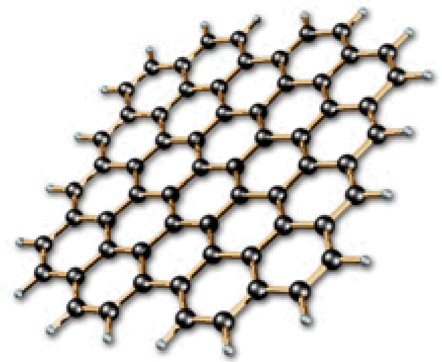

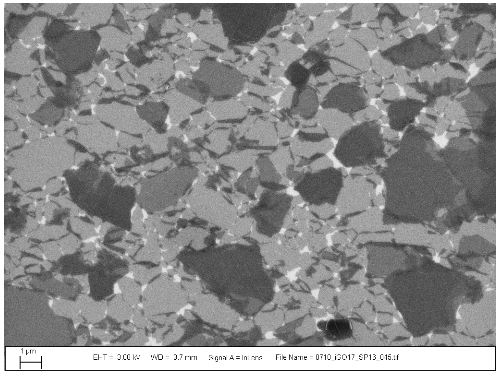

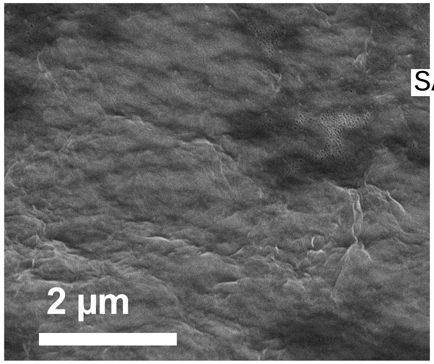

SAND2012-9065C

Langmuir-Blodgett Assembly of Graphitic Films

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

1. Sandia National Laboratories, Albuquerque, NM

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Rio Grande Symposium on Advanced Materials, Oct. 22, 2012

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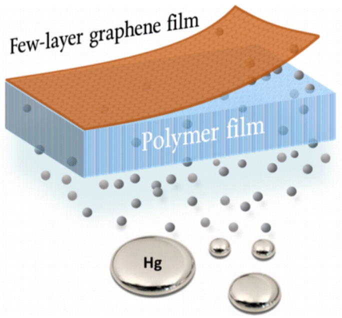
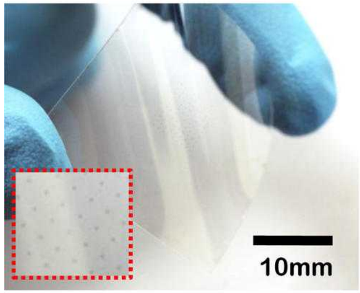
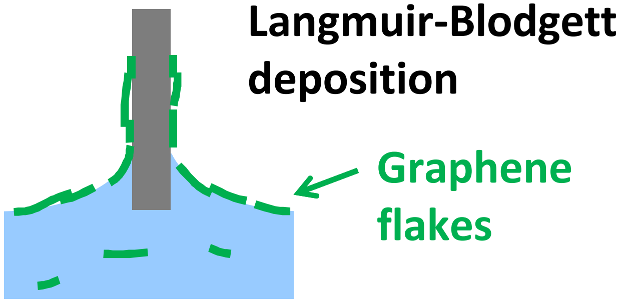
Assembly of graphitic membranes

1. Motivation

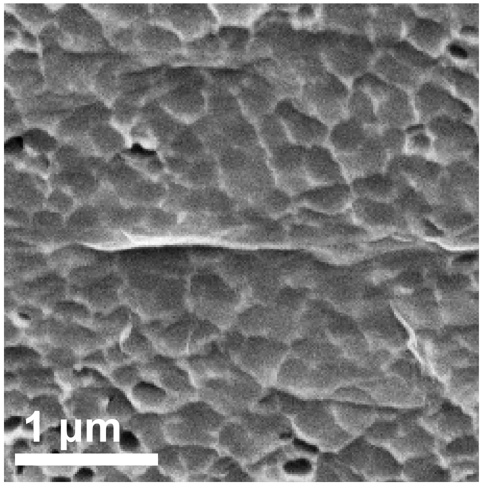




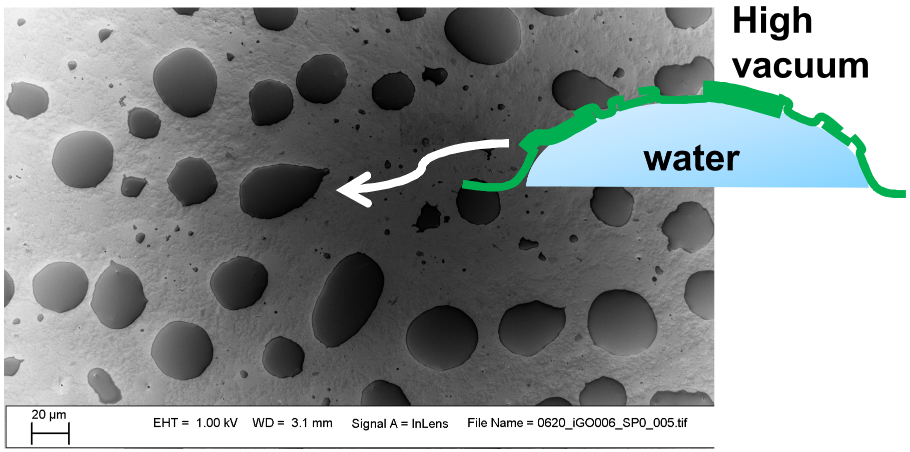
2. Experimental methods



3. Controllable deposition

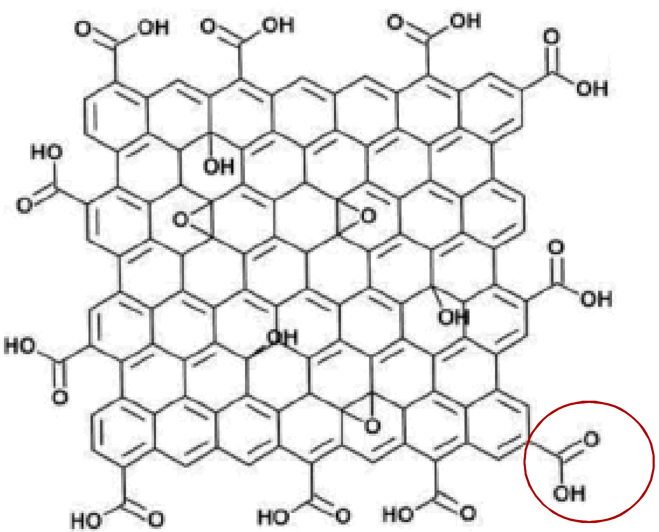


4. Permeation barrier



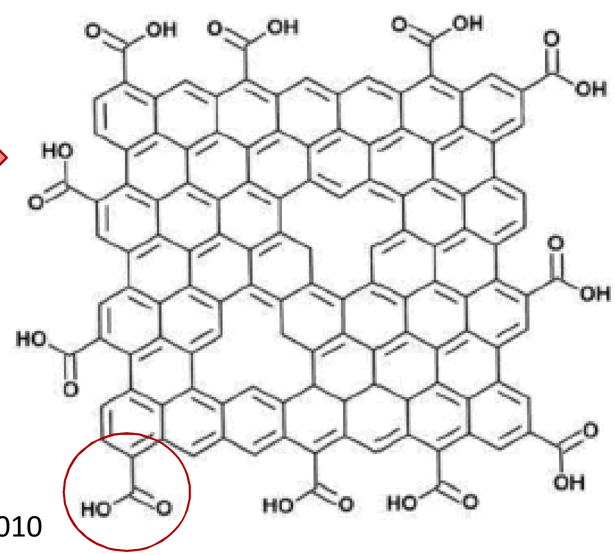
Compare properties of GO and RGO films

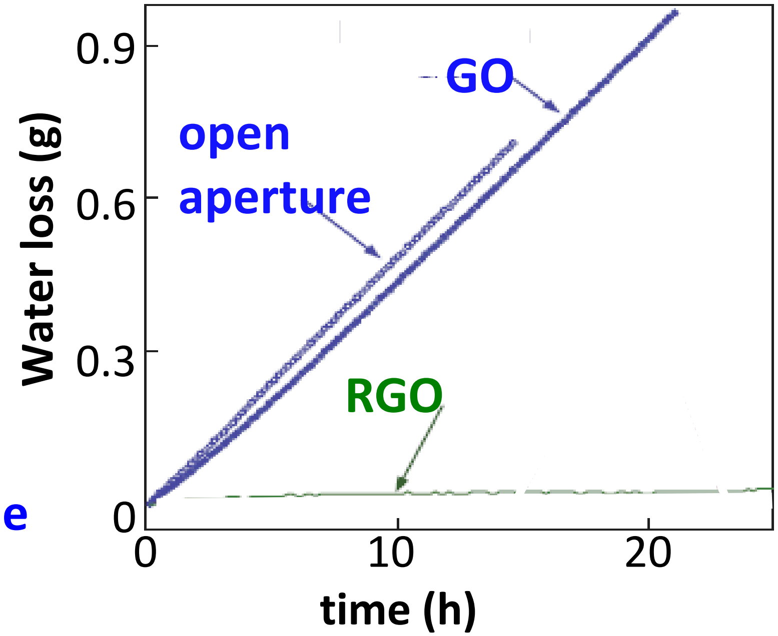
Graphene Oxide (GO)

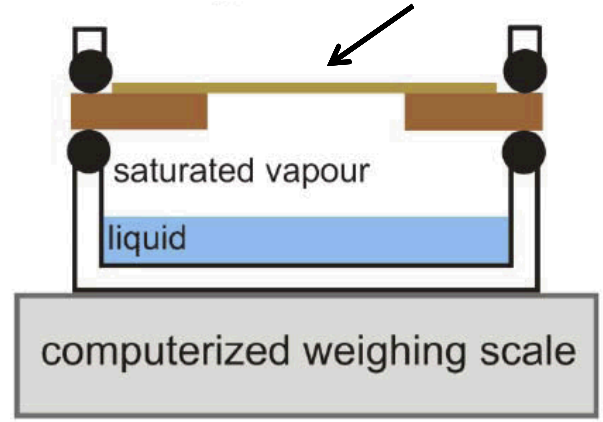


+ 80 ^{o}C and
Ascorbic acid
(Vitamin C)

Reduced Graphene Oxide (RGO)





