will appear with a bright contrast in the DF-TEM image, and the rest will have a darker contrast. In our DF-TEM analysis, we used the objective aperture to block the direct beam to only allow diffracted beams from graphene grains with specific horizontal plane orientations to contribute to the DF-TEM images (figures 5 and S8). Panel I of figure 5c shows three positions we used for the objective aperture (in red, green, and blue) and from which diffracted beams are used to form the DF-TEM images. The corresponding DF-TEM images are shown in panels II, III, and IV of figure 5c (panel borders are highlighted by matching colors). In these images, the bright contrast areas correspond to graphene grains with an orientation that diffracts the electrons to the position where we positioned the objective aperture. The color of the frame indicates which diffracted beams of the panel I were used to create the image. Graphene has a six-fold rotational symmetry, so the three DF-TEM images of Figure 5c map all the possible graphene grain orientations. To visualize grain boundaries between graphene grains with different orientations, we false colored the bright contrast areas of panels II, III, and IV of Figure 5c with red, blue, and green color, respectively, and combined them into the single image shown in Figure 5b. Such image processing is helpful to visualize graphene grain boundaries (dividing line between two differently colored areas) and vacancy defects (uncolored dark contrast areas). We note that the resolution of this analysis in terms of graphene grain orientation is determined by the size of the objective aperture (represented by the colored circles in the panel I of Figure 5c). The analysis does not differentiate graphene grains in the same orientation.

5. References

1. X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, Science 2009, 324, 1312–1314.
2. S. Huang, S. Li, L.F. Villalobos, M. Dakhchoune, M. Micari, D.J. Babu, M.T. Vahdat, M. Mensi, E. Oveisi, K.V. Agrawal, Sci. Adv. 2021, 7, eabf0116.
3. L.F. Villalobos, S. Huang, M. Dakhchoune, G. He, W.-C. Lee, K.V. Agrawal, Carbon 2021, 173, 980–988.
4. K.-J. Hsu, L.F. Villalobos, S. Huang, H.-Y. Chi, M. Dakhchoune, W.-C. Lee, G. He, M. Mensi, K.V. Agrawal, ACS Nano 2021, 15, 13230–13239.
5. J.W. Suk, A. Kitt, C.W. Magnuson, Y. Hao, S. Ahmed, J. An, A.K. Swan, B.B. Goldberg, R.S. Ruoff, ACS Nano 2011, 5, 6916–6924.
6. D. Zhao, H. Liu, C. Sun, L. Xu, Q. Cao, Combust. Flame 2018, 197, 471–486.
7. R. Yang, J. Catal. 1983, 82, 245–251.
8. R. Yang, L. Zhang, Y. Wang, Z. Shi, D. Shi, H. Gao, E. Wang, G. Zhang, Adv. Mater. 2010, 22, 4014–4019.
9. S. Huang, M. Dakhchoune, W. Luo, E. Oveisi, G. He, M. Rezaei, J. Zhao, D.T.L. Alexander, A. Züttel, M.S. Strano, K.V. Agrawal, Nat. Commun. 2018, 9, 2632.
10. Z.H.H. Zhu, J. Finnerty, G.Q.Q. Lu, R.T.T. Yang, Energy & Fuels 2002, 16, 1359–1368.
11. C. Jia, J. Jiang, L. Gan, X. Guo, Sci. Rep. 2012, 2, 707.
12. X. Yang, B. Hu, Y. Jin, W. Zhao, Z. Luo, Z. Lu, L. Fang, H. Ruan, Adv. Mater. Interfaces 2017, 4, 1601065.
6. Author contributions

M.R. and K.V.A. conceived the research, designed the experiments and wrote the manuscript. M.R. performed the CO$_2$ etching experiments, DF-TEM characterization, and STM imaging. L.F.V. carried out the AC-HRTEM sample preparation and imaging. K.J.H. measured the XPS data. L.F.V. and K.J.H. performed the O$_3$ treatment experiments. All authors discussed the results and commented on the manuscript.