Interlayer Elasticity and Friction in 1D and 2D Van der Waals Materials

Elisa Riedo

CUNY - Advanced Science Research Center

The City College of New York

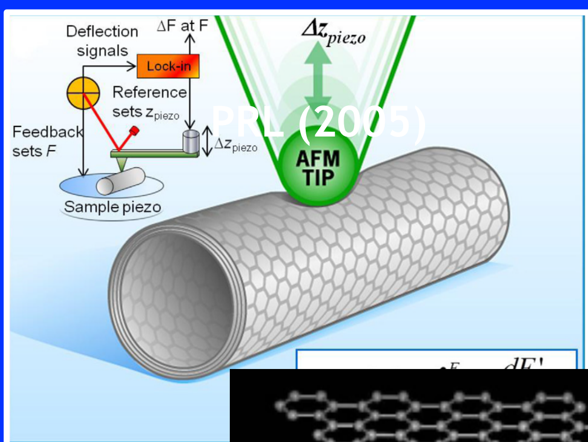
Georgia Institute of Technology

Georgia Tech

the City College of New York

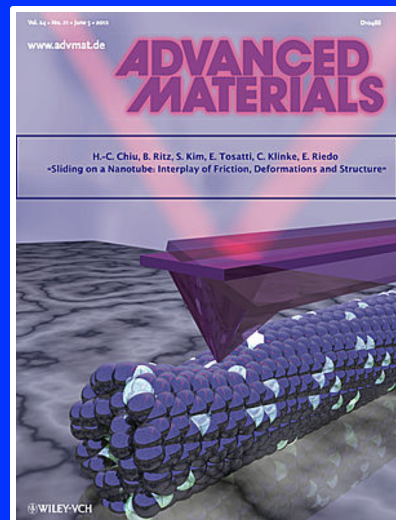
Nanomechanics by Atomic Force Microscopy

Radial Elasticity of NTs

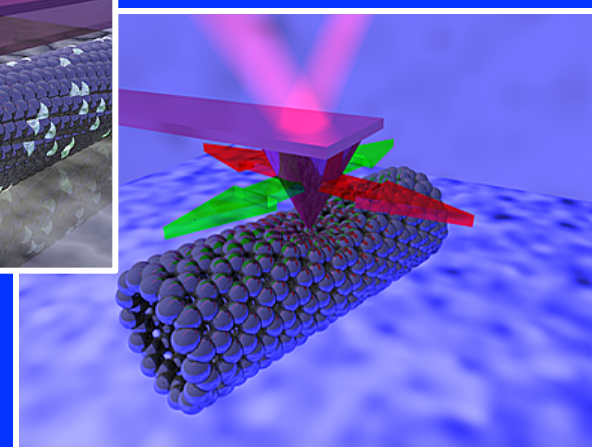


PRL (2005)

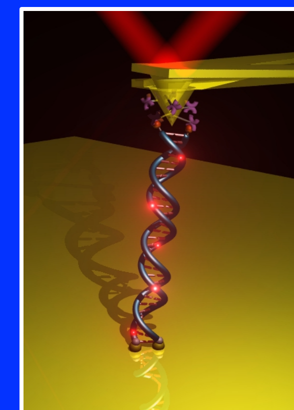
Friction Anisotropy in NTs



Nature Material (2010)

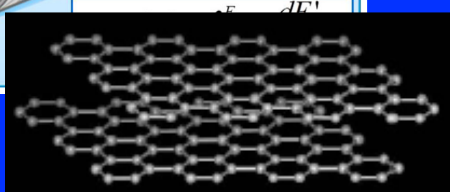


Stretching Modulus of short DNA strands



Nanoscale (2014)

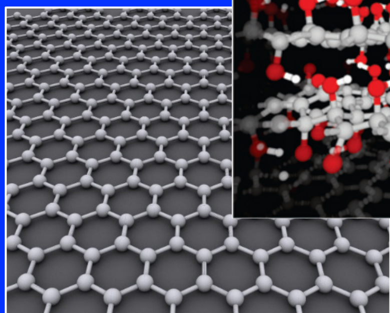
2D Materials



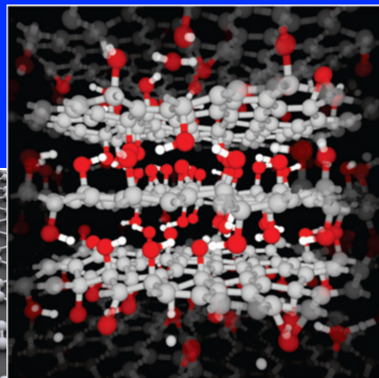
Nature Material (2015)

Office of Basic Energy Sciences

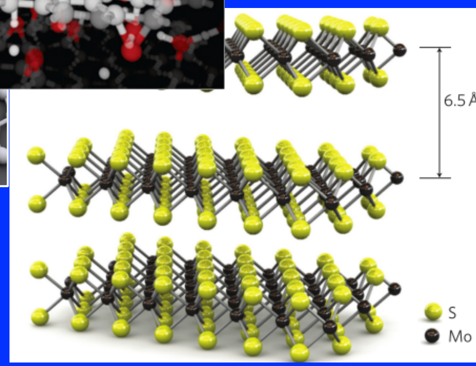
2D and 1D Layered Materials



Graphene

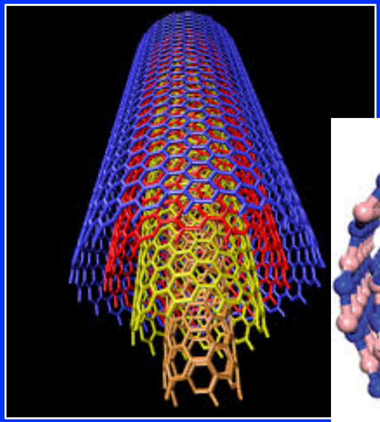


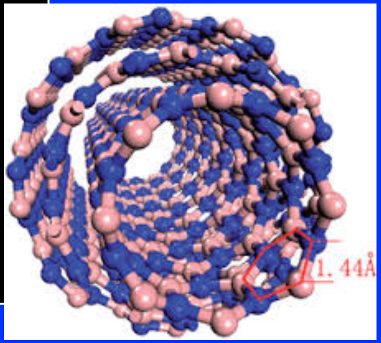
Graphene Oxide



MoS_2

C- Nanotubes





BN- Nanotubes

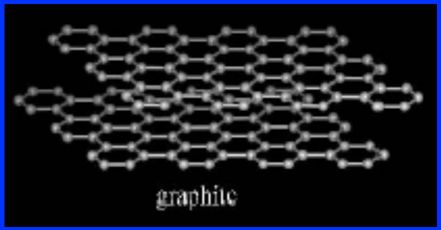
Key-Property:

Strong In-Plane bonds and

Weaker Interlayer Interaction (Van der Waals force)

$C_{11} = 1.06$ TPa

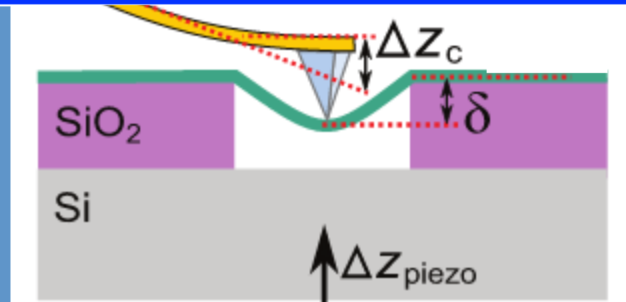
↔ $E_{//}$



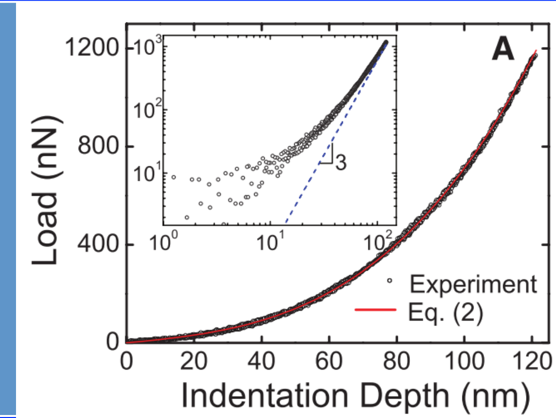
$C_{33} = 36$ GPa

↕ $E_{\perp}$

$E_{//}$



C. Lee *et al.*, Science (2008)

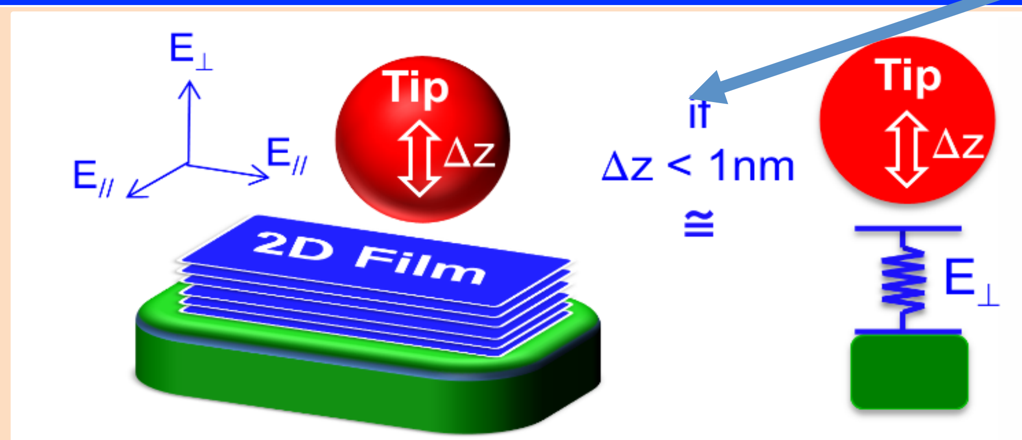


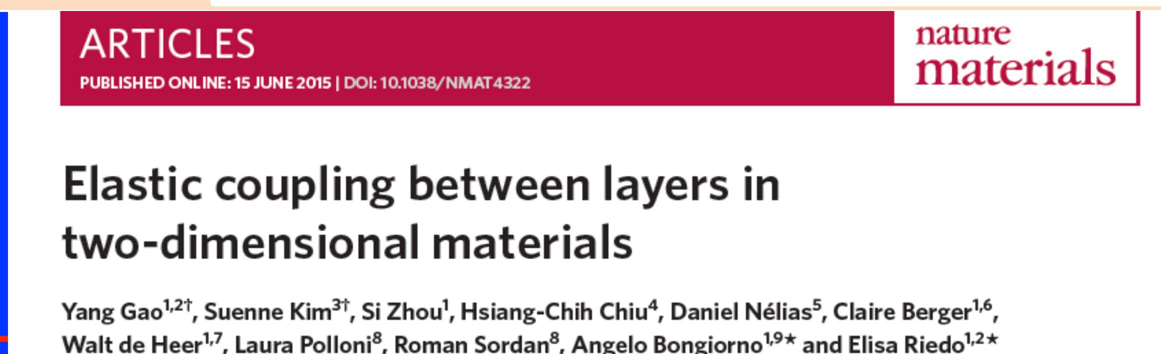
1. ~~ΔZ ~ 10 to 100nm~~; 2. ~~material suspended~~; 3. Only $E_{//}$ but not $E_{\perp}$!