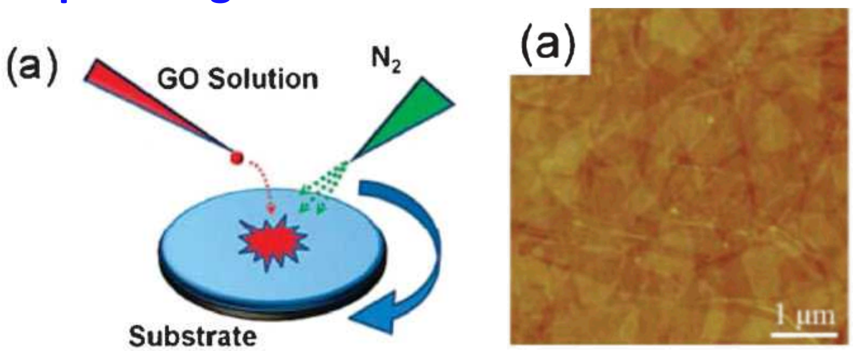


R. Nair *et al. Science* 2012

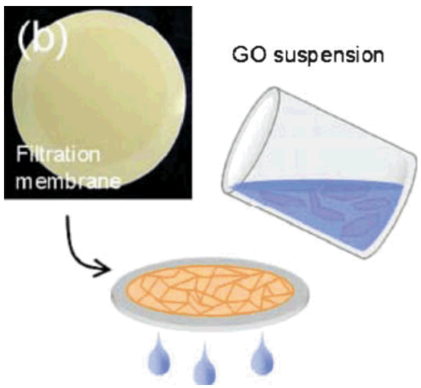
G. Eda and M. Chhowalla, *Adv. Mater*. 2010
M. Fernandez-Merino *et al., J. Phys. Chem. C* 2010

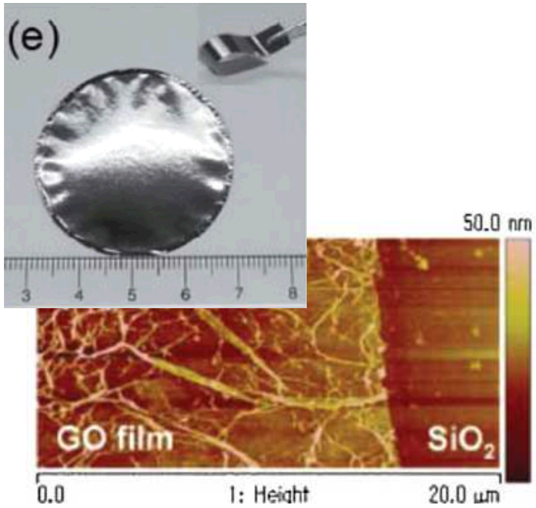
Assembly of GO and RGO films

Drop casting[1]

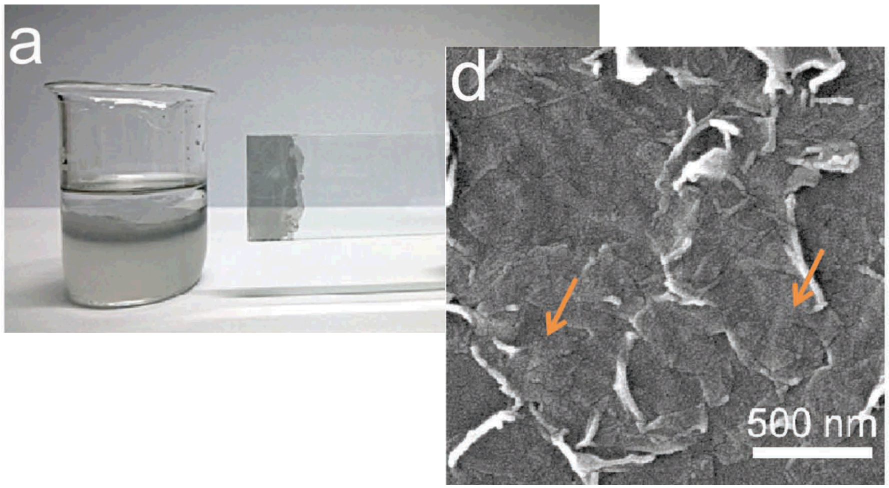


Vacuum filtration[2]

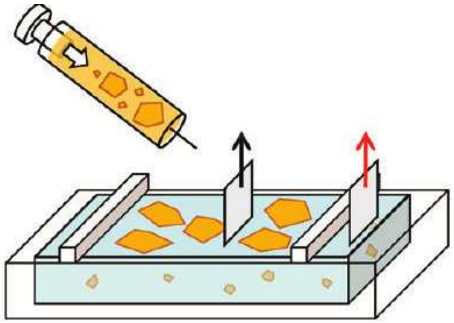


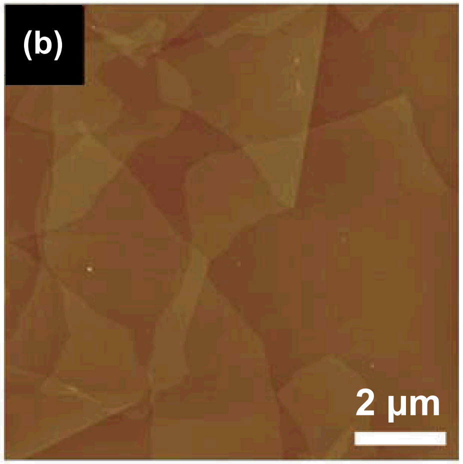


Assembly at an oil-water interface[3]



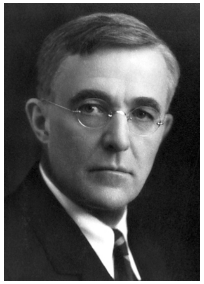
Langmuir-Blodgett deposition[4]





[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.

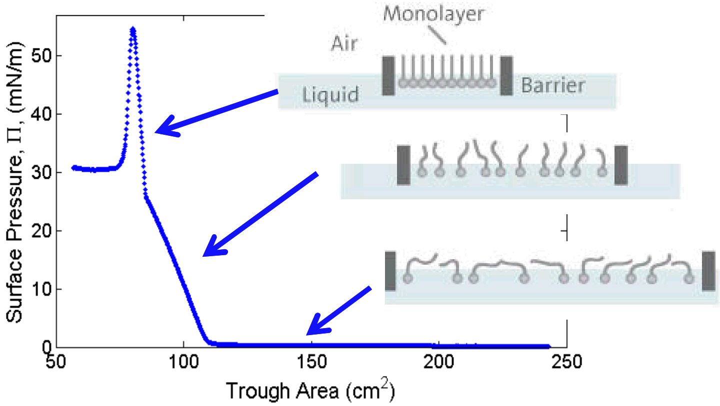
Dense, ordered molecular monolayers assembled using Langmuir-Blodgett deposition

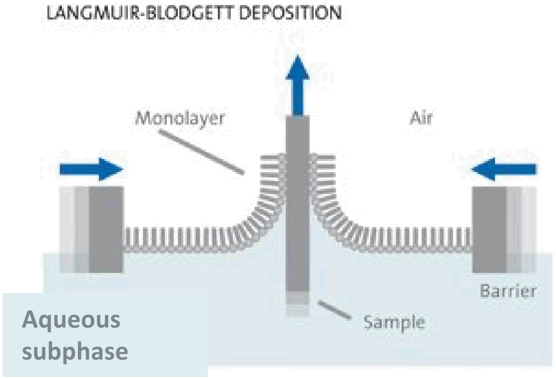


Irving Langmuir

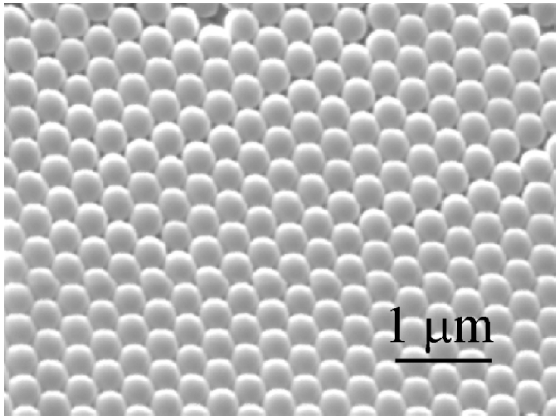
Katherine Blodgett

Compression of an amphiphilic molecule

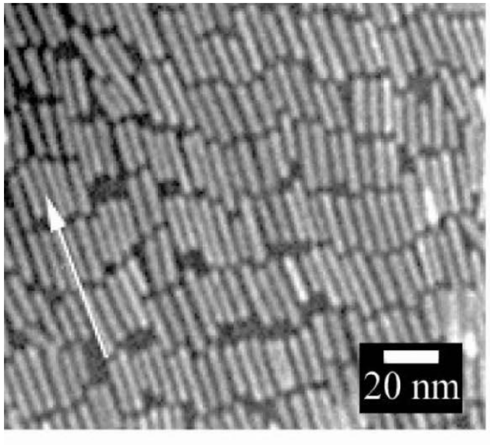




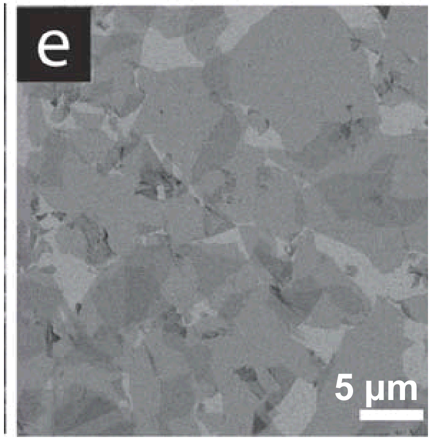
Synthetic opals[1]



$BaCrO_4$ nanorods[2]



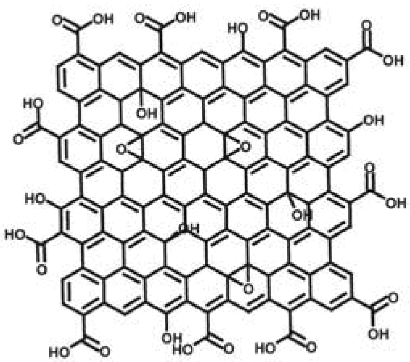
Overlapping GO flakes[3]

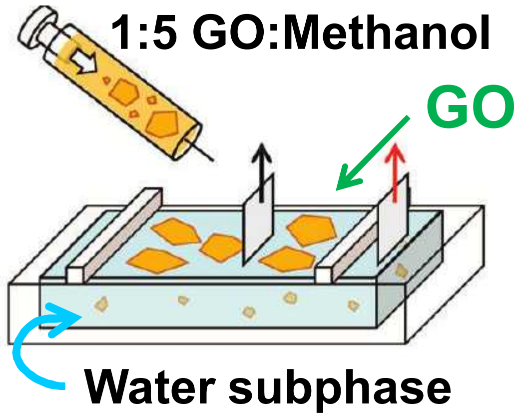


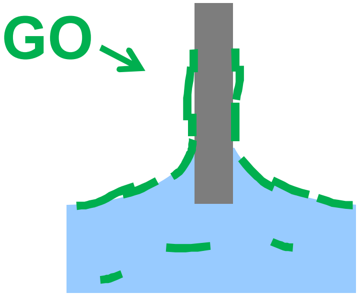
[1] M. Bardosova, et al. *Thin Solid Films*, 2003 [2] F. Kim *et al. JACS*, 2001 [3] L. Cote *et al. Soft Matter* 2010.

