Electronic Supplementary Material (ESI) for Nanoscale.


# Controlled Formation of Closed-Edge Nanopores in Graphene

# Supporting Information

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**S1. Binding surface adsorbates to graphene by electron beam irradiation**

The low magnification image shown in figure S1a demonstrates the contrast between electron beam irradiated area and pristine area. Figure S1(b) and (c) are magnified images of the yellow and blue boxed regions respectively. The darker contrast dots are the inorganic nanocrystals on the surface of graphene. Panel c shows the electron beam sputtered region and the red dotted highlighted region shows the surface hydrocarbon layer created during imaging at RT, which still remains when temperature increased back to 800°C. Panel b is the non-irradiated area and the surface carbon contamination evaporates off again when temperature increases.

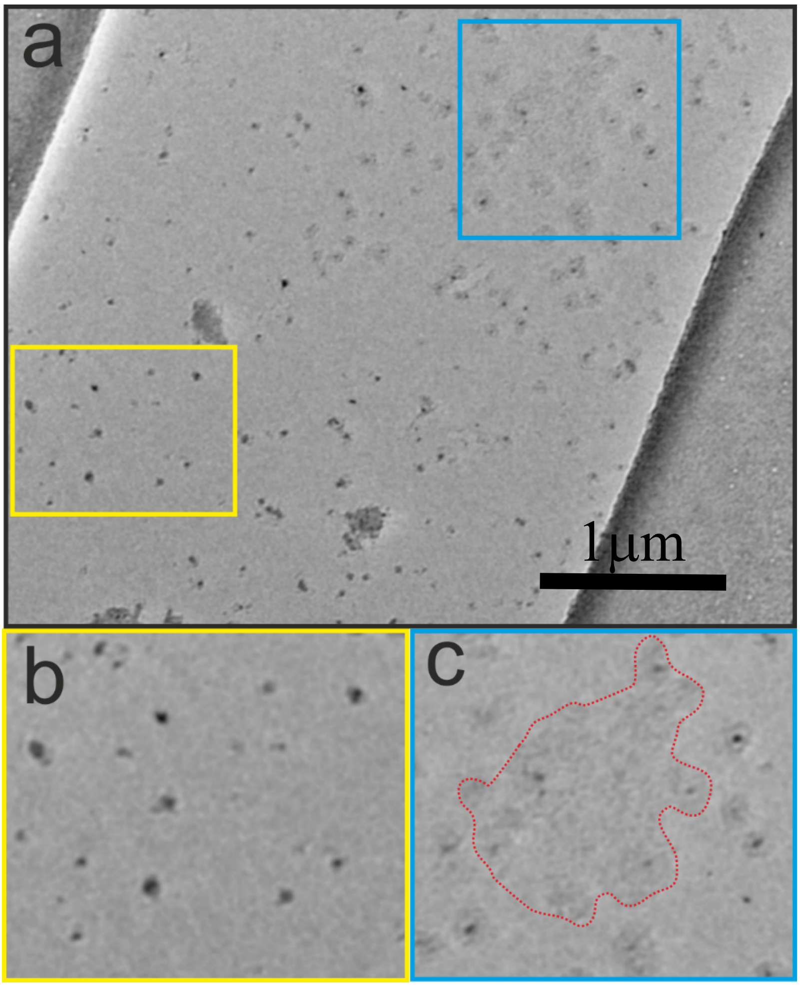


**Figure S1 low magnification electron beam sputtering effect study.** (a) Low magnification image of graphene suspended across a window on SiN TEM grid for heating experiments. (b) and (c) correspond to the magnified image of the yellow and blue highlighted region in (a).

## S2. Image processing

The images in the main text are processed in order to ease interpretation. The raw image is initially subject to a Bandpass filter with 100px to 1px mask size, this helps to reduce the uneven illumination. Then a Gaussian Blur with a sigma radius of 3px was applied to enhance signal to noise ratio. Then a figure look-up-table color pallet was applied to enhance visual contrast.