< 0.3 nm

Supported on substrate

$E_{\perp}$




ARTICLES

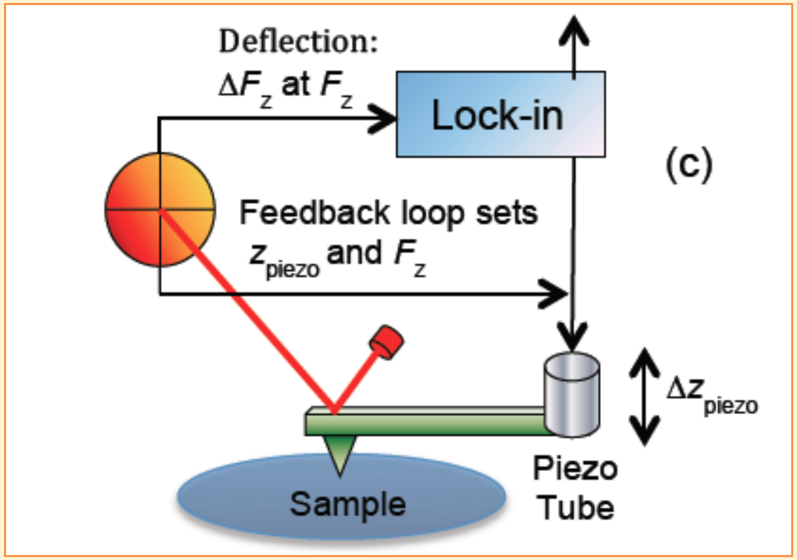
PUBLISHED ONLINE: 15 JUNE 2015 | DOI: 10.1038/NMAT4322

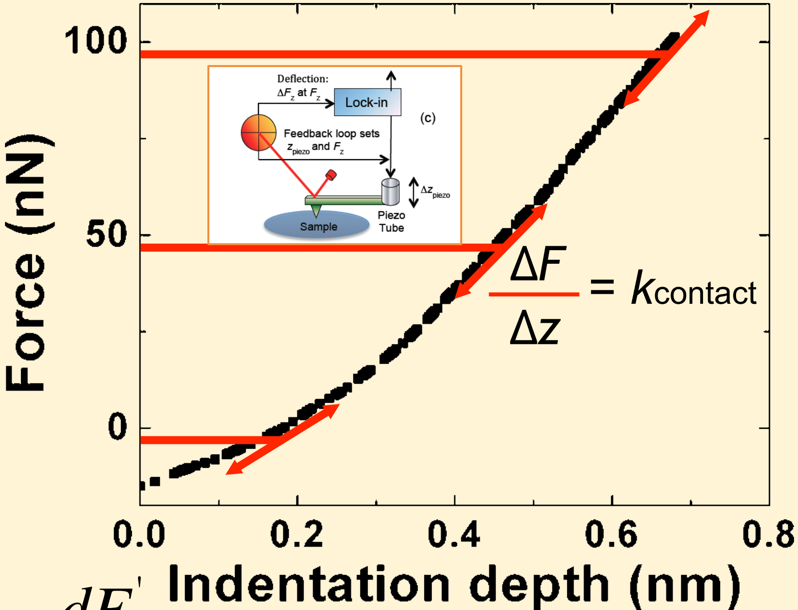
nature materials

Elastic coupling between layers in two-dimensional materials

Yang Gao[1,2†], Suenne Kim[3†], Si Zhou[1], Hsiang-Chih Chiu[4], Daniel Nélias[5], Claire Berger[1,6], Walt de Heer[1,7], Laura Polloni[8], Roman Sordan[8], Angelo Bongiorno[1,9*] and Elisa Riedo[1,2*]

Modulated NanoIndentation (MoNI)





$$z(F) - z(F=0) = \int_{F(z=0)}^{F_{max}} \frac{dF'}{k_{contact}(F')}$$

A new technique-***Modulated NanoIndentation*** (MoNI):

FIRST experimental measurement of the local perpendicular-to-the-plane elastic modulus $E_\perp$ of 2D material at **0.1 Å** resolution

Y. Gao, S. Zhou, S. Kim, H.-C. Chiu, D. Nélias, C. Berger, W. de Heer, L. Polloni, R. Sordan, A. Bongiorno and E. Riedo, Nature Mat. (2015)

M. Lucas, W.J. Mai, R.S. Yang, Z.L. Wang, E. Riedo, Phil. Mag. 87, 2135 (2007)

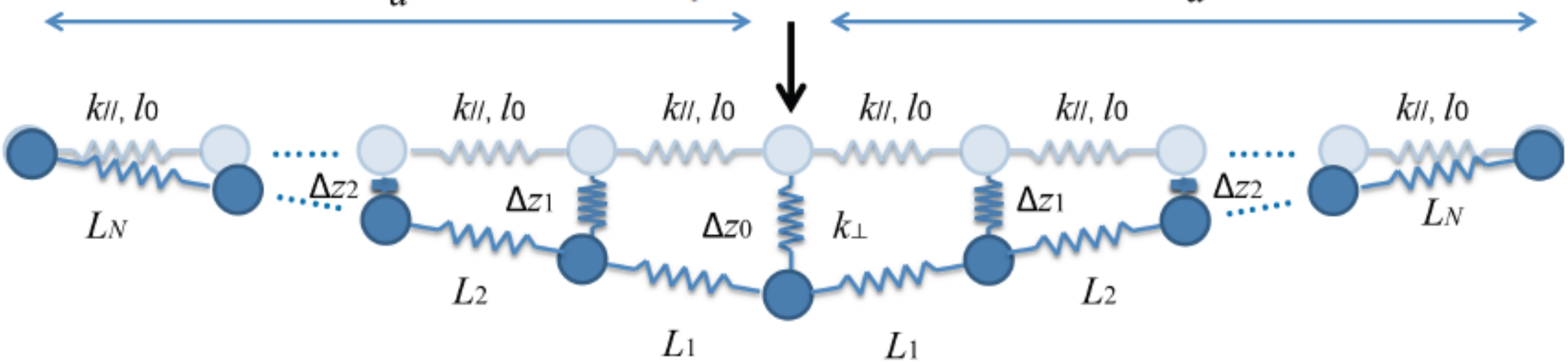
M. Lucas, K. Gall, and E. Riedo, J. Appl. Phys. 104, 113515 (2008)

I. Palaci, C. Klinke, H. Brune, E. Riedo, Phys. Rev. Lett. (2005)

Back-of-the-envelope Calculations

What do we measure when we indent a nano-size tip for indentations smaller than interlayer distance ?

$$F_{\perp} + F_{//,z} = F_0$$



$$\frac{F_{\perp}}{F_{//,z}} = \frac{\Delta z_0 \times k_{\perp} \times N}{2k_{//} \times \frac{\Delta z_0}{N} \times \frac{\Delta z_0}{a} \times \frac{\Delta z_0}{a}} = \frac{k_{\perp}}{2k_{//}} \cdot \frac{N^2 a^2}{\Delta z_0^{\;2}}$$

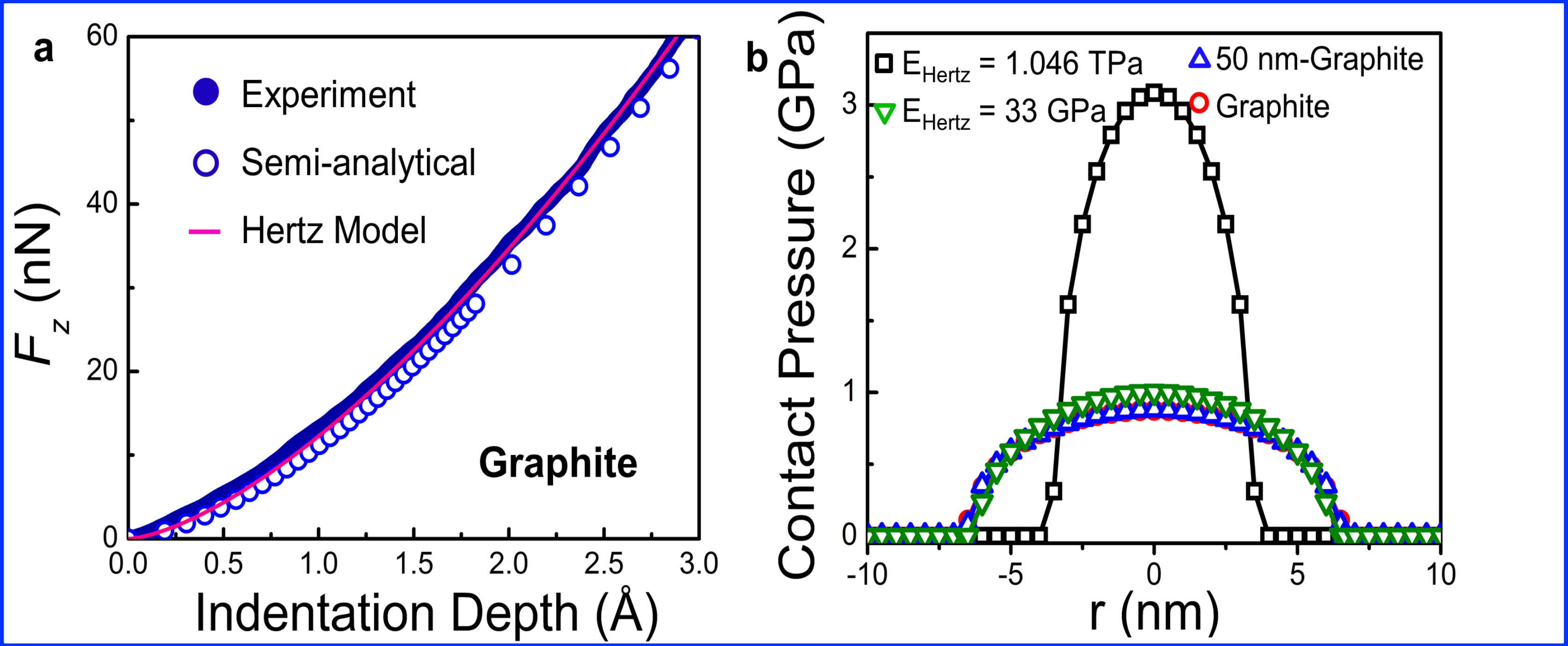
IF $\Delta Z < 3$ Å

$$F_{\perp} / F_{//,z} = 10^4 >> 1$$

For sub-nm indentations << film thickness,
the force vs. indentation curves are mainly sensitive to $E_{\perp}$ **!**

MoNI Å – depth indentations in 2D films

For sub-nm indentations << film thickness,
the force vs. indentation curves are mainly sensitive to $E\perp$!



