Ultimate Permeation Across Atomically Thin Graphene Porous Membrane

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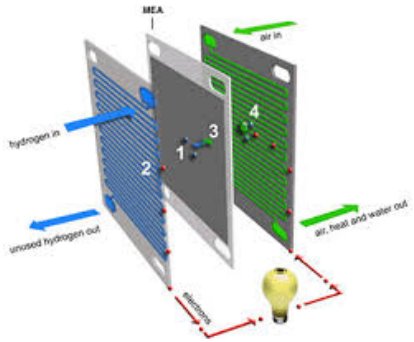
Outline

- Introduction into membrane technology
- Membrane transport theory
- Graphene – A superior membrane material
- Graphene membrane fabrication
- Graphene membrane characterization

Prominent membrane applications

- Gas separation
  - Flue gas treatment
  - Natural gas separation
- Water treatment
  - Micropollutant filtration
  - Desalination
- Energy harvesting
  - Ion conducting membranes
  - Osmotic current generation

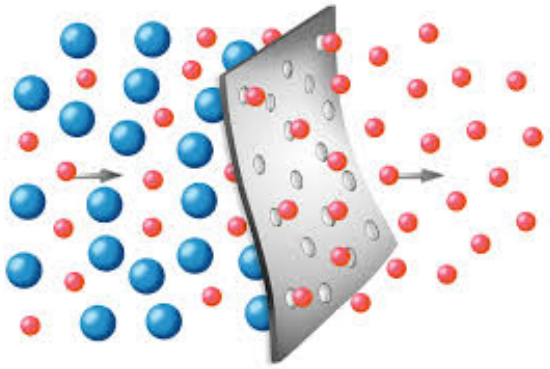


E. Drioli, A. I. Stankiewicz, F. Macedonio, Journal of Membrane Science 380, 1–8 (2011).

Ideal picture of a membrane

Intuitive picture:

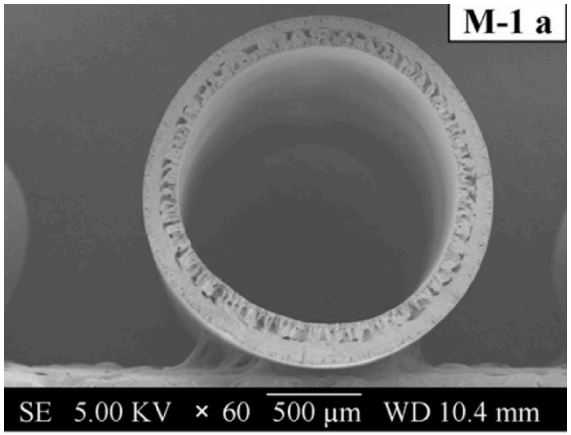
- 2D sheet
- Separating two compartments
- Passing fluid is sieved (size exclusion)



Feed Permeate

Technical picture

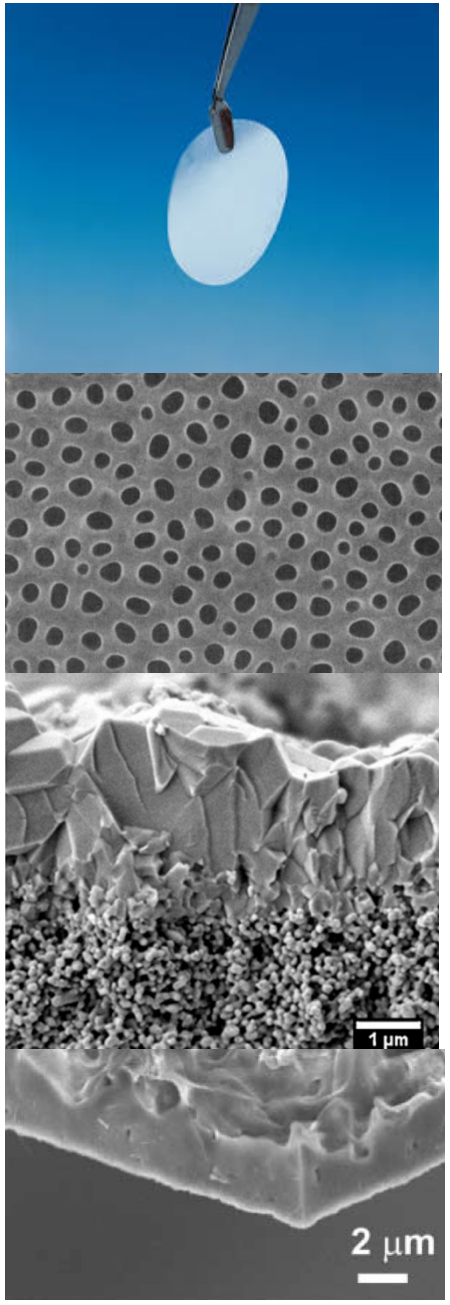
- High permeance
  high throughput at low pressure
- High selectivity
  only desired species passes
- Hollow fiber assembly



D. Hou, J. Wang, X. Sun, Z. Ji, Z. Luan, Journal of Membrane Science 405, 185–200 (2012).

Common membrane materials

- Conventional membranes
  - Polymer membranes
  - Track etched membranes
  - Anodic aluminum oxide membranes
- Zeolites membranes
- Carbon molecular sieves (CMS)
- CNT membranes



R. C. Furneaux, W. R. Rigby, A. P. Davidson, Nature 337, 147–149 (1989).
Y. Li, F. Liang, H. Bux, W. Yang, J. Caro, Journal of Membrane Science 354, 48–54 (2010).
J. K. Holt, H. G. Park et al., Science 312, 1034–1037 (2006).

Membrane transport theories

Polymer Membranes

- Examples: PDMS, Nafion, PMSP membranes
- Solution diffusion transport
  - Permeating species *i* is dissolved in membrane material
  - Diffusion of dissolved species *i*
  - Henry's law: $$j_i = D_i \frac{dc_i}{dx}$$
  - Fick's law of diffusion: $$p_i = S_i c_i$$
- Membrane flux

$$j_i = D_i \frac{\Delta c_i}{l} = D_i S_i \frac{\Delta p_i}{l}$$

- Typical gas permeance:
  - 2×10^{-8} mol/m^2/Pa/s (H_2 in PMSP)

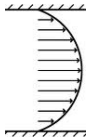
$$\frac{j_i}{\Delta p_i} = D_i S_i \frac{1}{l}$$

K. Nagai, A. Higuchi, T. Nakagawa, J. Polym. Sci. B Polym. Phys. 33, 289–298 (1995).

Membrane transport theories

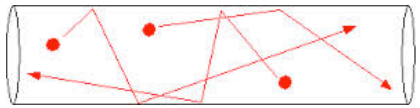
Porous Membranes

- Examples: track etched, anodic alumina, zeolite membranes
- Convective transport through pore
  - Transport path is approximated by cylindrical pore with diameter d
    - Hagen-Poiseuille (continuum theory)



$$Q_{HP} = \frac{\pi}{8\mu}\left(\frac{d}{2}\right)^4 \frac{\Delta p}{l}$$

    - Knudsen diffusion (gas kinetic theory)



$$Q_{Kn} = \frac{2\pi}{3}\left(\frac{d}{2}\right)^3 \sqrt{\frac{8}{\pi MRT}} \frac{\Delta p}{l}$$

- Membrane flux of solute species i with concentration c_i and size d_i

$$j_i = \frac{Q}{A_{pore}} c_i K_i(d, d_i)$$

- Typical permeance: 4×10^{-7} mol/m^2/Pa/s (H_2 in Zeolite)

Z. Tang, J. Dong, T. M. Nenoff, Langmuir (2009).

Can we do better?

YES!

We have to get thinner membranes!

Effect of thickness

Membrane performance is limited by thickness!

