Supporting information

Hydrocarbon Contamination in Angström-scale Channels

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S1. Fabrication of Å-slit channel devices

Graphite bulk crystals are obtained from Manchester Nanomaterials. Two dimensional (2D) crystals were mechanically exfoliated using scotch tape to expose a fresh crystal on SiO₂/Si wafers with ~290 nm thickness of SiO₂. Photoresist (S1813) and developer (MF319) for photolithography and polymethyl methacrylate (950k) resist for electron beam lithography (EBL) were purchased from Microposit[®]. Reactive ion etching (RIE) was used for dry etching silicon nitride (SiN_x) and 2D crystals. Micron size rectangular holes in the SiN_x membrane were etched using RIE with a mixture of SF₆ and CHF₃ gases. Graphite was etched using RIE with oxygen gas.



Figure S1. Device fabrication flow-chart for making Å-channels. Devices are made using previously reported nanofabrication procedures and the fabrication steps are illustrated with the black arrows.¹ The bottom and top 2D crystals in the fabrication of channel devices are chosen to be either graphite or hexagonal boron nitride (hBN) whereas the spacer 2D crystals are always monolayer or few layer think graphene. **Step 1:** A long rectangular hole in a freestanding silicon nitride (SiN_x) membrane (~ 500 nm thick) was covered with the bottom 2D crystal. **Step 2:** The rectangular hole was projected on the bottom crystal layer using RIE (oxygen plasma for graphite, CHF₃/oxygen plasma for hBN) from the backside of SiN_x membrane. **Step 3:** The spacer 2D crystal, pre-patterned by EBL using polymethyl methacrylate (PMMA) as a resist and exposed to oxygen plasma to make parallel long stripes with ~ 130 (±10) nm wide and ~ 130 (±10) nm spacing was transferred on to this projected the aperture in the bottom crystal. **Step 4:** This spacer of graphite strips was etched from backside of the membrane to remove exposed graphite on the hole area. **Step 5:** The hole was covered with a relatively thick (~ 200 nm) top 2D crystal. **Step 6:** In some of the devices where top crystals had thin or uneven edges, a metal mask was deposited after a photolithography patterning. **Step 7:**

RIE was employed to remove the unmasked thin edges of the top crystal to open channels' entries. After each 2D crystal (bottom, spacer and top) transfer, the SiN_x/Si wafer chip with rectangular hole was annealed in 10% hydrogen-in-argon at 400 °C for 4 hours. The final devices contained between ~ 100 and ~ 2000 channels in total on either side of the rectangular hole.

S2. Helium flow measurements

The device with Å-channels on SiN_x/Si wafer was clamped between O-rings to separate two oil-free chambers (loading and vacuum chambers) as depicted in Fig. S2. In this setup, the only pathway between the chambers is through the channels. Both the chambers were evacuated using a bypass loop connected to a vacuum pump. The chambers were evacuated before every experiment. The vacuum (bottom) chamber was maintained at a pressure of around 10^{-6} bar and connected to a mass spectrometer. The loading (top) chamber was equipped with an electrically controlled dosing valve that provided the controlled pressure *P* inside, which was monitored by a pressure gauge. Helium gas was released into the loading chambers and the applied pressure was varied in a controlled fashion (~ 6 mbar/s) using an electrically controlled gas dosing valve (VAT Group). Our Å-slit channel devices were sufficiently robust to withstand applied pressure up to two bar.



Figure S2. (a) Schematic representation of helium gas flow measurements using Å-channel devices. (b) The picture of our experimental setup with helium leak detector and voltage operated valve to selectively inject helium gas and hexane in to the loading chamber.

S3. Storage and revival of Å-slit channels

After the devices were made using the nanofabrication steps (described above in Fig. S1) in the cleanroom (class 100), they were stored at ambient conditions on the laboratory bench top. These channels (in fact any 2D materials surfaces) can be contaminated with airborne hydrocarbons in the atmosphere. To protect from the hydrocarbon adsorption and resulting clogging of channels, the devices were stored in activated carbon (Merck, "charcoal activated for analysis"). For measurements, the devices were taken out, washed with water, and IPA and dried under flow of nitrogen gas. Most of the charcoal particles were removed in this cleaning procedure but few particles were left on the devices as depicted in Fig. S3b. We have found that storage in water (in combination with 400 °C annealing) also enables the channels to remain open for few weeks to months.



Figure S3. Optical image of as fabricated Å-channel device before (a) and image of the same device stored in charcoal for a year (b).

S4. Airborne contamination in monolayer graphite device

We monitored the airborne contamination of a freshly fabricated monolayer graphite device (channel height $h \sim 0.4$ nm). The channel shows some variation of the helium permeance monitored for 270 days and could be revived by combination of storage in charcoal and high temperature (400 °C) annealing.



