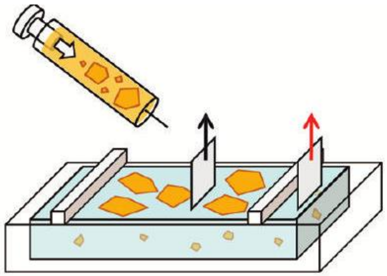
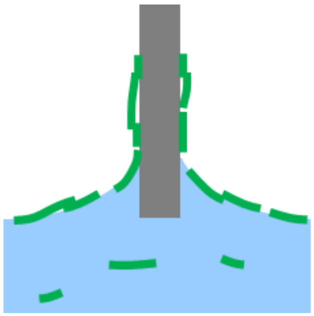
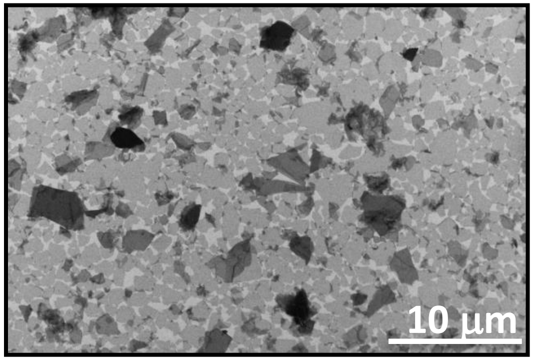
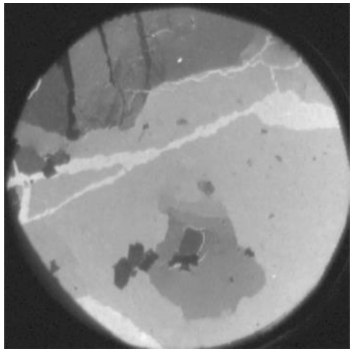








Langmuir-Blodgett assembly and characterization of nanosheets

<u>Laura Biedermann</u>, Calvin Chan, Katie Harrison, Paul Kotula, and Kevin Zavadil

Electrical, Optical, and Nanomaterials

Sandia National Laboratories, Albuquerque, NM

Anthony Dylla and Keith Stevenson

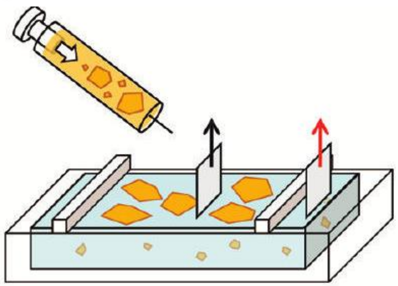
Dept. of Chemistry and Biochemistry, the University of Texas at Austin

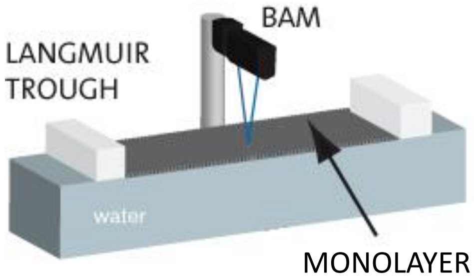
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

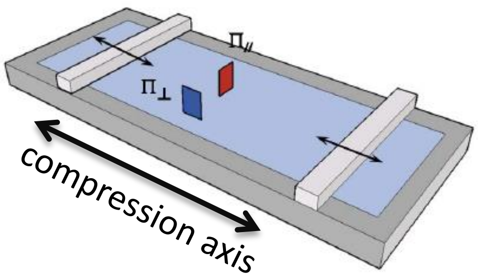
Langmuir-Blodgettry of graphene oxide (GO) and TiO_2(B) nanosheets

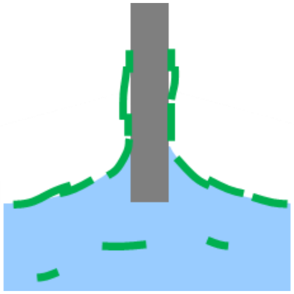
Sandia National Laboratories

- **How to characterize Langmuir-Blodgett (L-B) monolayers**



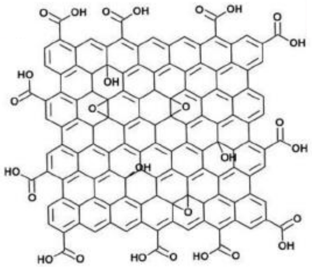


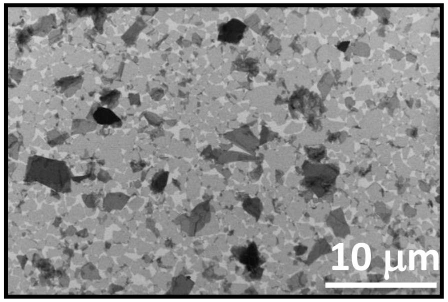




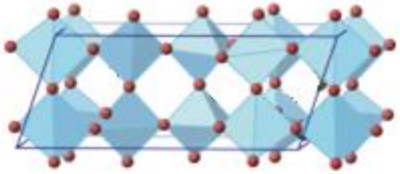
- **Optimization of L-B deposition for 2D-nanosheets**

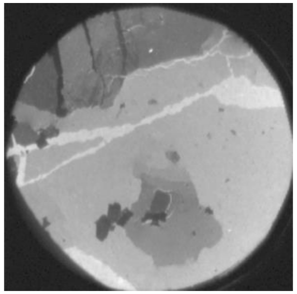
GO





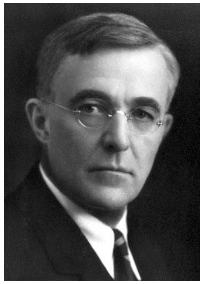
TiO_2(B)





- **Utility of L-B deposition in preparing nanosheets for surface analysis**

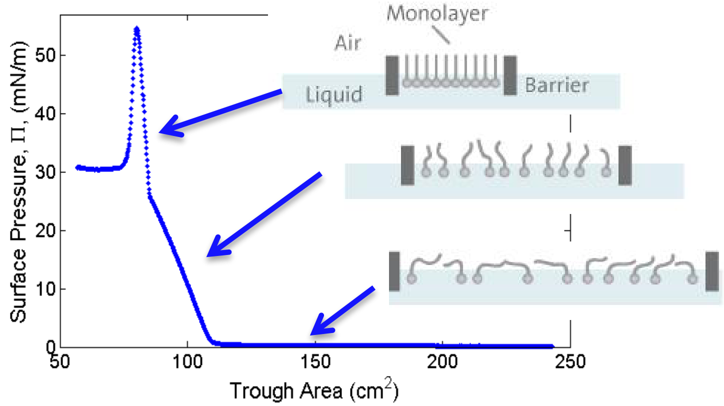
Dense, ordered molecular monolayers assembled using Langmuir-Blodgett deposition

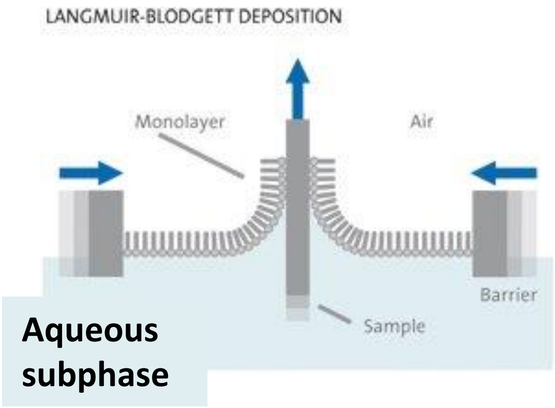


Irving Langmuir

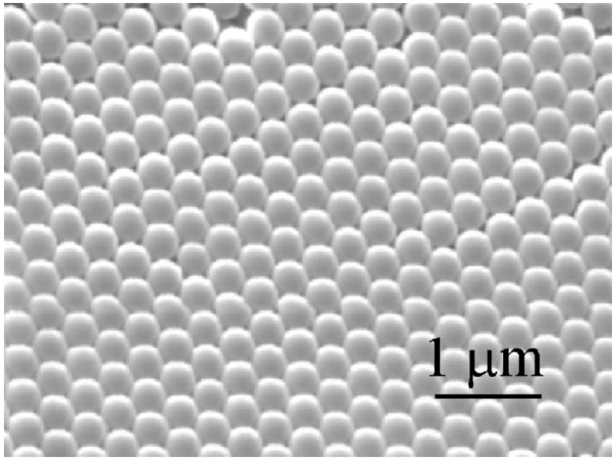
Katherine Blodgett

Compression of an amphiphilic molecule

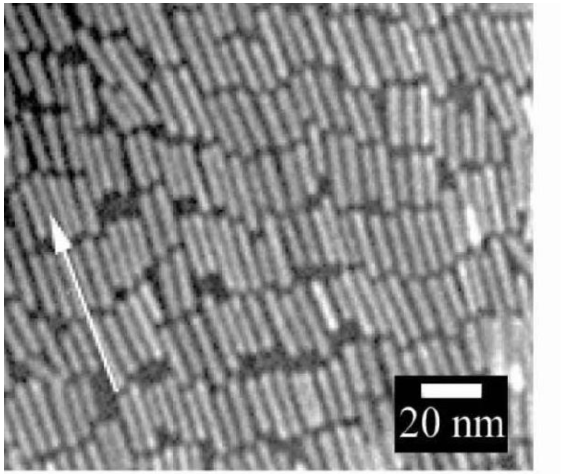




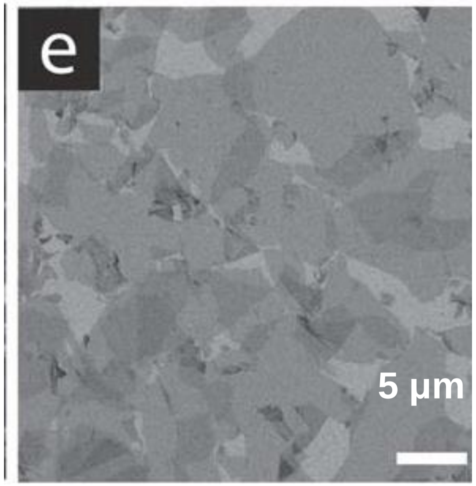
Synthetic opals[1]



$BaCrO_4$ nanorods[2]