Graphite: $E_{//}$ = 1.046 TPa and $E\perp$ = (36.4±1) GPa

Hertz model as if graphite was isotropic
<u>with modulus = 33 GPa → WORKS!</u>
or 1.046 TPa → Not good

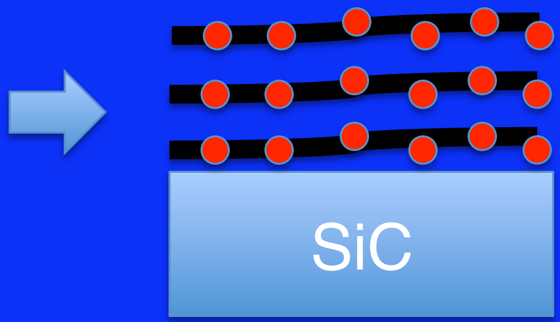
2D Films: Graphene and Graphene Oxide

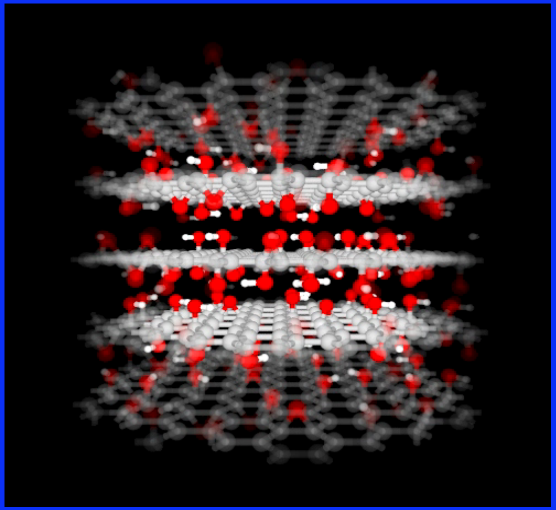
Graphene

Interlayer distance
~ 3 A

Graphene Oxide

Interlayer distance
~ 9 A





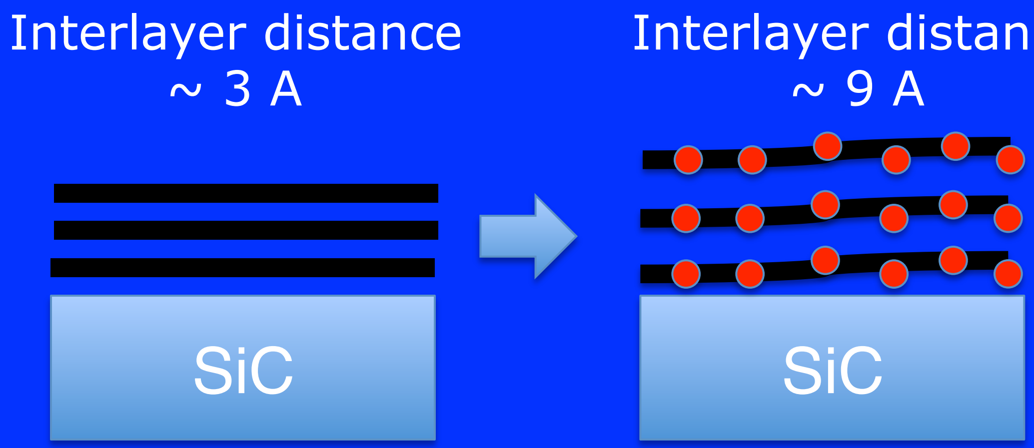
DFT Calculations From
Bongiorno's Lab

**Controlled Functionalization of Graphene
has been explored as a route to produce
Graphene-based materials
with tunable mechanical, optical and electron transport properties**

for Energy, Sensors, MEMS and Electronic Applications.

Epitaxial Multilayer Graphene Oxide (EGO)

Chemical (Hummers) Mild Oxidation of Epitaxial Graphene on SiC



- uniform films
- insulating
- transparent
- reproducible
- many potential applications

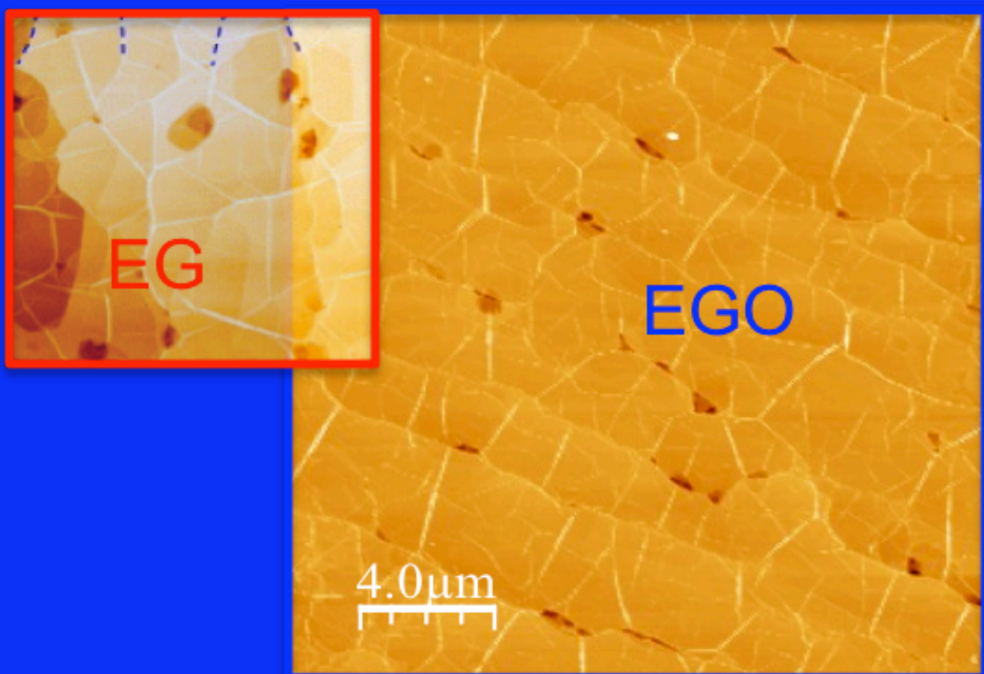
Nature Materials **11**, 544 (2012)
Adv. Funct. Mat. (2015)
Science (2010)

Graphene films are epitaxially grown on the C-surface of a SiC .

First, EG films are dipped into a $H_2SO_4/NaNO_3$ solution placed in an iced water bath. Second, $KMnO_4$ is added to the solution. The mixture is then transferred to a 35 C water bath for about 20 minutes. DI water (23 ml) is added slowly to the mixture. Finally, after 15 minutes, warm DI water (70 ml) and H_2O_2 (1.5 ml) are added to terminate the reaction. The sample is then brought in air, rinsed with DI water, and dried in a high purity nitrogen gas.

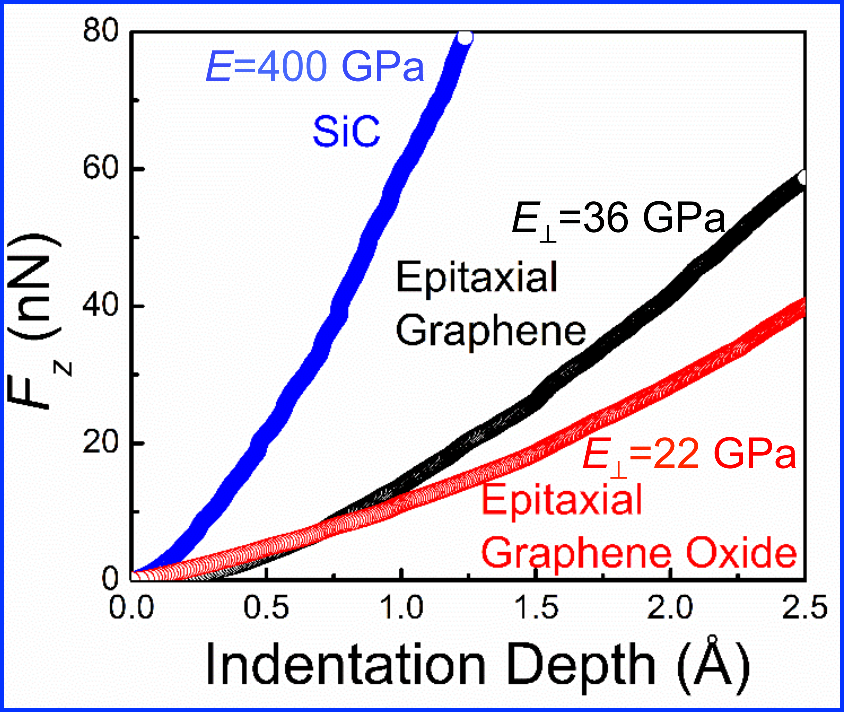
Epitaxial Multilayer Graphene Oxide (EGO)

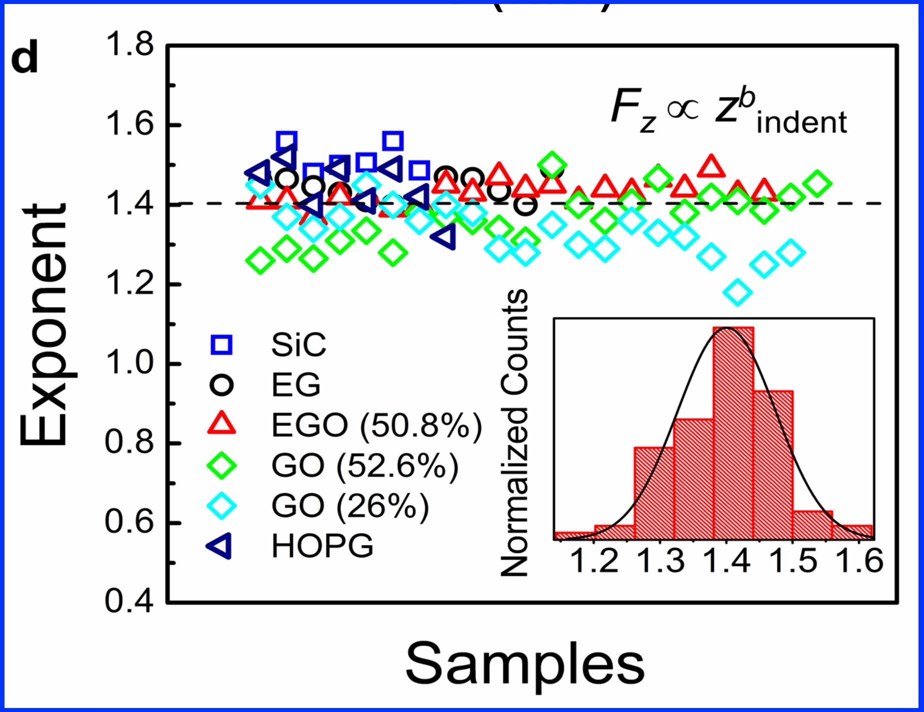
Chemical (Hummers) Mild Oxidation of Epitaxial Graphene on SiC



