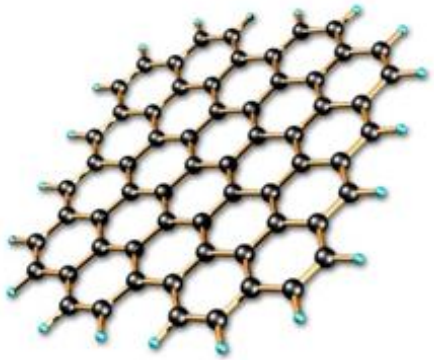
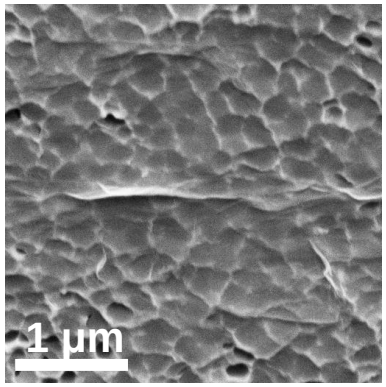




SAND2012-10172C

Gas permeability of graphene oxide membranes

Laura B. Biedermann[1], Jordan A. Fleischer[1,2], Katherine L. Harrison[1], and Kevin R. Zavadil[1]

1. Sandia National Laboratories, Albuquerque, NM

2. U. Michigan at Ann Arbor, Ann Arbor, MI

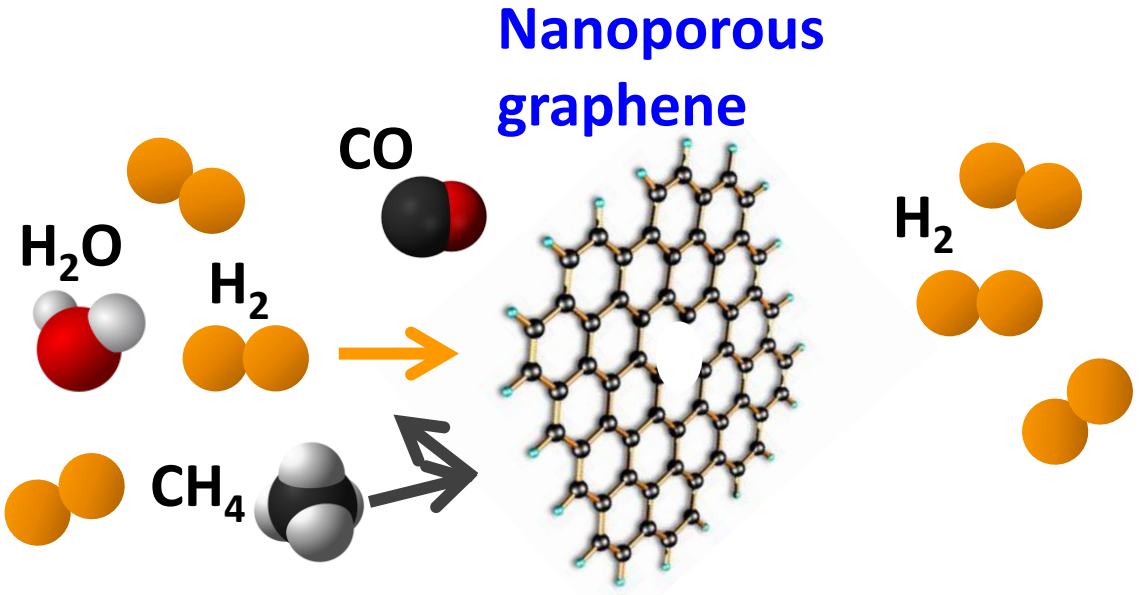
MRS Fall Meeting, Symposium T **November 28th, 2012**

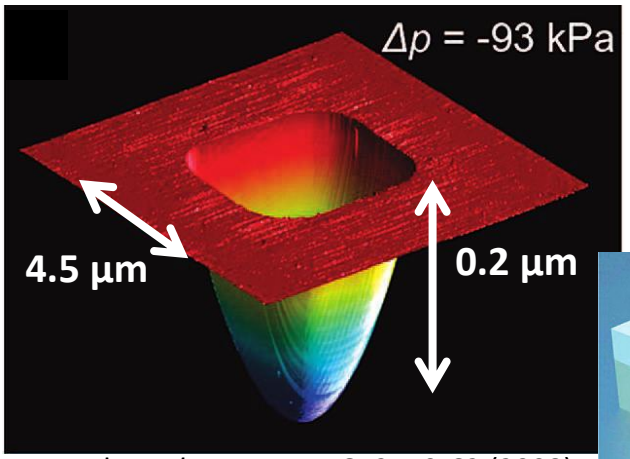
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC0494AL85000.

Permselective gas membranes enable energy technology

Steam reforming of natural gas:

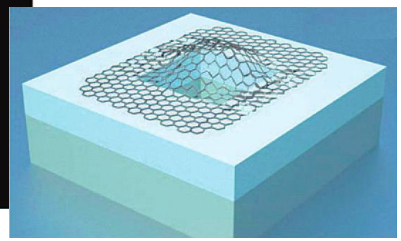
$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$





J. Bunch *et al.*, *Nano Lett* **8,** 2459-62 (2008).

A pristine graphene membrane is impervious to gasses

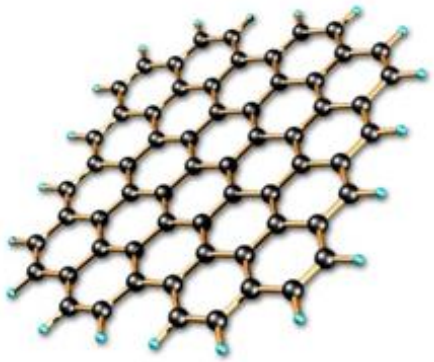


AFM image of a graphene monolayer under Δp = 700 torr

Graphene oxide is a one-atom thin solution-processable membrane material.

Graphene

sp^2 bonded carbon atoms

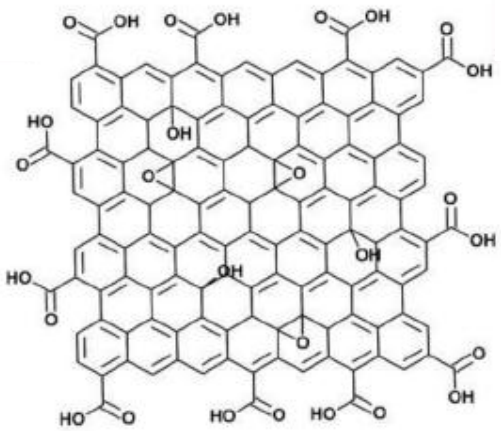


Natural graphite

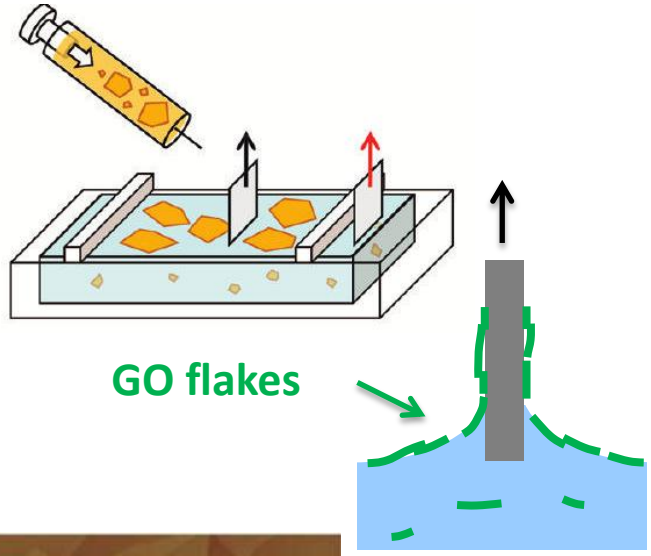
G. Eda and M. Chhowalla, *Adv. Mater*. 2010

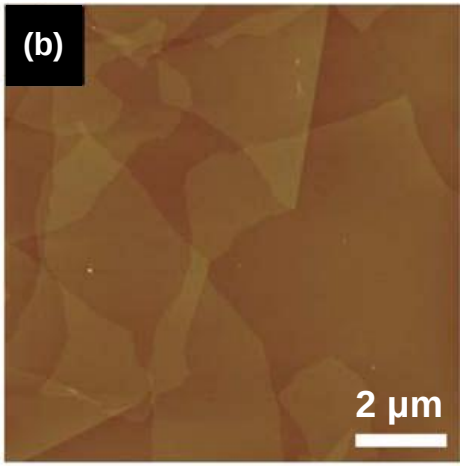
Chemical oxidation

Graphene Oxide (GO)



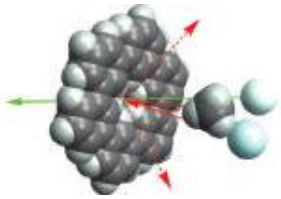
Langmuir-Blodgett deposition





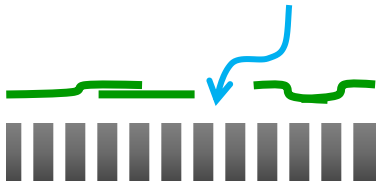
L. Cote *et al.*
Soft Matter 2010.