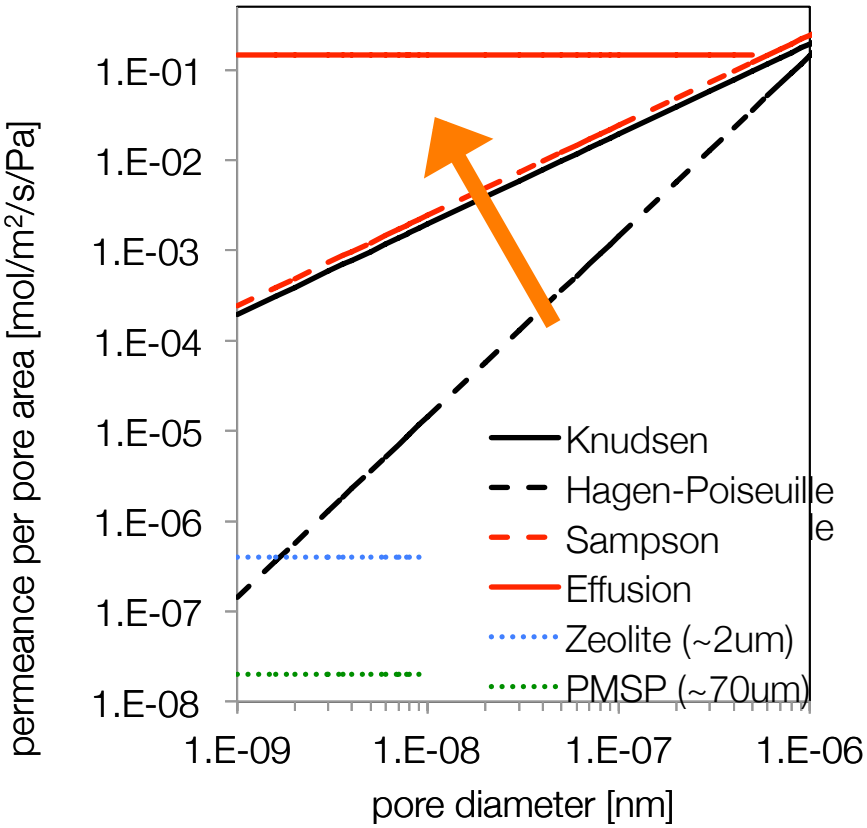
$$\frac{j_i}{\Delta p} \propto \frac{1}{l}$$

- Example for /=1um

Zero thickness flow theory

- Sampson's Model
- Effusion theory

Does it work in reality?



Ultimate Permeation Across Atomically Thin Porous Graphene

Kemal Celebi,[1]* Jakob Buchheim,[1]* Roman M. Wyss,[1] Amirhossein Droudian,[1] Patrick Gasser,[1] Ivan Shorubalko,[2] Jeong-Il Kye,[3] Changho Lee,[3] Hyung Gyu Park[1]†

A two-dimensional (2D) porous layer can make an ideal membrane for separation of chemical mixtures because its infinitesimal thickness promises ultimate permeation. Graphene—with great mechanical strength, chemical stability, and inherent impermeability—offers a unique 2D system with which to realize this membrane and study the mass transport, if perforated precisely. We report highly efficient mass transfer across physically perforated double-layer graphene, having up to a few million pores with narrowly distributed diameters between less than 10 nanometers and 1 micrometer. The measured transport rates are in agreement with predictions of 2D transport theories. Attributed to its atomic thicknesses, these porous graphene membranes show permeances of gas, liquid, and water vapor far in excess of those shown by finite-thickness membranes, highlighting the ultimate permeation these 2D membranes can provide.

Recent advances in graphene synthesis and processing (*1*–*3*) have enabled demonstrations of atomically thin two-dimensional (2D) membranes showing mechanical sturdiness and hermetic sealing (*4*, *5*). Initial attempts to endow mass permeability to the otherwise impermeable graphene have been based on formation of a single aperture (*6*) and randomly etched or defect-originated pores (*7*, *8*). However, the macroscopic quantification of mass transport through such 2D pores is extremely challenging because the task demands a large number of pores with controlled dimensions.

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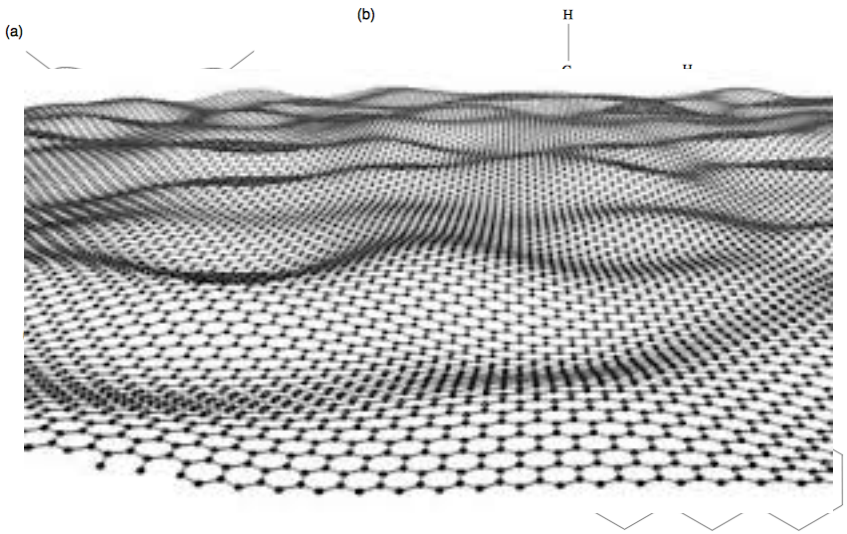
We have developed a facile and reliable method for making 2D membranes (Fig. 1, A to G). This process uses chemical vapor deposition (CVD) optimized to grow graphene with minimal defects and good grain connectivity in order to prevent undesirable crack formation (*9*). A clean transfer process places two layers of graphene consecutively onto a SiN_x frame punctured with 49 pores each of 4 μm in diameter (Fig. 1D), forming freestanding graphene layers that are thinner than 1 nm. This double transfer strengthens the freestanding graphene and keeps it from leakage through random defects (*10*, *11*). Cleanliness and quality of graphene are found to be crucial during this graphene transfer process because grain boundary defects, polymer residues, or dust particles can induce crack formation while perforating the graphene. Scanning electron microscope (SEM) images (Fig. 1E and fig. S1) support that our transfer process produces crack-free graphene over the length scale of the entire frame. The freestanding film of double-layer graphene remains impermeable to gases and water. Nanopores were then drilled with a focused ion beam (FIB) to produce porous membranes (Fig. 1, F and G). We used Ga-based FIB to perforate apertures between 14 nm and 1 μm in diameter and He-based FIB for <10-nm-pore drilling. Low exposure doses (5×10^{-6} to 5×10^{-5} pA/nm^2 for Ga^+ ions and 6×10^{-3} pA/nm^2 for He^+ ions) enabled fast and precise drilling, resulting in well-defined pore diameter distributions (Fig. 1, H to K).