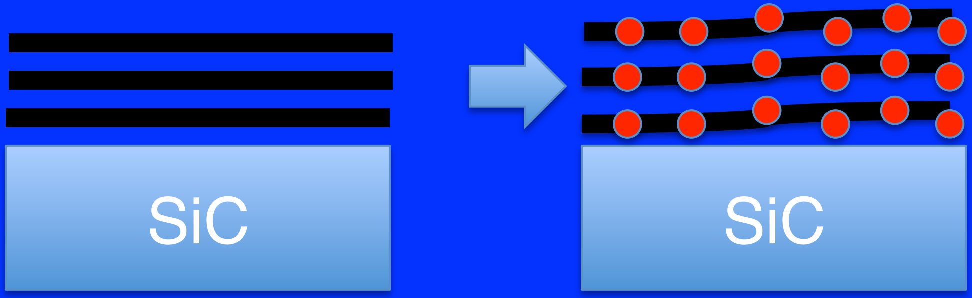
- uniform films
- insulating
- transparent
- reproducible
- many potential applications

SiC, Epitax-Graphene (10-L), Epitax Graphene Oxide (10-L)





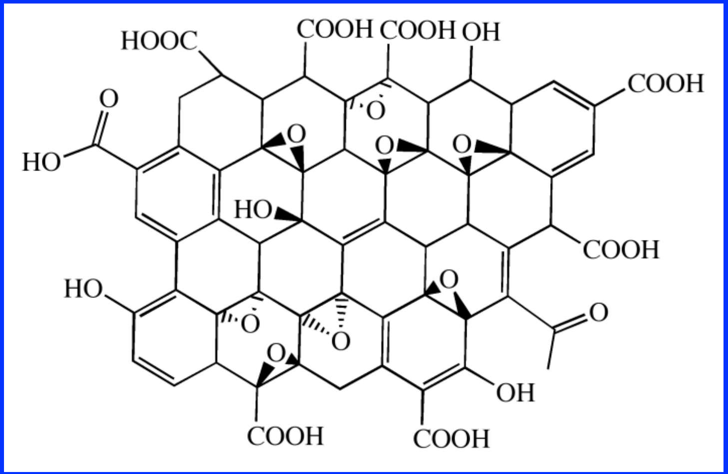
Riedo et al. Nature Materials **11**, 544 (2012)
Riedo et al. Adv. Funct. Mat. (2015)



Epitaxial Graphene (EG)

Epitaxial Graphene Oxide (EGO)

Conventional Graphene Oxide Flakes



(1) Oxidation of bulk graphite:
The Hummers method
A Wet Chemistry Strong Acids Process

(2) Exfoliation in water

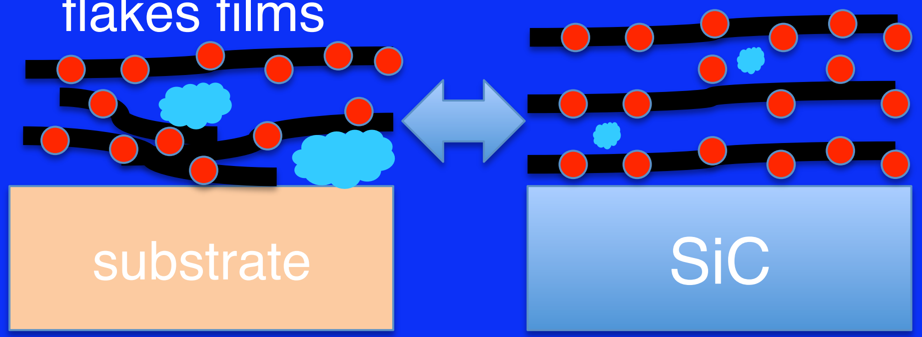
(3) Filtration and Deposition on a Substrate

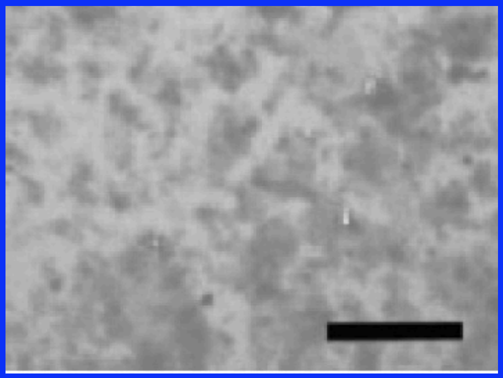
R.Ruoff, et. al. Nature 448, 457 (2007).

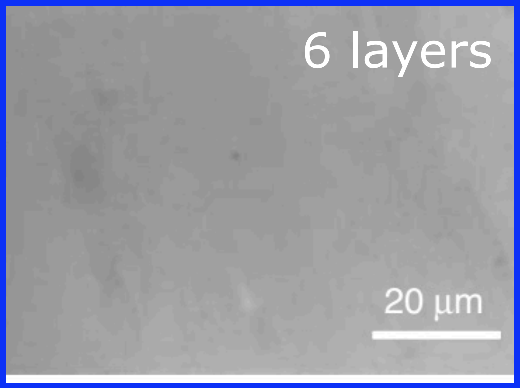
Epitaxial GO versus Flakes GO

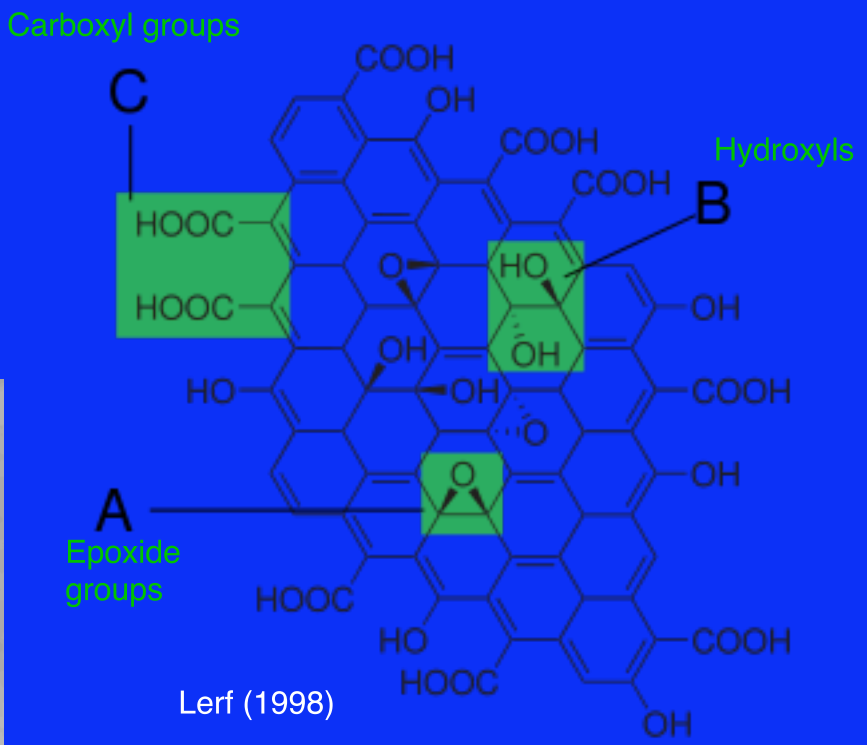
Conventional GO flakes films

Epitaxial GO films





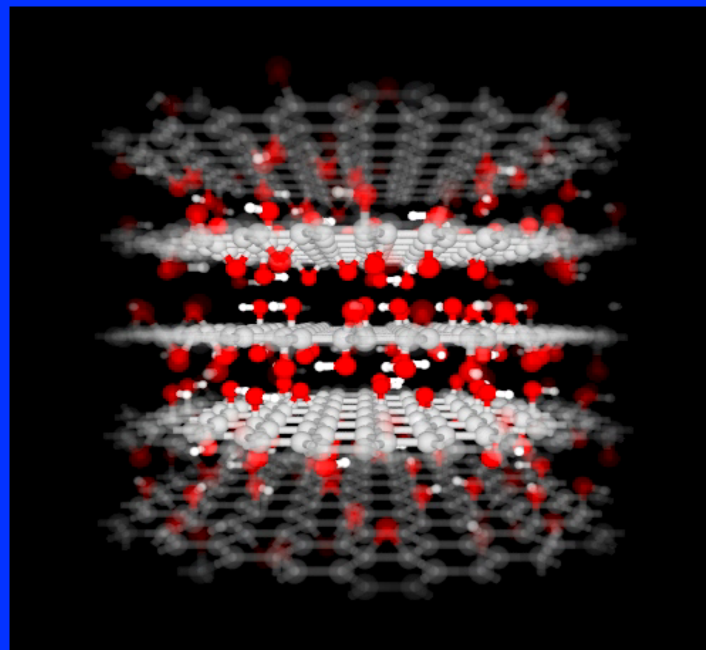




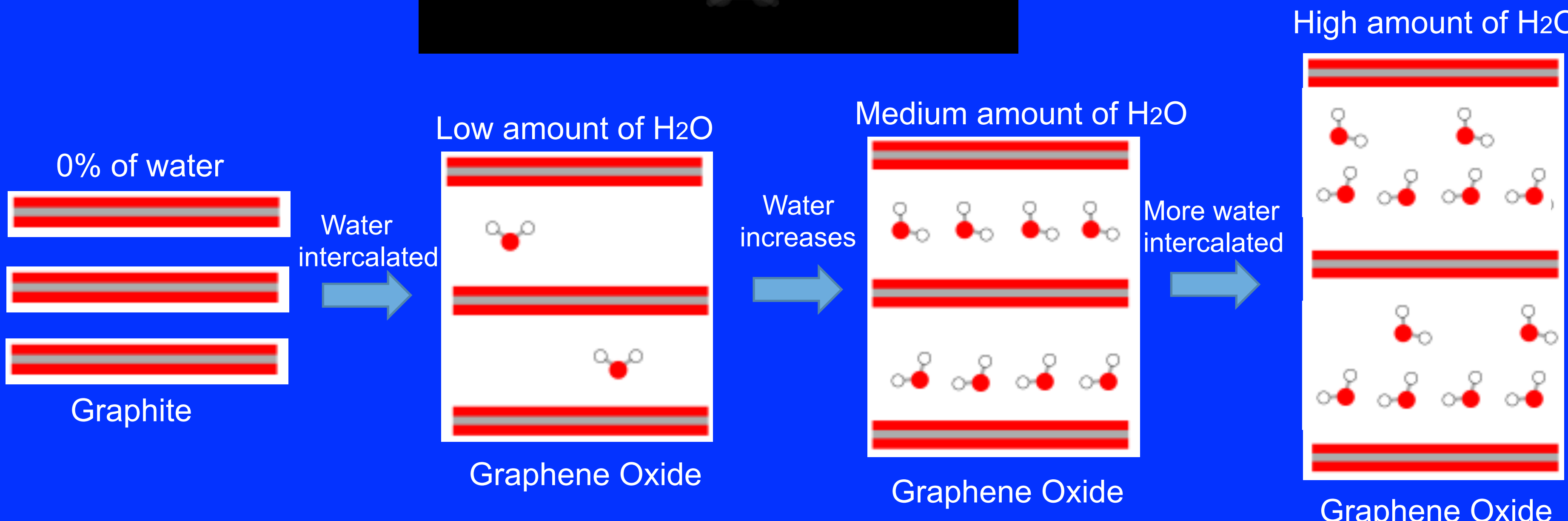
EGO films:

No edges (no carboxyl groups), uniform surface, control over number of layers, little water

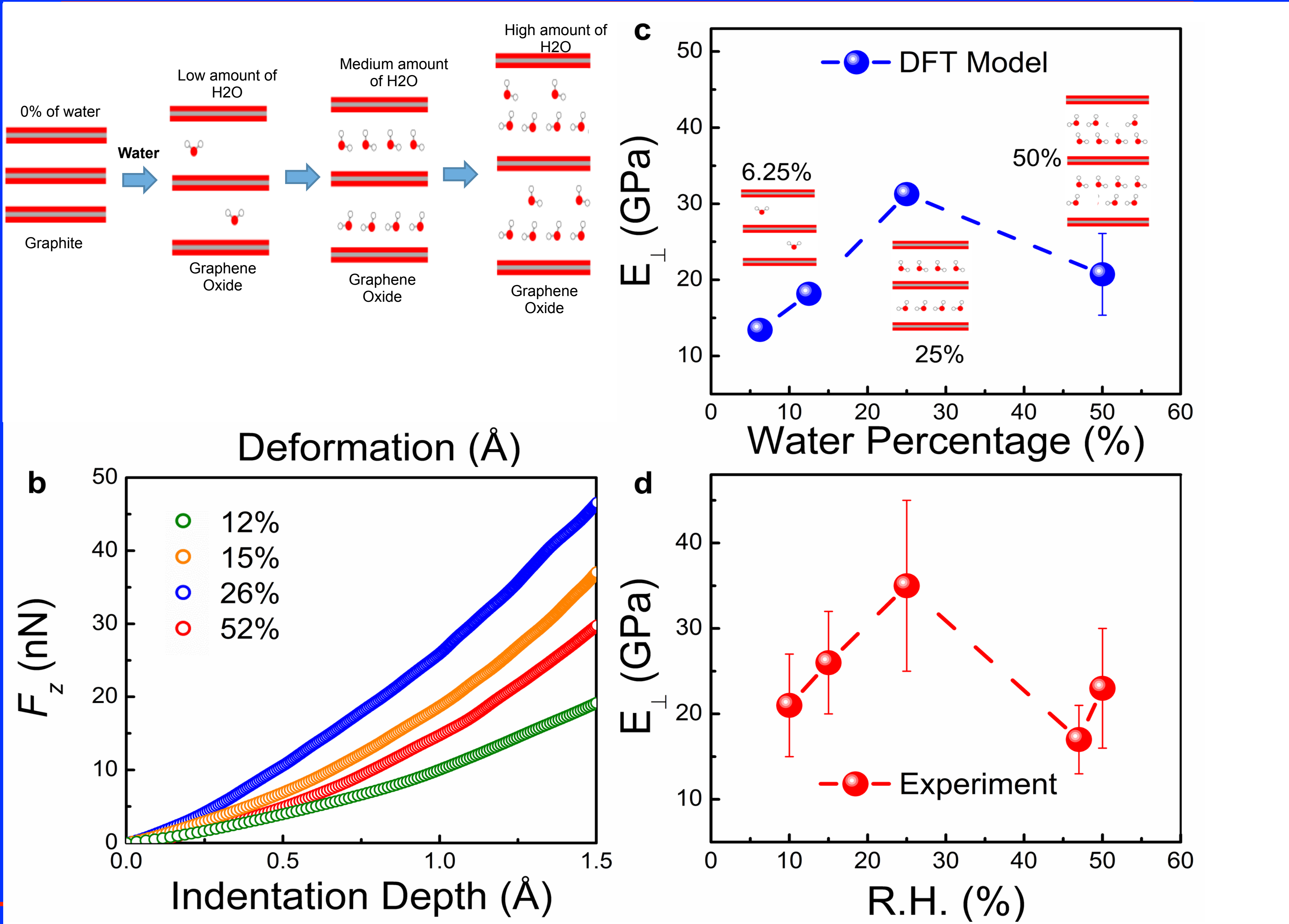
Conventional Graphene Oxide Flakes and Intercalated Water



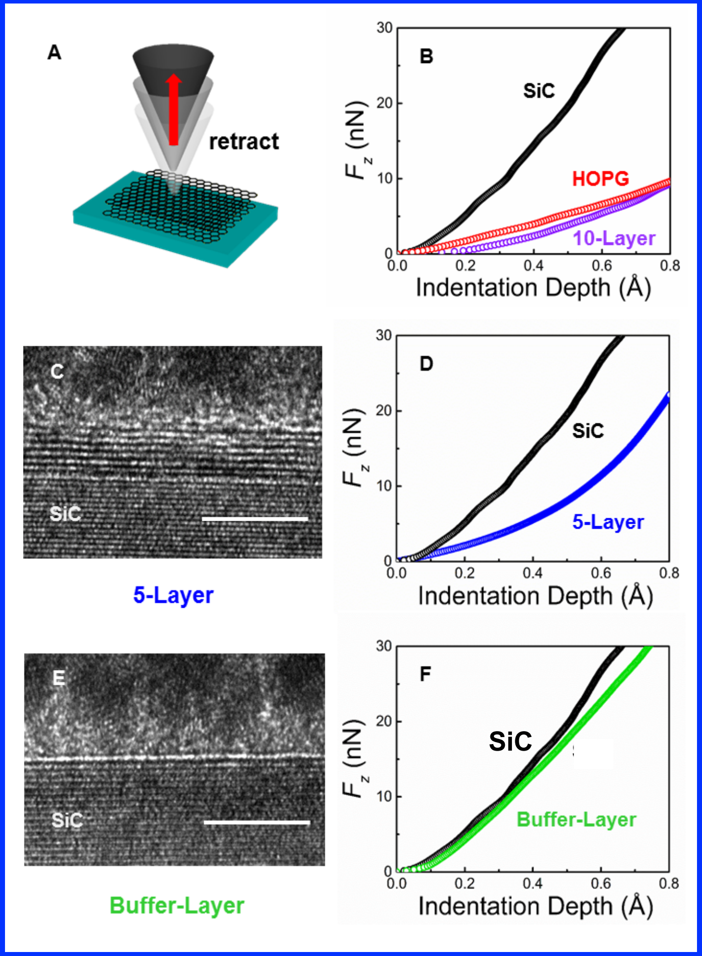
DFT Simulations from Bongiorno's group

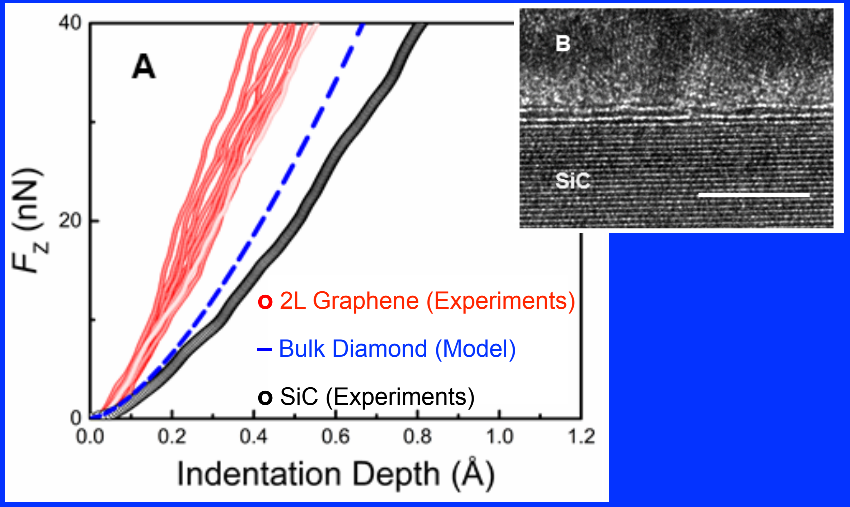


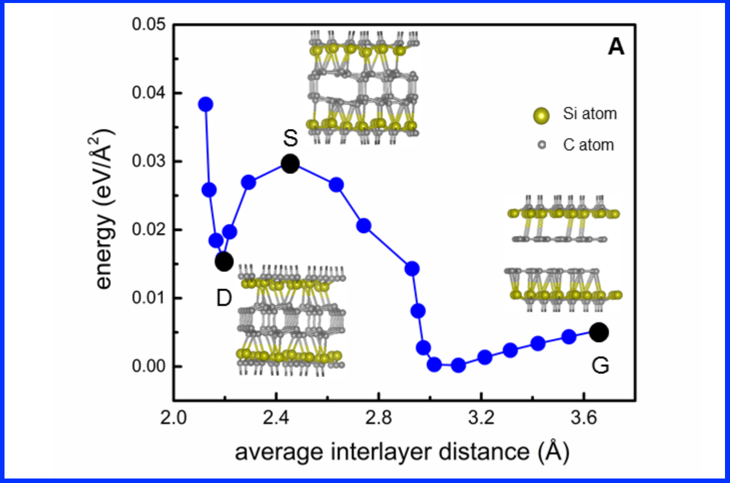
Graphene Oxide Interlayer Elasticity and Water



Inducing a diamond-stiff phase in two-layer graphene: the fingerprint of diamene





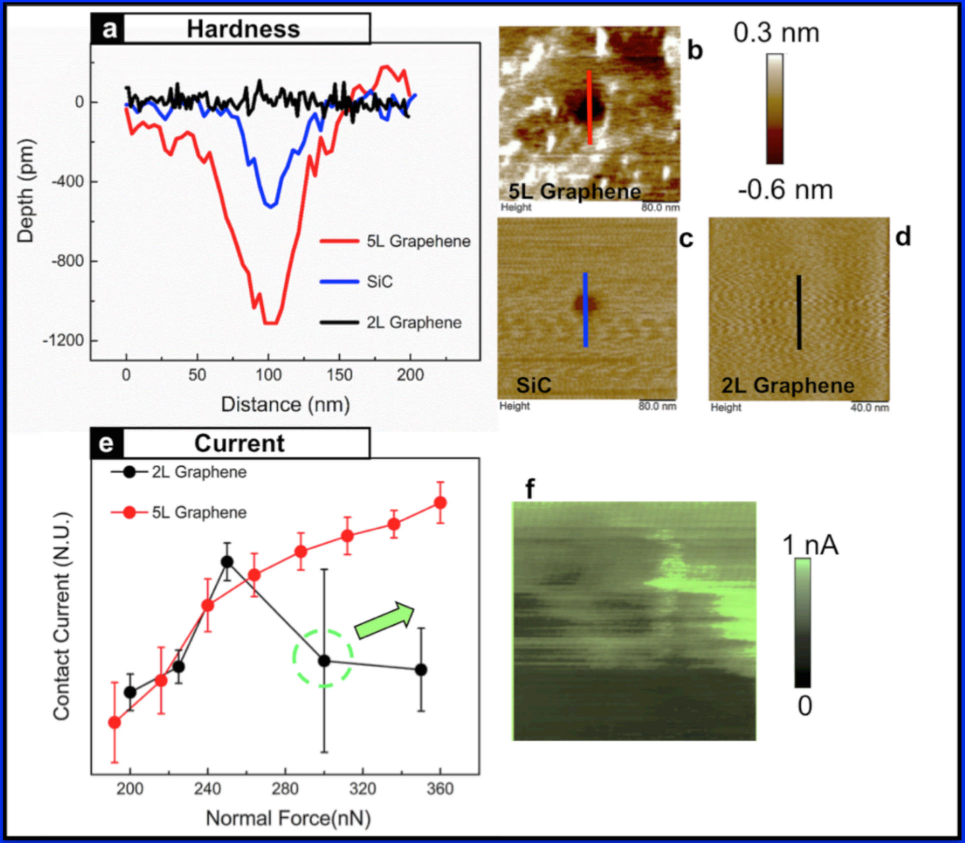


Under Review

Yang Gao*, Tengfei Cao*, Claire Berger, Walt de Heer, Tosatti, Angelo Bongiorno and Elisa Riedo