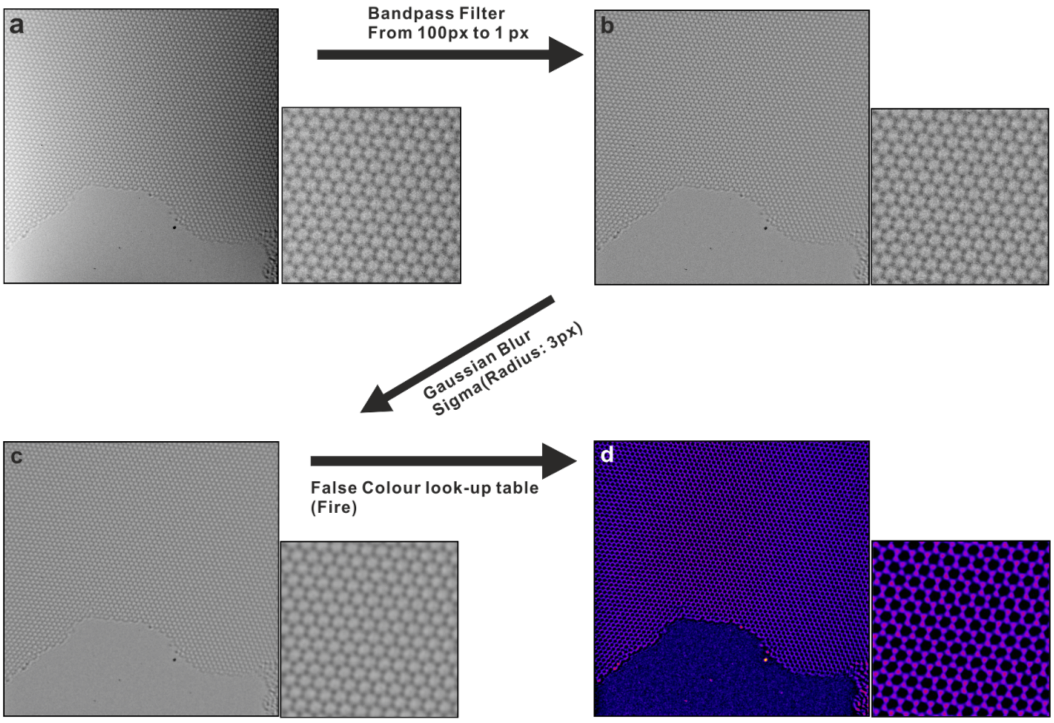


**Figure S2. Image processing.** (a) An unprocessed TEM image. (b) All the images in the main text have been initially subjected to a bandpass filter (ImageJ, filter large structures at 100px and small at 1px) to remove brightness variations. Gaussian blurr with the sigma radius of 3.0 is applied to the image. (c) A false colour look up table (fire) is applied to the image and brightness and contrast adjusted to enhance visual contrast. The insets in each panel show the magnified image of a region in (a-d) respectively.

## S3. Closed edge graphene nanoribbon

The nanoribbon created betwen two graphene nanopores is seen in figure S3a. This helps us further identify the atomic configuration of the edges, i.e. open or closed edge. In figure S3b, the lower boundary of the nanoribbon shows an array of periodically separated bright spots, indicating a closed edge. Multi-slice image simulations are shown in figure S3 (c-i). This analysis helped us further confirm the closed edge formation on the edge and identify closed edges are also formed on other nanopores based on the unique feature of periodic array of bright dots.