The large number of pores (~10^3 to 10^6 per membrane) allows gas flows detectable with conventional mass flow meters. The membranes are mechanically sturdy enough to stand pressure differences of up to 2 bar (higher pressure not tested). N_2 flow shows linear pressure dependence (figs. S2 and S3), resulting in pressure-independent permeance. N_2 flux displays diameter dependence characterized by two asymptotic theories: free molecular transport (effusion) and modified Sampson's model (*12*, *13*) for small- and large-size apertures, respectively (Fig. 2A). For apertures smaller than 50 nm, the mean free path (λ) becomes larger than the aperture diameter (d), and the probability of having intermolecular collisions in the vicinity of the aperture decreases. Here, the transport enters the molecular flow regime featured by effusion for small apertures. Knudsen numbers (λ/d) for membranes (7.6 nm < d < 50 nm) are between 1 and 10, which is well within the molecular flow regime, and so the flow can be explained by the effusion mechanism, which is purely dependent on the probability of a molecule hitting the aperture. This can be quantified by the effusion flux, $Q_E = \bar{u}\Delta n/4 = \Delta P/\sqrt{2\pi m k_B T}$, where n is the gas number density, $\bar{u}$ is the mean molecular speed, P is the pressure, k_B is the Boltzmann constant, T is the temperature, and m is the molecular weight. As the pore diameter enlarges, more molecules interact with one another near the aperture, causing a transition from effusion to a more collective flow. However, collective flow models based on pore wall interactions (the Hagen-Poiseuille model) are not suitable to explain the flow behavior for atomically thin membranes. Such flows through an

Graphene



- Structure
  - sp^2 C bond – “benzene rings”
  - 1 atom layer thick 2D crystal
  - Honeycomb lattice

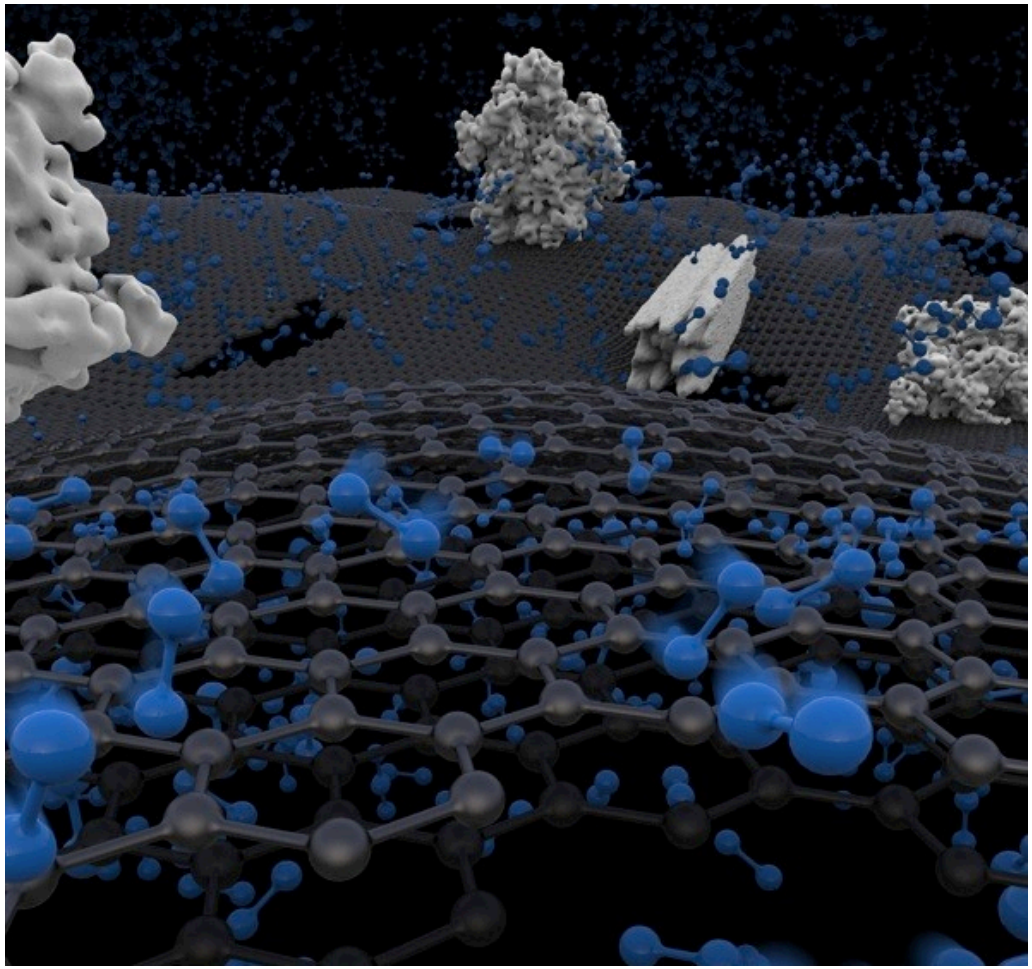
- Properties
  - Very high electron mobility: ~$1x10^4$ $cm^2/V/s$
  - Superb mechanical properties:
    - Young’s Modulus: ~1TPa
    - Tensile strength: ~130GPa
  - Gas/liquid tight
    - Impermeable to He
  - Chemically stable

A perfect membrane material

K. S. Novoselov et al., Science 306, 666–669 (2004).
C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 321, 385–388 (2008).
J. S. Bunch et al., Nano Letters 8, 2458–2462 (2008).
D.-E. Jiang, V. R. Cooper, S. Dai, Nano Letters 9, 4019–4024 (2009).

How to make a membrane from graphene?

- Graphene synthesis
- Graphene transfer
- Pore fabrication



K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).

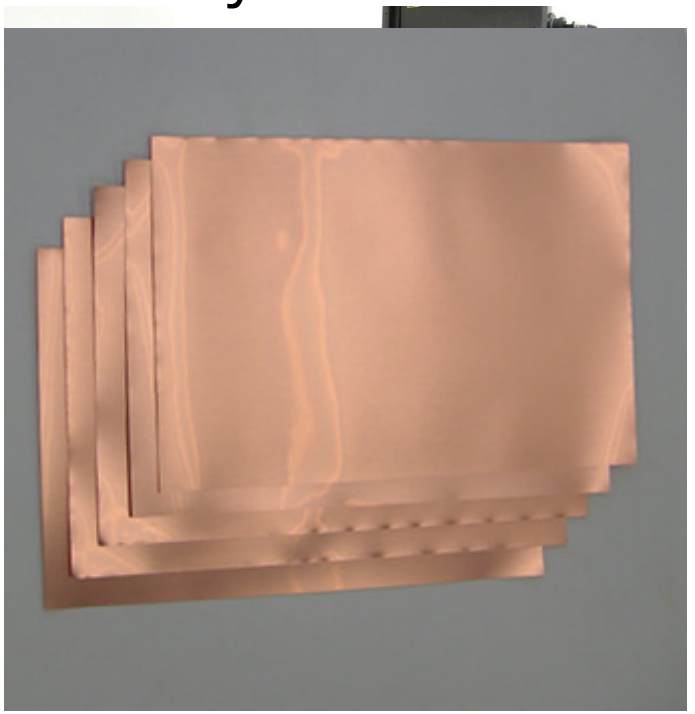
Membrane fabrication – Graphene synthesis

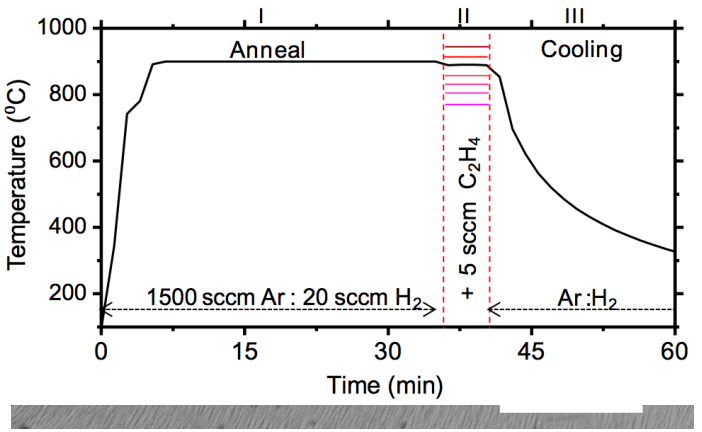
Chemical Vapor Deposition

- Large scale synthesis
- Monolayer multi crystalline graphene
- Substrate: Cu foil
- Growth conditions:
  - ~850-950°C @ 4mbar pressure
  - 30min annealing in 1:15 H_2:Ar
  - Carbon precursor Ethylene for 3min