Inducing a diamond-stiff phase in two-layer graphene:

the fingerprint of diamene



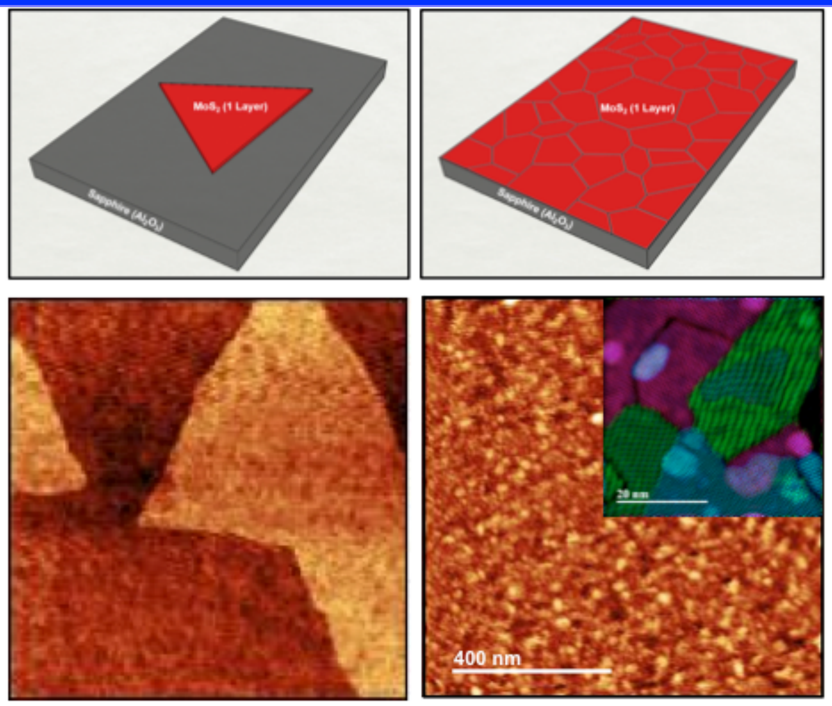
Under Review

Yang Gao*, Tengfei Cao*, Claire Berger, Walt de Heer, Tosatti, Angelo Bongiorno and Elisa Riedo