Permeation pathways through a supported GO membrane



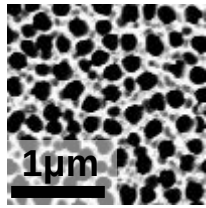
d ~ 0.3 nm
Kn >> 10

d ~ 1 nm
Kn > 10

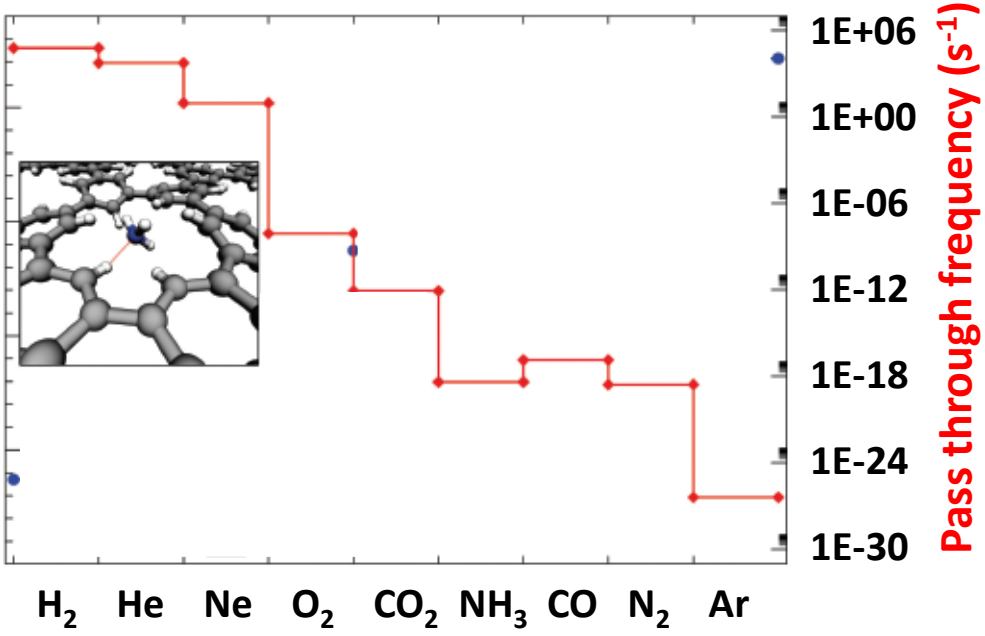


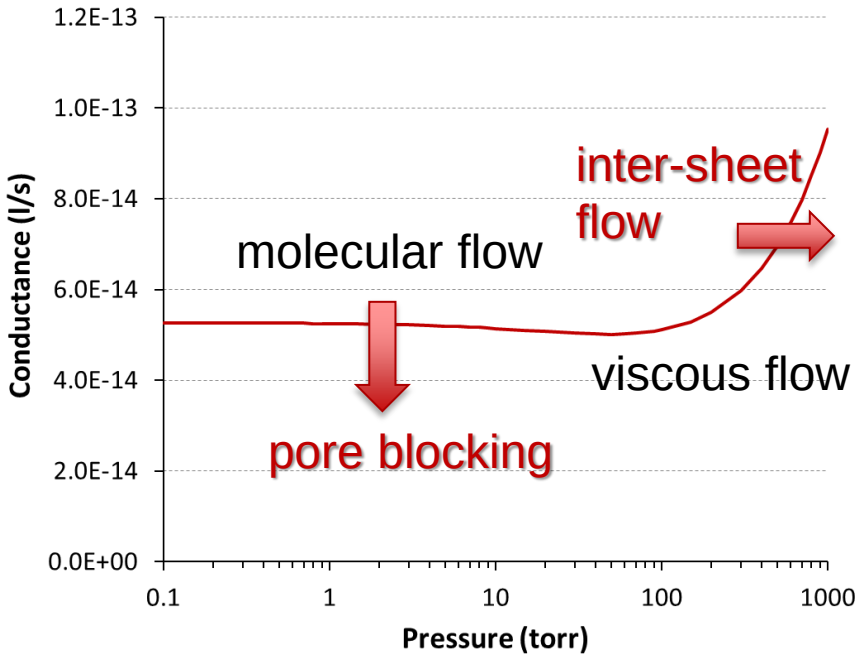
d ~ 20—200 nm
Kn ~ 10

Anodisc



For H_2/CH_4 and He/CH_4, selectivity > 10^{20}





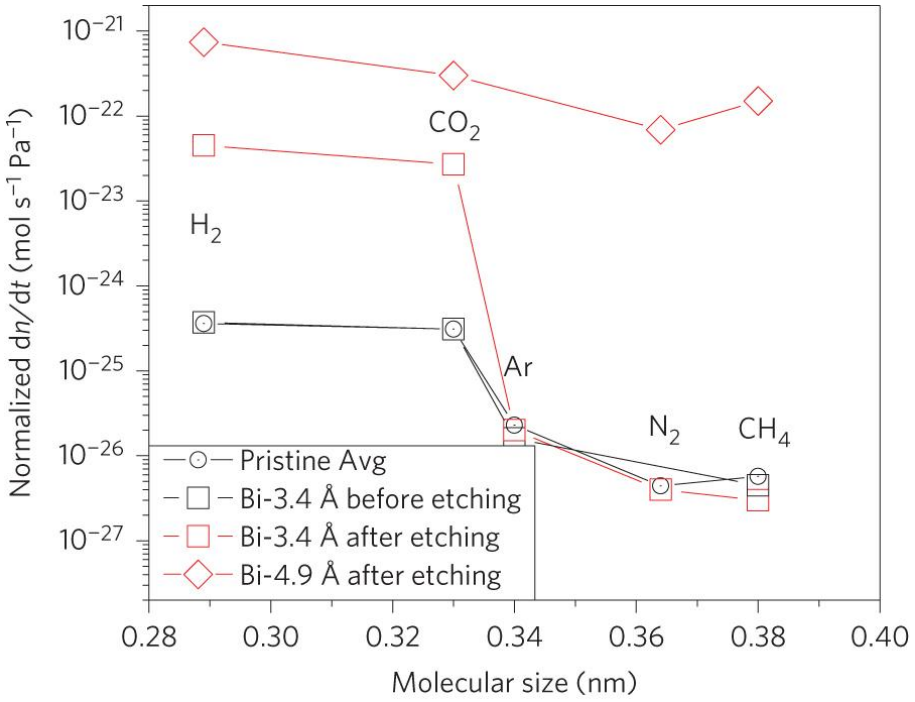
[1] S. Blankenburg *et al*. *Small* **6** (2010); [2] D. Jiang *et al. Nano Lett.* **9** (2009); [3] J. Schrier, *J. Phys. Chem. Lett.*, **1** (2010).

Membrane relaxation experiments have shown size-selective permeation

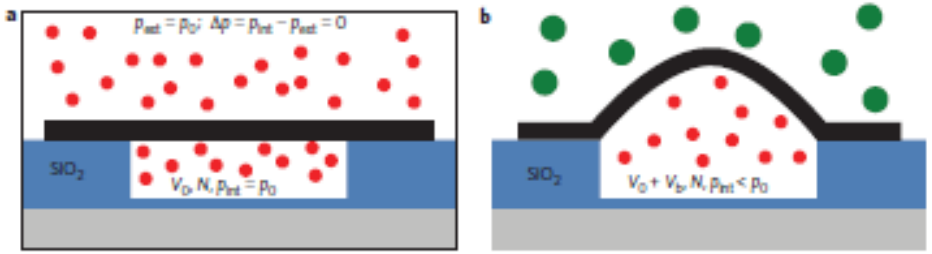
LETTERS
PUBLISHED ONLINE: 7 OCTOBER 2012 | DOI: 10.1038/NNANO.2012.162
nature nanotechnology

Selective molecular sieving through porous graphene

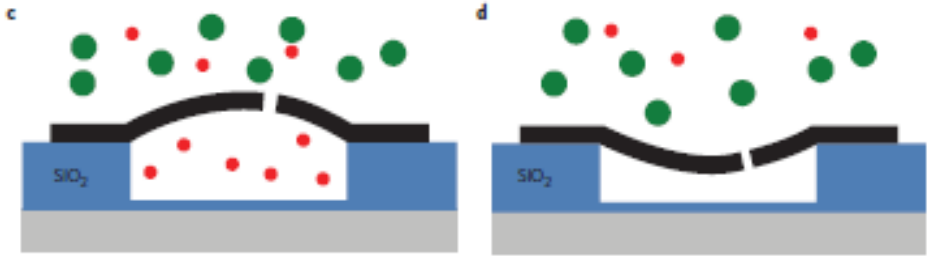
Steven P. Koenig, Luda Wang, John Pellegrino and J. Scott Bunch*



Oxidation generates nanopores, permitting size-selective permeation



Pristine graphene is impervious

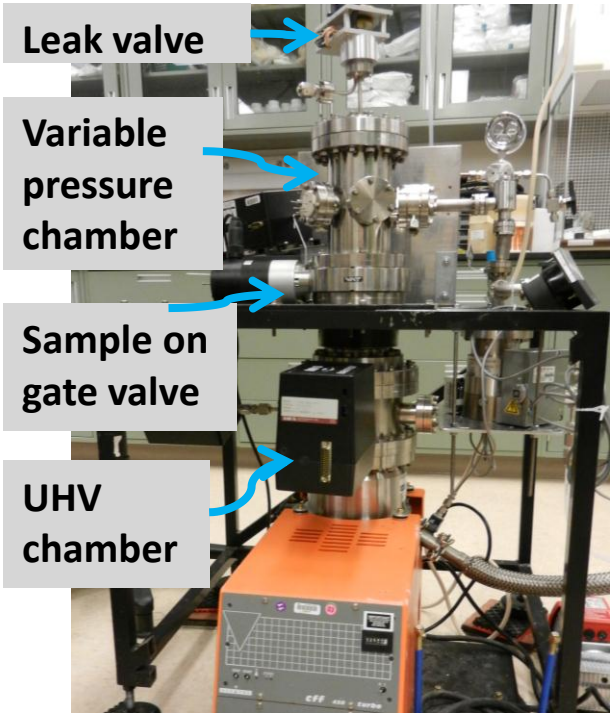


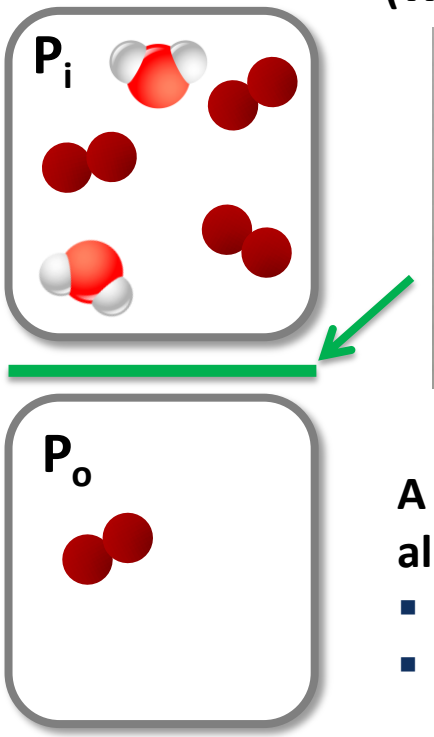
Small gases permeate through nanopores

High dynamic range of permeability allows flow channel differentiation

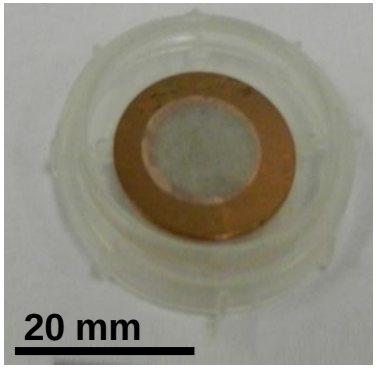
Sandia National Laboratories

Permeation System





GO membrane on porous alumina oxide (Whatman Anodisc)