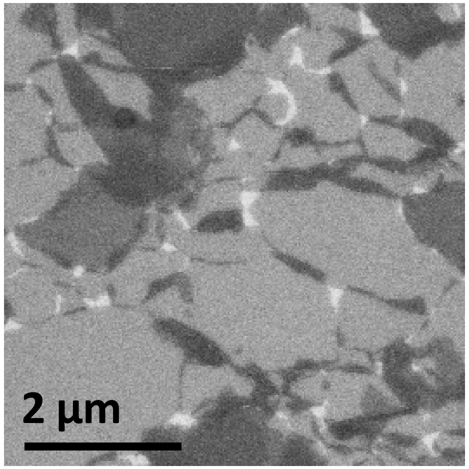
Stable graphene oxide surface phase enables Langmuir-Blodgett assembly

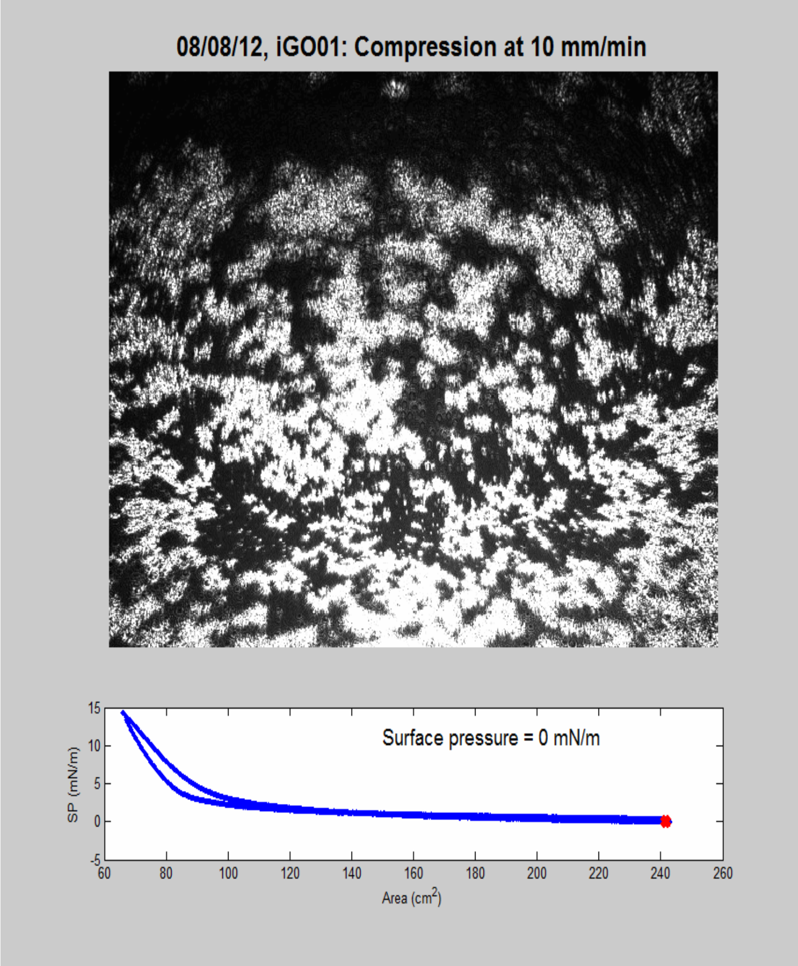
GO structure









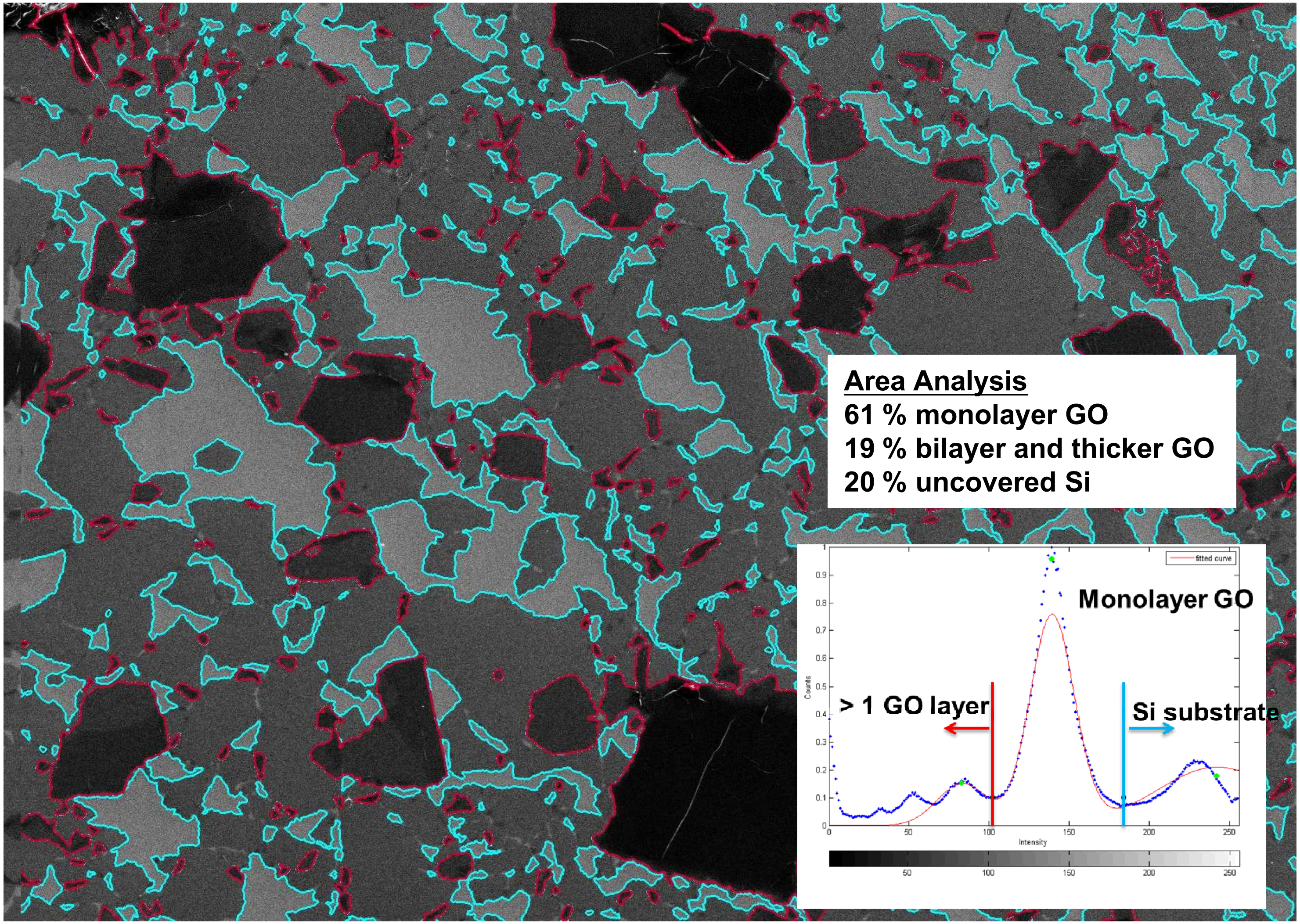


Goal: Optimize deposition to generate continuous GO and RGO films

Control of Graphene Oxide Coverage

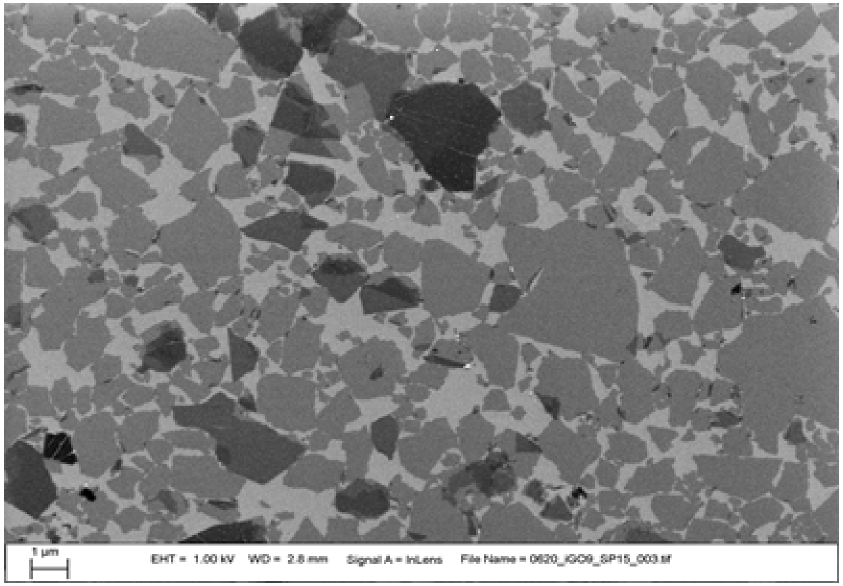
Adjusted Parameter	Effected Property	Impact to Coverage
Initial GO concentration	Amount of flakes in solution	Peak SP at lower concentration ✓
Centrifugation	Flake size	Large flakes yield higher coverage ✓✓
Addition of HCl, NaOH, or NH_2O_4	Excess charge on flake	Basic conditions show higher coverage
Surface Pressure	Flake Density	Increased coverage until plateau ✓
Dipping speed	Dynamics of flake attachment	Higher coverage with slower dip ✓
Number of dips	Layers of flakes	More dips yield higher coverage ✓✓

Determination of Graphene Coverage



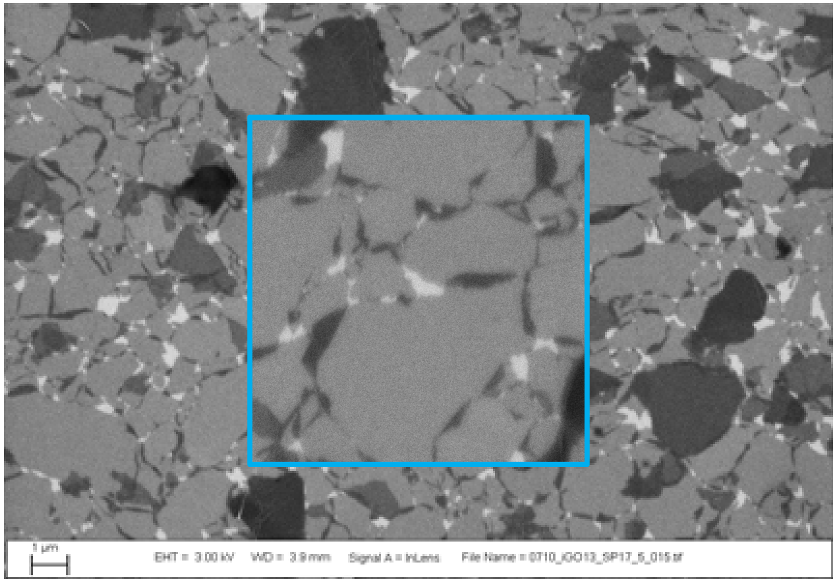
More continuous GO films are possible through controlling flake size