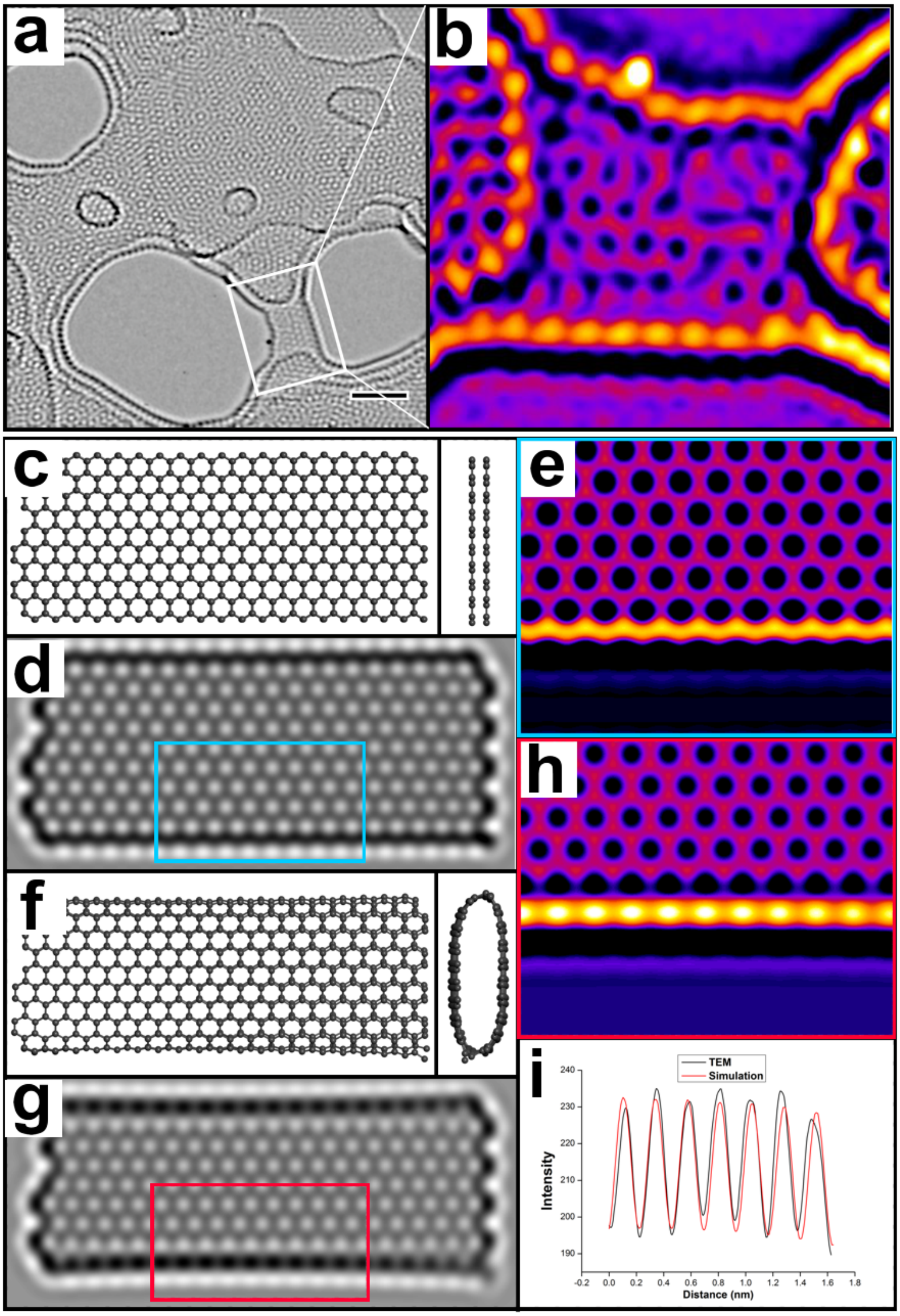


**Figure S3. Modelling and simulation of open and closed edge graphene nanoribbon.** (a) A TEM frame with the white box highlights a closed edge bilayer graphene nanoribbon. A magnified image is shown in (b). (c) is the atomic model of an open edge bilayer nanoribbon with its side view shown in the inset. The multi-slice image simulation of the model is shown in (d), and the magnified area of the blue box highlighted region shown in (e). (f-h) are the same analysis applied to the closed edge nanoribbon.