A precision permeation system allows for high pressure differentials

- $P_i/P_o \sim 10^{11}$ Torr
- $P_i \sim 1000$ Torr

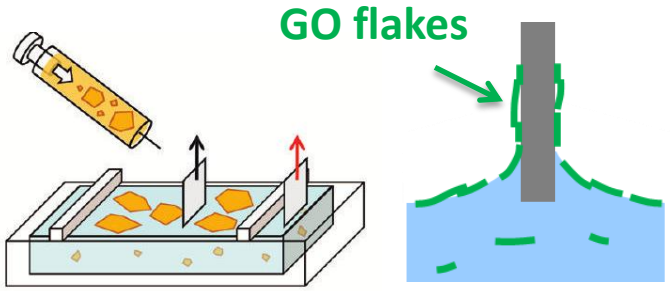
System design following P. Galambos, K. Zavadil, R. Shul, *et al.* Proc. SPIE (1999).

Tunability of Langmuir-Blodgett deposition allows GO assembly on varied surfaces

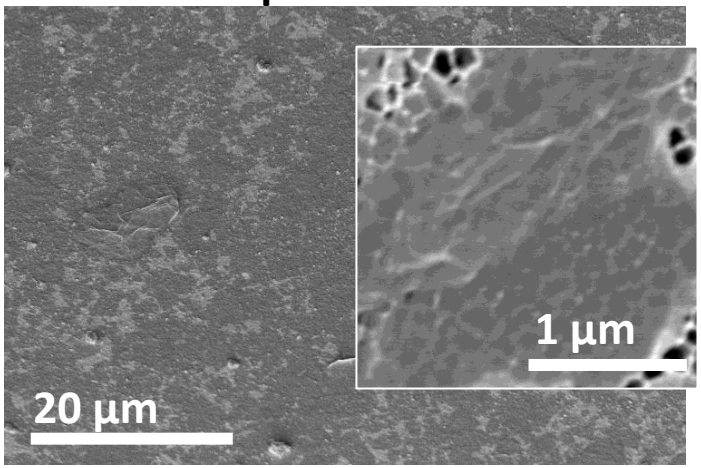
Spreading solution:

1:5 Aqueous GO in methanol

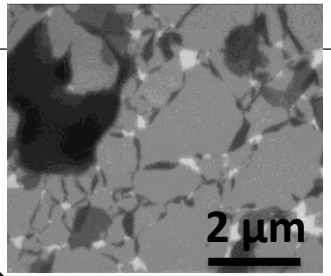
DI water subphase



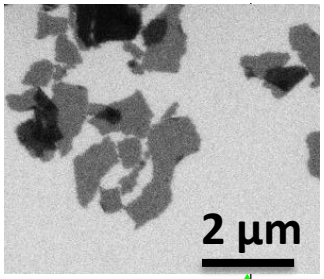
86 % GO on porous Anodisc



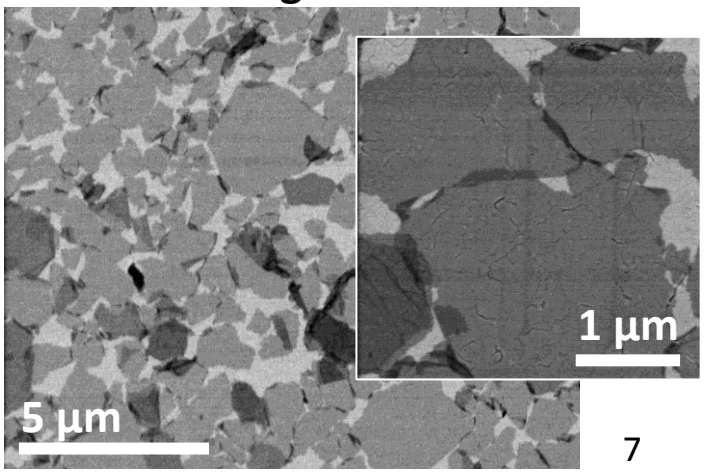
97 % GO on Si



9 % GO on Si



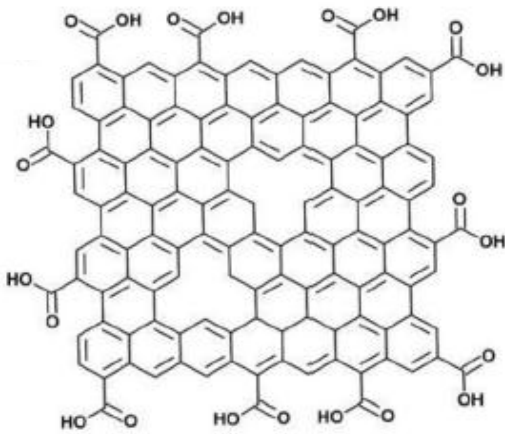
84 % GO on gold

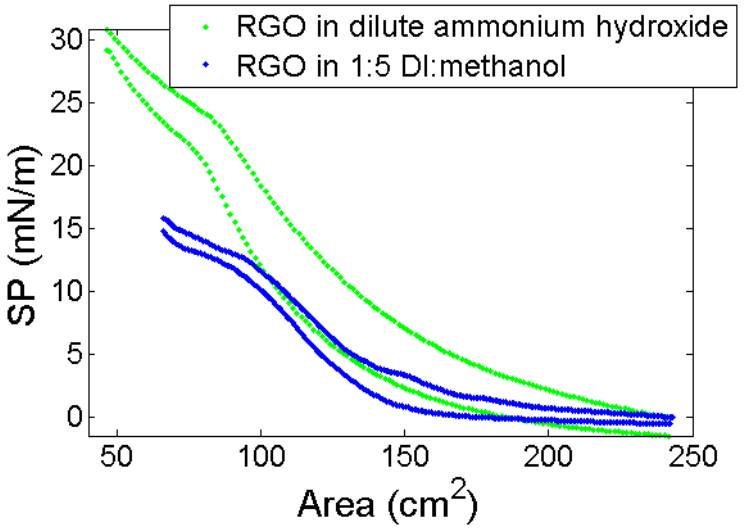


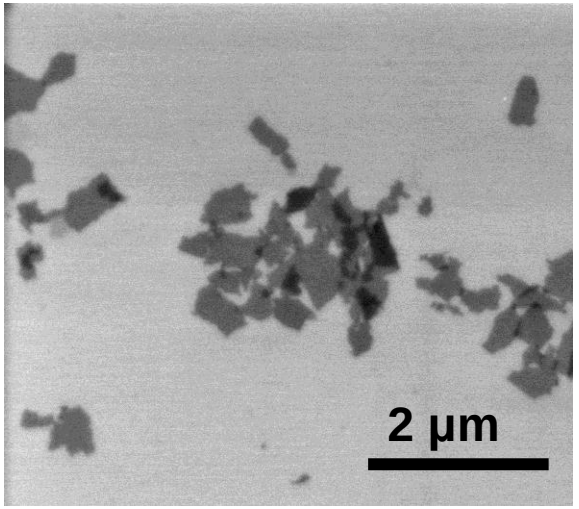
RGO surface phase is stable, yet deposition is challenging

With NH_4OH, stable RGO monolayer, yet poor deposition

RGO structure

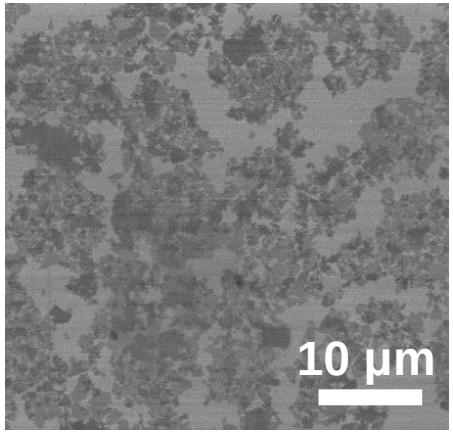




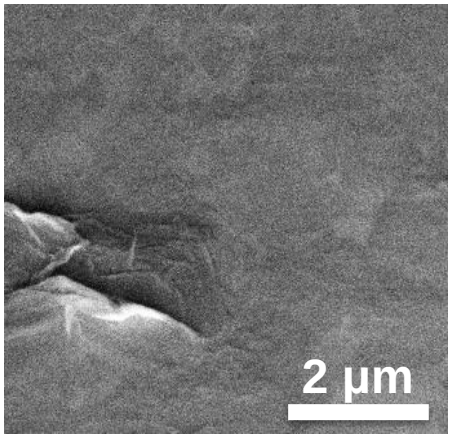


With methanol, RGO flakes cluster together, increasing deposition on Si and Anodisc.