Initial GO size distribution



78 % GO coverage
for deposition at 15 mN/m

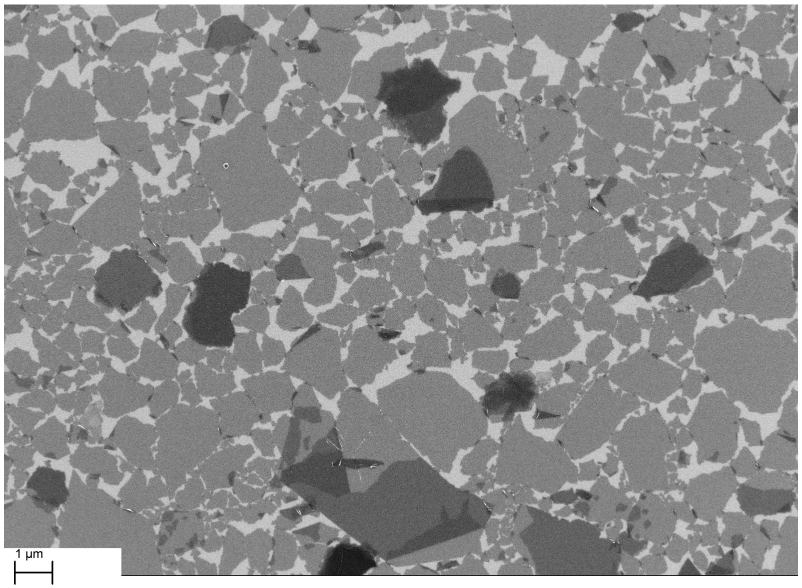
After removing smallest GO flakes



97 % GO coverage
for deposition at 17.5 mN/m

Multiple dips can result in higher surface coverage

First dip at 14 mN/m

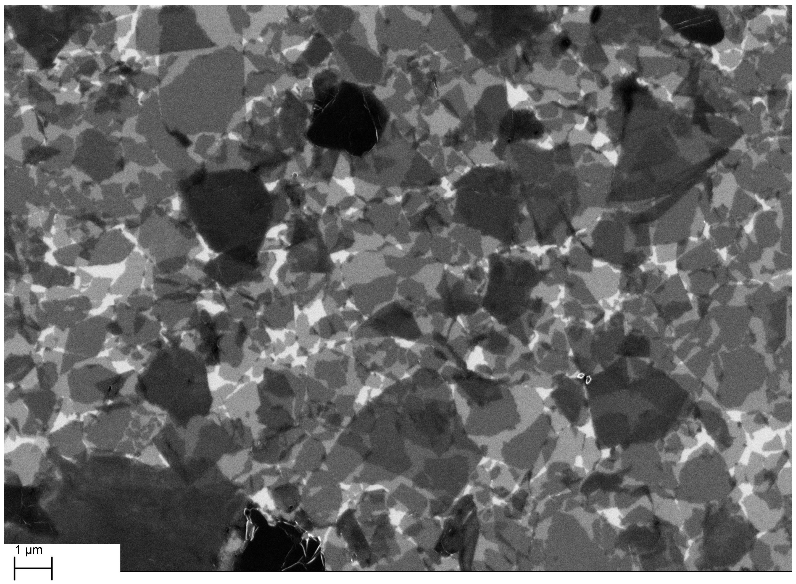


83 % coverage

75 % monolayer GO

12 % thicker and overlapped GO

Second dip at 17.5 mN/m



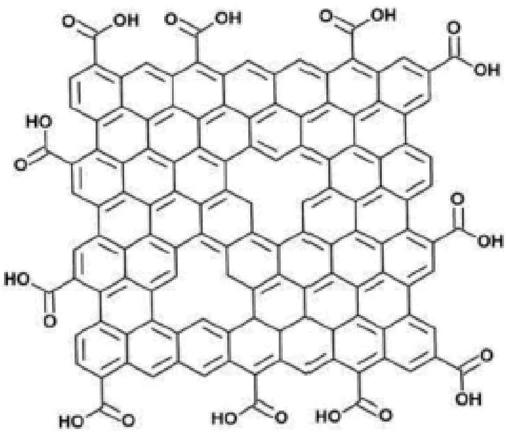
94 % coverage

20 % monolayer GO

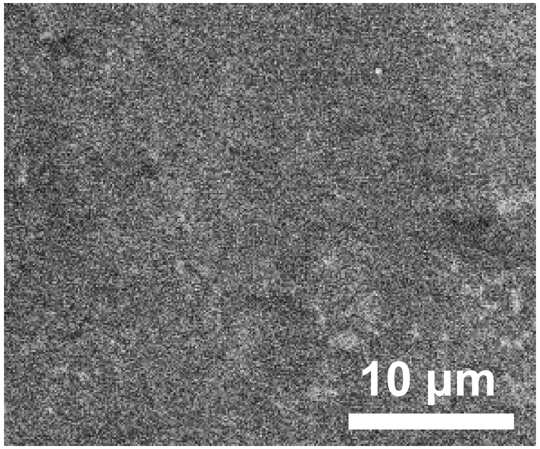
74 % thicker and overlapped GO

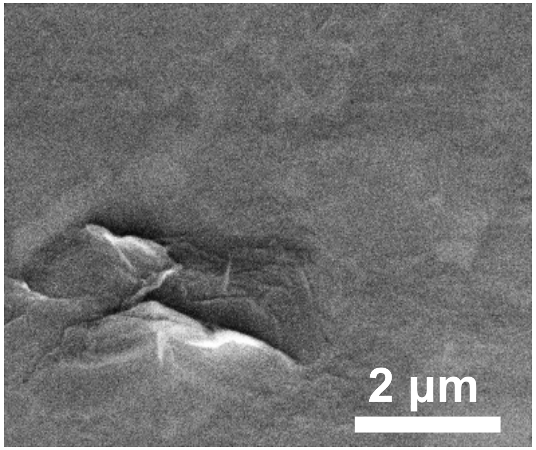
RGO surface phase is stable, yet deposition is challenging

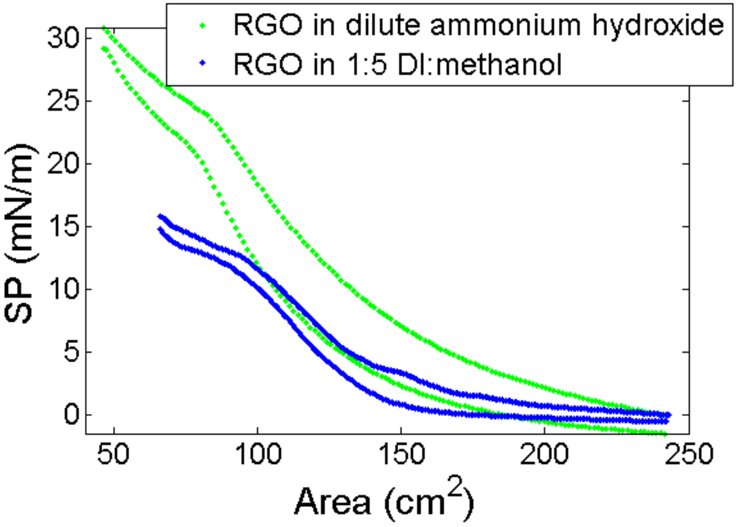
RGO structure



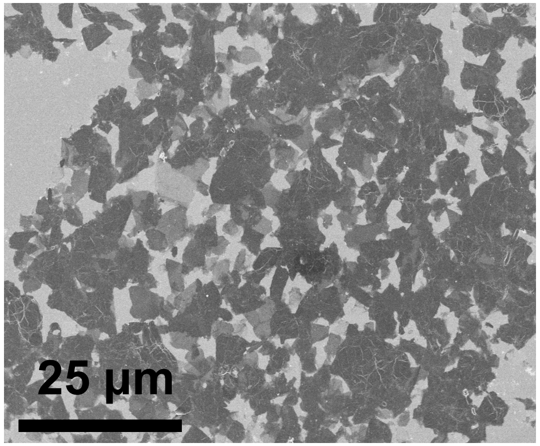
High coverage, but wrinkled RGO flakes with methanol spreading solvent.





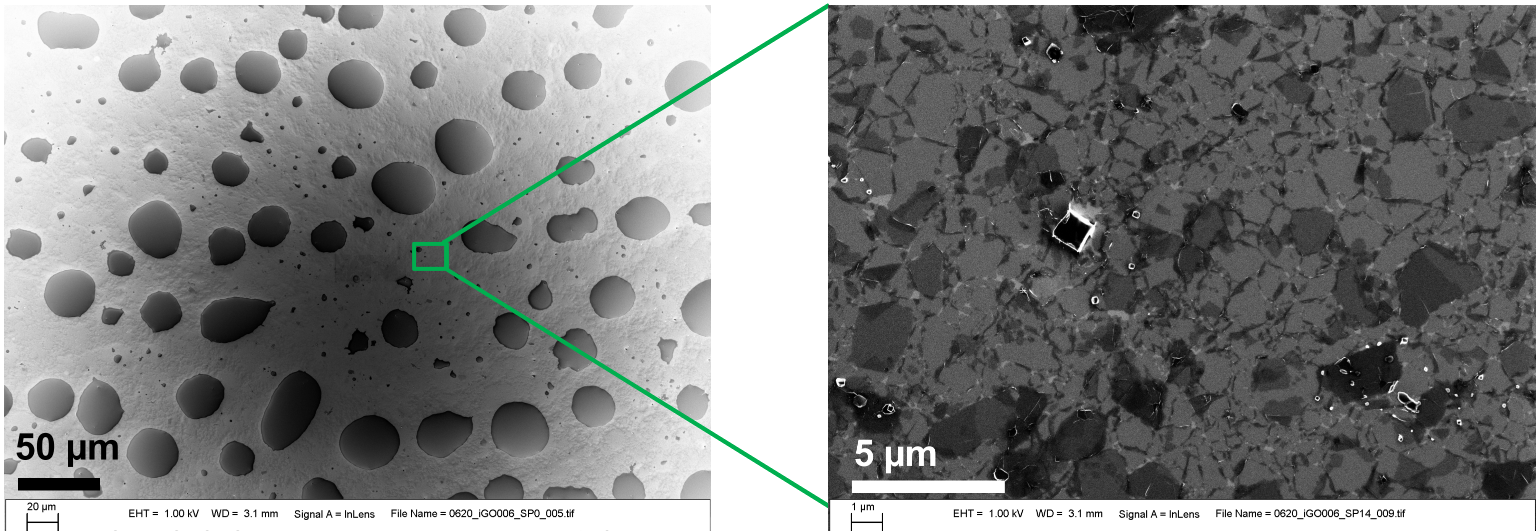


Low coverage of flat RGO with dilute ammonium hydroxide as a spreading solvent.



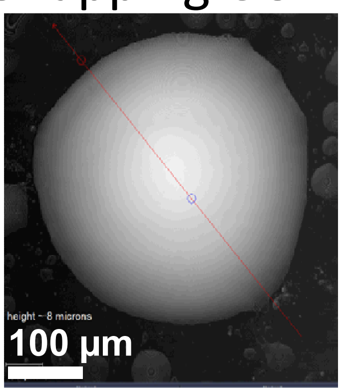
Hydrophobic surfaces yield best transfer for aqueous RGO

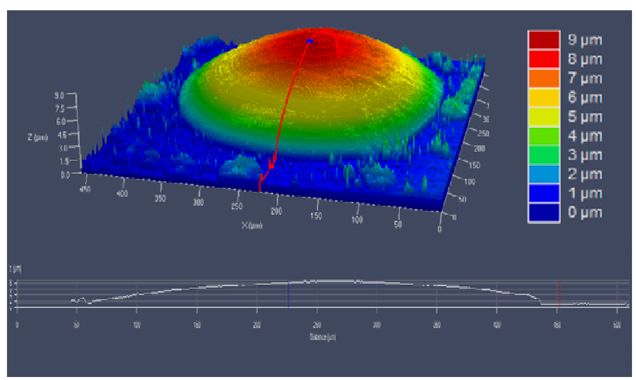
Demonstration of GO as permeation barrier

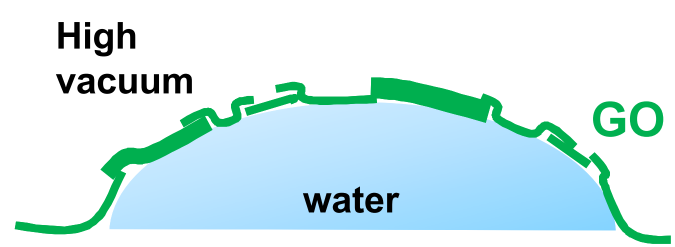


Water bubbles are trapped by overlapping GO flakes.