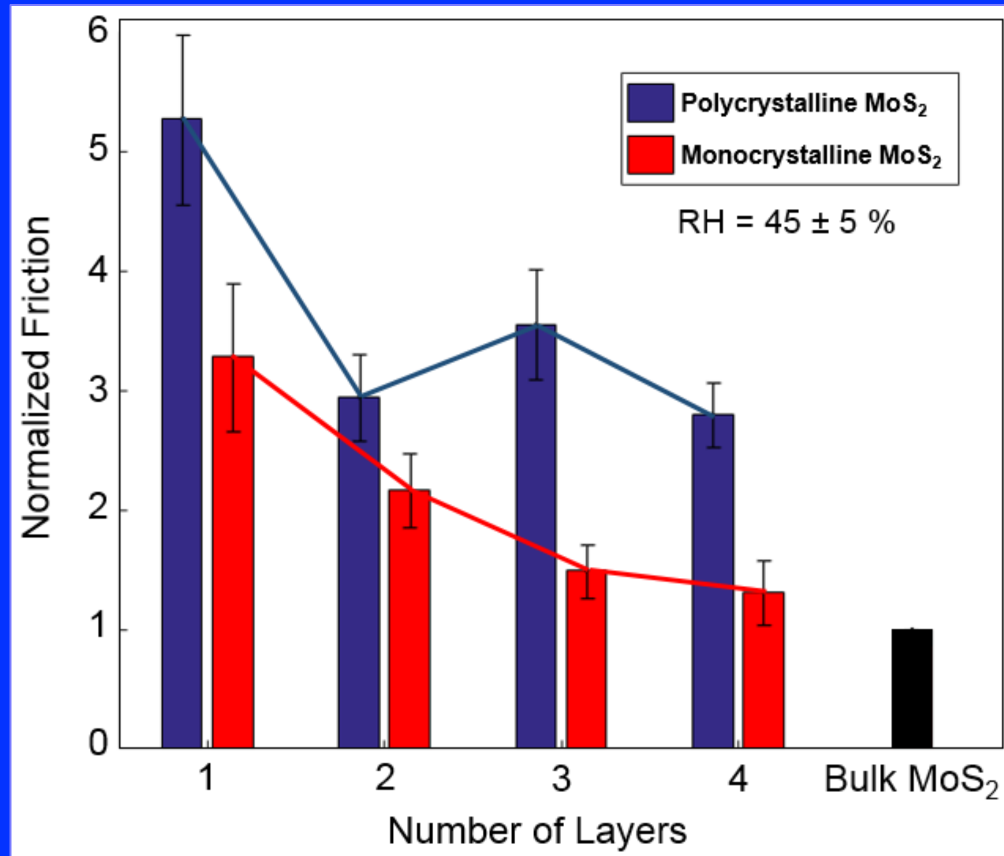
Oscillatory friction behavior

for even and odd number of layers

in polycrystalline MoS_2

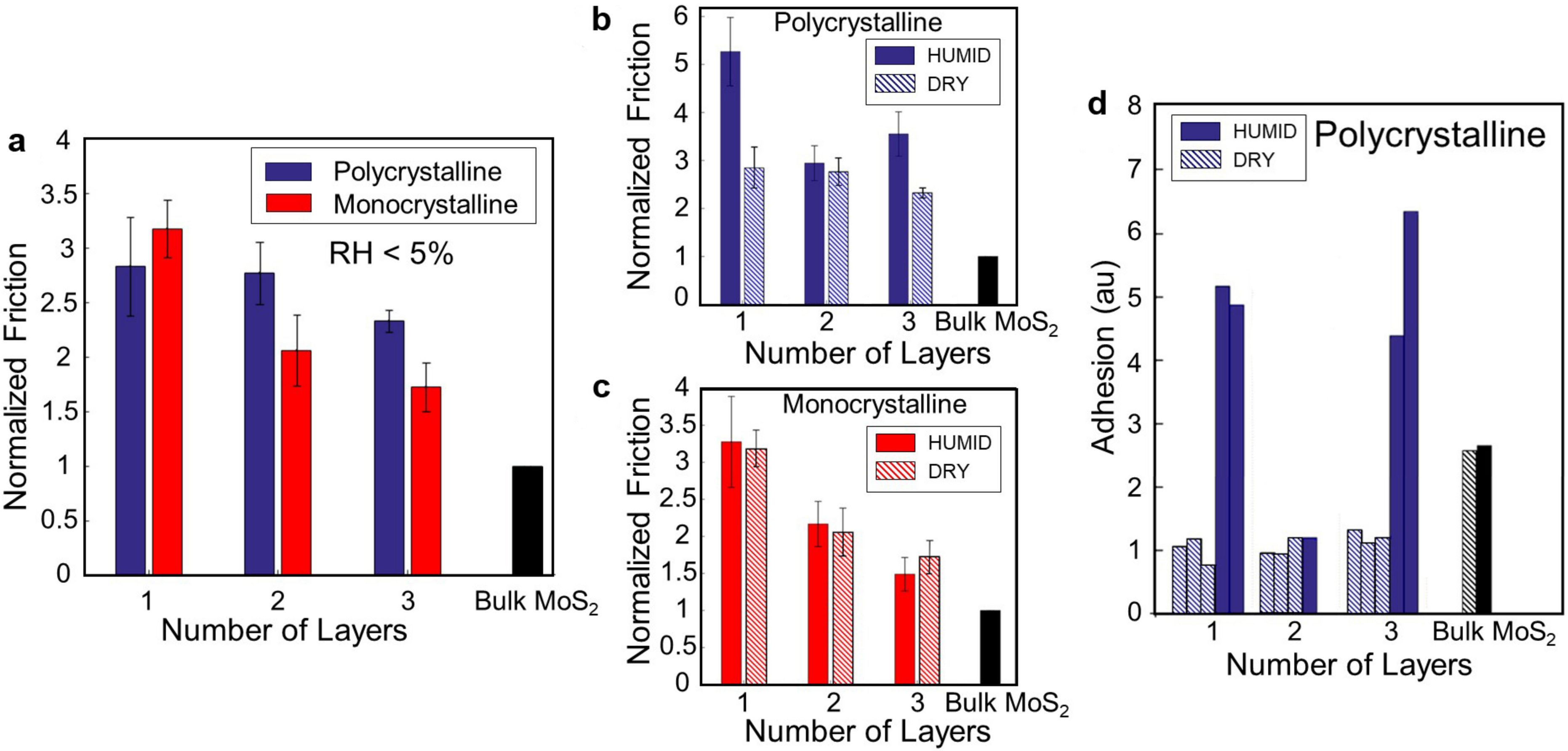


Monocrystalline MoS_2 Polycrystalline MoS_2



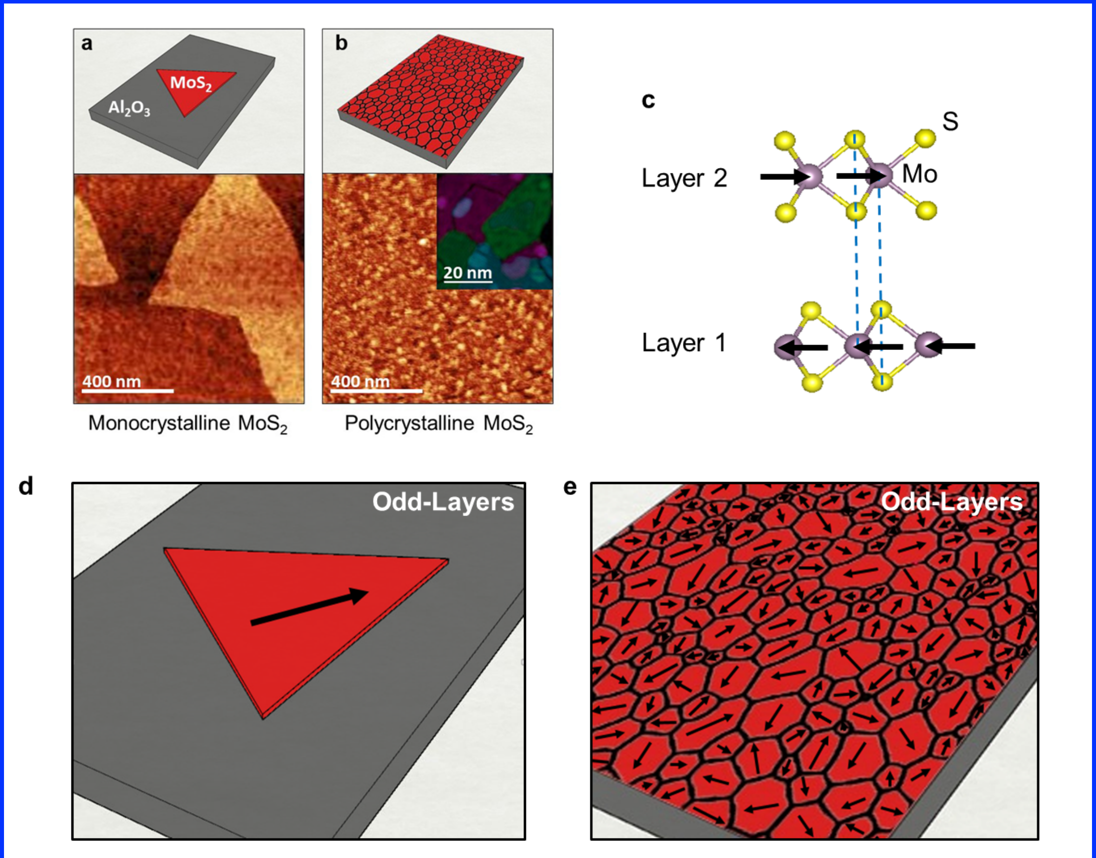
Broken Symmetry for 1 and 3 Layers:

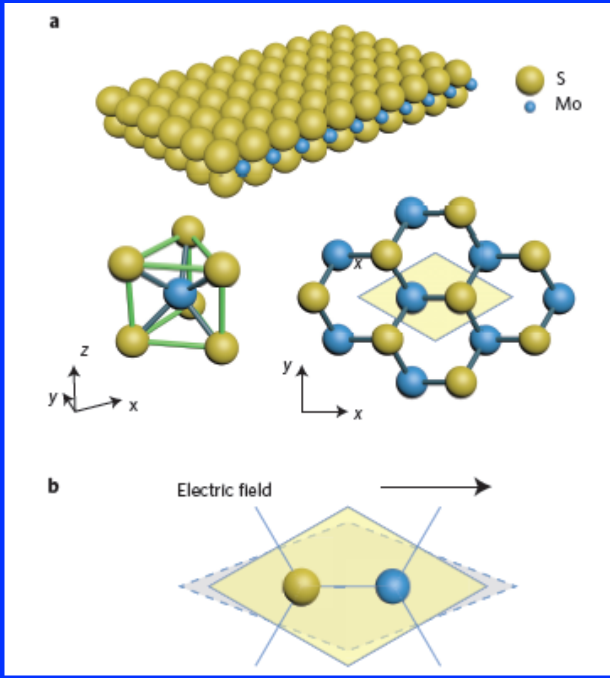
Permanent Dipole in the grains → Water Adsorbs more!



Broken Symmetry for 1 and 3 Layers:

Permanent Dipole in the grains → Charges at Grain Boundaries



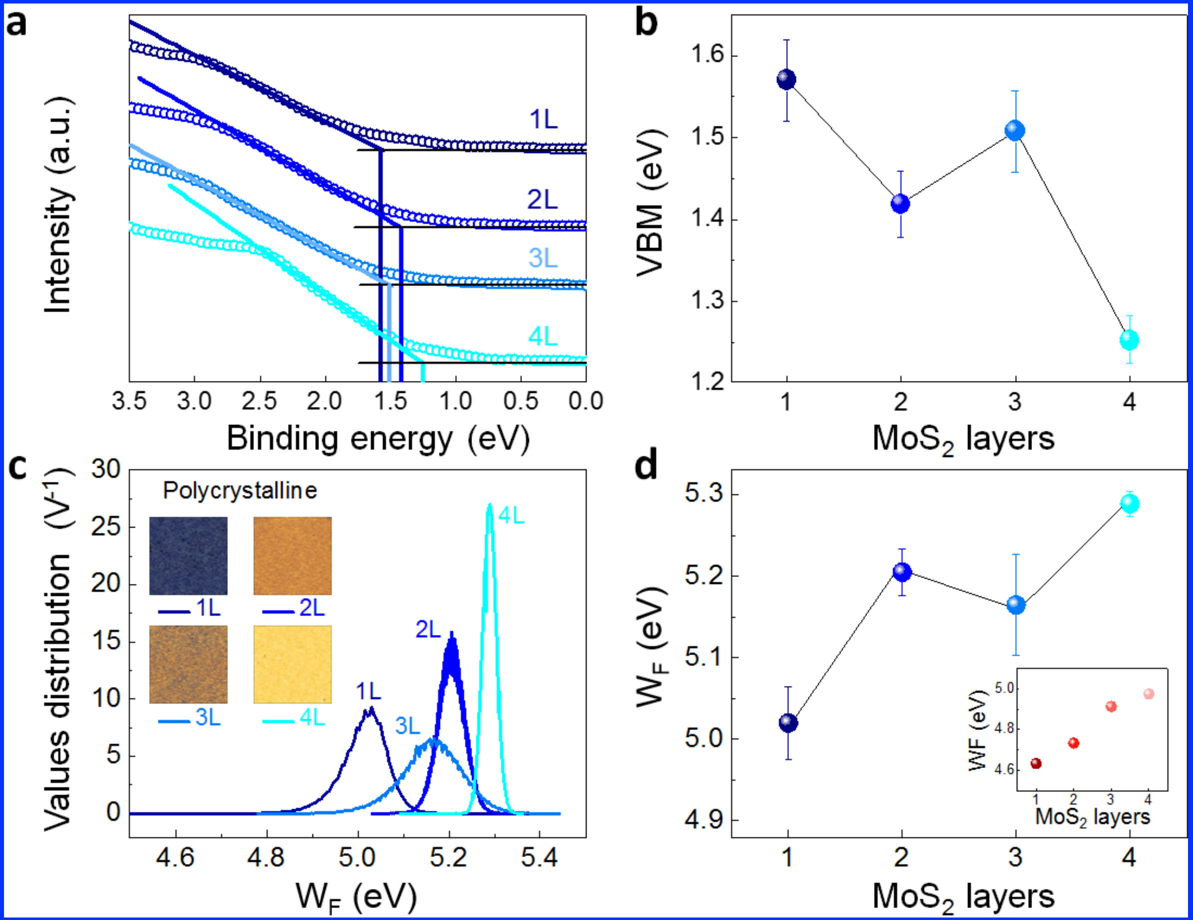


Submitted

Francesco Lavini, Annalisa Calo', Yang Gao, Edoardo Albisetti, Tai-De Li, Tengfei Cao, Linyou Cao, Carmela Aruta, and Elisa Riedo

Broken Symmetry for 1 and 3 Layers:

Permanent Dipole in the grains → Charges at Grain Boundaries



Submitted

Francesco Lavini, Annalisa Calo', Yang Gao, Edoardo Albisetti, Tai-De Li, Tengfei Cao, Linyou Cao, Carmela Aruta, and Elisa Riedo

Conclusions

★We can **measure Elastic Coupling and Van Der Waals** Interaction between atomic layers in 2D layered materials

★**Interlayer elasticity** is extremely sensitive to **intercalated molecules** e.g. water, in between the planes.

★Pressure Induced Room-temperature **diamond-stiff phase** in two-layer graphene: the fingerprint of diamene

★**Oscillatory friction** behavior for even and odd number of layers in polycrystalline MoS_2 → Permanent Dipole in the grains

Acknowledgments

Riedo Group

Yang Gao
Dr. Robert Szoszkiewicz
Dr. Debin Wang
Dr. Marcel Lucas
Dr. Tai-De Li
Dr. Soo-Young Kim
Dr. Suenne Kim
Dr. Douglas Chiu
Li Xu
Edoardo Albisetti