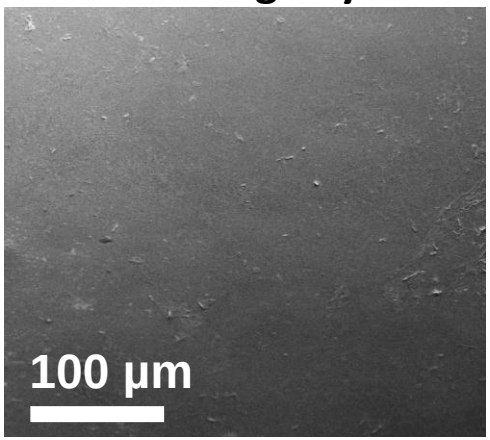
RGO on Si, 0 mN/m

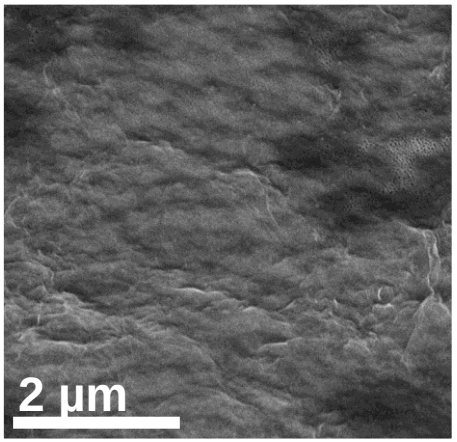


RGO on Si, 10 mN/m

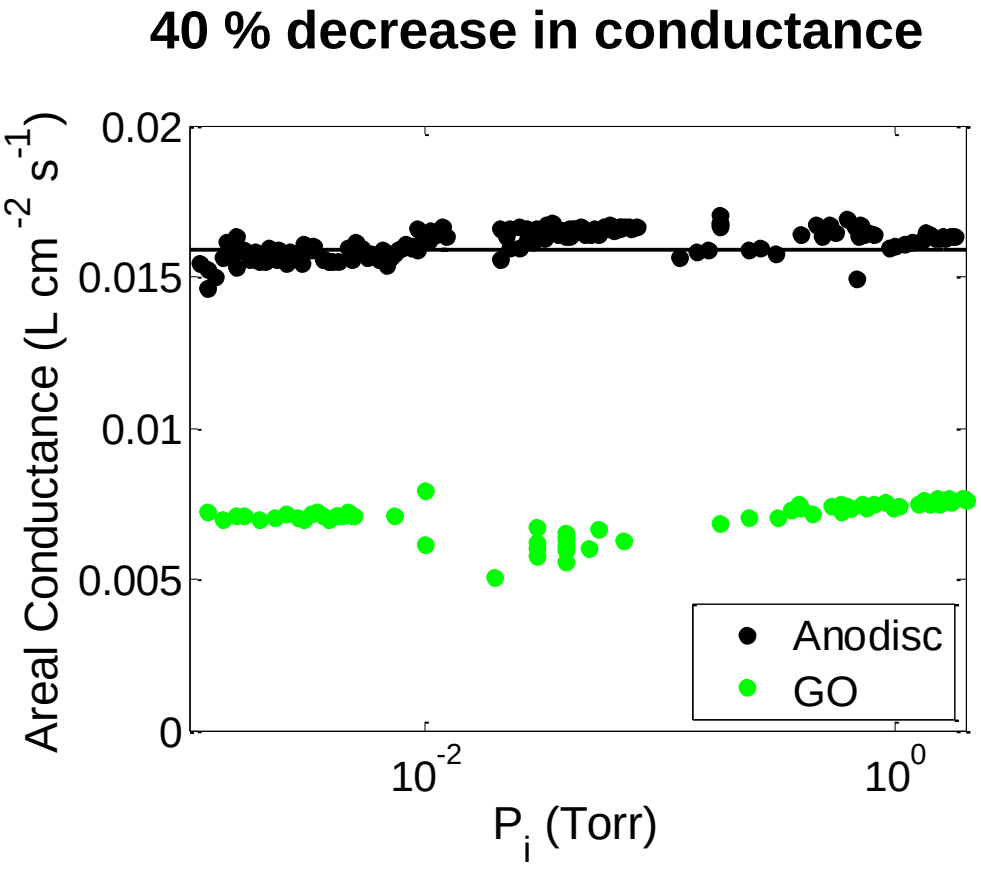


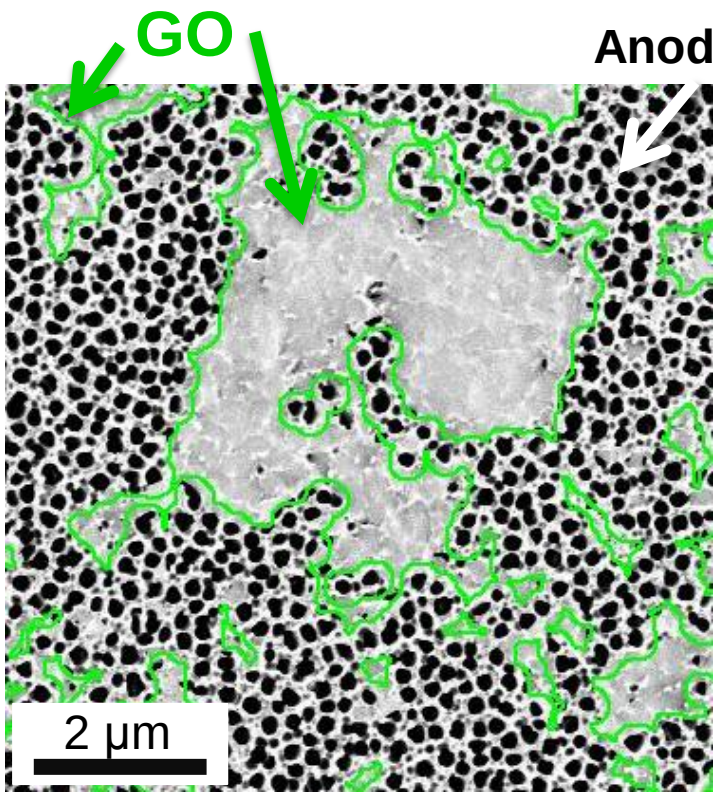
>95 % coverage by RGO on 200-nm Anodisc





Preliminary permeation results demonstrate decreased conductance due to GO membrane



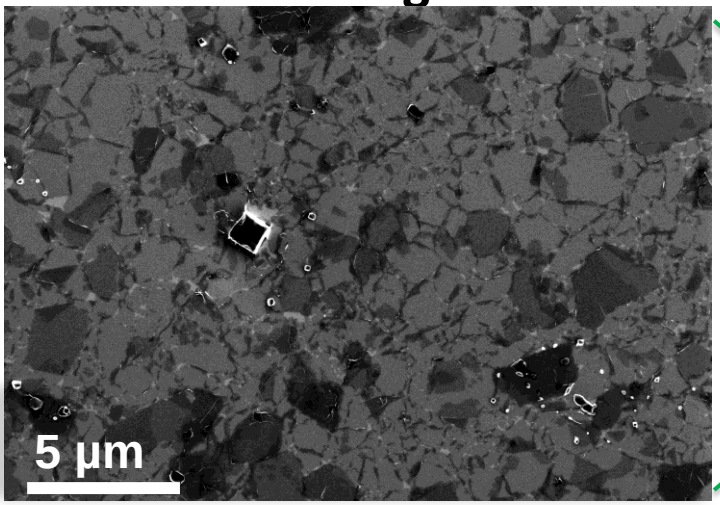


15 ± 5 % GO coverage
on this side of the sample.

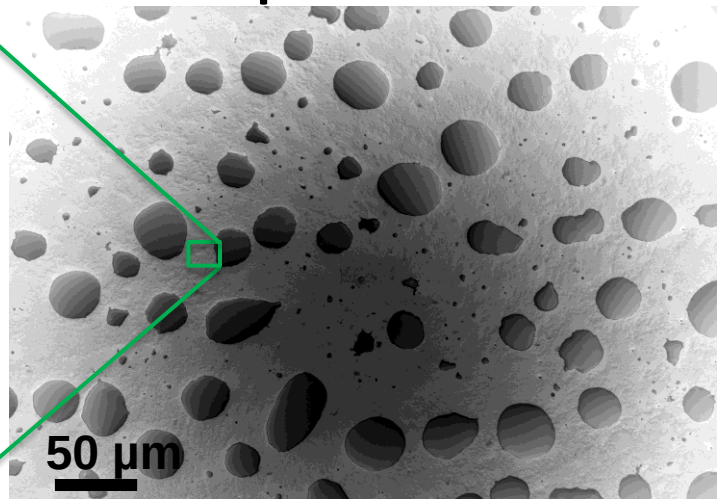
Ordered assembly of GO necessary to prevent permeation of water

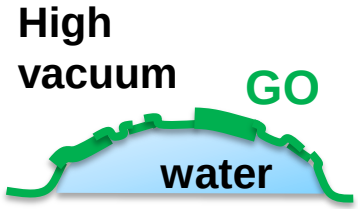
Sandia National Laboratories

98 % GO coverage on Si.

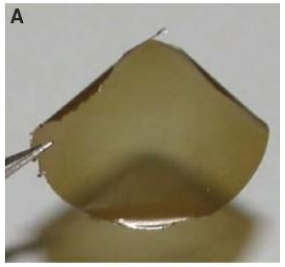


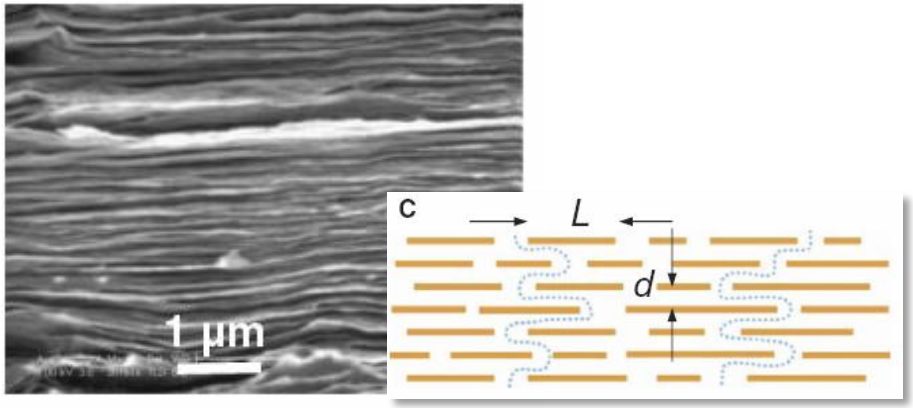
GO overlaps to encase bubbles

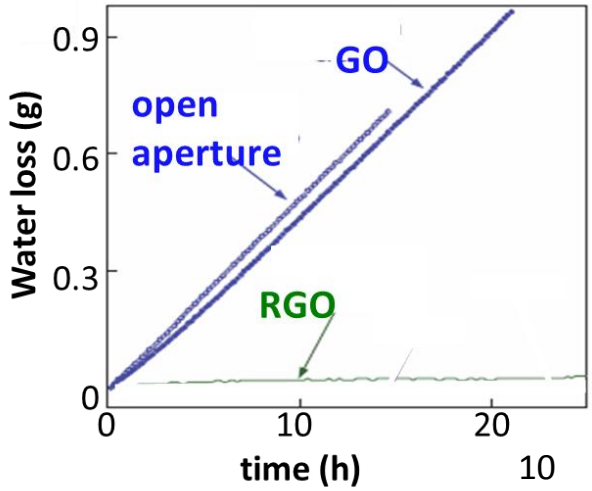




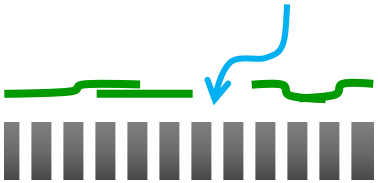
Unimpeded Permeation of Water Through Helium-Leak–Tight Graphene-Based Membranes
R. R. Nair *et al.* *Science* **335**, 442 (2012);