Key achievement:

- Full coverage monolayer graphene



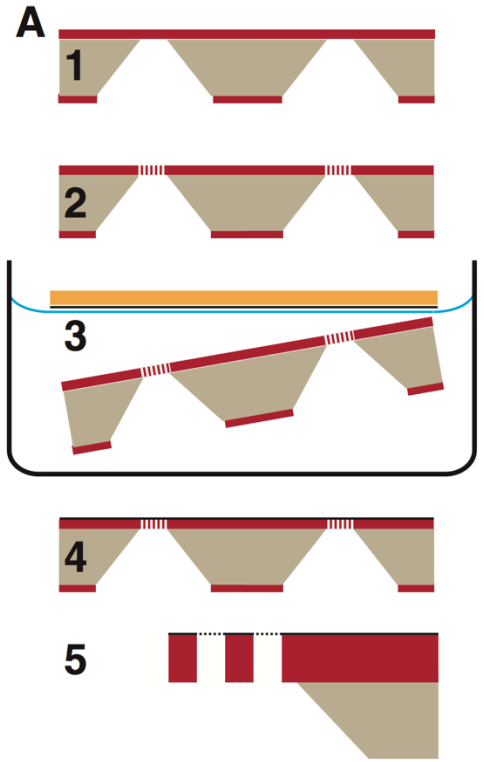


K. Celebi et al., Nano Letters 13, 967–974 (2013).

Membrane fabrication – Graphene transfer

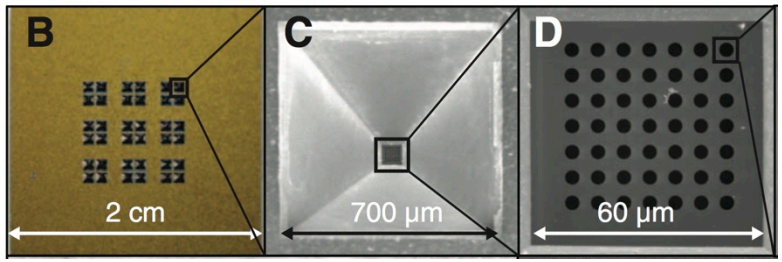
Transfer from Cu foil to target substrate

- Target substrate
  - Patterned Si chip with porous SiN_x membranes
- Transfer of two layer graphene layer
  1. Spin coat PMMA on graphene Cu foil
  2. Immerse in Cu etchant
  3. Scoop floating graphene PMMA with another graphene Cu foil
  4. Etch again the Cu foil
  5. Scoop floating graphene graphene PMMA with target substrate
  6. Remove PMMA by thermal decomposition

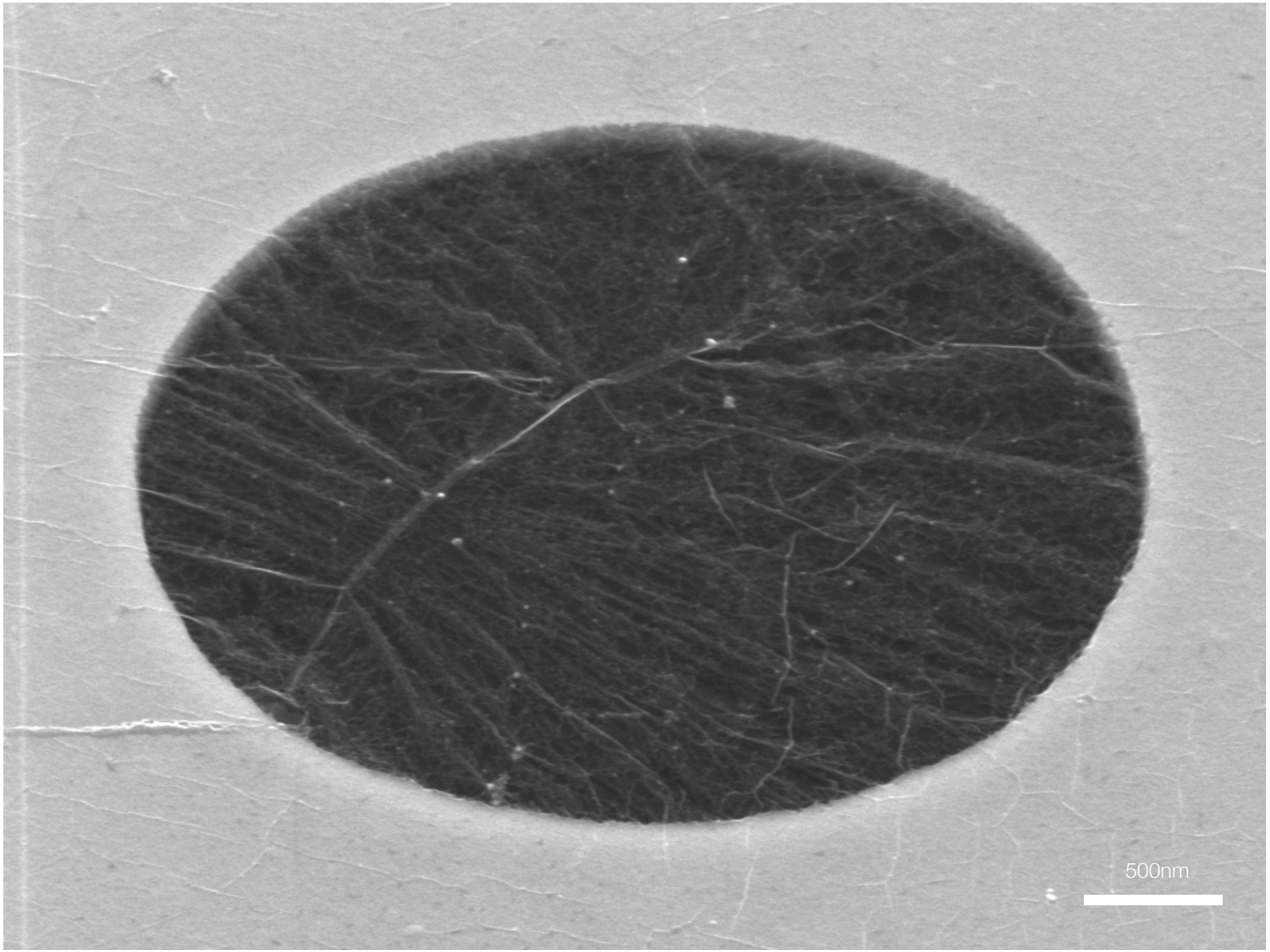


Key Achievement:

- Defect free large area transfer



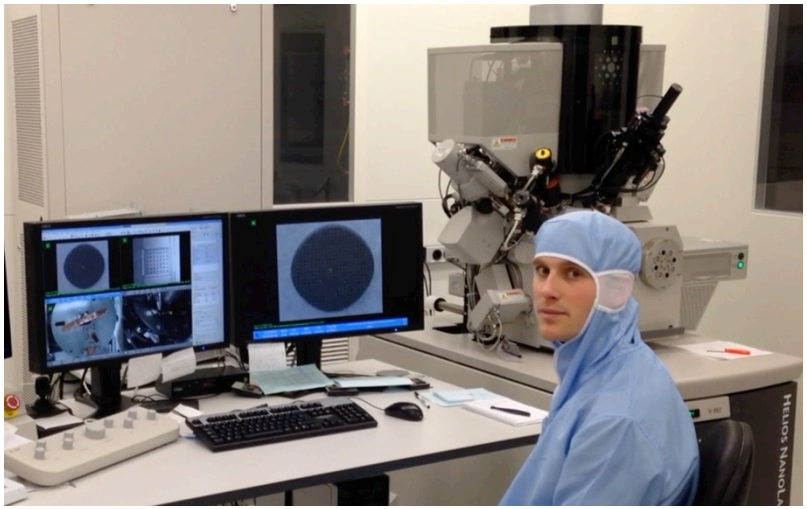
K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).