**S4. AC-TEM frames of results shown in Figure 5 of main text.**

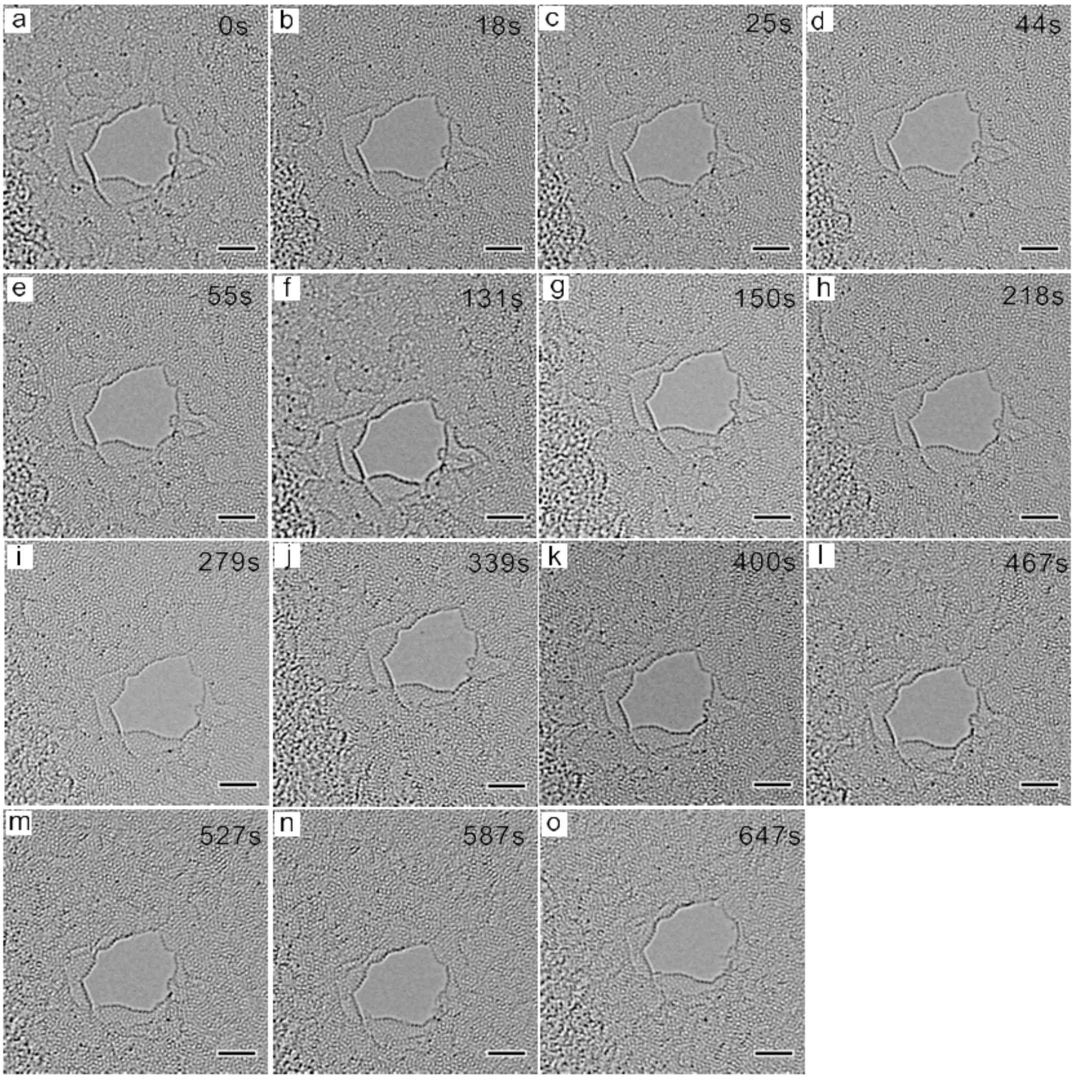


**Figure S4.** (a)-(o) Full series of AC-TEM images from which three were taken for figure 5(d)-(f) in the main text. All scale bars = 2nm.

## S5. Extended-period stability test of closed edge nanopore.

The stability of the nanopores are tested for an extensive period of time to evaluate the practicality of using them in applications. Six different sized nanopores were initially created using a focused electron beam in a TEM, and then we have applied the stabilization processes discussed in the main text. After two days of exposure to atmospheric conditions the same nanopores were imaged again and showed no sign of filling with amorphous contamination.