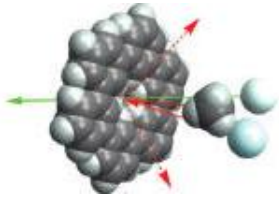


Optimizing permeation pathways through a GO membrane



Transition regime

Free-molecular regime

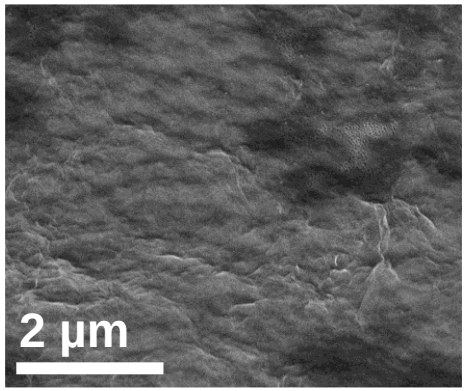


Size-selective permeability

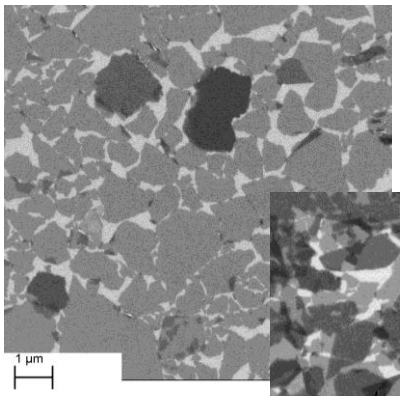
Optimized substrates

Microchannel plate?

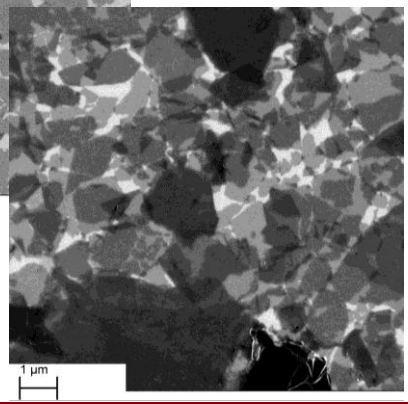
Polycarbonate track etched filter?



Tunable assembly



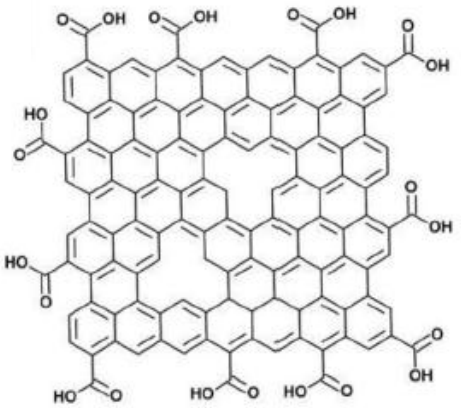
83% GO
One dip



94% GO
Two dips

UV-oxidative etching

Chemical reduction, GO→ RGO



Conclusions

Demonstrated L-B assembly of GO and RGO films on a porous substrate

- Pathway for supported membrane structures

Achieved Langmuir-Blodgett deposition of RGO membranes, which hasn't been reported before.

- RGO membrane assembly requires a network of overlapping flakes.

Discovered smoothly overlapping graphitic membranes restrict water permeation.

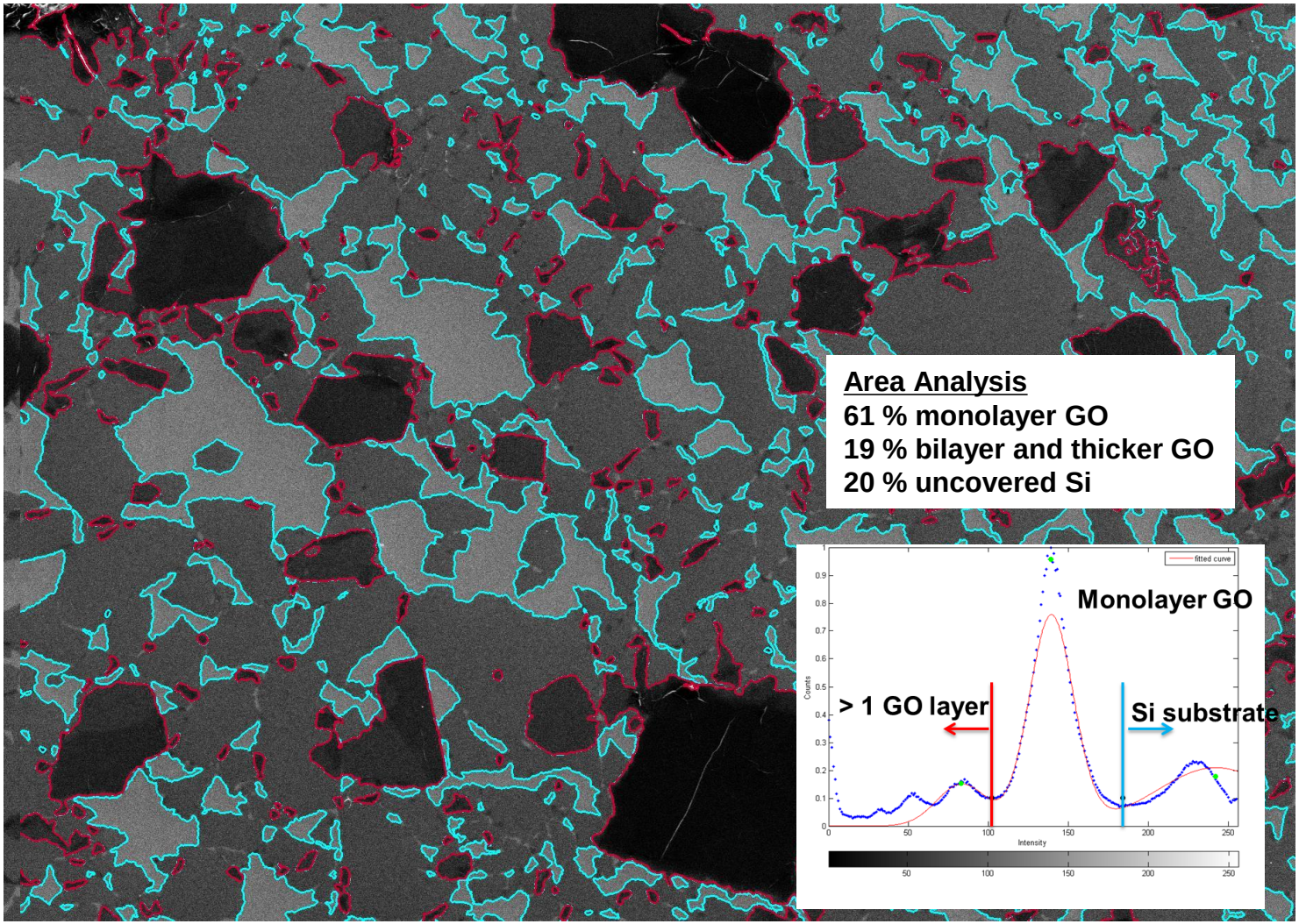
Acknowledgements

Graphene oxide: Tim Lambert

Experimental assistance: Susan Brozik, Ron Goeke, Stephen Rose, Cody Washburn, and Dave Wheeler

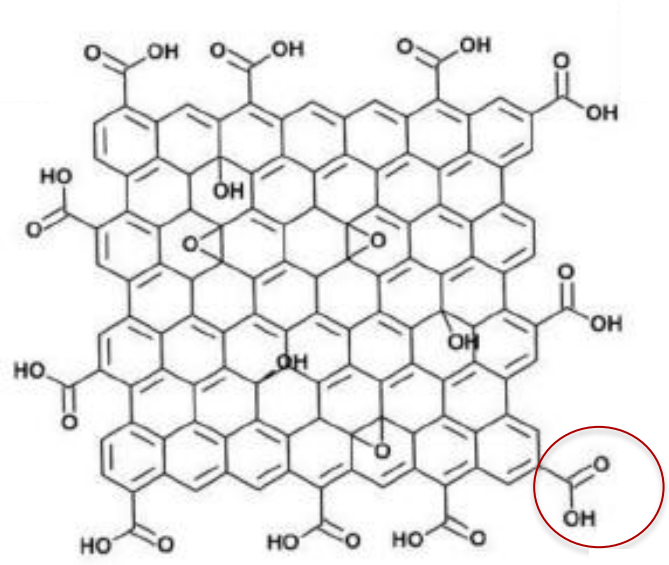
Scanning electron and optical microscopy: Bonnie McKenzie and Alice Kilgo