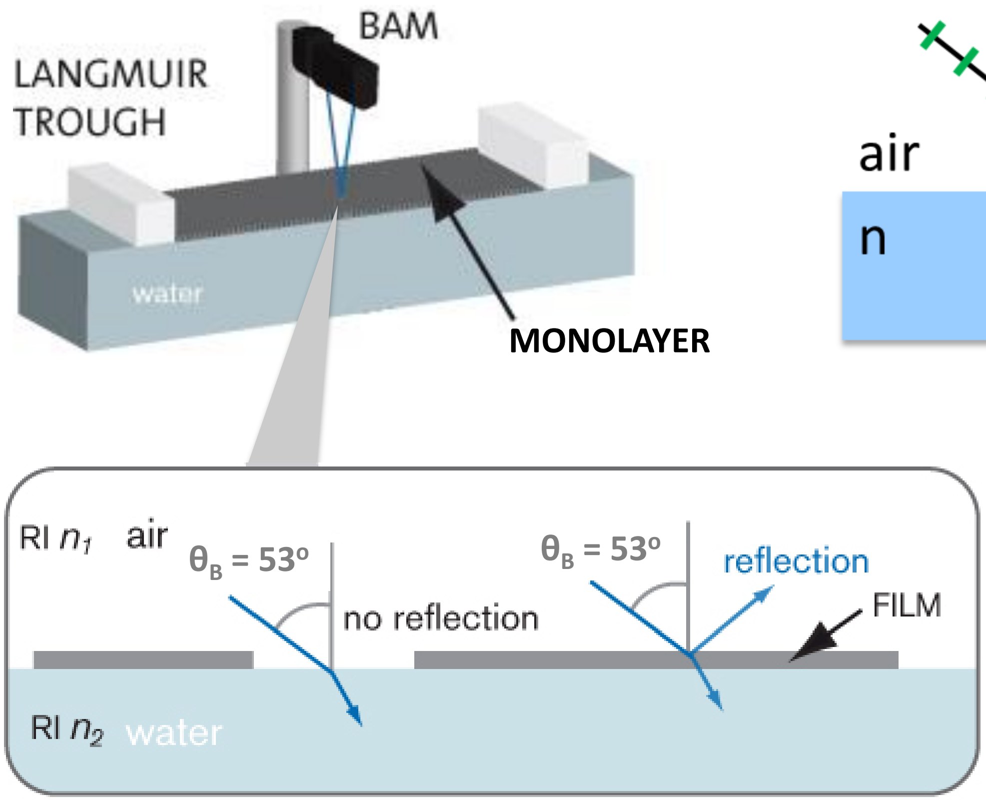
Overlapping GO flakes[3]

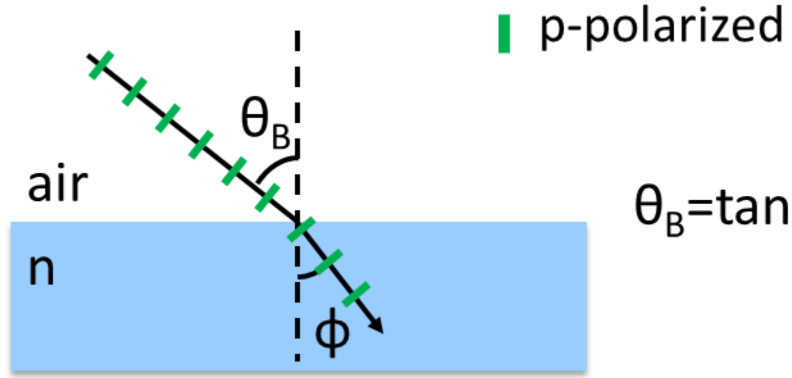


[1] M. Bardosova, et al. *Thin Solid Films*, 2003 [2] F. Kim *et al. JACS*, 2001 [3] L. Cote *et al. Soft Matter* 2010.

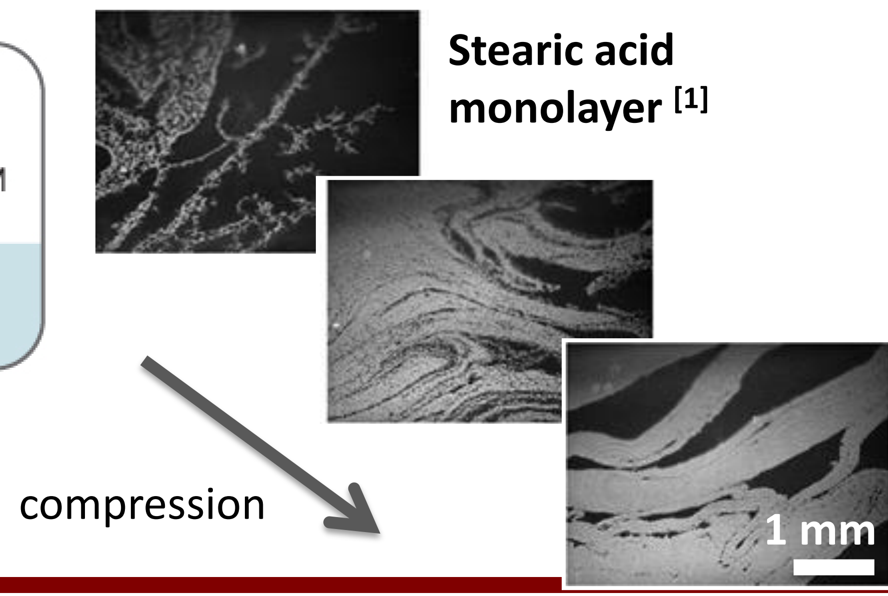
Brewster-Angle microscopy (BAM) allows observation of monolayer interactions

Sandia National Laboratories





$$\theta_B = \tan^{-1} n$$

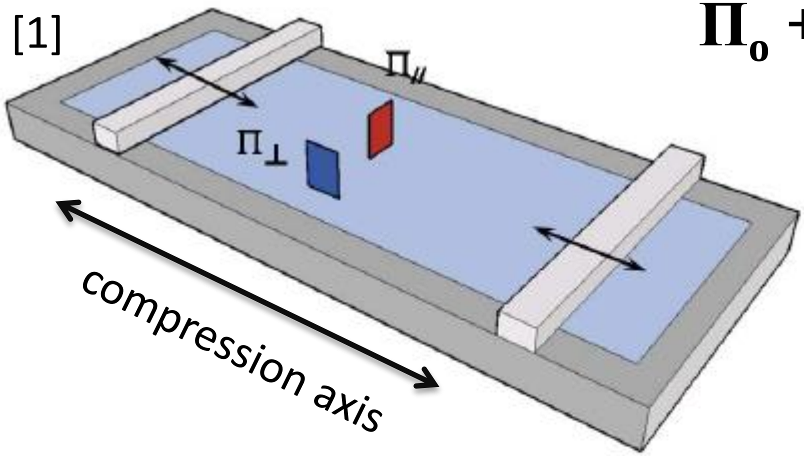


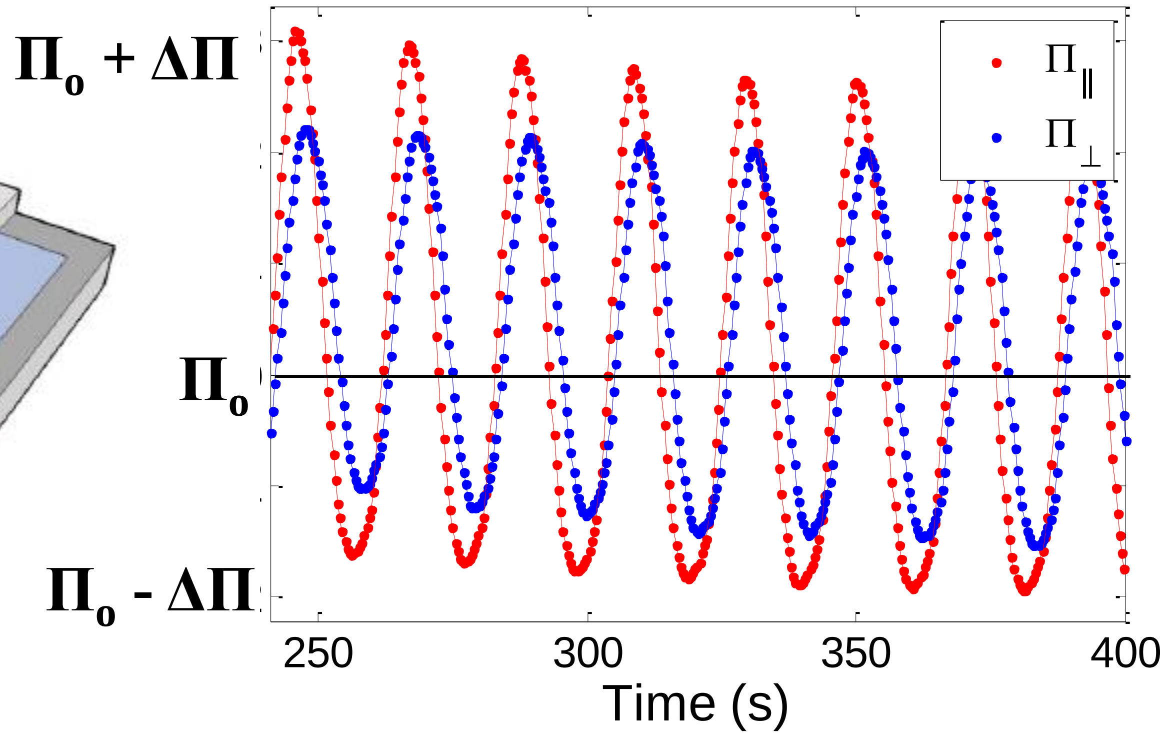
Stearic acid monolayer [1]

[1] www.ksvnima.com

Dynamic measurements of monolayer elasticity

[1]