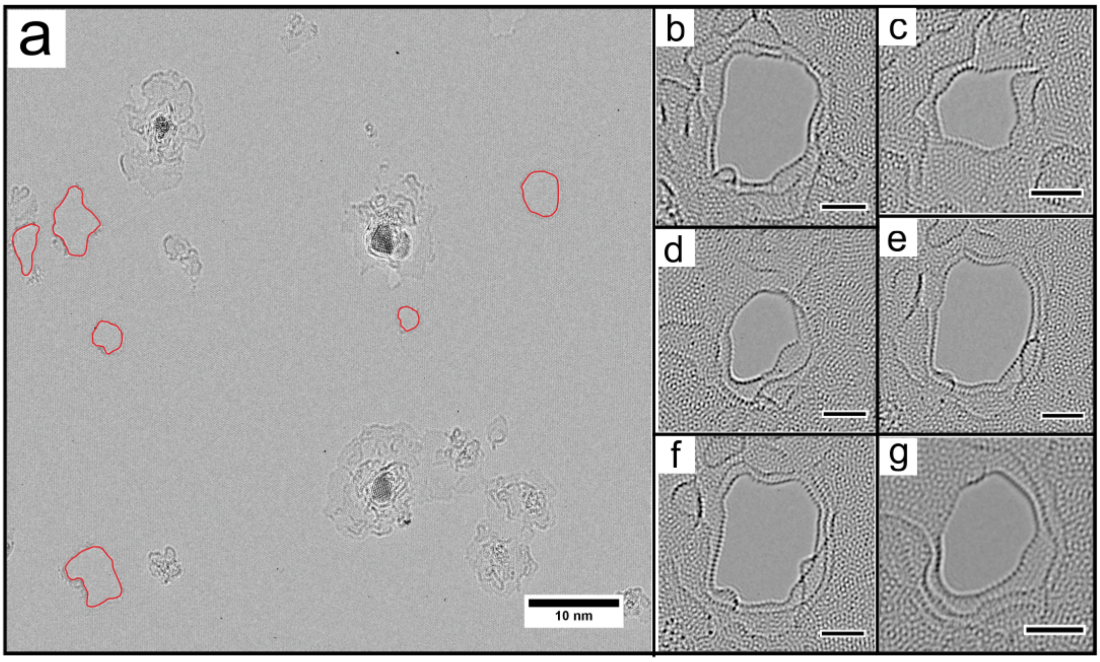


**Figure S5. Long term stability test of closed-edge nanopores.** (a) Low magnification TEM image of the as-created nanopores in graphene at 800°C. These were then turned into closed edge nanopores using the mentioned fabrication method and left in air for two days. (b)-(g) show the same nanopores after two days in air.