500nm

Membrane fabrication – Graphene patterning

Focused Ion Beam (FIB) patterning

- Highly flexible direct patterning tool
- Localized ion sputtering with Ga or He ions
- Ion energy 30keV
- Areal dose to pattern double layer free standing graphene
  - Ga FIB: 4×10^{15} to 2×10^{16} cm^{-2}
  - He FIB: 5×10^{17} to 4×10^{18} cm^{-2}



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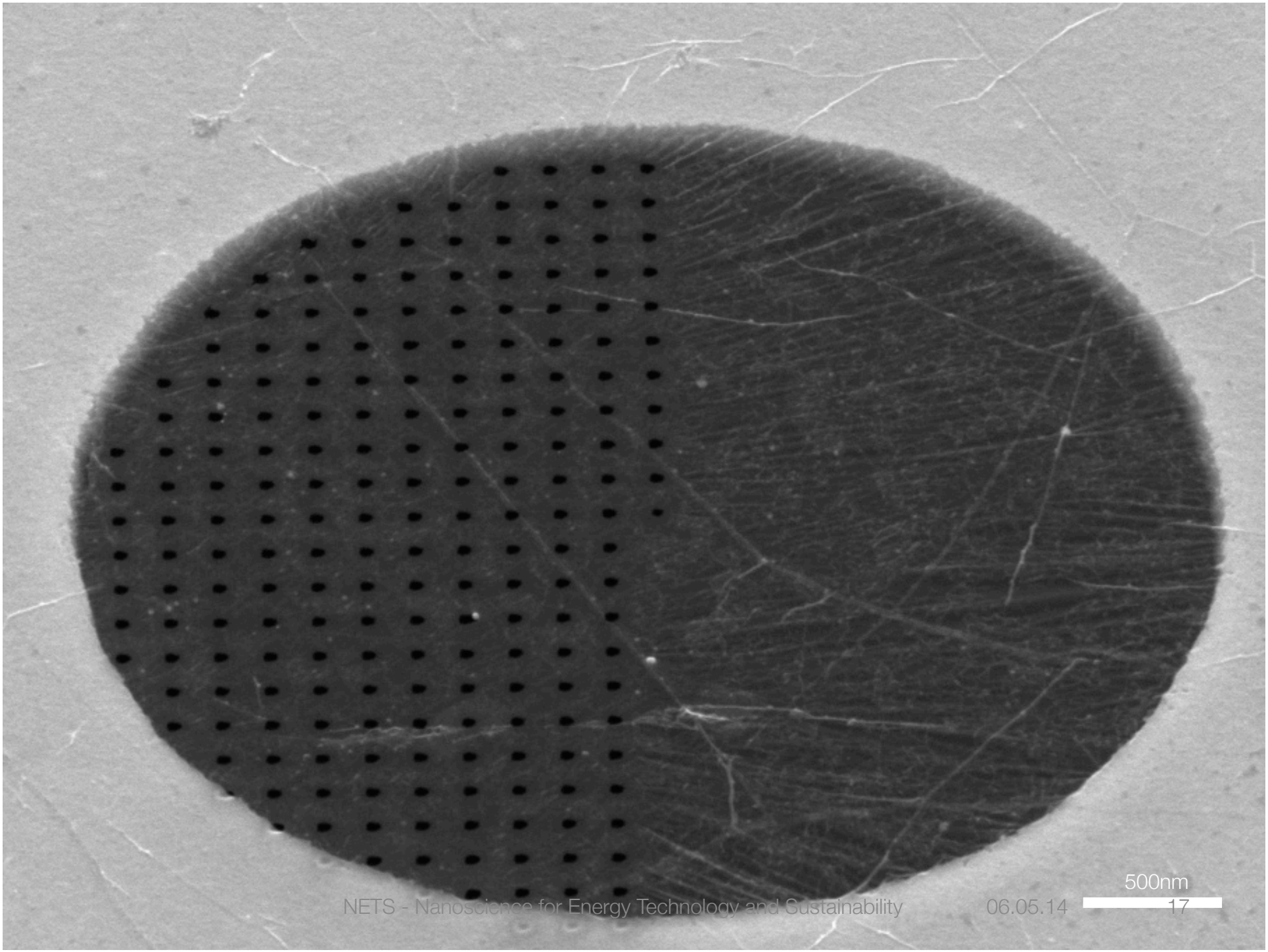
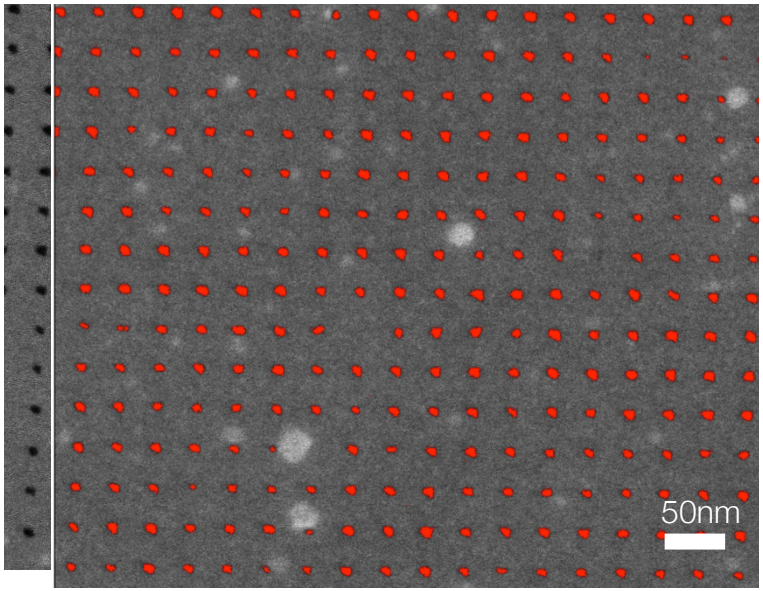
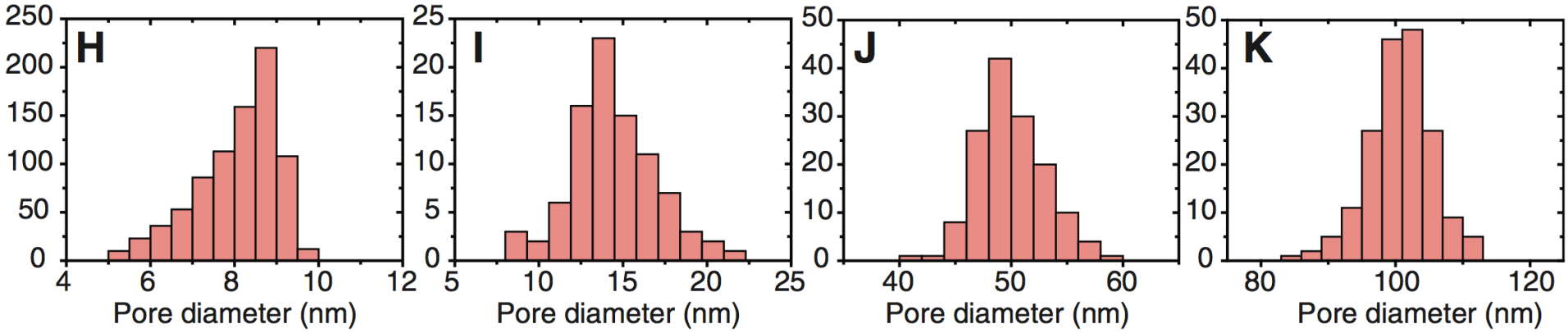

500nm

Membrane characterization – Pore sizes

- Pore sizes from 7.5nm to 1um
- 100 to 1 000 000 pores
- Narrow pore size distribution
- Membrane porosity 3-10%





K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).