[2]

$$|\varepsilon^* + G^*| = A_o \frac{\Delta\Pi_{\parallel}}{\Delta A}$$

$$|\varepsilon^* - G^*| = A_o \frac{\Delta\Pi_{\perp}}{\Delta A}$$

ε, compression modulus

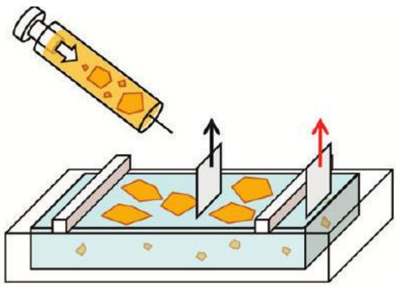
G, shear modulus

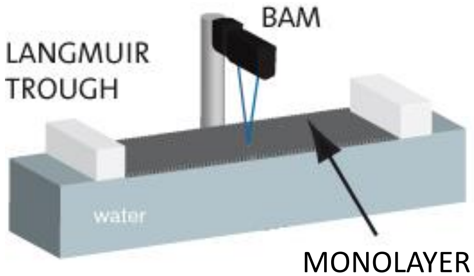
[1] D. Zang *et al., Eur. Phys. J. E* **31**, 125-34 (2010) [2] P. Cicuta and E. Terentjev.*, Eur. Phys. J. E* **16**, 147-58 (2005)

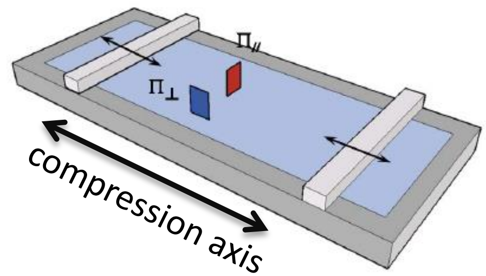
Langmuir-Blodgettry of graphene oxide (GO) and TiO_2(B) nanosheets

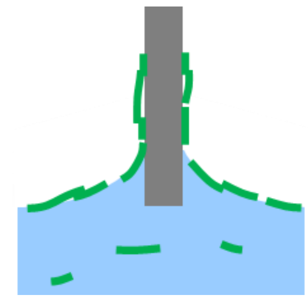
Sandia National Laboratories

- What is Langmuir-Blodgett (L-B) deposition?



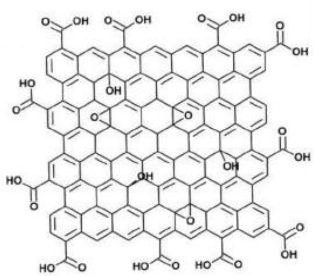


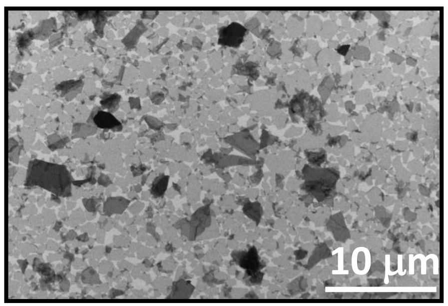




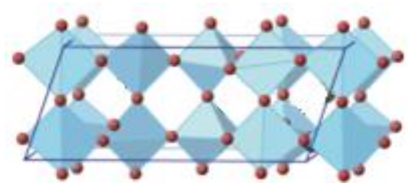
- **Optimization of L-B deposition for 2D-nanosheets**

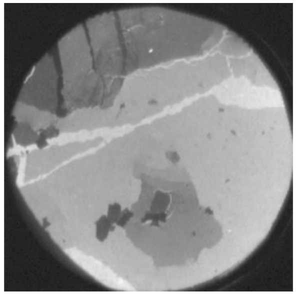
GO





TiO_2(B)



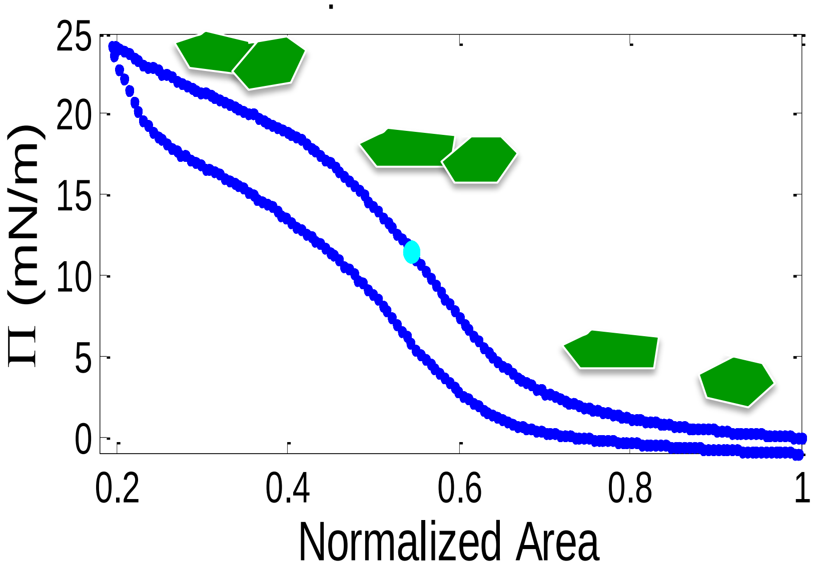


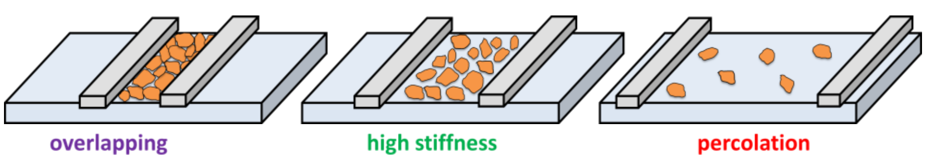
- Utility of L-B deposition in preparing nanosheets for surface analysis

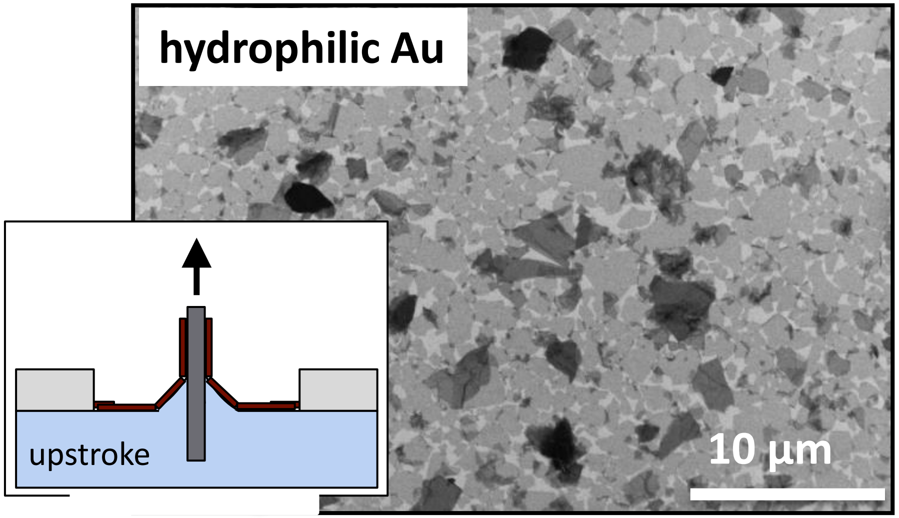
Graphene oxide: How to achieve excellent monolayers on diverse substrates?

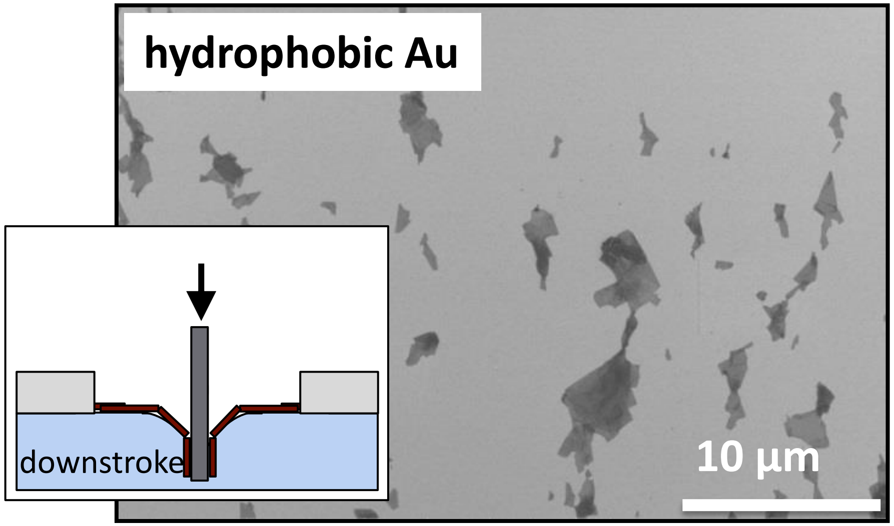
Langmuir-Blodgett deposition:

1) Prepare GO monolayer
2) Compress to desired surface coverage
3) Transfer monolayer to substrate