**S6. AC-TEM images of results shown in Figure 6 of main text**.

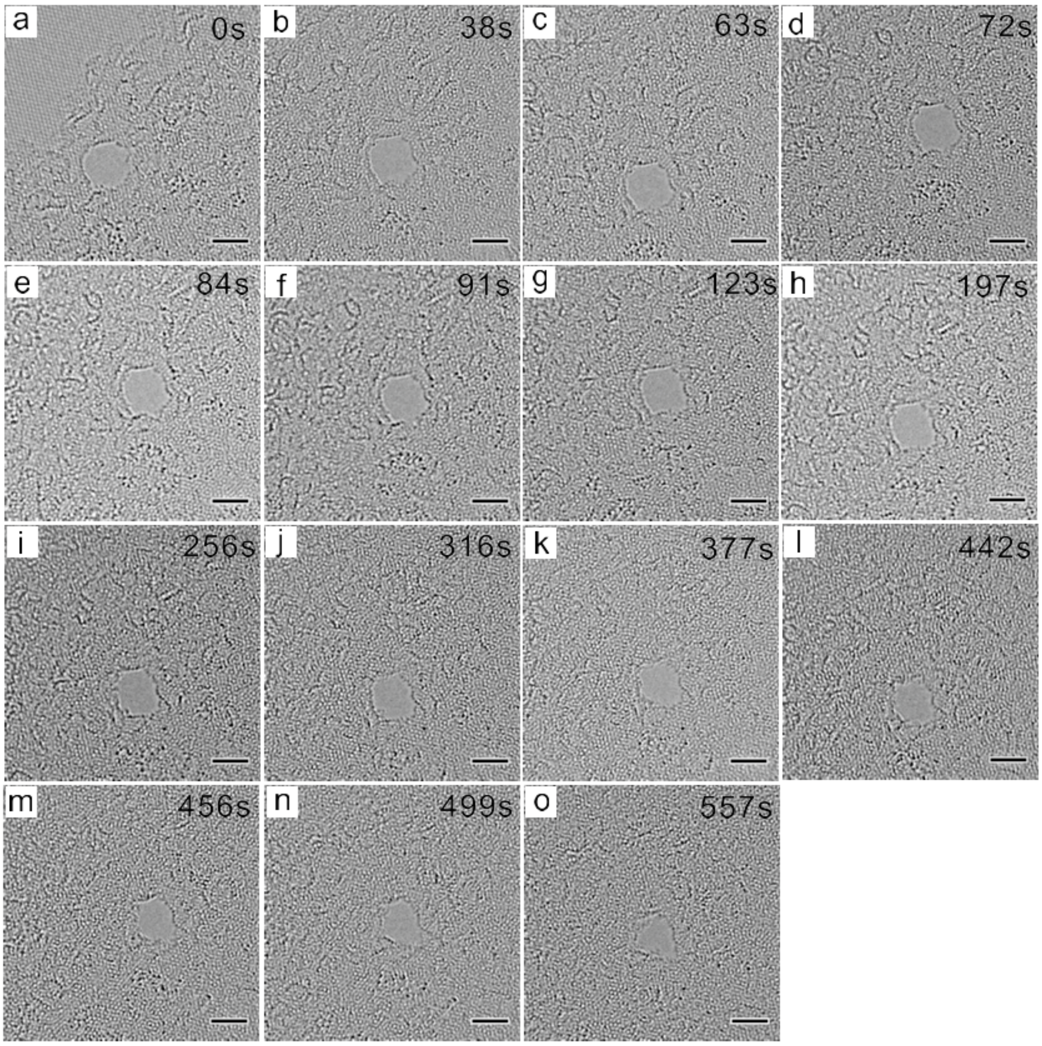


**Figure S6.** Images of graphene nanopores at room temperature after open edge nanopore fabrication at 800°C. All scale bars = 2nm.