Membrane characterization – Gas permeance

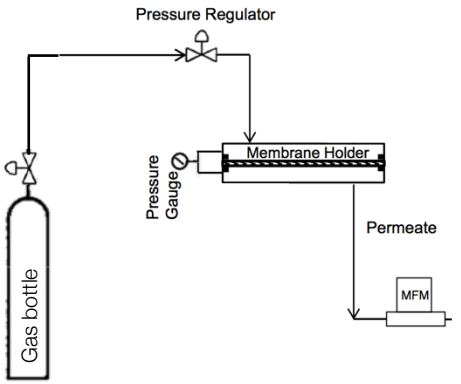
Measuring single and mixture gas flow through porous graphene membrane

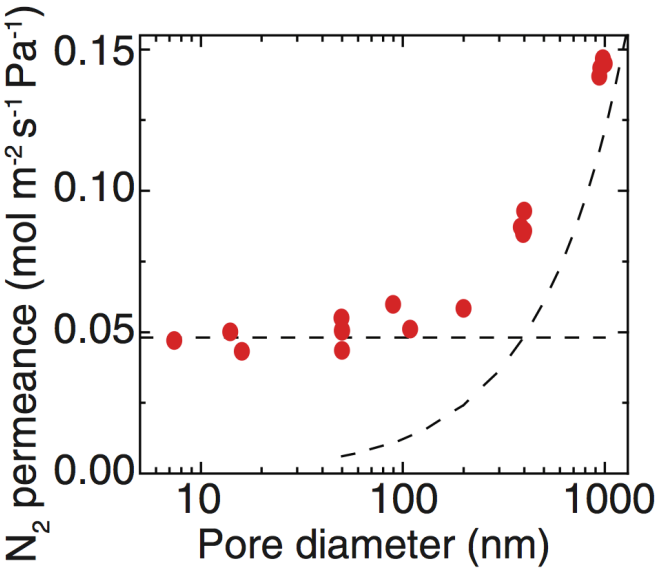
- Large pores – Sampson Model (continuum theory)

$$\frac{j_{Sampson}}{\Delta p} = \frac{1}{3\mu\pi}\frac{d}{2}\frac{1}{V_M}$$

- Small pores – Effusion (gas kinetic theory)

$$\frac{j_{Effusion}}{\Delta p} = \sqrt{\frac{1}{2\pi MRT}}$$





K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).

More on flow theory

- Sampson's model
  - Solution for flow through infinitesimal thin orifice
  - Continuum theory in for viscosity dominate flow (Stoke's Flow)
  - Flow constriction at entrance and exit are causing the resistance

$$Q_{Sampson} = \frac{1}{3\mu\pi}\left(\frac{d}{2}\right)\Delta P$$

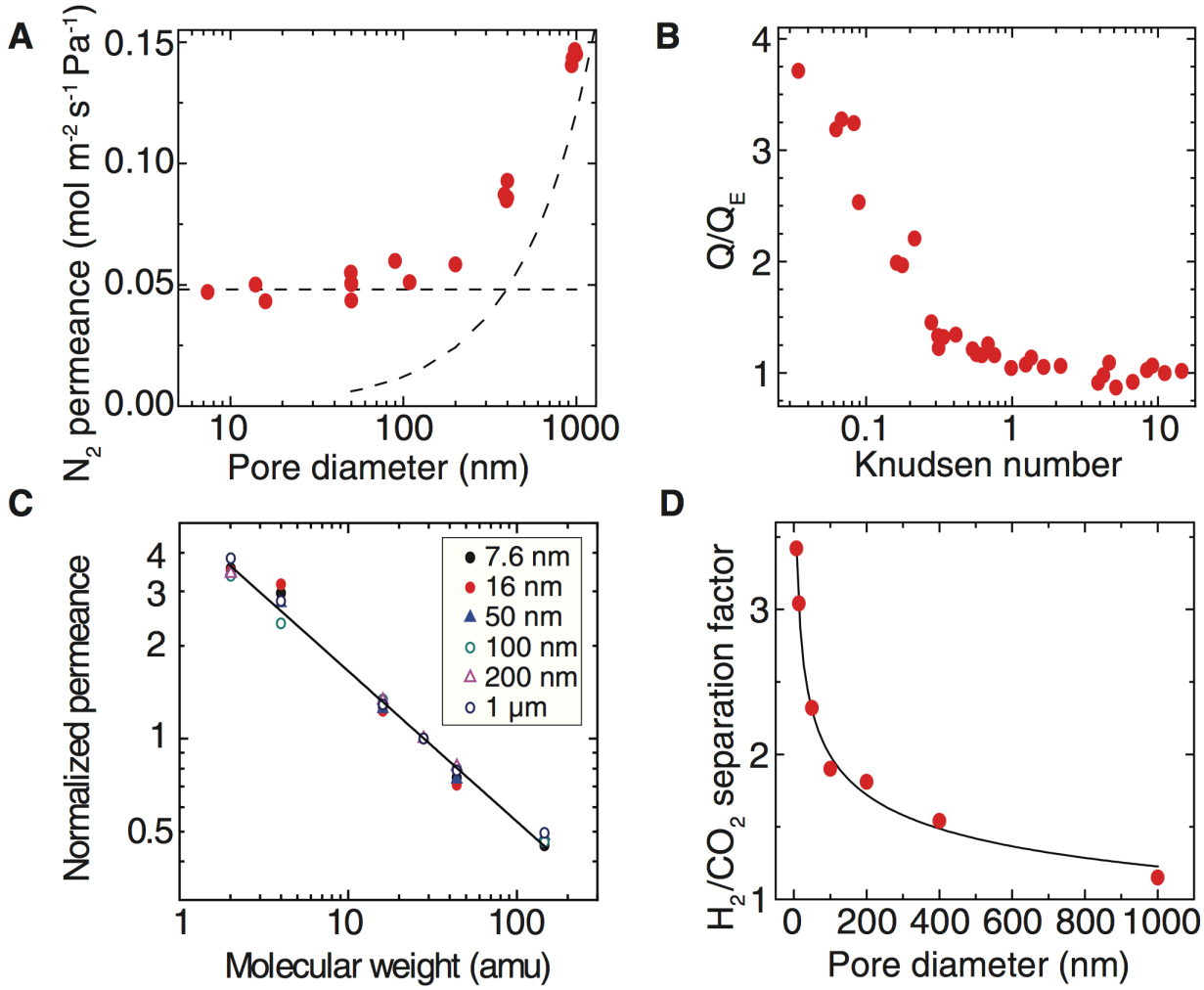
- Effusion theory
  - Gas kinetic theory – valid for $Kn=\lambda/d \gtrsim 1$
  - Collision density of gas molecules with pore area defines permeation

$$Q_{Effusion} = \frac{1}{4}\bar{u}\Delta n A_{pore} = \sqrt{\frac{\pi}{2MRT}}\left(\frac{d}{2}\right)^2 V_M \Delta P$$

R. A. Sampson, Philosophical Transactions of the Royal Society of London. A, 449–518 (1891).
K.-K. Tio, S. S. Sadhal, Appl. Sci. Res. 52, 1–20 (1994).
M. Knudsen, Ann. Phys. 333, 999–1016 (1909).

Membrane characterization – Gas permeance

- Transition from continuum to molecular flow regime
- There is no Knudsen Minimum for ultra thin membranes
- Gas permeance scales with $M^{-0.5}$
- Gas separation approached ideal selectivity for smaller pore sizes



K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).