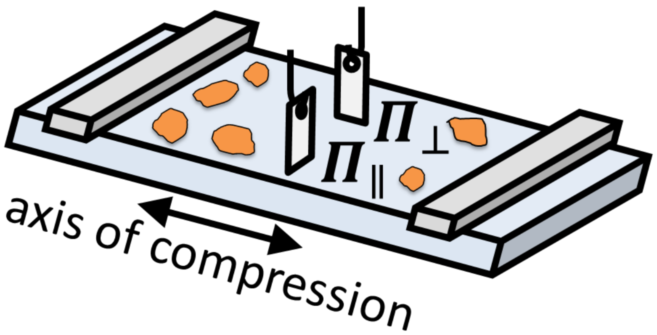


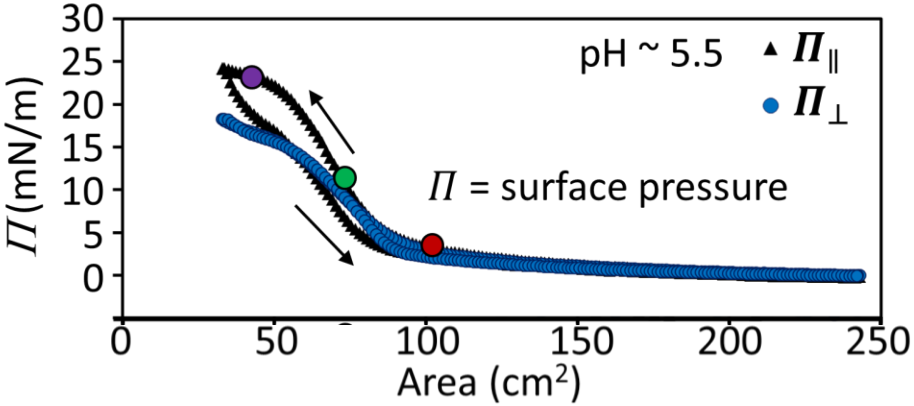


with Katie Harrison and Kevin Zavadil

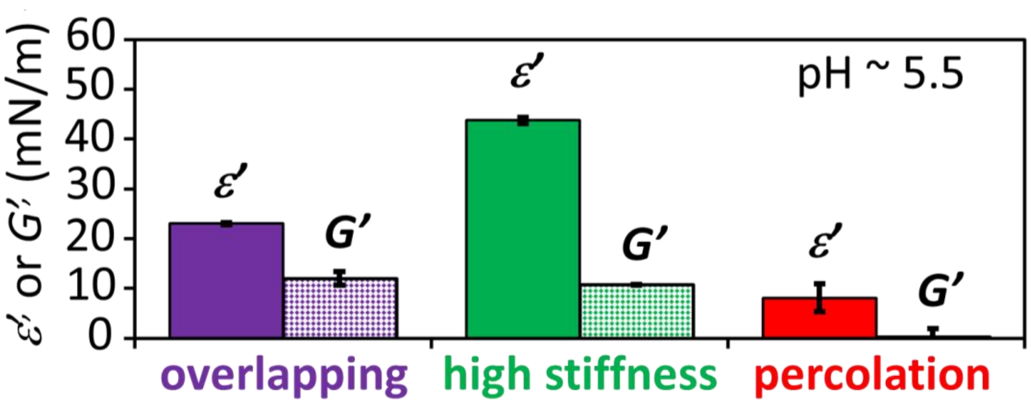
Elastic moduli measurements show GO monolayer behaves as a 2D-solid

Asymmetry in surface pressure ($\Pi_{\parallel}$ vs $\Pi_{\perp}$) indicates finite shear modulus, *G'*





Shear moduli, ε* and *G, calculated from oscillatory barrier measurements[1]**



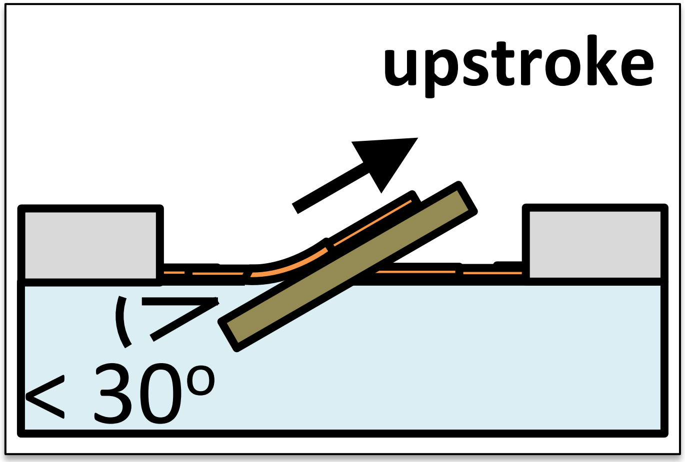
Finite G'→

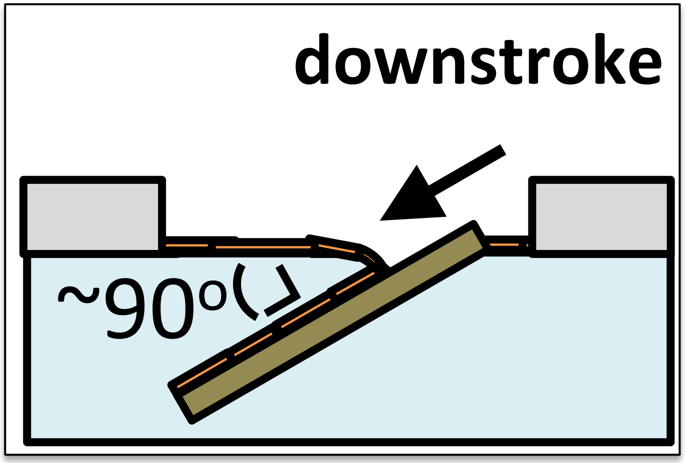
GO monolayer interacts as a 2D-solid

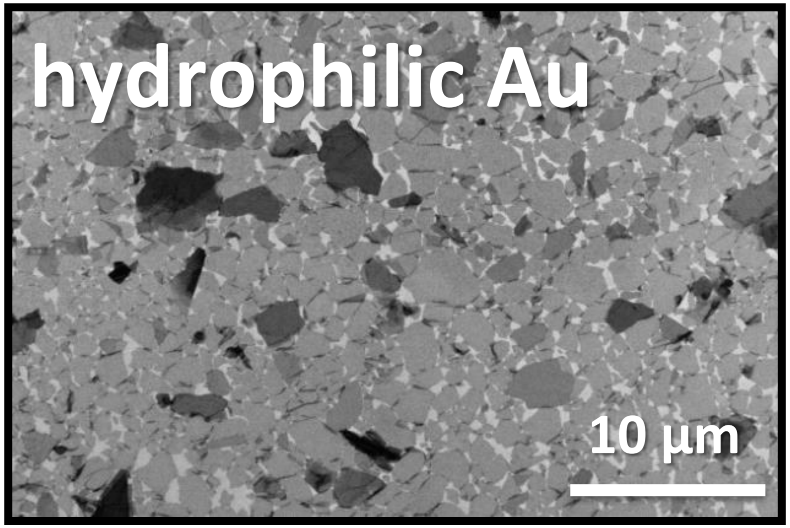
[1] Please ask for details – supporting info

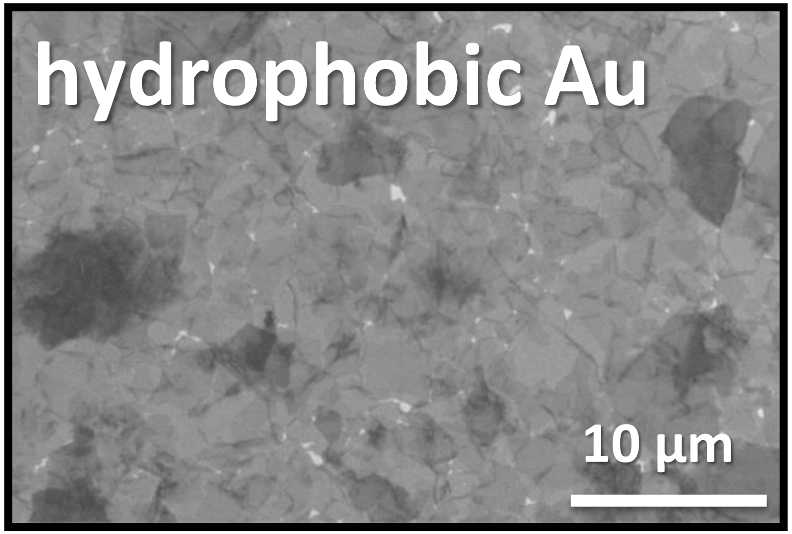
with Katie Harrison and Kevin Zavadil

To improve GO deposition, minimize strain







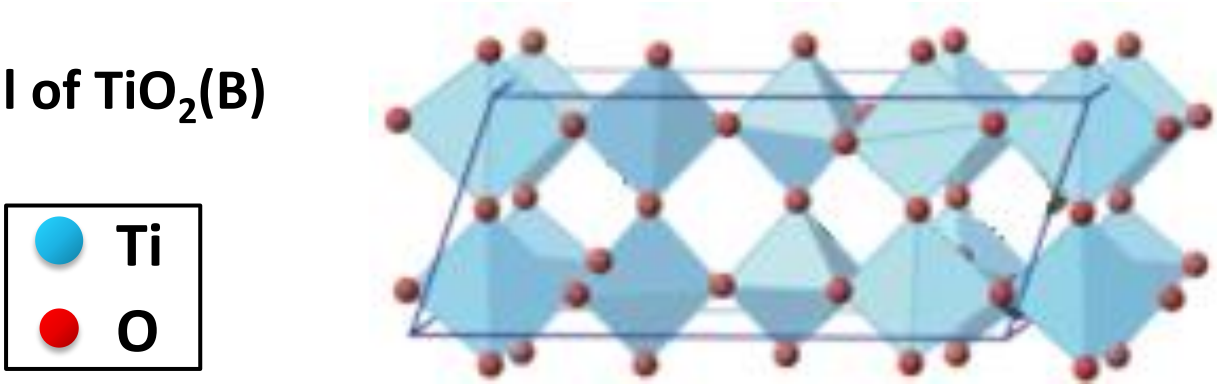


Angled dip developed by Katie Harrison

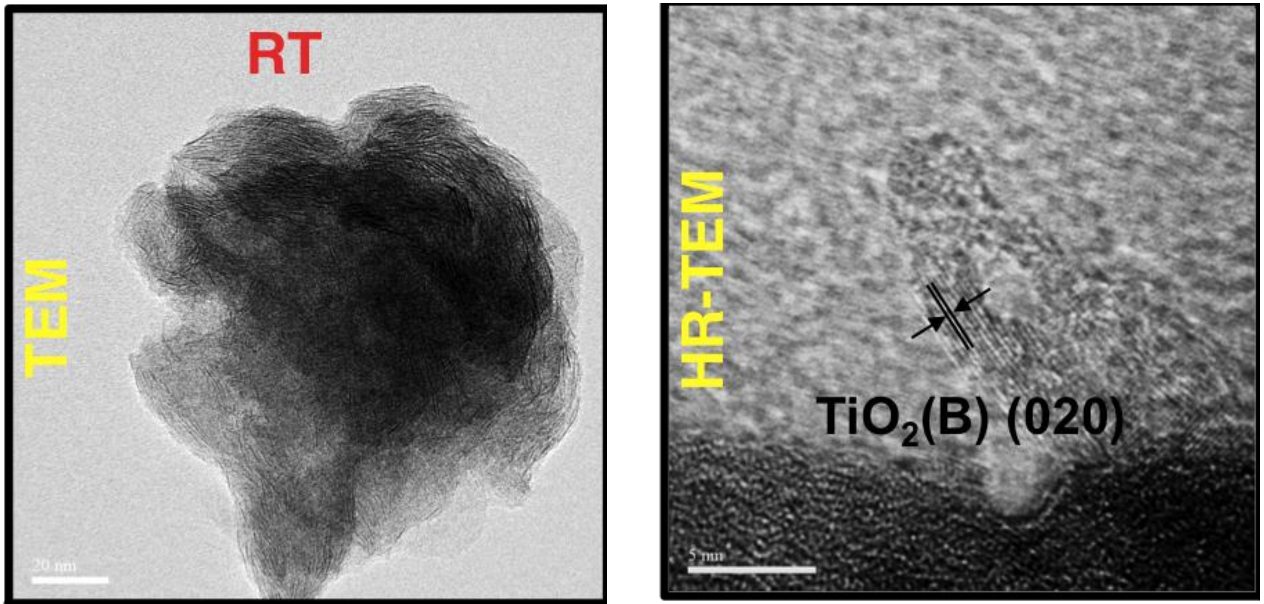
with Katie Harrison and Kevin Zavadil

Problem: TiO_2(B)-nanosheets form clusters when solution-deposited

Unit cell of TiO_2(B)