98 % GO coverage between bubbles.

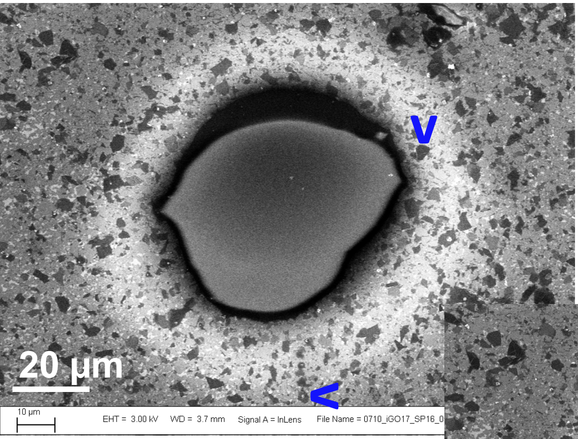


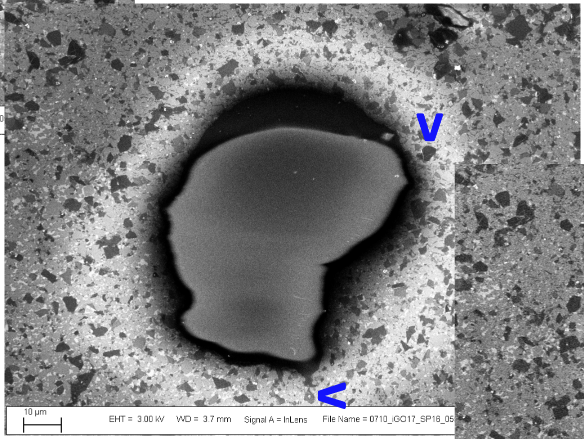


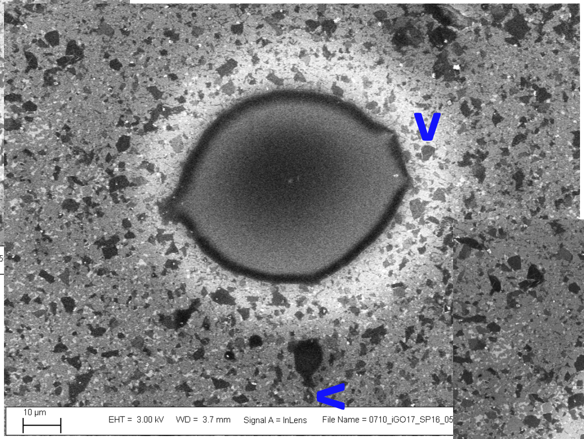


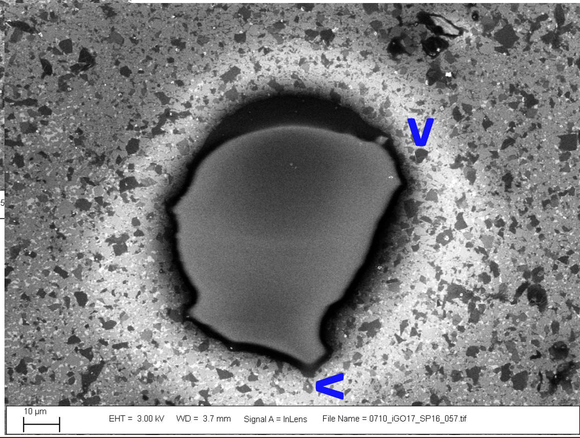
An unusually large bubble is 8-µm tall and 450- µm in diameter.

Composite GO membranes can stretch without bursting





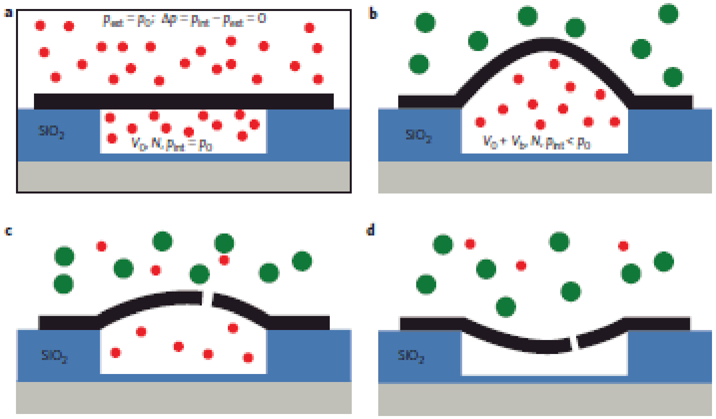




A 3 keV SEM beam, slowly rastered across the bubble, heats and charges the trapped water.

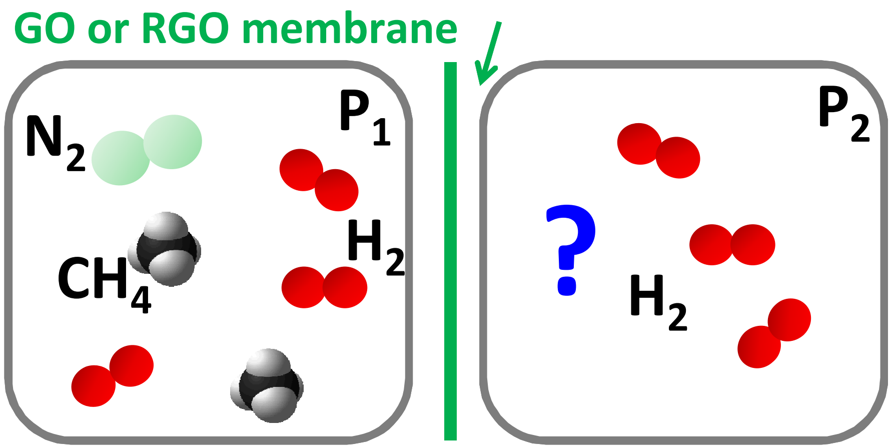
Are GO and RGO membranes permselective?

Size-selective permeation of H_2 through graphene recently reported



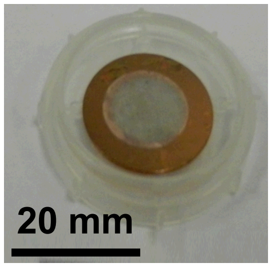
S. Koenig *et al., Nature Nano.*2012 (Adv. Online)

Compare the permeability of GO and RGO films on porous supports.

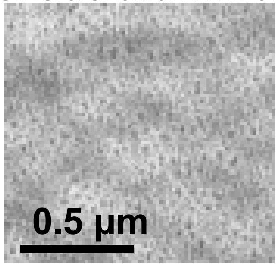


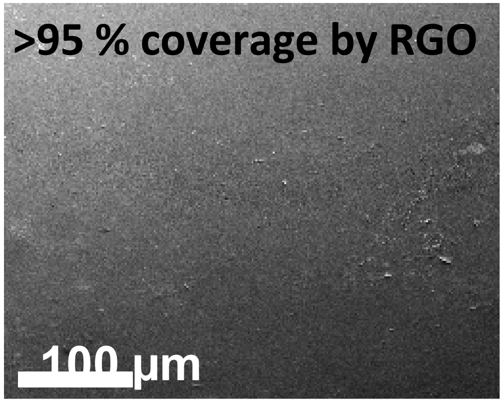
P_1/P_2 ~ 10^8 Torr, P_1 ~ 1 Torr

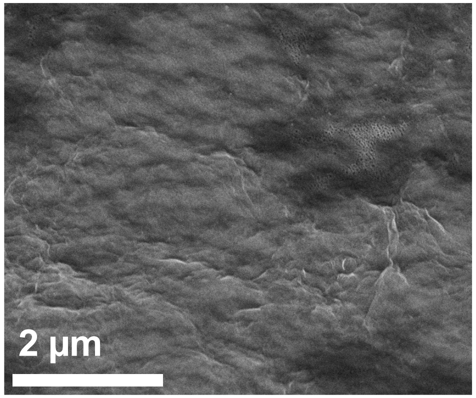
Progress towards continuous GO and RGO films on porous supports



Porous alumina





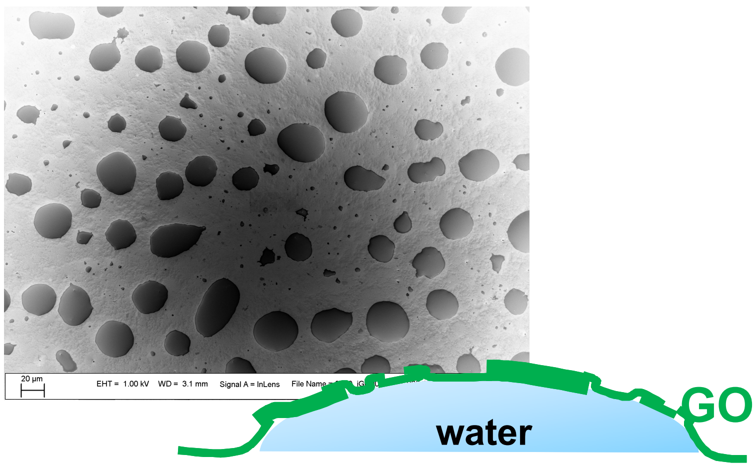


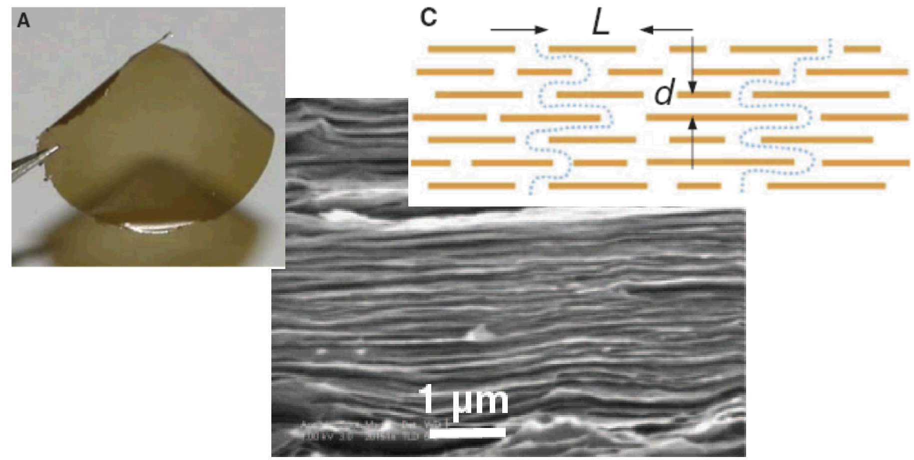
Conclusions

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.