More on gas separation

Gas separation:

- Size of H_2 molecule 2.6Å
- Size of CO_2 molecule 3.3Å
- Pore size 7.6nm to 1um

Contradicting results

- Single gas permeances scales $M^{-0.5}$ for all pore sizes
- Permselectivity ->

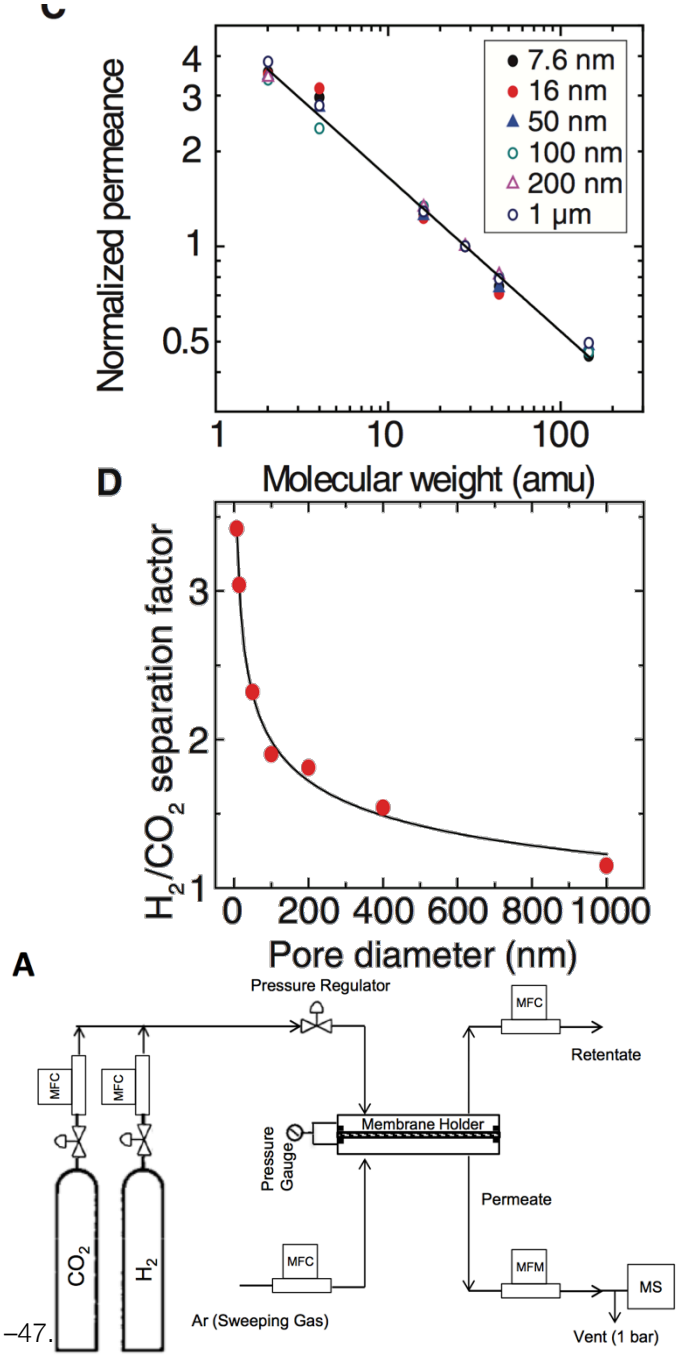
$$\frac{j_A}{j_B} = \sqrt{\frac{M_B}{M_A}}$$

Separation factor

- True mixture separation measurement
- Compare feed composition and permeate composition

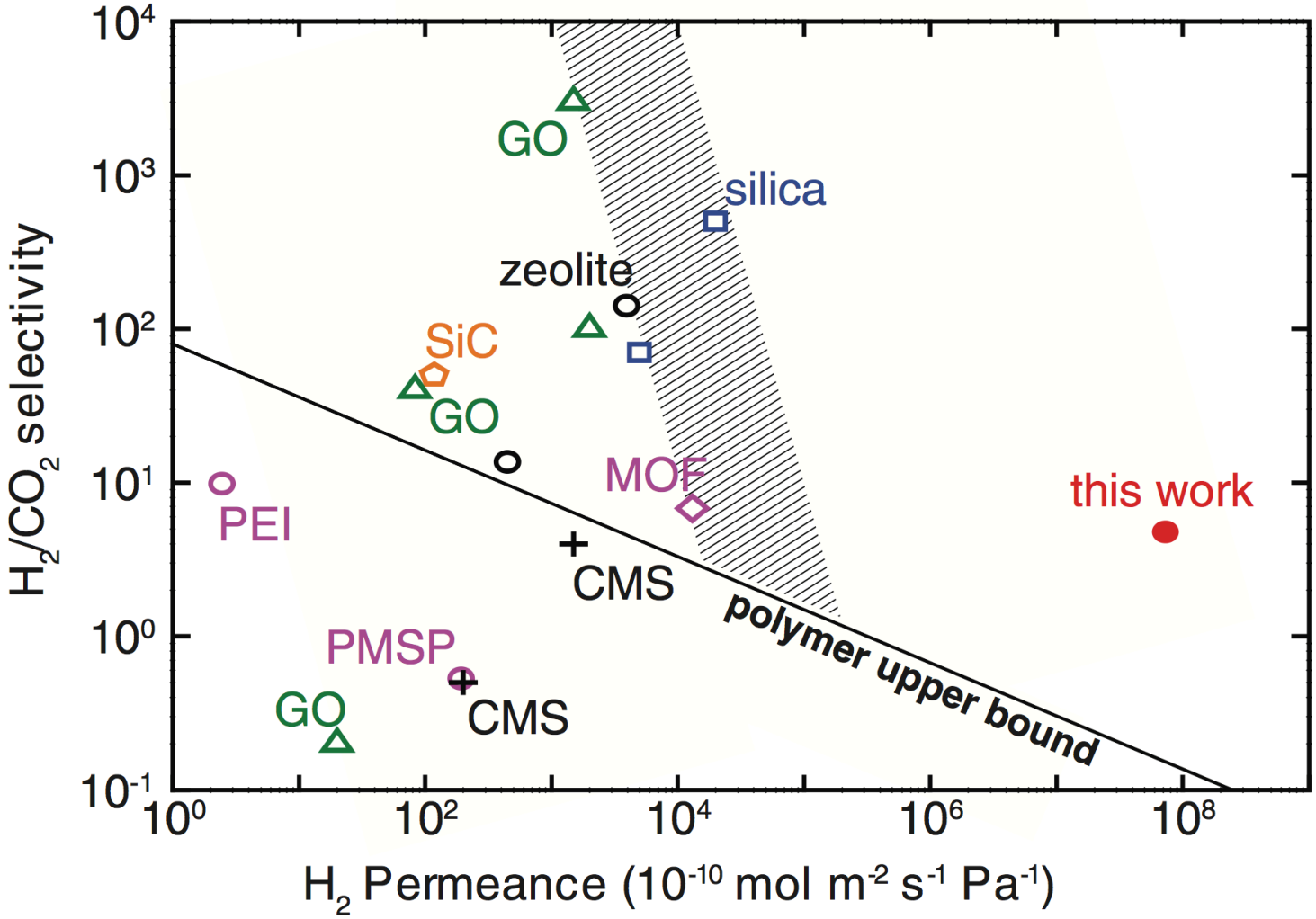
$$\alpha = \frac{\gamma_A/\gamma_B}{x_A/x_B}$$

Gas separation based on suppression of momentum exchange between gas species



K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).
S. Matteucci, et. al., in Materials Science of Membranes for Gas and Vapor Separation 2006, pp. 1–47.

Membrane characterization – Performance



K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).