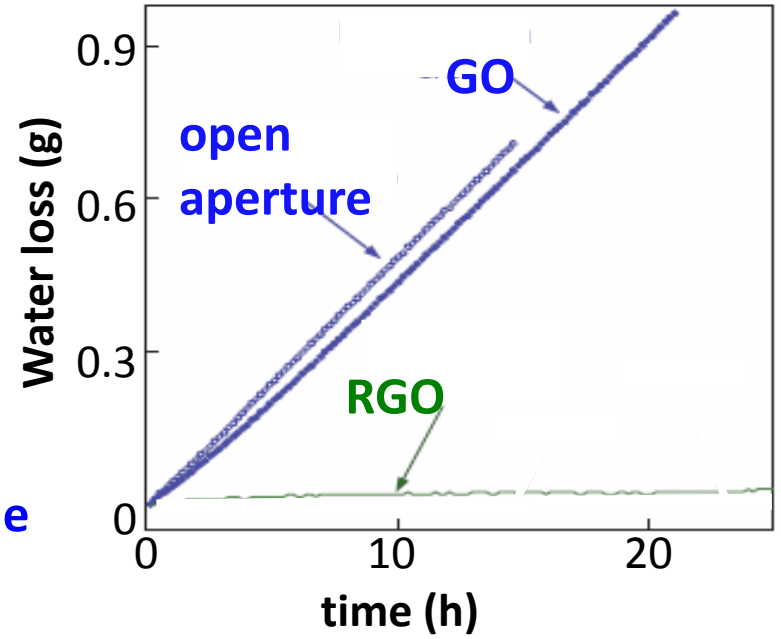
Determination of Graphene Coverage



Compare properties of GO and RGO films

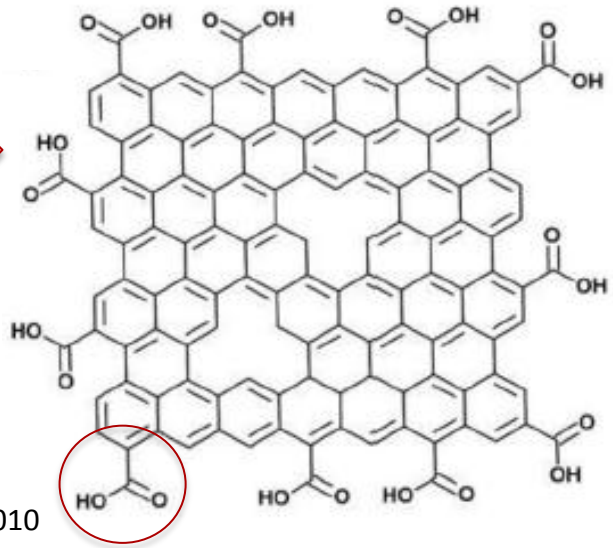
Graphene Oxide (GO)

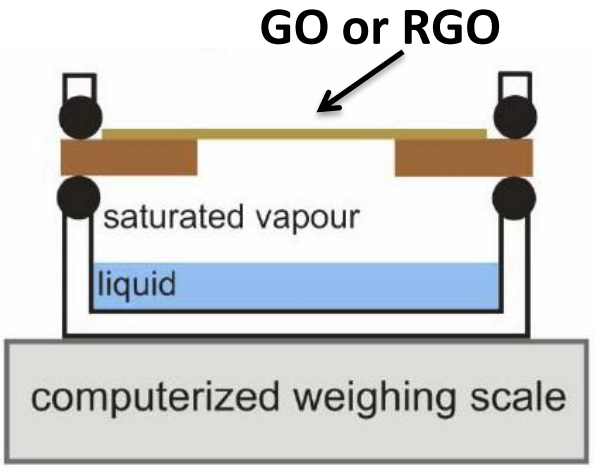




Reduced Graphene Oxide (RGO)

+ 80 °C and Ascorbic acid (Vitamin C)





G. Eda and M. Chhowalla, *Adv. Mater*. 2010
M. Fernandez-Merino *et al., J. Phys. Chem. C* 2010

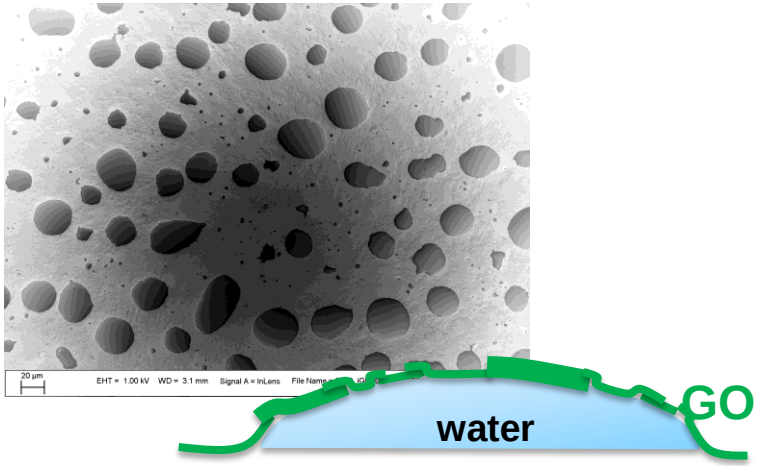
R. Nair *et al. Science* 2012

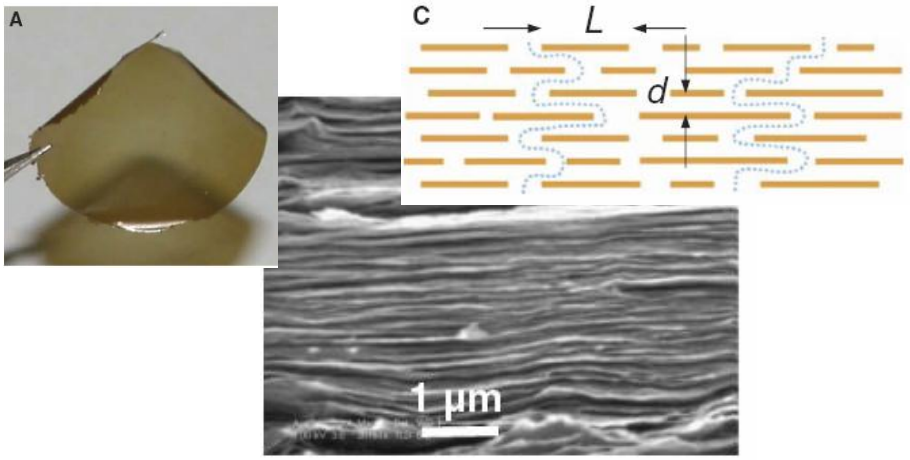
Conclusions

Optimized deposition of GO on a variety of substrates, including porous alumina.

Achieved Langmuir-Blodgett deposition of RGO membranes, which hasn't been reported before.

Discovered both GO and RGO membranes restrict water permeation.