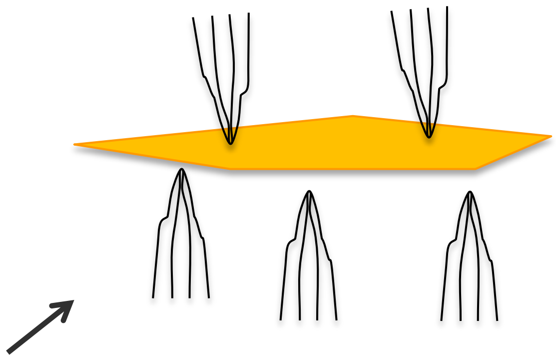
Crumpled TiO_2(B) nanosheet clusters



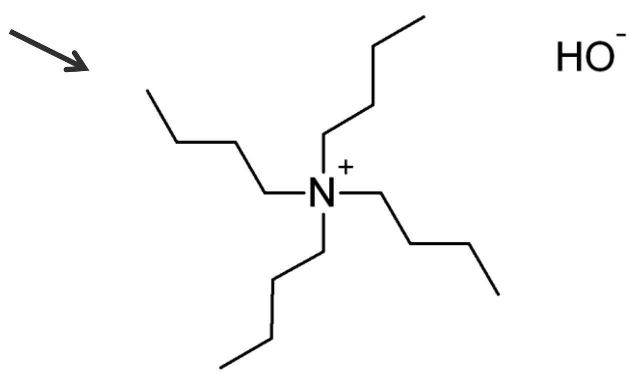
Dylla et al., "Electrochemical and Raman Spectroscopy Identification of Architectural and Morphological Transformations in Nanostructured TiO_2(B)," *submitted* (2013)

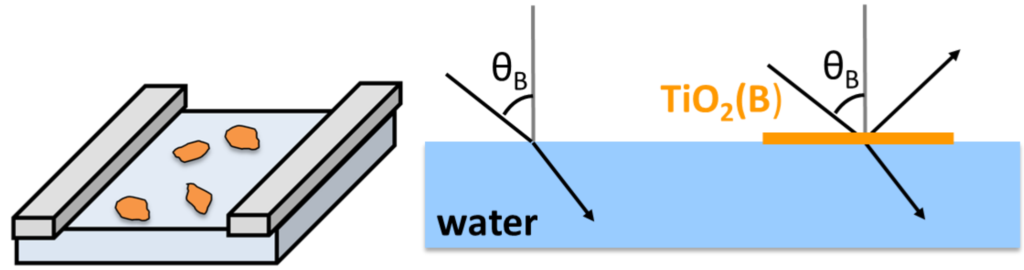
TiO_2(B): Amphiphilic surfactants allow formation of oxide nanosheet monolayers

TiO_2(B)-NS in TBAOH:H_2O spreading solvent

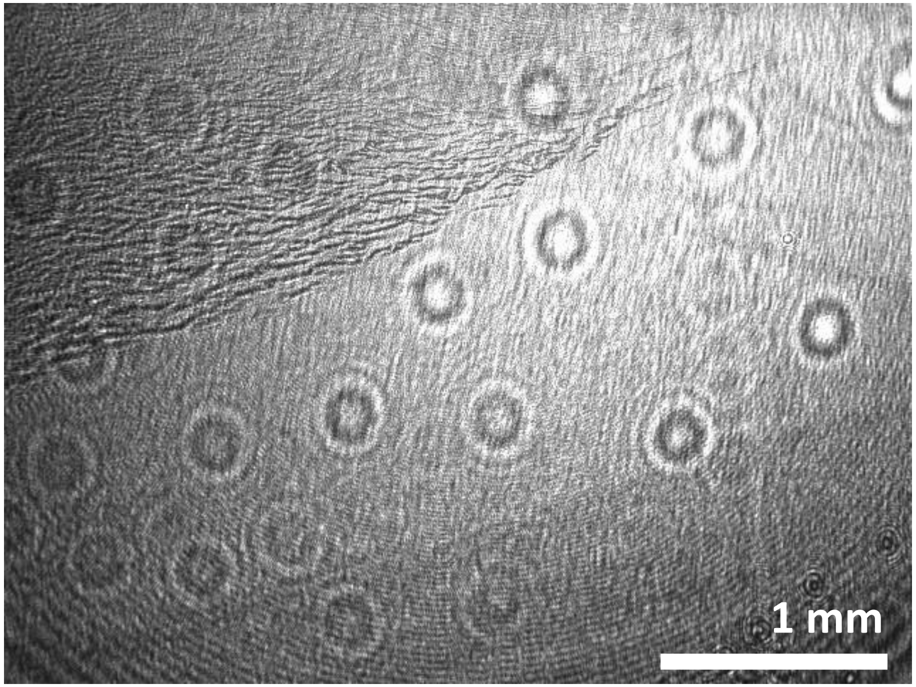


TBAOH: tetrabutylammonium hydroxide



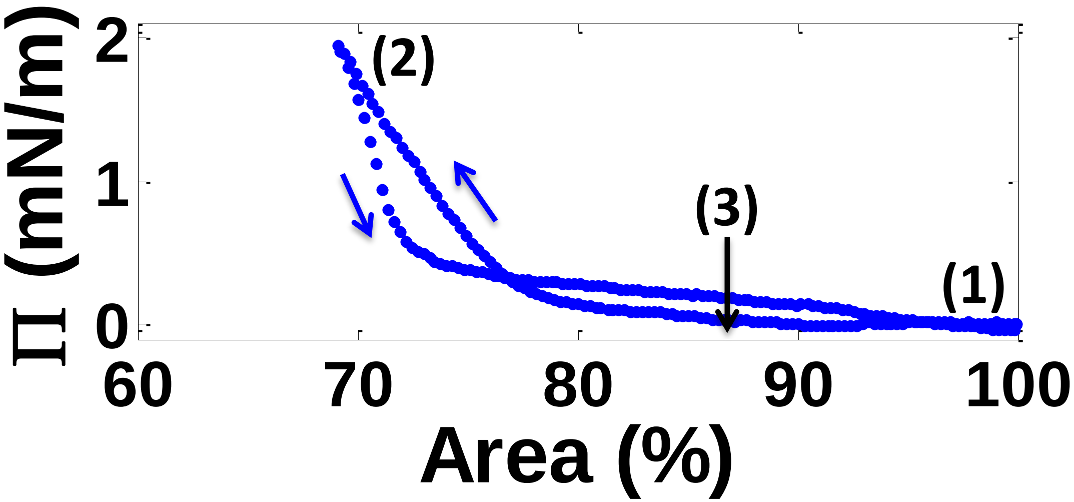


BAM of diffuse TiO_2(B) monolayer

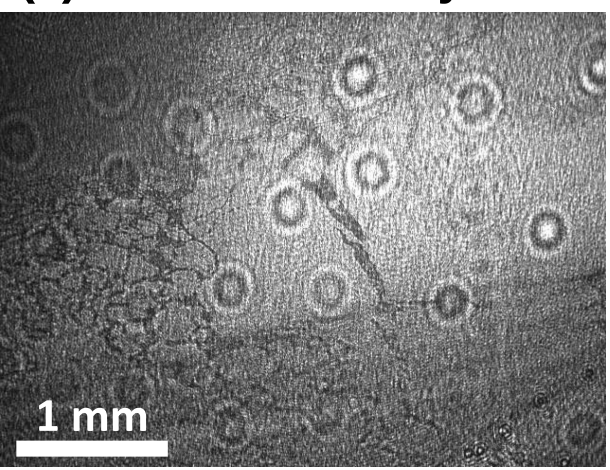


TiO2(B) synthesis by Anthony Dylla and Keith Stevenson, UT Austin

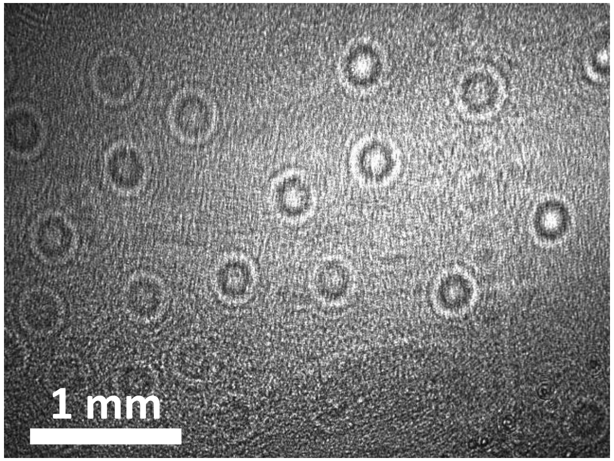
BAM shows stages of TiO_2(B) monolayer formation