Membrane characterization – Water permeance

Feed side wet

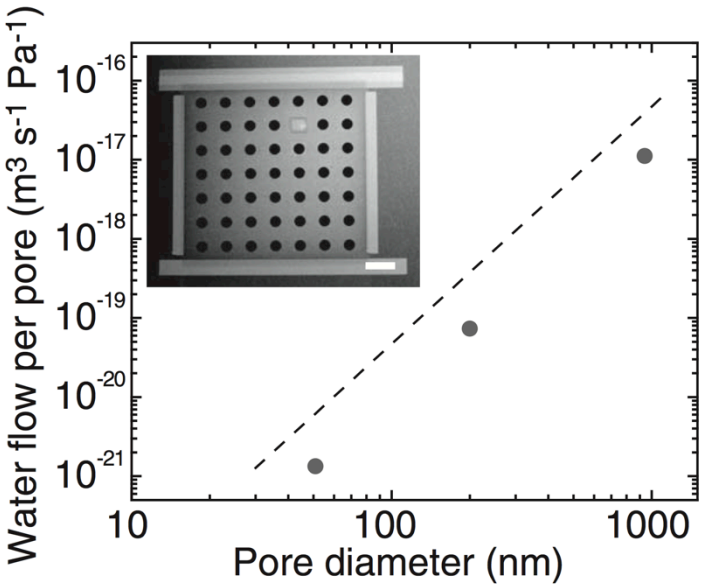
Feed + Permeate side wet

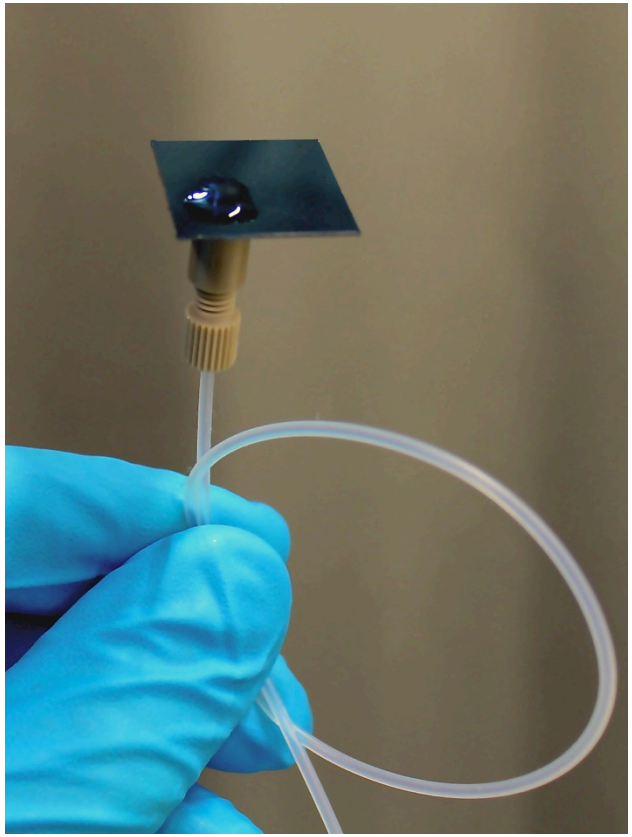
- Membrane does not allow liquid water to pass if only one side is wetted! (up to 2 bar pressure drop)
- Capillary pressure at meniscus at pore mouth counteracts feed pressure

Membrane characterization – Water permeance

Water flux through porous graphene

- Flow initiation only when both permeate and feed side are wetted
- Follows Sampson's flow model





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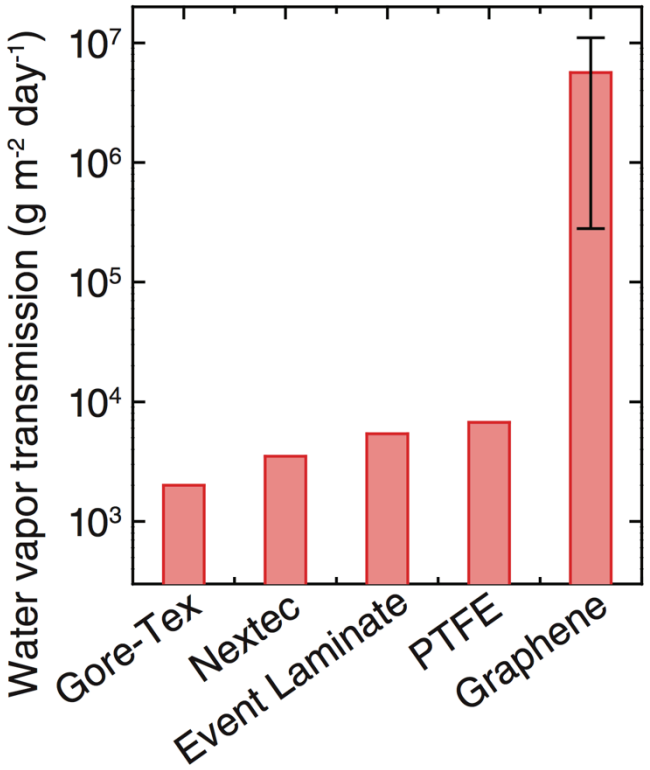
Membrane characterization – Water vapor permeance

Finding:

- Membrane is water tight (if only one side of graphene is wet)

What about water vapor?

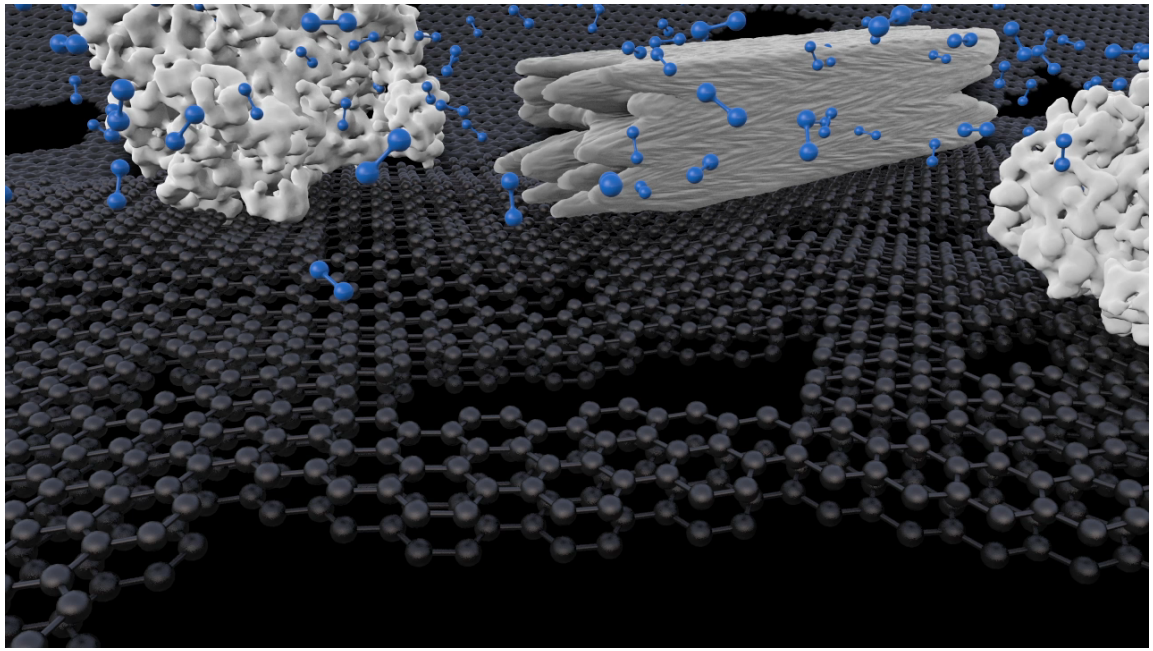
- Water vapor permeates at extraordinary high rate
- O(10^4) higher!!



➔Promising waterproof breathable membrane

K. Celebi, J. Buchheim et al., Science 344, 289–292 (2014).

Conclusion



- Graphene is promising membrane material
- Thinnest possible membrane synthesized
- Porous graphene membranes show ultimate gas permeation
- Porous graphene can serve as very efficient filter for gas separation and water treatment
- Porous graphene can serve as next generation waterproof fabric

Acknowledgments

Supporters:

Binnig Rohrer Nanotechnology Center

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