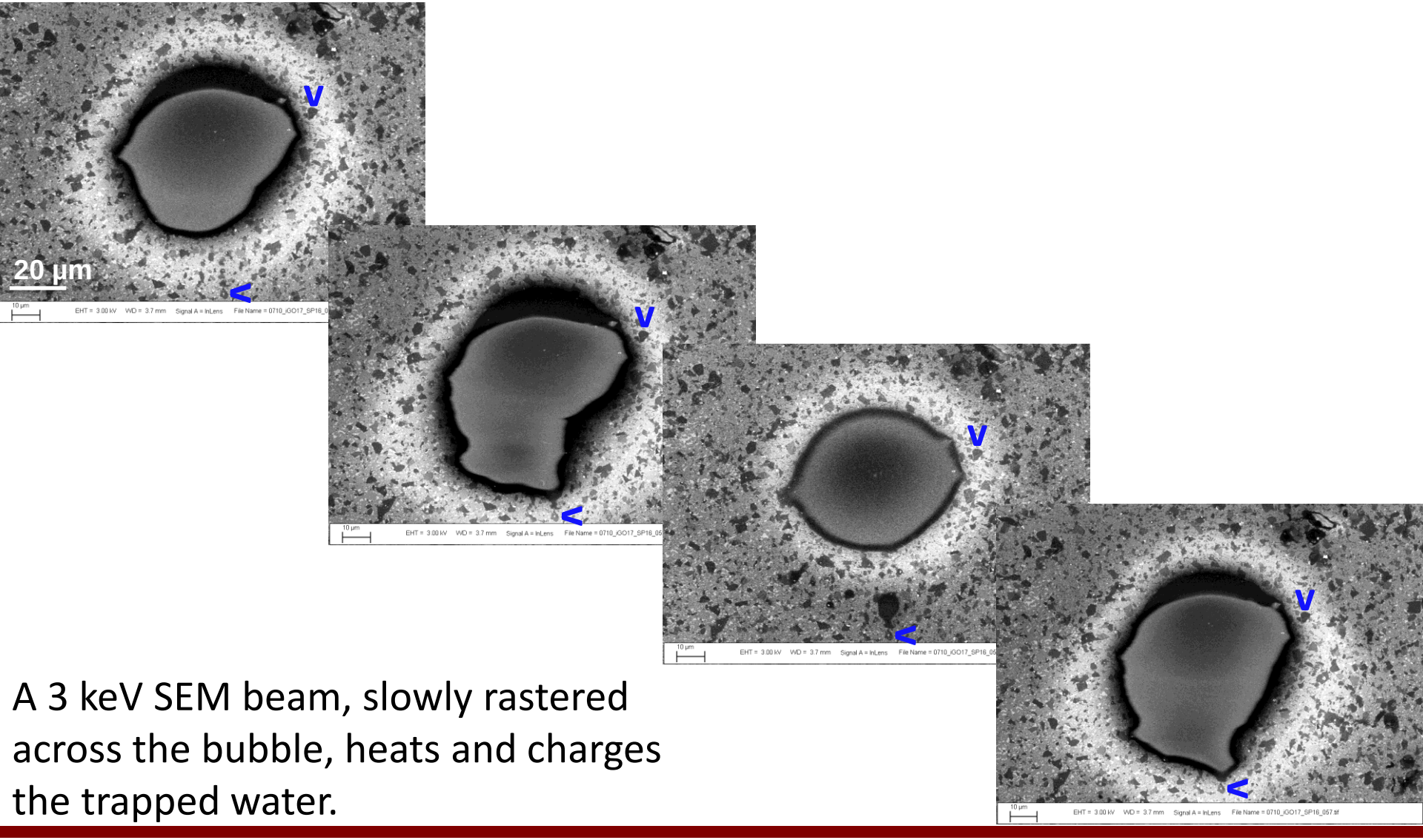
Acknowledgements

Graphene oxide: Tim Lambert

Experimental assistance: Susan Brozik, Cody Washburn, and Dave Wheeler

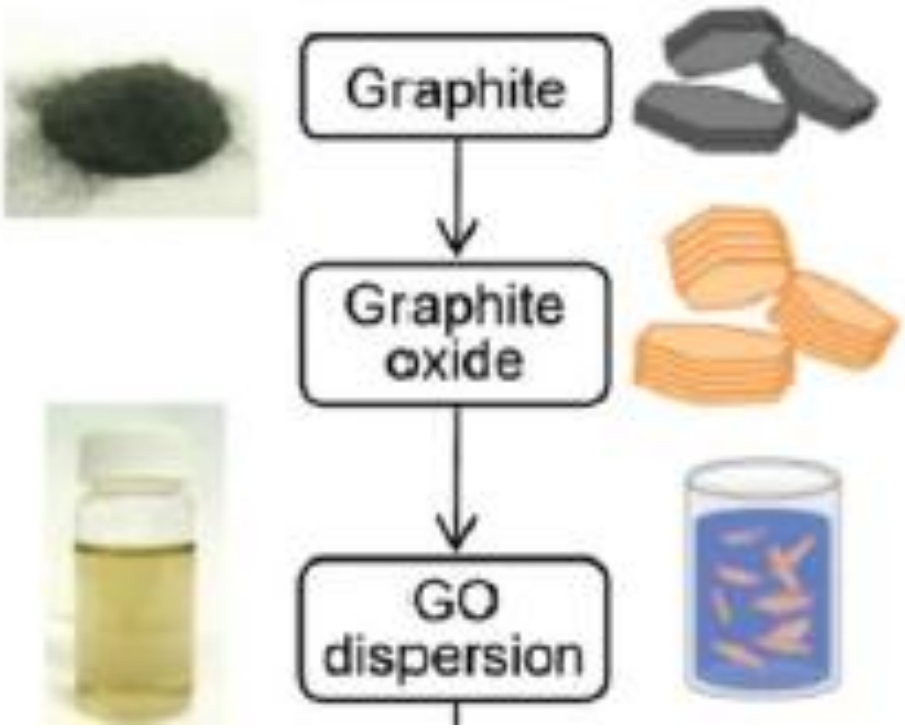
Scanning electron and optical microscopy: Bonnie McKenzie and Alice Kilgo

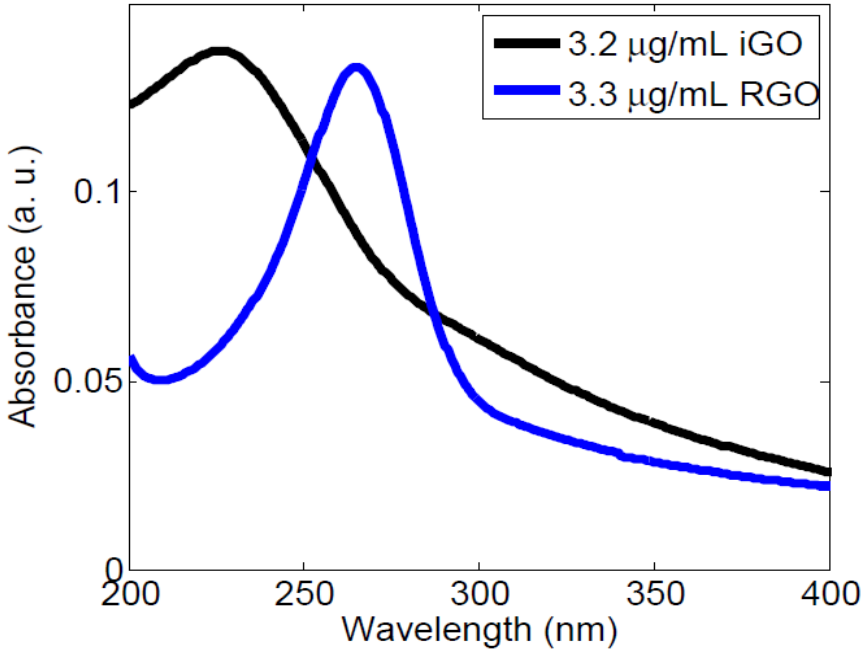
Composite GO membranes can stretch without bursting

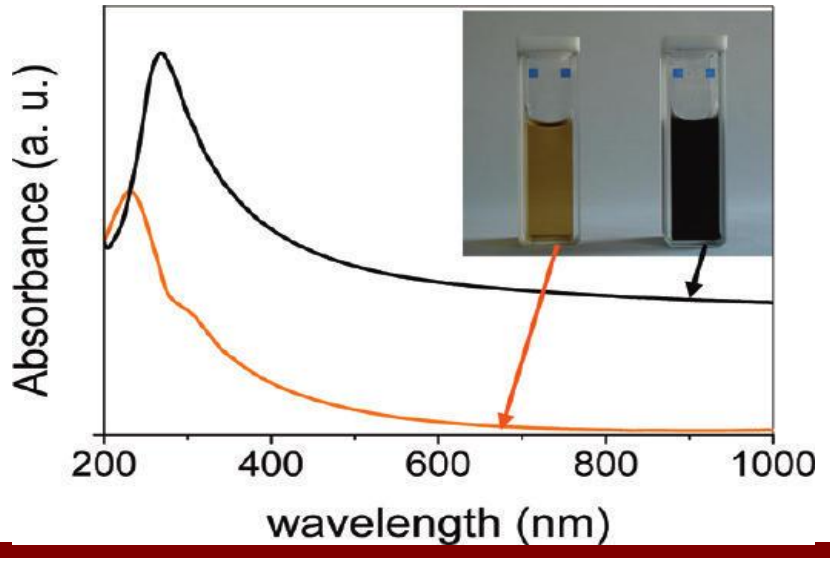


A 3 keV SEM beam, slowly rastered across the bubble, heats and charges the trapped water.

Natural graphite is oxidized via Hummer's method



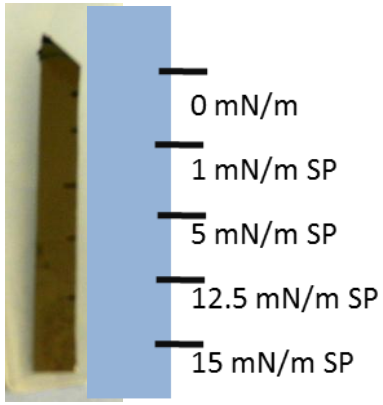


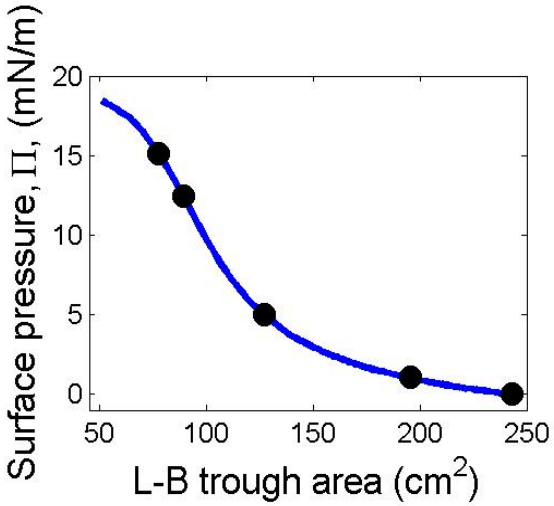


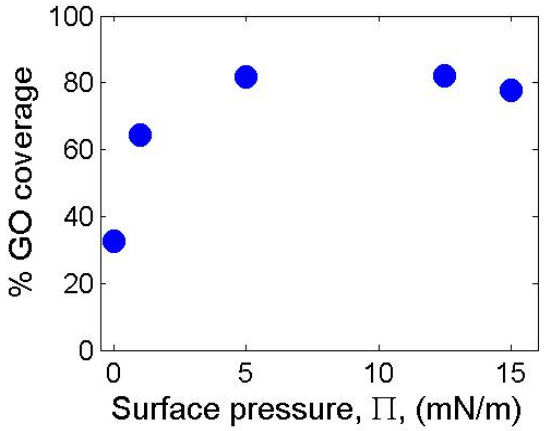
Oxidized using a mixture of $NaNO_3$, H_2SO_4, and KMn04.
Diluted and heated with H_2O and H_2O_2
Filtered and rinsed with HCl

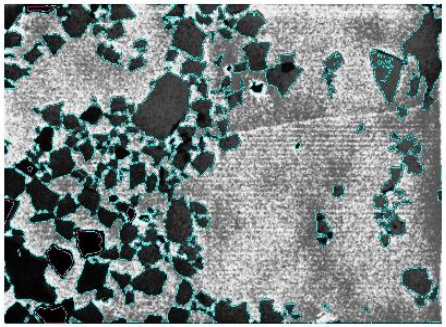
Paredes *et al., Langmuir* 2009.