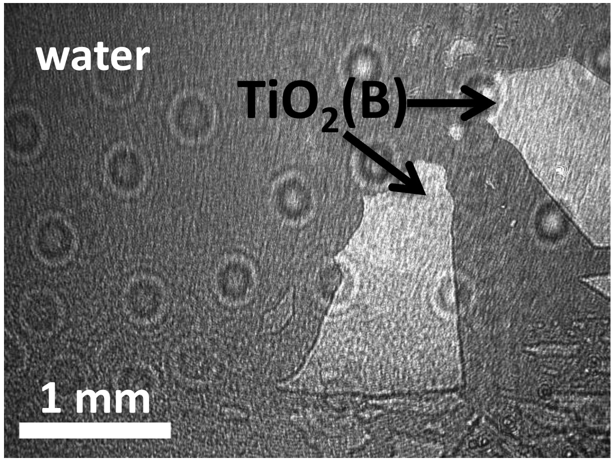
(1) Diffuse monolayer



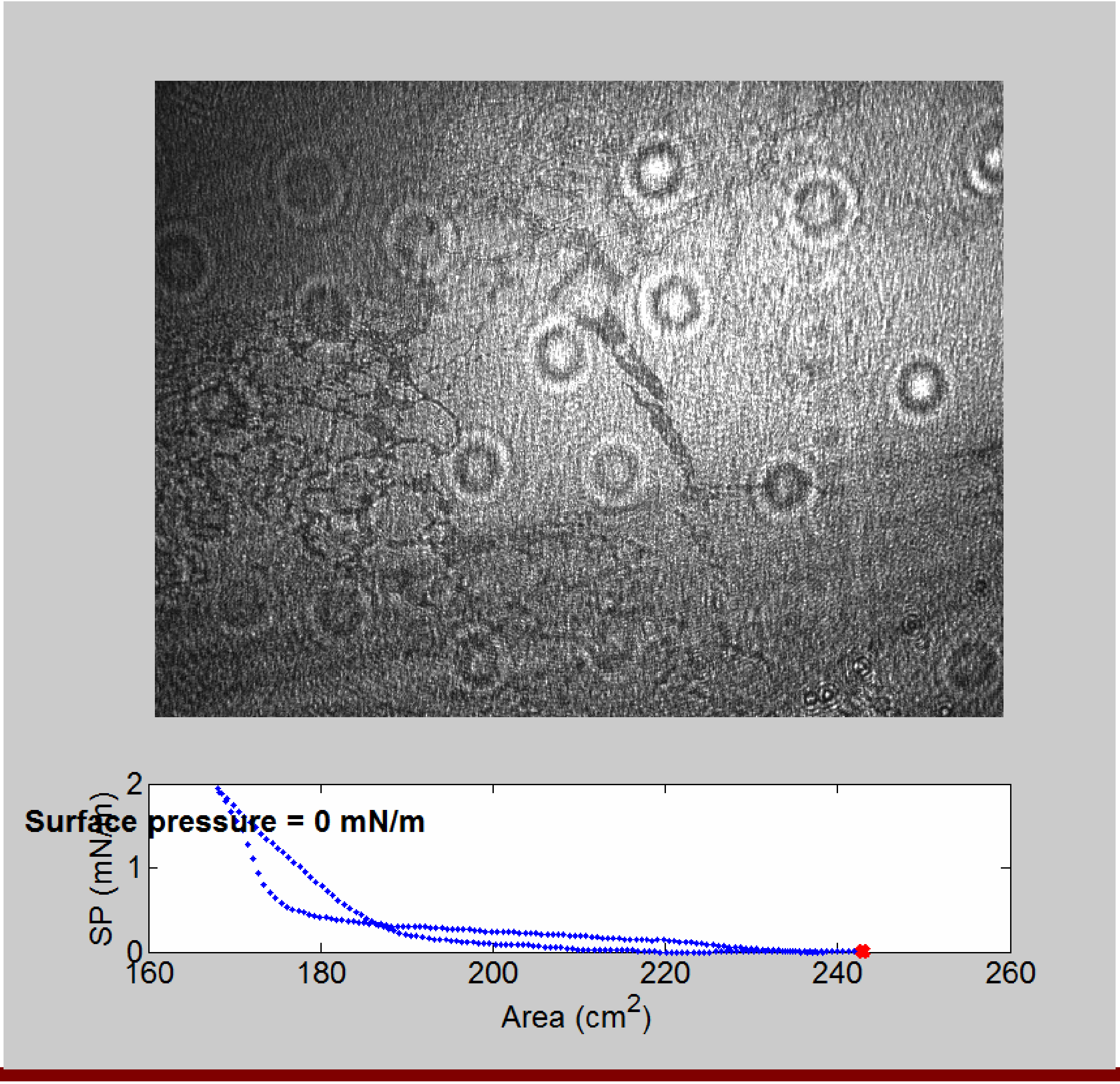
(2) Compressed TiO_2(B)