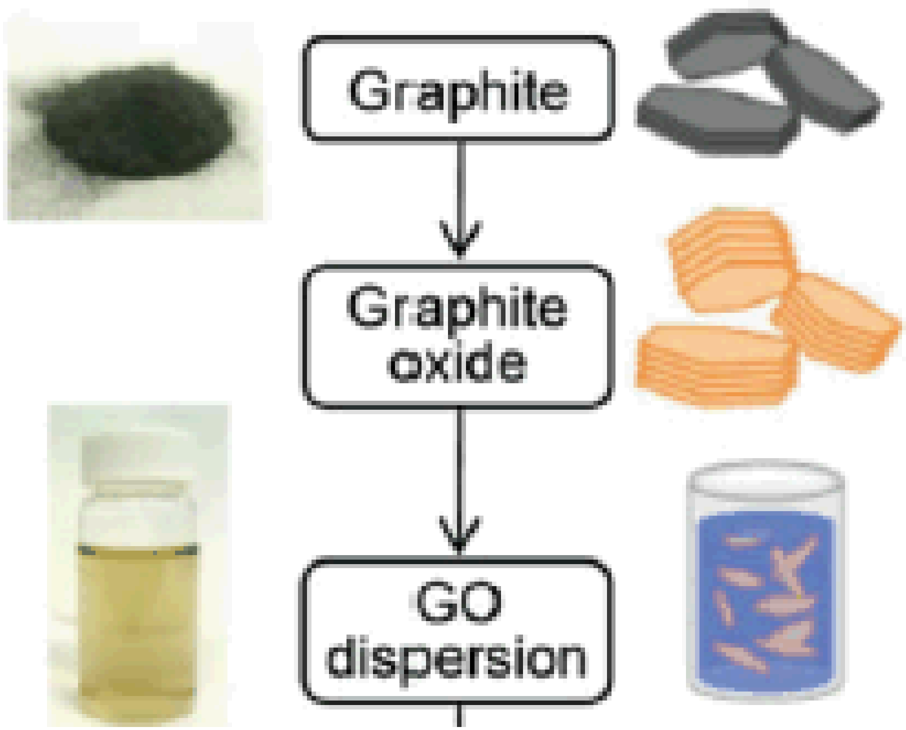
Acknowledgements

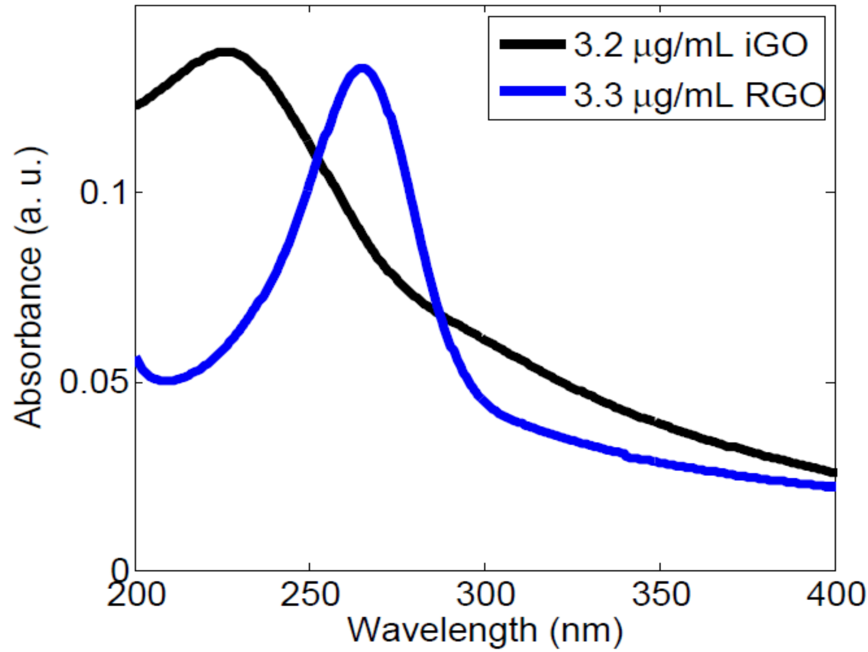
Graphene oxide: Tim Lambert

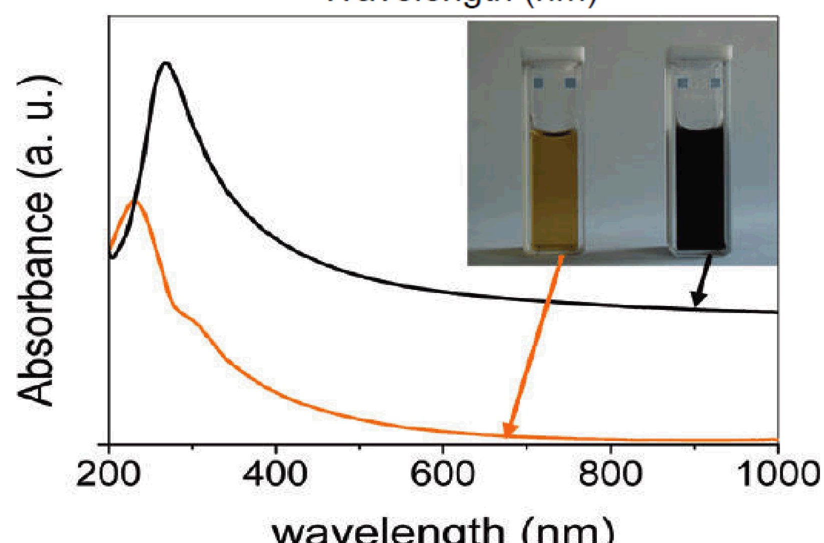
Experimental assistance: Susan Brozik, Cody Washburn, and Dave Wheeler

Scanning electron and optical microscopy: Bonnie McKenzie and Alice Kilgo

Natural graphite is oxidized via Hummer's method





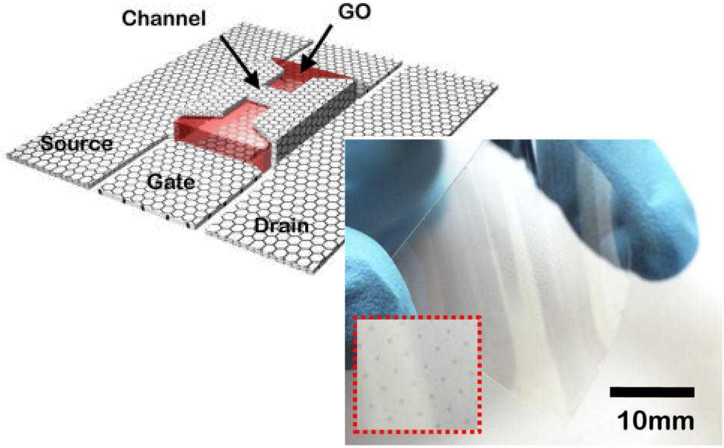


Oxidized using a mixture of $NaNO_3$, H_2SO_4, and KMn04.
Diluted and heated with H_2O and H_2O_2
Filtered and rinsed with HCl

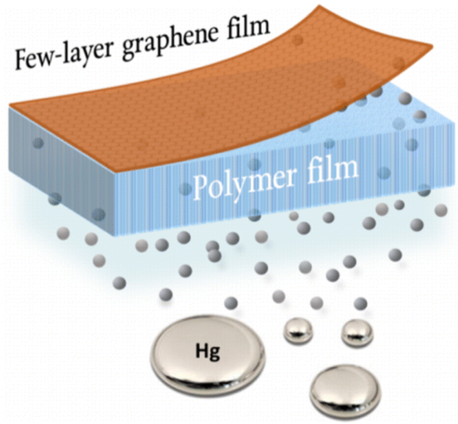
Paredes *et al., Langmuir* 2009.

Transparent graphitic films are ideal for flexible electronics and barrier membranes

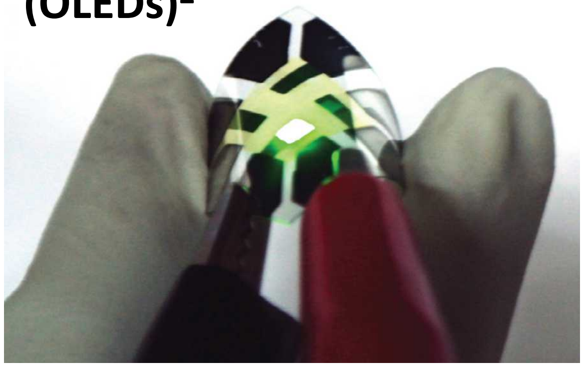
Dielectric for flexible electronics[1]



Environmental barrier[4]



Anode for organic LEDs (OLEDs)[2]



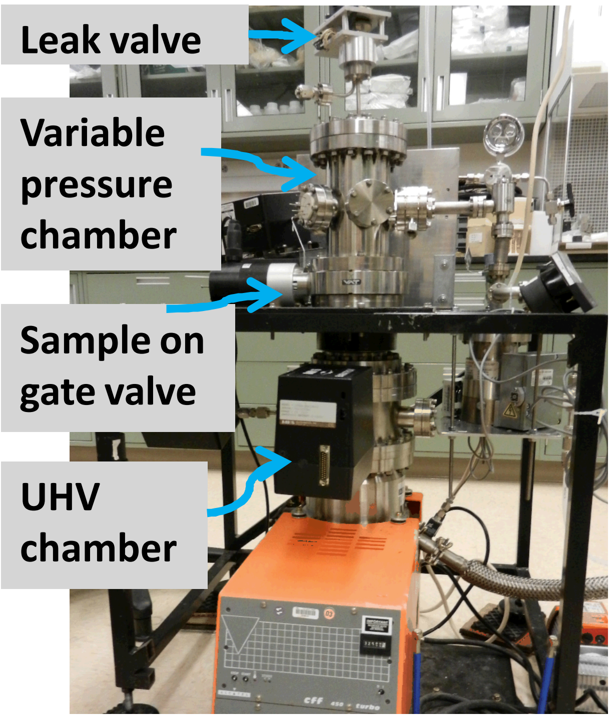
Window electrode for solar cells[3]

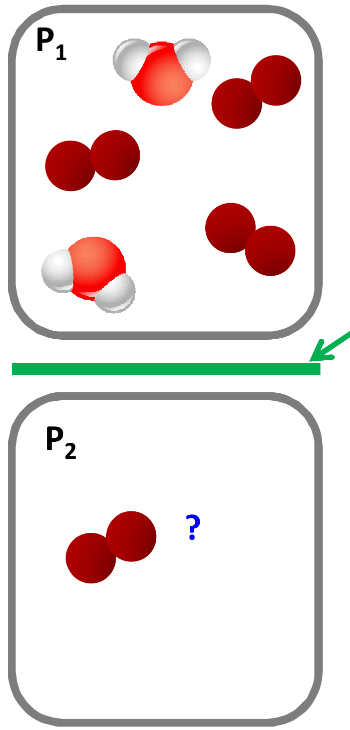
[1] S.-K. Lee *et al. Nano Lett.* v. 12, 3472-6, 2012.
[2] T. H. Han *et al., Nat. Photonics* v. 6, 105-10. 2012
[3] G. Eda and M. Chhowalla, *Adv. Mater*. 2010
[4] F. Guo *et al. Enviro. Sci. Tech*. v. 46, 7717-24, 2012.

Approach to confirm size-selective permeation

Sandia National Laboratories

Permeation System





Compare the permeability of GO and RGO films supported on alumina membranes.