Figure S4. Helium flow through a Å-channels made with monolayer graphene spacer (height, $h \approx 0.4$ nm), top and bottom graphite walls. The bars represent He flows arbitrarily checked on different days through the same device, when it was stored under charcoal. The device was annealed before each measurement.

S5. Hexane exposure and clogging of graphite Å-slit channels

The Å-channel graphite device (both bottom and top layers made by graphite crystals) were exposed to hexane in the same experimental set-up used for He gas flows as described in the above section (S2) with slight modification. Additional valve and liquid hexane reservoir with < 1 mL capacity were attached to loading chamber (Fig. S2). After the initial He flow measurements through Å-channels, both chambers were evacuated, and hexane was released in to the input chamber. The channel was exposed to vaporized hexane for 60 seconds while the applied pressure in the top input chamber raised up to ~ 200 mbar at temperature T ~ 26 (±1) °C, which is approximately equal to the vapor pressure of hexane and this pressure is sensitive to the experimental temperature. After the chamber was evacuated to remove the hexane for 10 minutes, helium conductance data was measured. Helium flow was recorded using Helium leak detector while input of Helium from a balloon was controlled by electrical voltage gated valve. Opening the electrical gate valve for introducing Helium into input chamber, and the leak detector measurements were started simultaneously. LabVIEW program

was used to interface both the pressure and leak rate measurements which are recorded every second. Blank silicon substrates were used to demonstrate the increase in the vapour pressure of hexane with increase in temperature.



Figure S5. (a) Effect of temperature on the vapour pressure of hexane. (b) Time trace plot of the helium flow for 5-layer graphite device.

S6. Hexane exposure on a control aperture

Control devices, SiN_x membranes without channels, were used to check the measurement set-up thoroughly for possible leaks. These control devices exhibited no noticeable He leak which confirms that the Å-channels were the only possible permeation path. The experimental accuracy of our helium flow measurements was tested using the reference devices containing few nanometres to micrometre sized circular apertures made in free-standing graphene on SiN_x membranes. We did the same sequence of steps, exposure to hexane, recovery by He flush and heat treatment of the substrate. We observe no discernible change in the flow through the aperture, confirming that the measurement setup does not show any flow reduction due to hydrocarbon adsorption on the chamber components or O-rings (Fig. S6).



Figure S6. Hexane exposure on an aperture of diameter, ~ 60 nm made in a free-standing graphene layer. The Helium flow remains constant after exposure to hexane and further recovery steps of He flush and heat treatment. This validates our experimental method that the observed changes of flow in the case of Å-channels are mainly due to the channel clogging and recovery.





Figure S7. Comparison of helium leak rate before and after exposure to hexane through various graphite Å-channel devices with heights, (a) $h \sim 1.7$ nm, (b) $h \sim 0.7$ nm. All the graphs represent the flows normalized per single channel, and per µm length of the channel.

S8. Hexane exposure and clogging of hBN Å-slit channels

The Å-channel hBN channels (both bottom and top layers made by hBN crystals) were exposed to hexane in the same experimental set-up used for He gas flows in graphite channel device (S7).



Figure S8. Comparison of helium leak rate before and after exposure to hexane through various hBN Å-channel devices with heights, (a) $h \sim 1.7$ nm, (b) $h \sim 0.7$ nm, and (c) $h \sim 0.4$ nm. All the graphs represent the flows normalized per single channel, and per µm length of the channel.



S9. Atomic force microscopy of spacers with varied heights

Figure S9. Atomic force micrographs and height profile of (a) monolayer spacer, (b) bilayer spacer, (c) five-layer spacer and (d) forty-layer spacer. Scale bar, 200 nm.

Table	S1.	Surface	roughness	of	monolayer,	bilayer,	five-layer	and	forty-layer	graphene
space	rs.									

Surface roughness	1-layer spacer	2-layer spacer	5-layer spacer	40-layer spacer
Rq	0.6 ± 0.1 Å	1.9 ± 0.2 Å	2.5 ± 0.4 Å	4.2 ± 0.3 Å
Ra	0.5 ± 0.1 Å	1.5 ± 0.1 Å	1.8 ± 0.2 Å	3.2 ± 0.3 Å

We analysed the surface roughness (e.g. root mean square roughness *Rq* and mean roughness *Ra*) based on the AFM images above (Fig. S9). For each spacer, we recorded the surface roughness value of individual spacer strip and the roughness value was obtained by averaging the data of at least five spacer strips.

S10. References

1. A. Keerthi, A. K. Geim, A. Janardanan, A. P. Rooney, A. Esfandiar, S. Hu, S. A. Dar, I. V. Grigorieva, S. J. Haigh, F. C. Wang and B. Radha, *Nature*, 2018, **558**, 420-424.