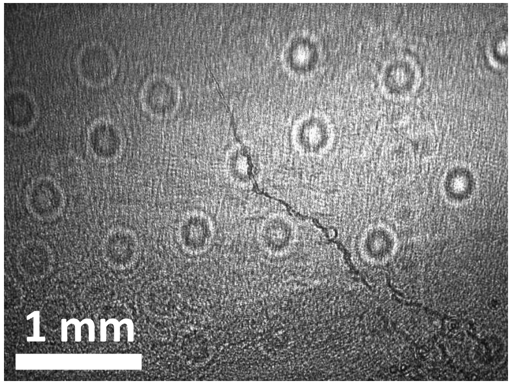


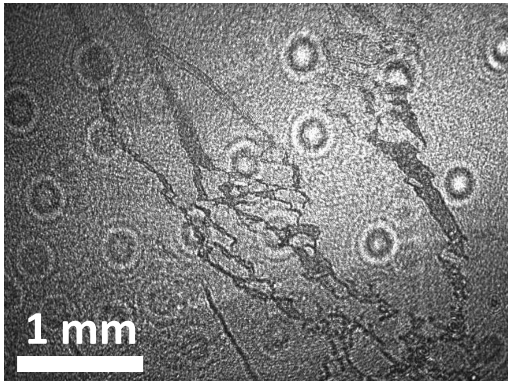
(3) Island formation

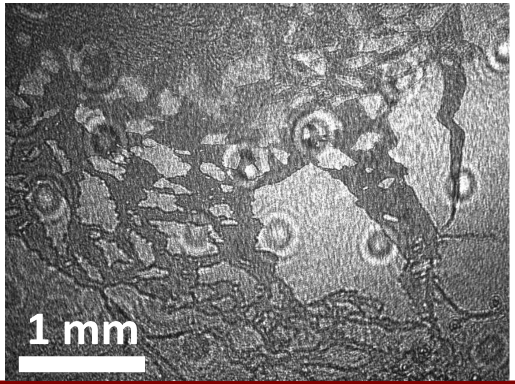


Monolayer fractures into islands upon expansion



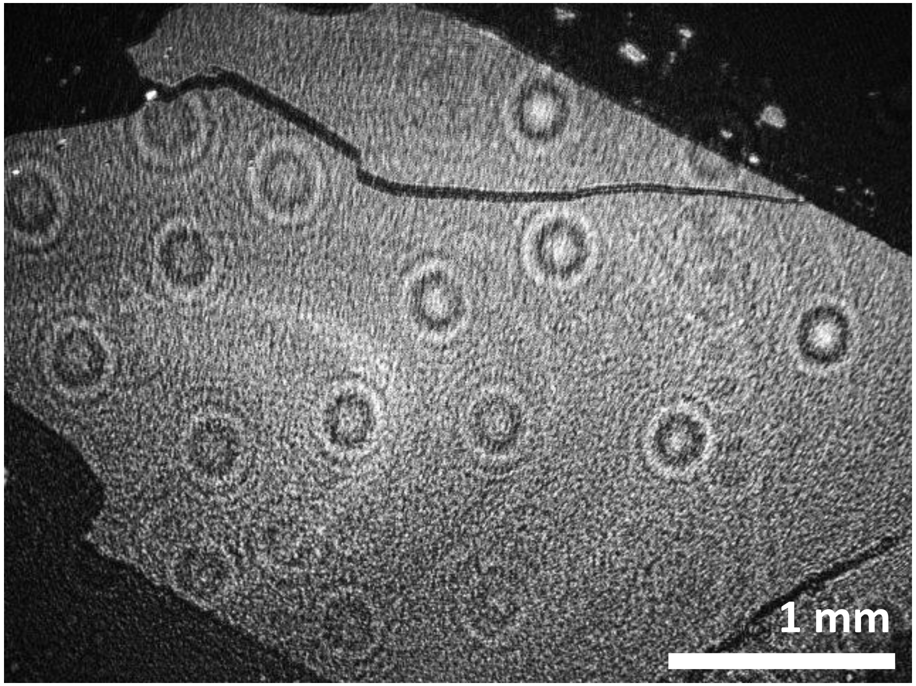




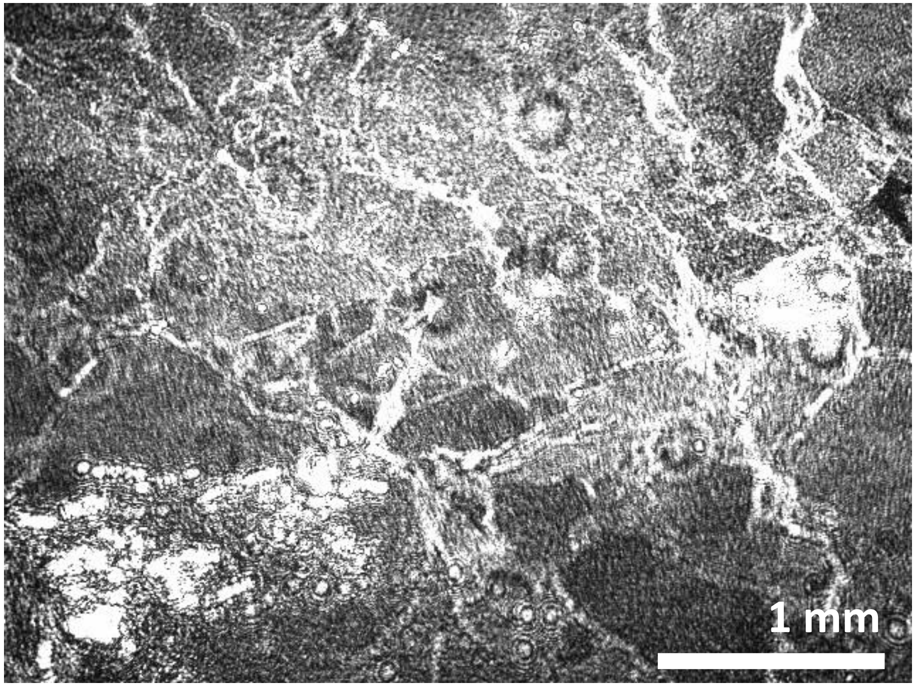


BAM observations guide TiO_2(B) deposition conditions

Gentle compressions (Π ~ 2—5 mN/m) drive monolayer formation

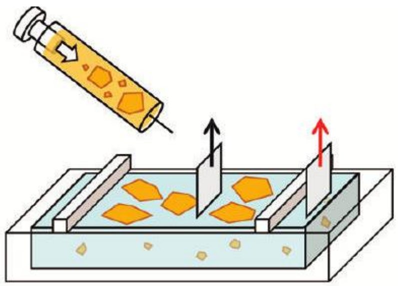
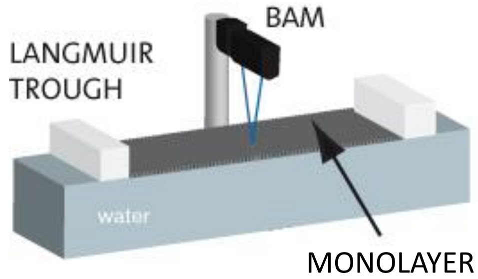


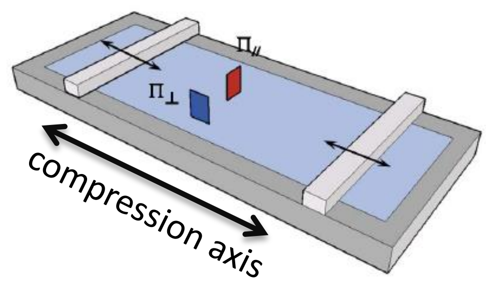
TiO_2(B) monolayer will collapse into multilayer structure under moderate and high compression (Π > 10 mN/m)

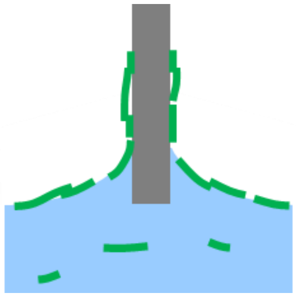


Langmuir-Blodgettry of graphene oxide (GO) and TiO_2(B) nanosheets

- What is Langmuir-Blodgett (L-B) deposition?

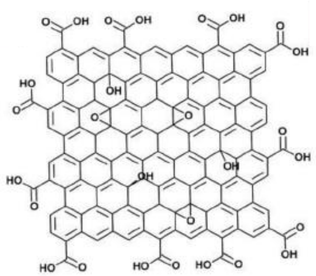
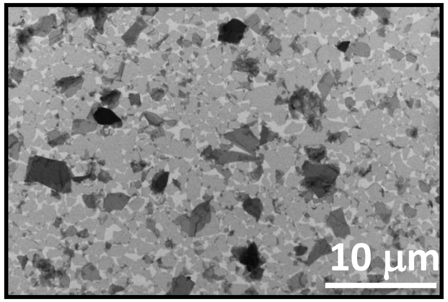





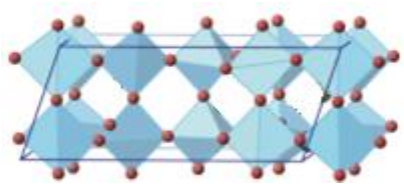
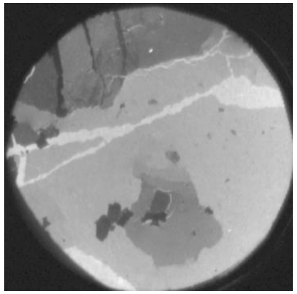


- Optimization of L-B deposition for 2D-nanosheets

GO

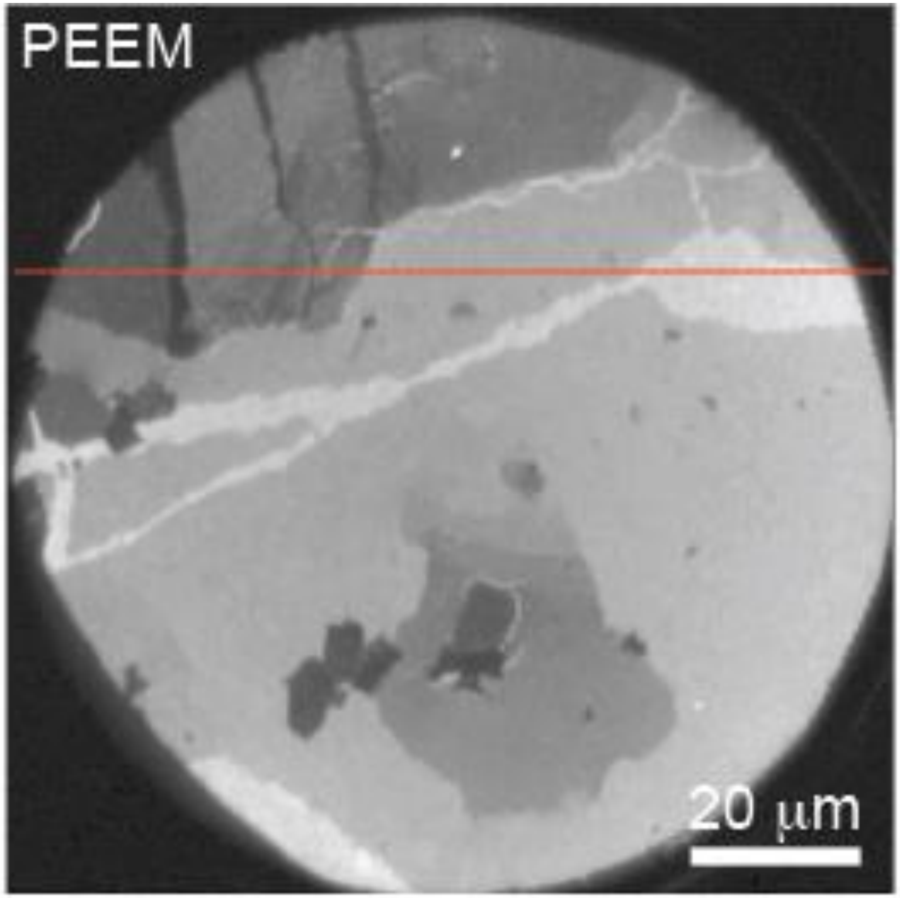



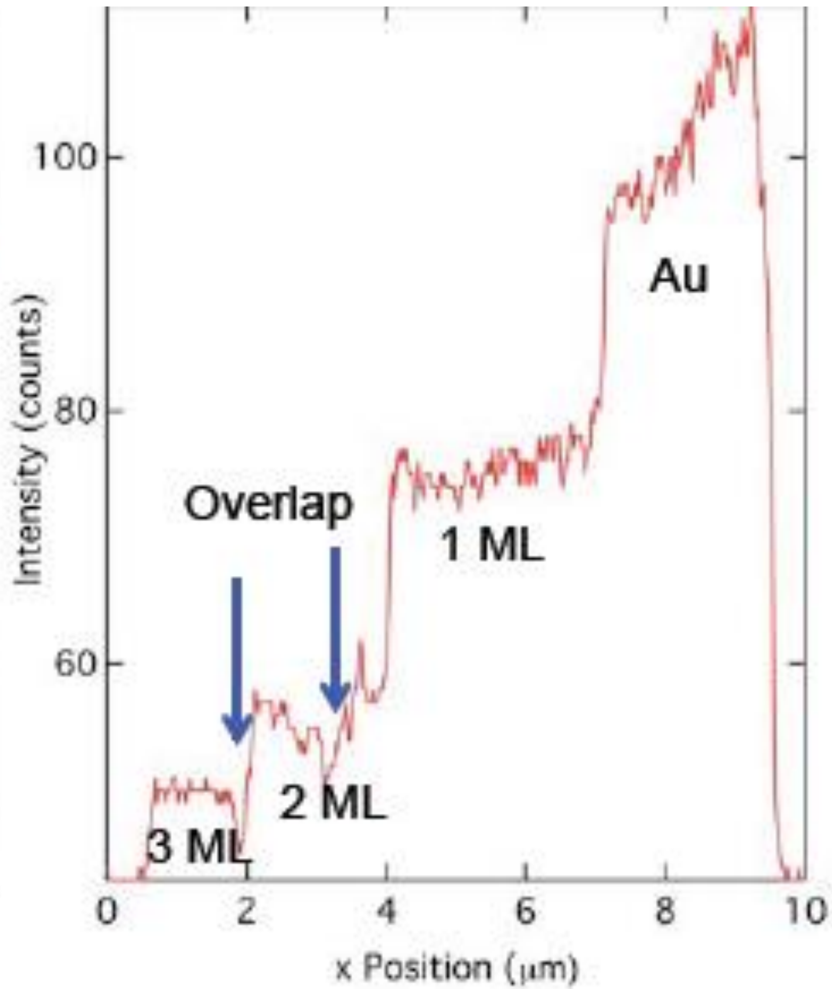
TiO_2(B)