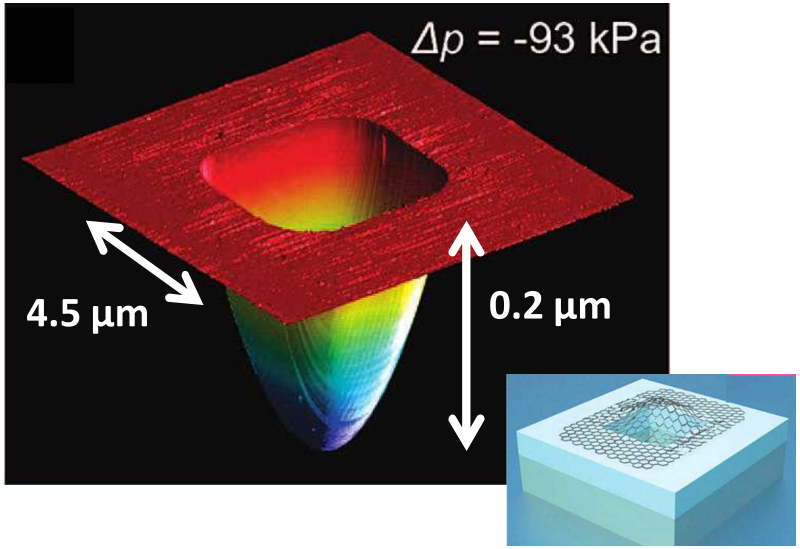
A precision permeation system allows for high pressure differentials

- $P_1/P_2 \sim 10^8$ Torr, $P_1 \sim 1$ Torr
- Permeation rates and composition will be detected using a mass spectrometer

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

Size-selective separation is expected in nanoporous graphene

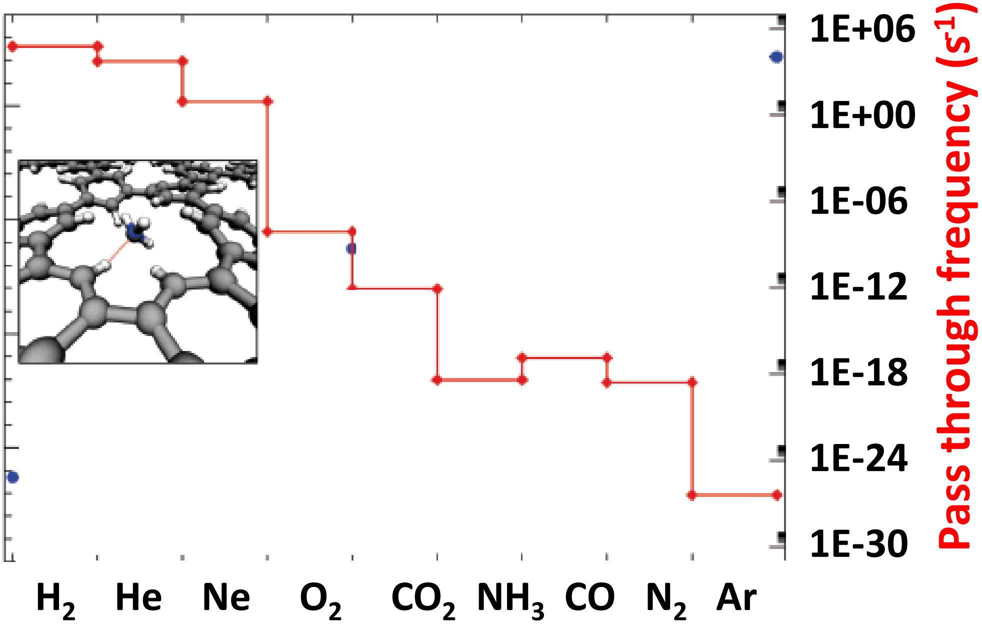
A pristine graphene membrane is impervious to gasses.



AFM image of a graphene monolayer under Δp = 700 torr

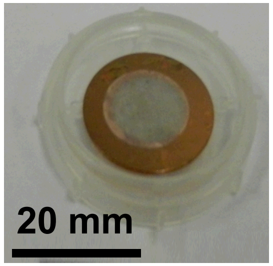
J. Bunch *et al.*, *Nano Lett* **8,** 2459-62 (2008).

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

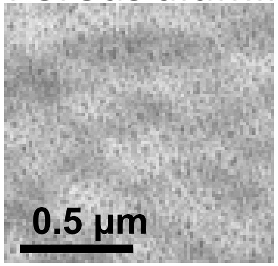


[1] S. Blankenburg *et al. Small* **6**, 2266-71 (2010)
[2] D. Jiang *et al. Nano Lett.* **9,** 1419-24 (2009)
[3] J. Schrier, *J. Phys. Chem. Lett.*, **1**, 2284-7 (2010)

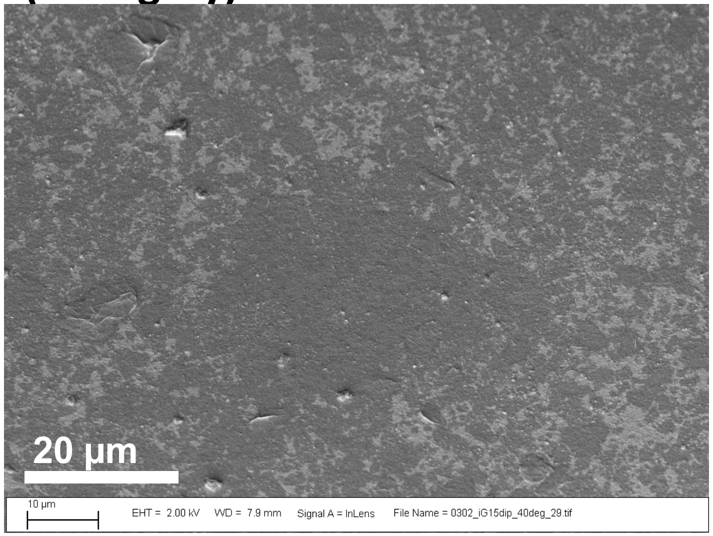
Progress towards continuous films on porous supports

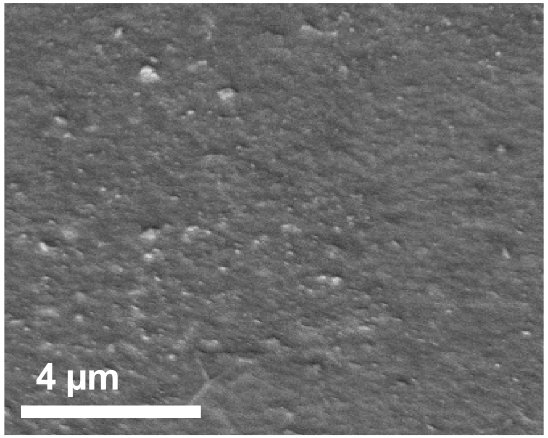


Porous alumina

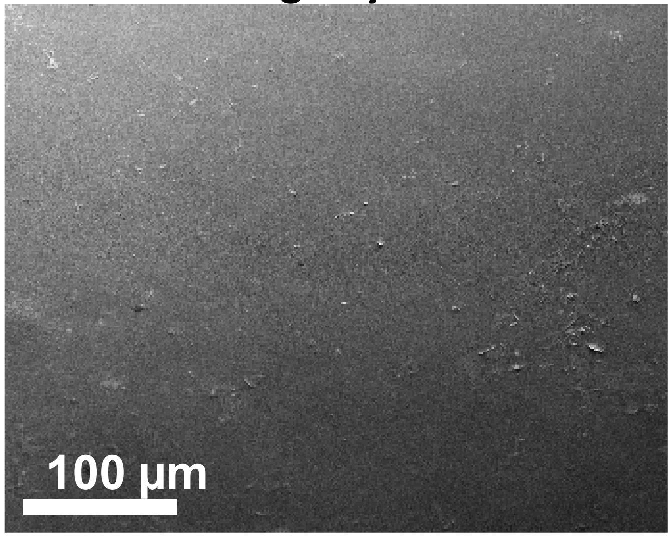


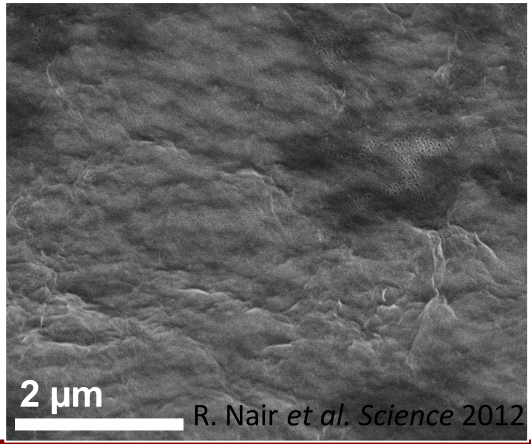
86 % coverage by GO flakes (dark grey)