**S7. AC-TEM frames of results shown in Figure S8**

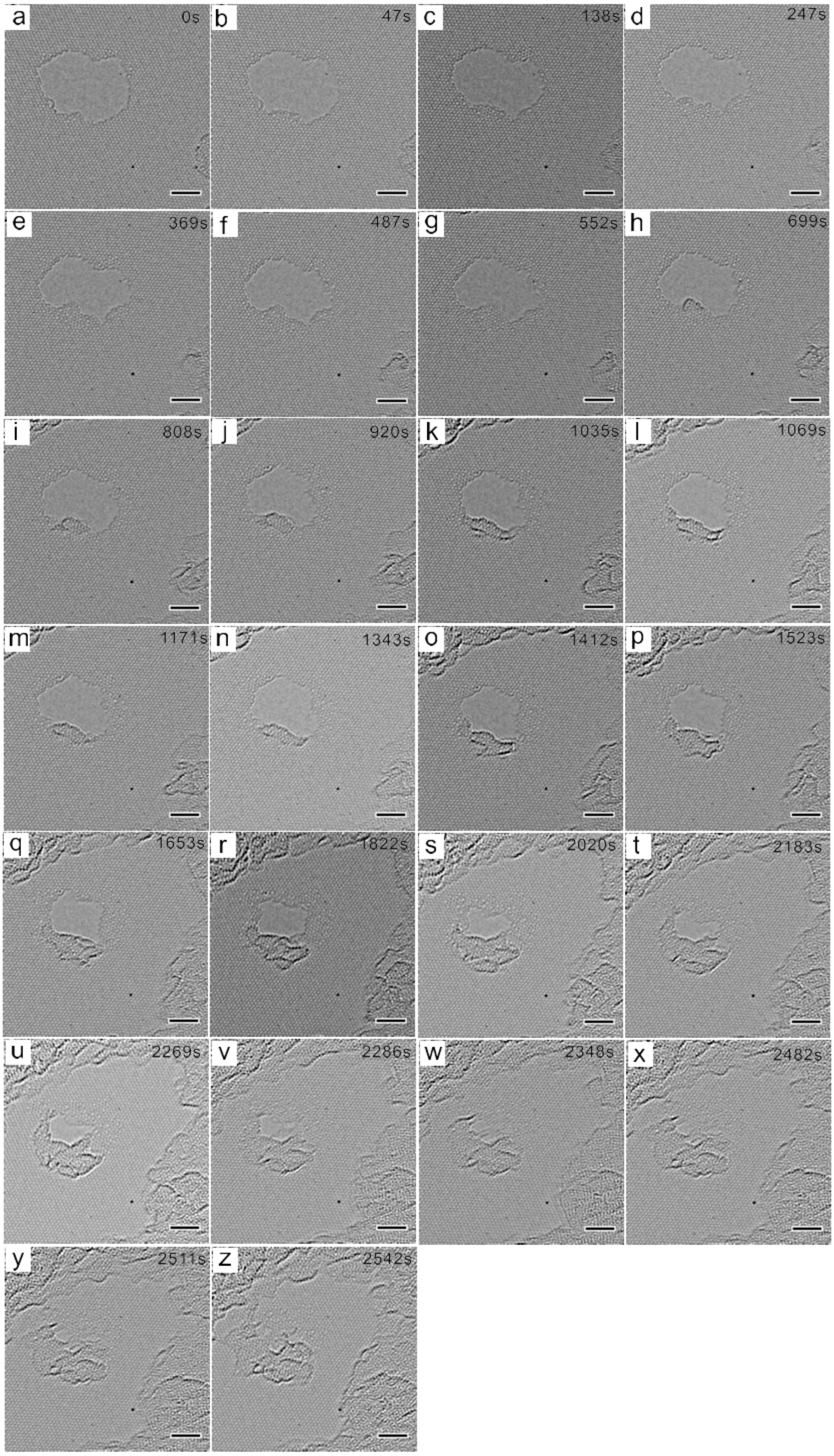


**Figure S7**. AC-TEM images of nanopores closing at 200°C. All scale bars = 2nm.

**S8. Filling of an open-edge graphene nanopore at 200 °C**

We now show a comparison experiment to demonstrate the effect of back filling at low temperature (200°C) if a closed edge had not been formed. Figure S8 a-c shows three selective frames in the AC-TEM time series with the comprehensive dataset shown in figure S7 of supporting information, the pore size again decreases with time because carbon atoms trapped by electron beam keep adhere to the reactive open edge. The nanopore filled up completely from what was a 22nm$^2$ pore over the course of ~40 minutes. This experiment testifies the significance of the closed edge formation technique developed in this report, in order to achieve a stable and durable nanopores in graphene.

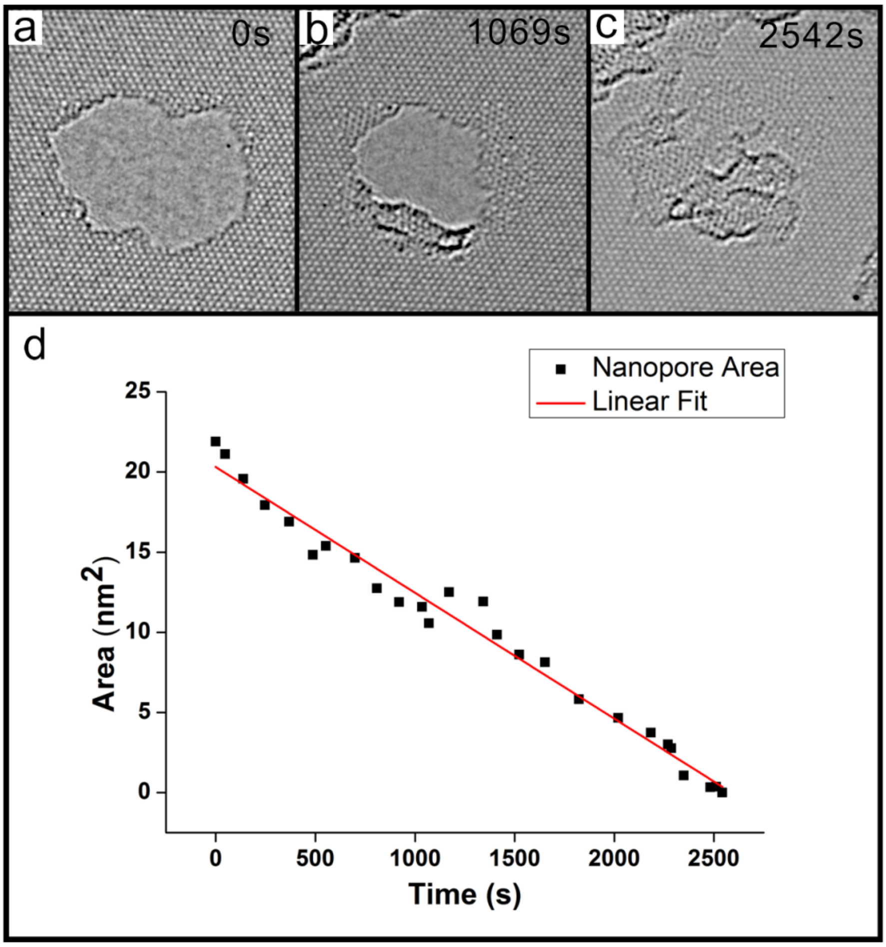


**Figure S8. Hole filling at 200°C** A nanopore was created at 800°C, then dropped to RT. (a – c) time series of AC-TEM images of the nanopore at 200°C. The change in area of the nanopore in each image as a function of time is plotted in (d) and fitted with a linear equation. All scale bars = 2 nm.