- **Utility of L-B deposition in preparing nanosheets for surface analysis**

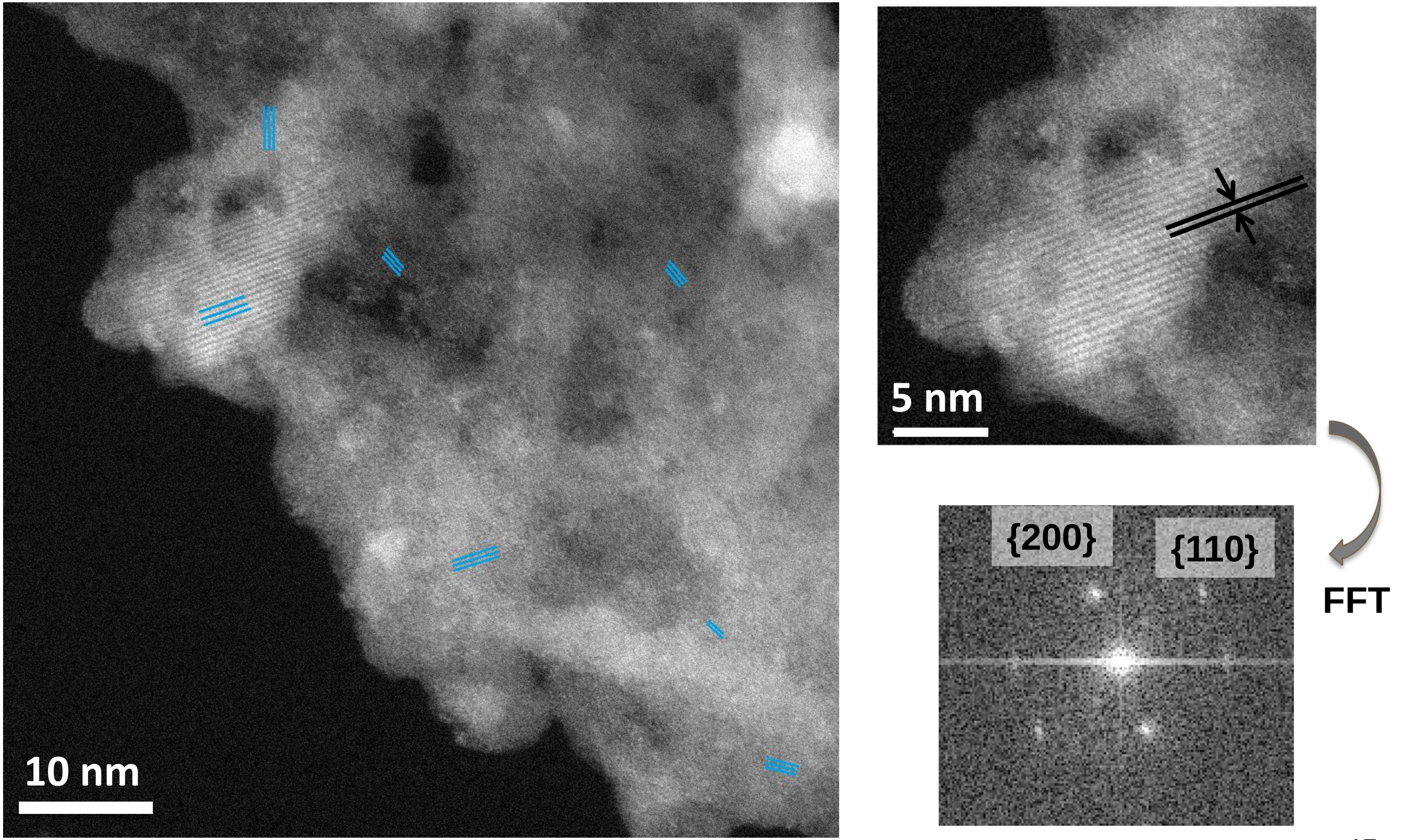
Photoemission electron microscopy shows large regions of monolayer TiO_2(B)





PEEM by Calvin Chan

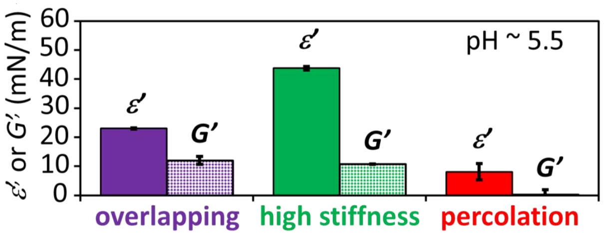
TEM confirms TiO_2(B) polymorph; nanocrystalline monolayer films

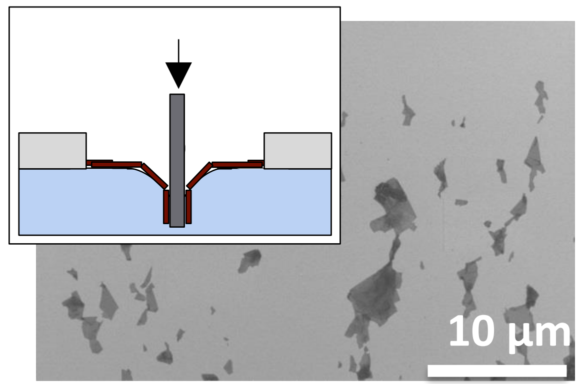


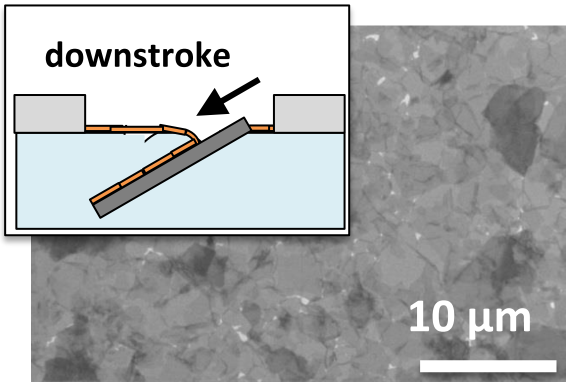
TEM by Paul Kotula

Control and characterization of 2D-nanosheet monolayers is crucial for uniform deposition

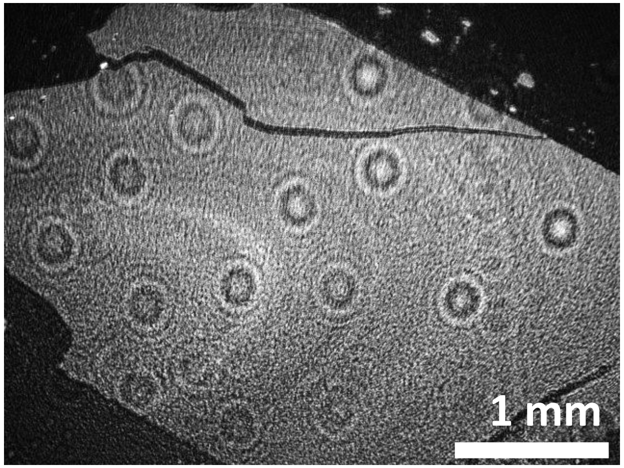
If the monolayer behaves as a 2D-solid, minimize strain during deposition

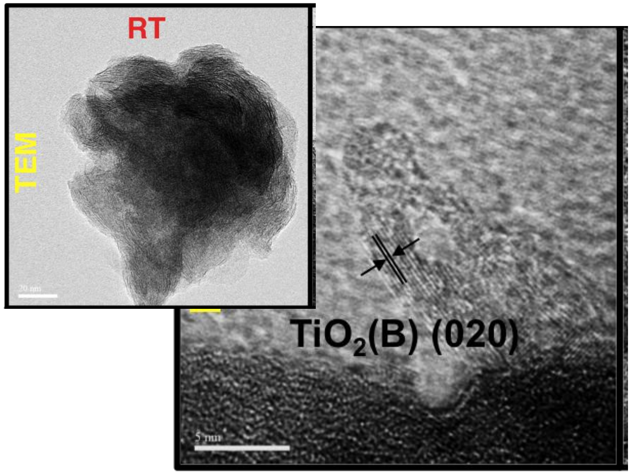


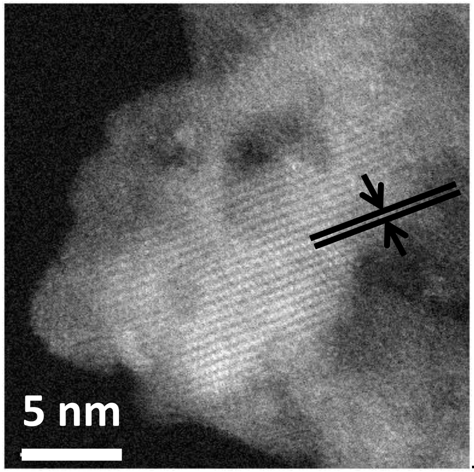




The air-water interface can stabilize colloidal nanosheet assemblies

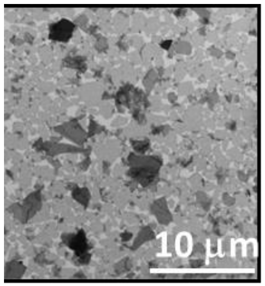


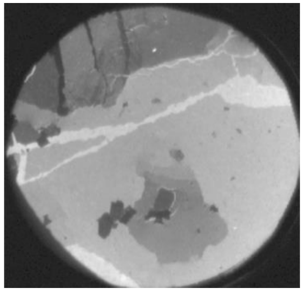


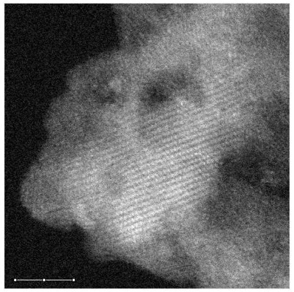


Acknowledgements

Sandia National Laboratories

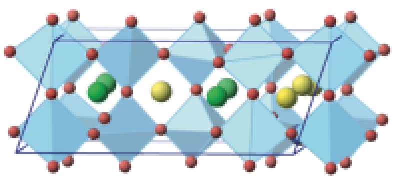


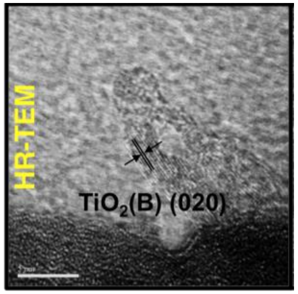




Calvin Chan, Katie Harrison, Paul Kotula, Kevin Zavadil

The University of Texas at Austin





Keith Stevenson, Anthony Dylla

G. Henkelman and P. Xiao

U.S. DEPARTMENT OF ENERGY

Sandia LDRD program

JCESR JOINT CENTER FOR ENERGY STORAGE RESEARCH

The Center for Integrated Nanotechnologies

CINT is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science.

EFRC CST

U.S. DOE, Office of Science, BES
Energy Frontiers Research Center on
"Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)"
[Award DE- SC0001091]

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-AC04-94AL85000.

lbieder@sandia.gov

Langiappe