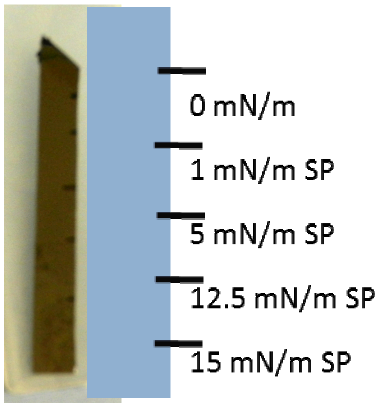
>95 % coverage by RGO

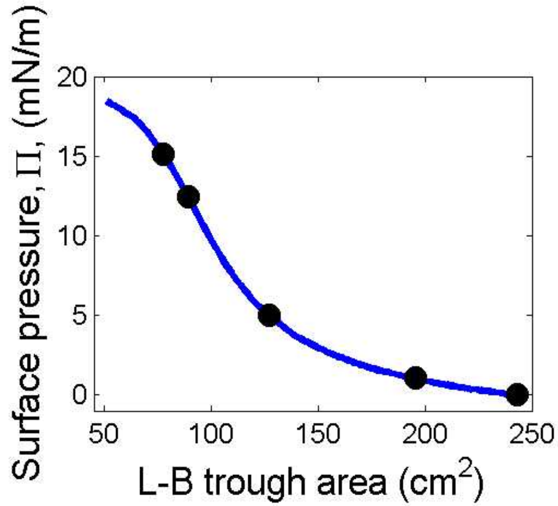


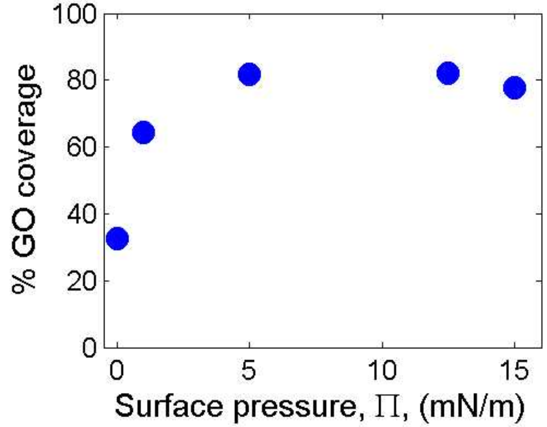


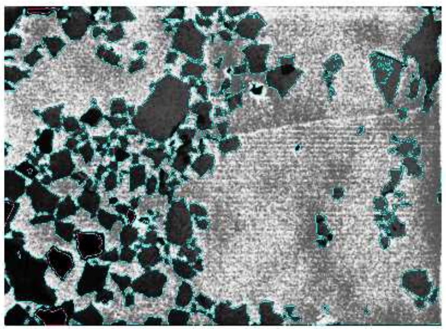
R. Nair *et al. Science* 2012

GO coverage can be controlled through surface pressure

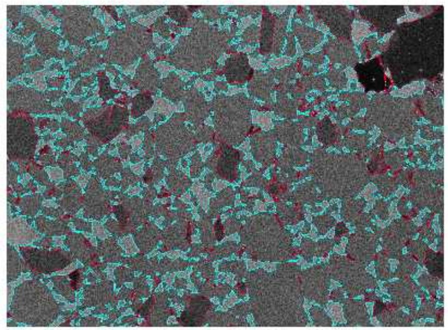








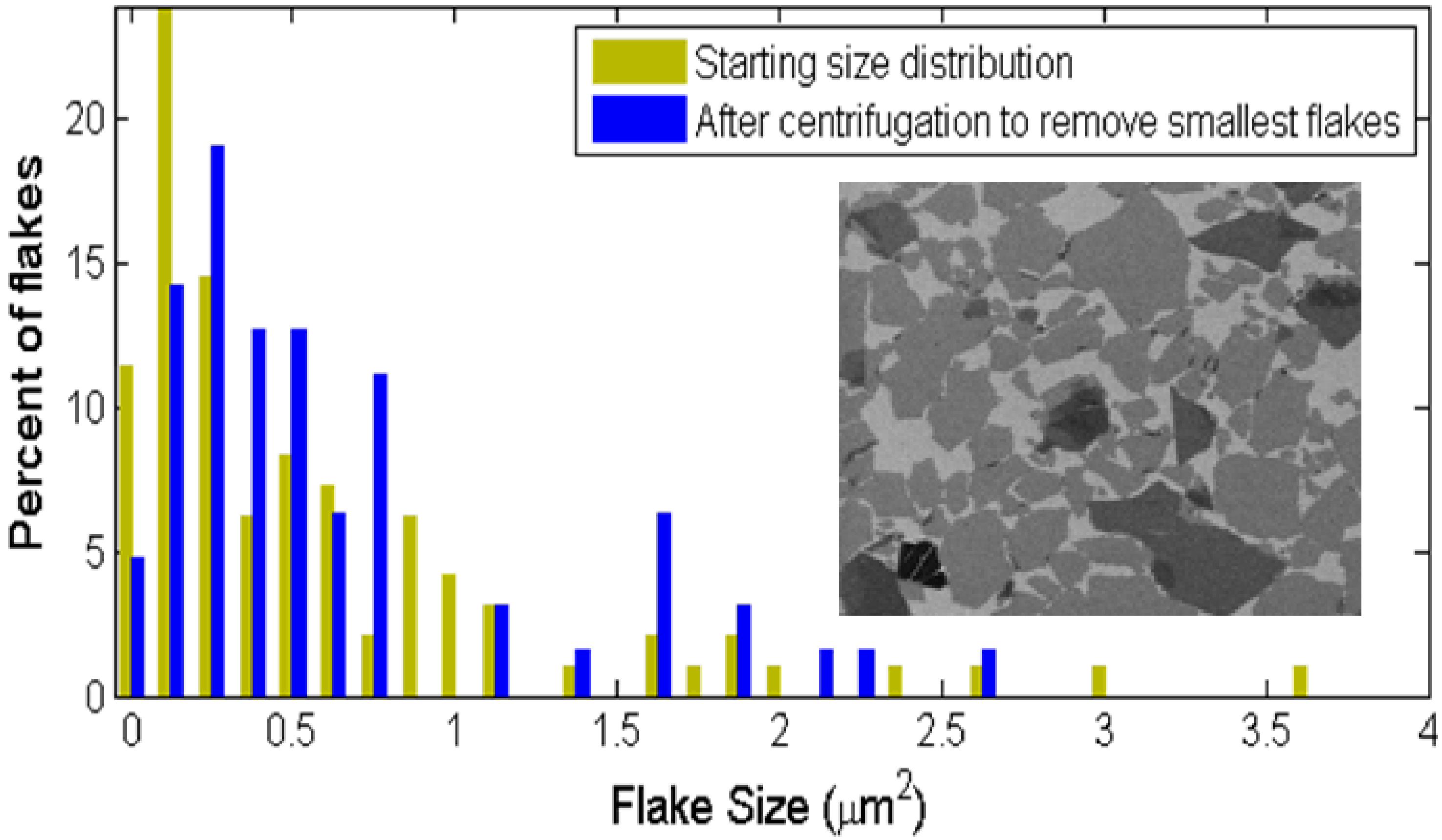
GO deposited at Π = 0 mN/m



GO deposited at Π = 12.5 mN/m

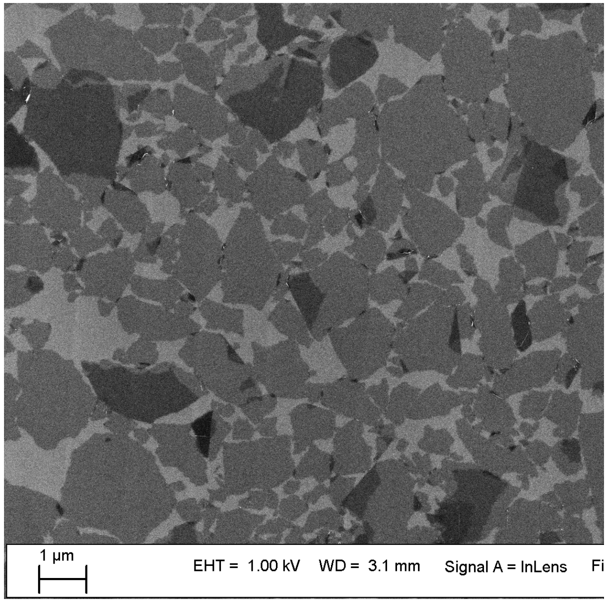
GO coverage plateaus at SP ≈ 5mN/m

Flake size can be controlled through separation techniques

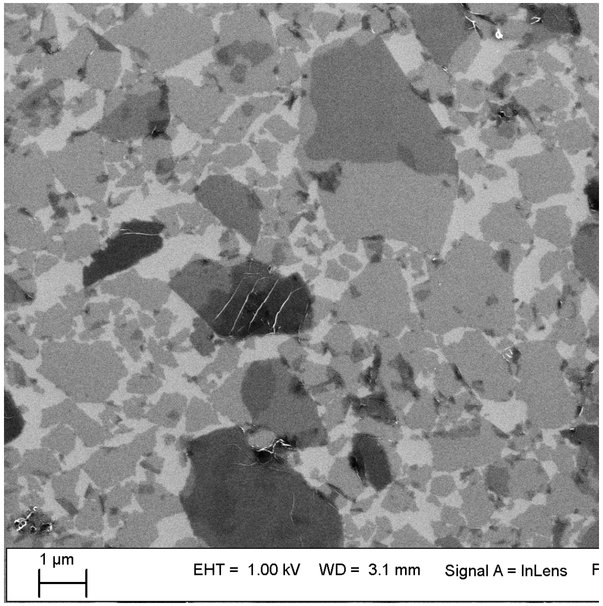


pH had minimal effect on coverage and overlap

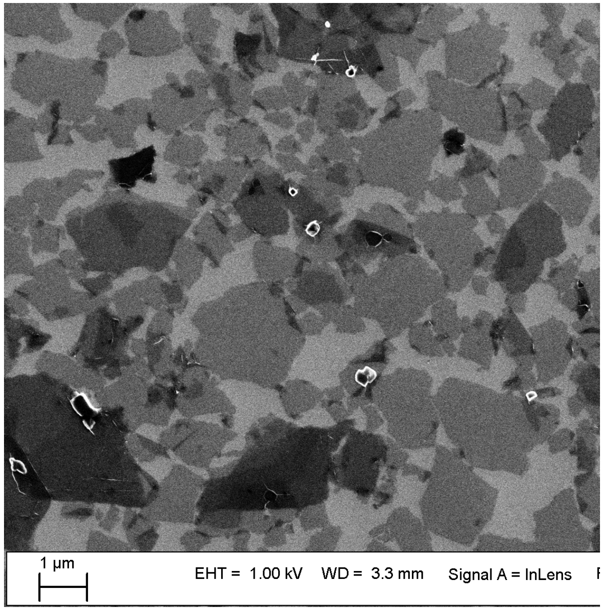
pH 10.1
SP = 12.5 mN/m
84 % coverage



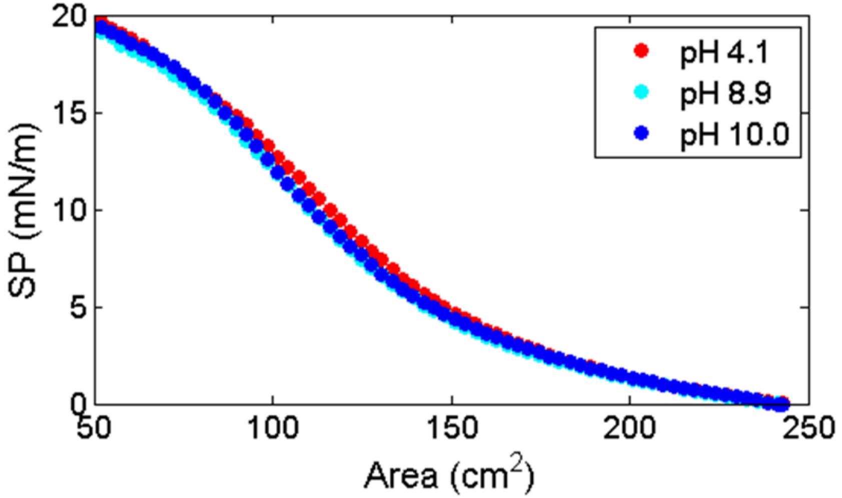
DI water (pH 5.8)
SP = 15mN/m
72 % coverage

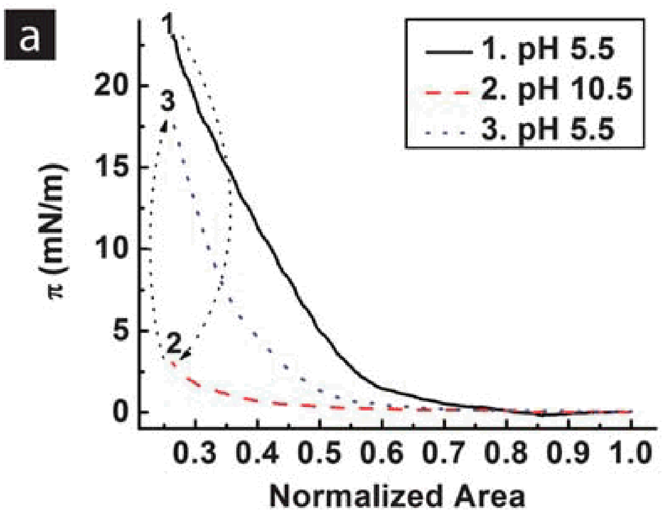


pH 4.3
SP = 14 mN/m
75 % coverage



pH had negligible effect on surface pressure, contrary to literature reports





L. Cote *et al. Soft Matter* ***6,*** *6015-6218 (*2010)

Slightly higher coverage achieved by slower dip speed