GO coverage can be controlled through surface pressure

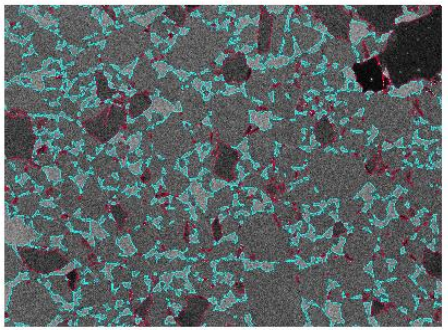








GO deposited at Π = 0 mN/m



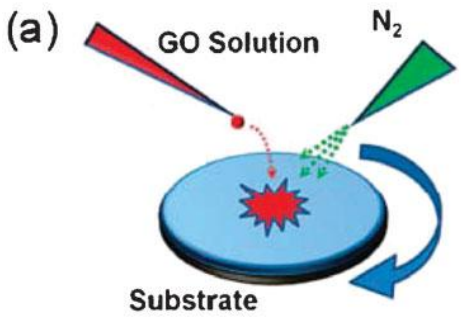
GO deposited at Π = 12.5 mN/m

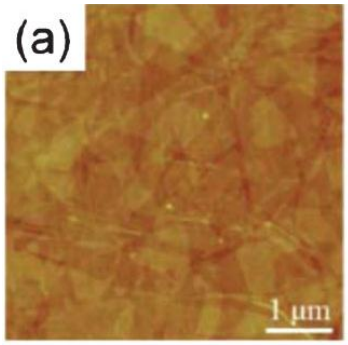
GO coverage plateaus at SP ≈ 5mN/m

Assembly of GO and RGO films

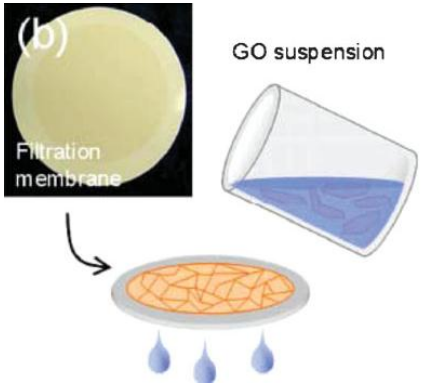
Sandia National Laboratories

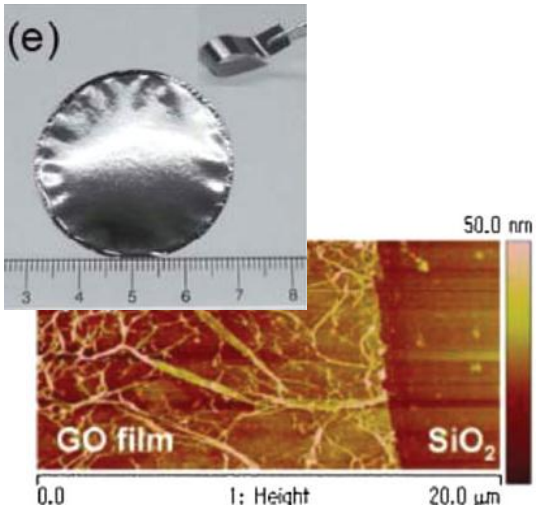
Drop casting[1]



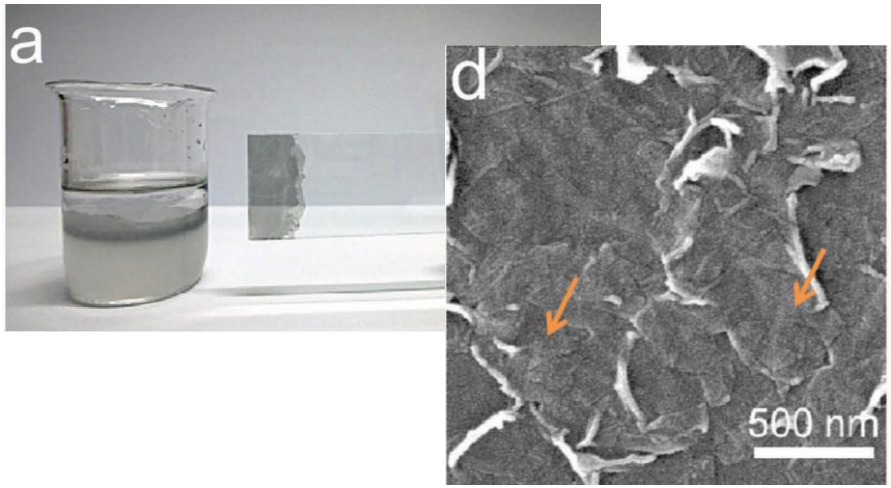


Vacuum filtration[2]

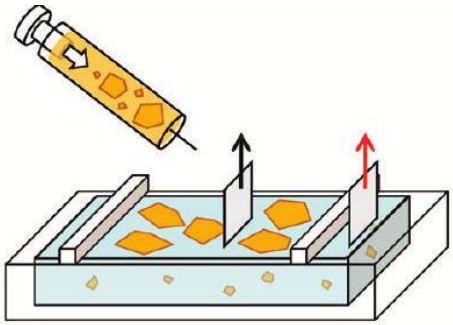


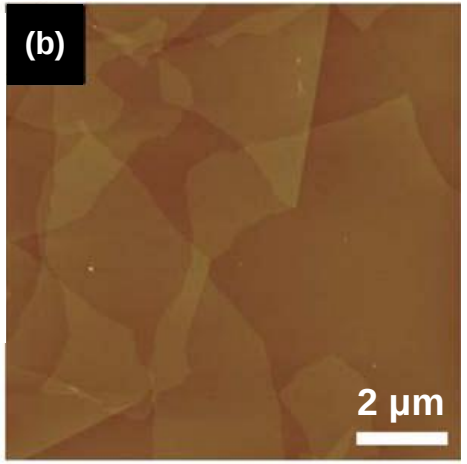


Assembly at an oil-water interface[3]



Langmuir-Blodgett deposition[4]



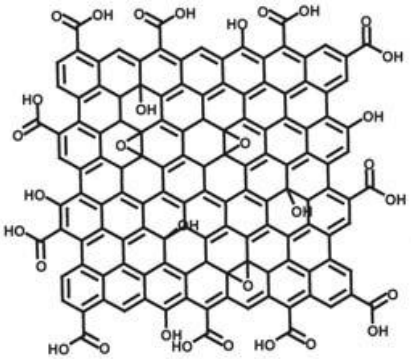


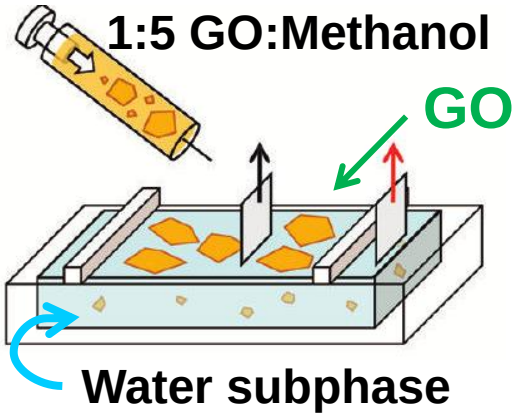
[1] G. Eda and M. Chhowalla, Adv. Mater. 2010
[2] S.-K. Lee *et al.* Nano Lett. 2012
[3] S. Gan *et al.* Adv. Mater. 2012
[4] L. Cote *et al.* Soft Matter 2010.

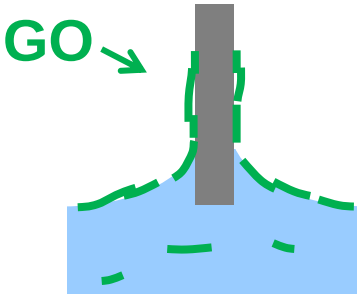
Stable graphene oxide surface phase enables Langmuir-Blodgett assembly

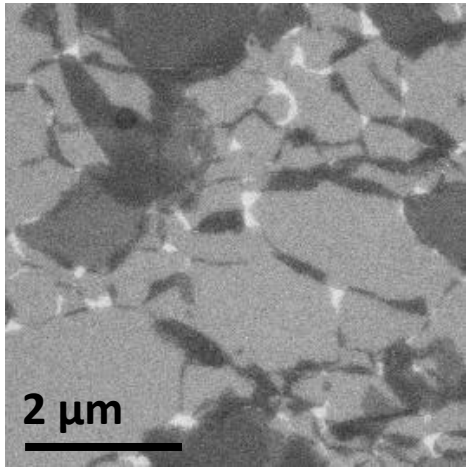
Sandia National Laboratories

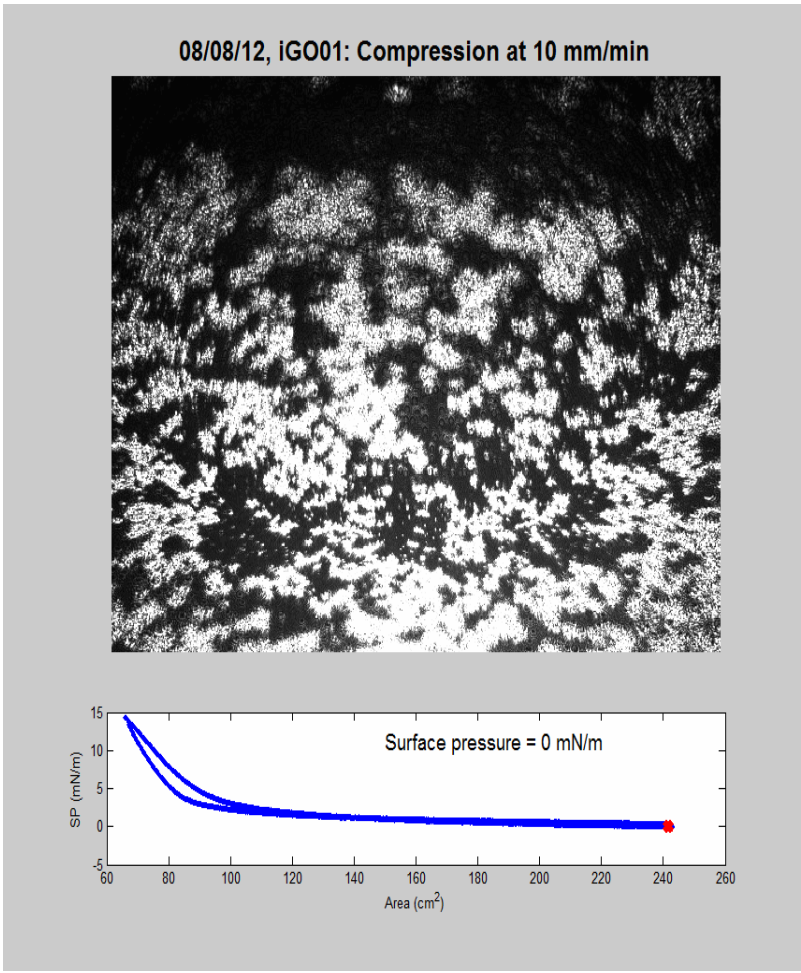
GO structure











Goal: Optimize deposition to generate continuous GO and RGO films