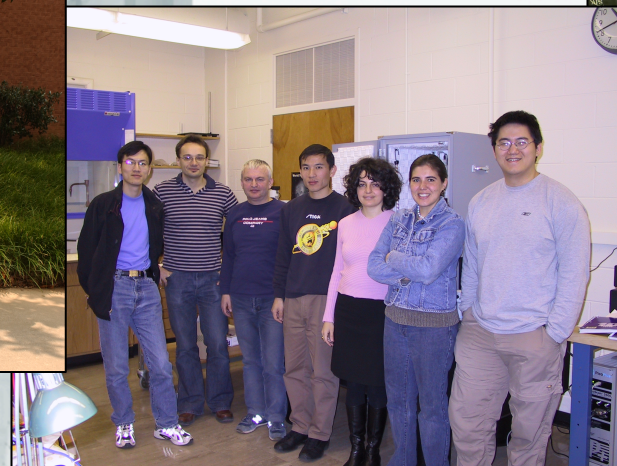
de Heer

Dr. Claire Berger
Yike Hu
Xiaosong Wu
Michael W. Sprinkle

Bongiorno

Si Zhou

Tosatti @ Sissa

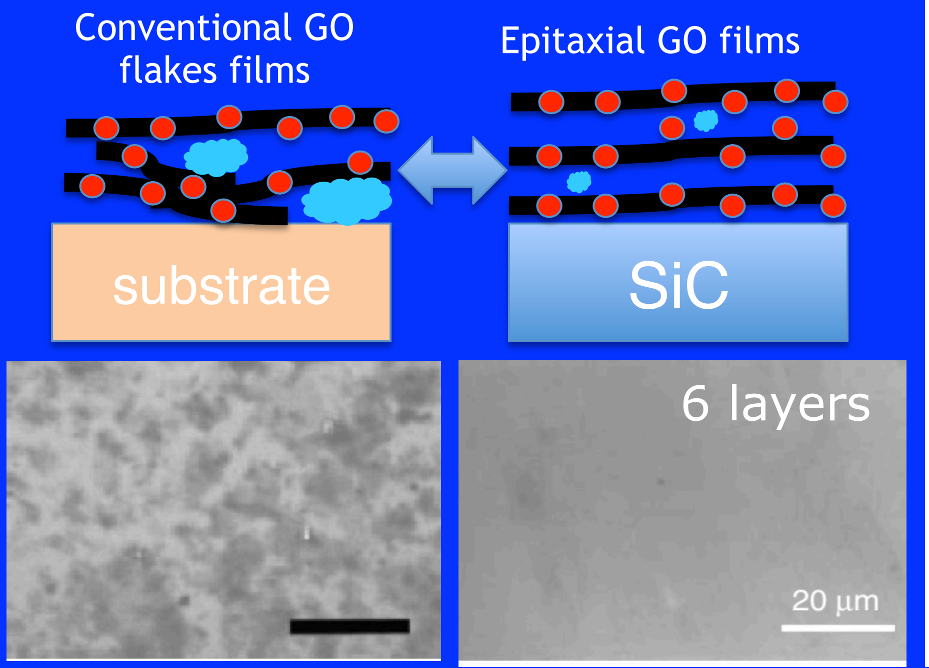



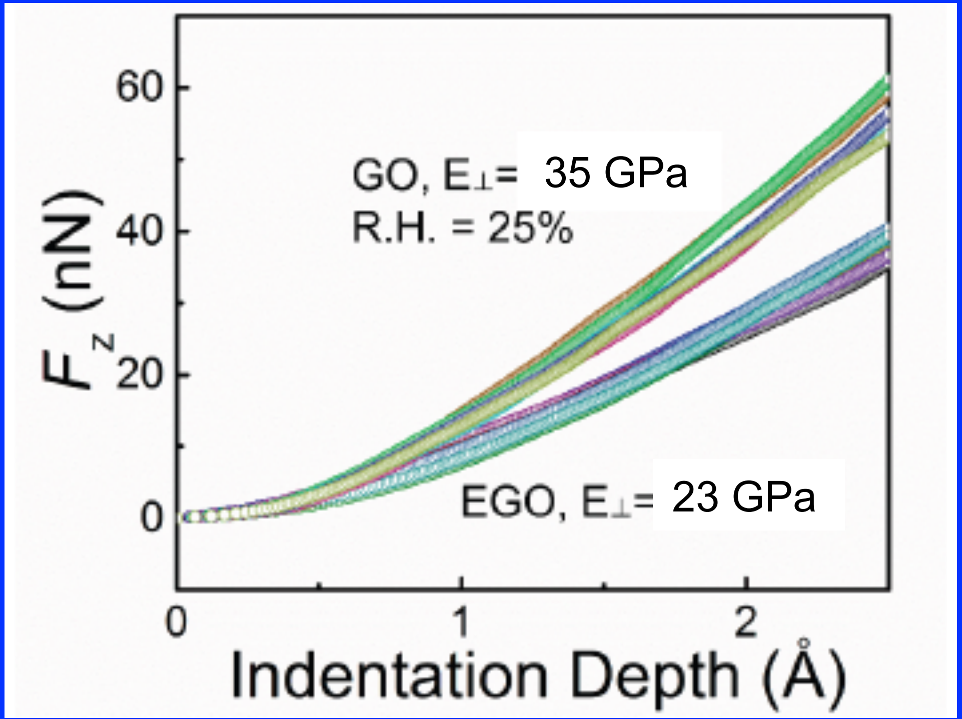


THANK YOU!

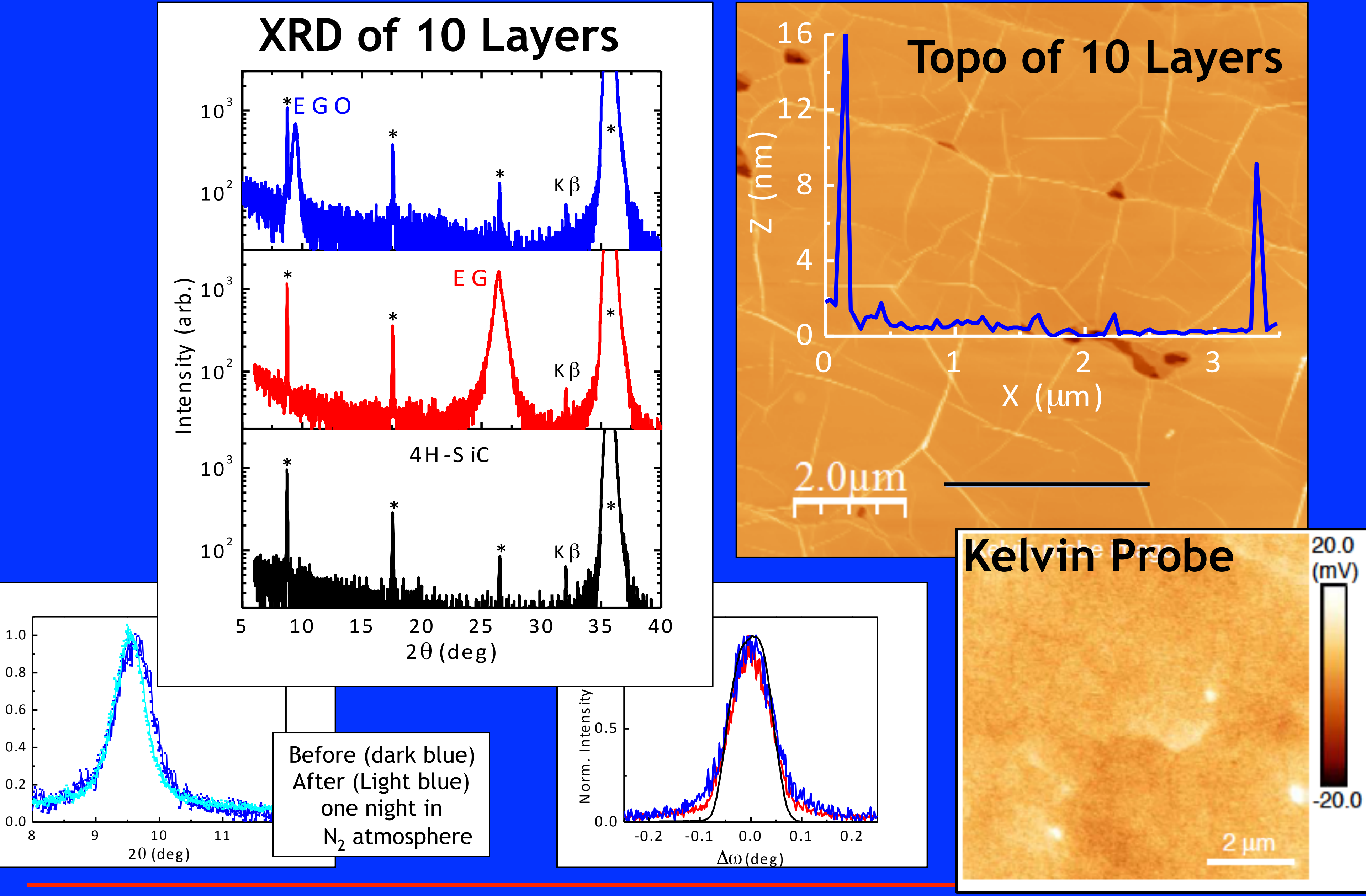
Graphene Oxide Interlayer Elasticity and Water

Relative Humidity		10 ± 2 %	15 ± 3 %	25 ± 3 %	35 ± 3 %	50 ± 3 %
$E_{\perp}$ (GPa)	10-layer EGO	22 ± 3	-	23 ± 4	19 ± 3	22 ± 3
	Conventional GO	21 ± 6	26 ± 6	35 ± 10	-	23 ± 7
	10-layer EG	-	-	36 ± 3	-	-
	HOPG	-	-	33 ± 3	-	-





Epitaxial Multilayer GO properties



Epitaxial Multilayer GO films

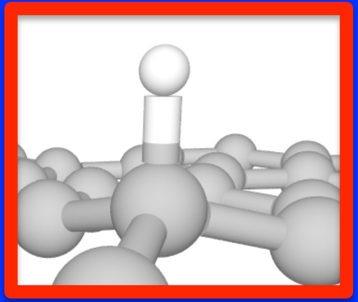
Summary

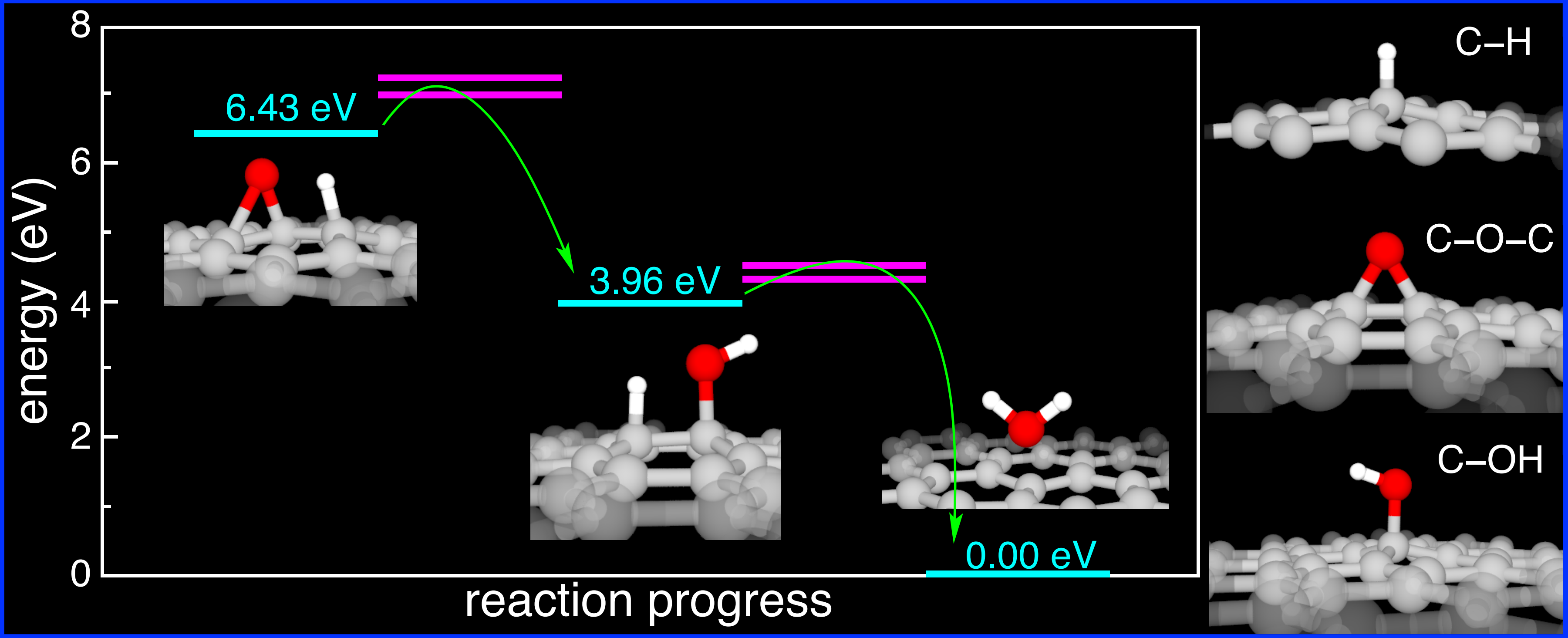
- Number of Layers : from 3 to 15
- Control over number of layers
- XPS shows about 0.4 O/C ratios
- No edges (no carboxyl groups)
- Little water, no more than 10% of C. As obtained from XPS, IR, XRD and Simulations
- Excellent Interlayer Registry
- Distance between the planes: ~ 9.3 A

→ How can we explain d=9.3A with so little water?

Origin of the room-temperature metastability of GO:

KEY ROLE of C-H groups!

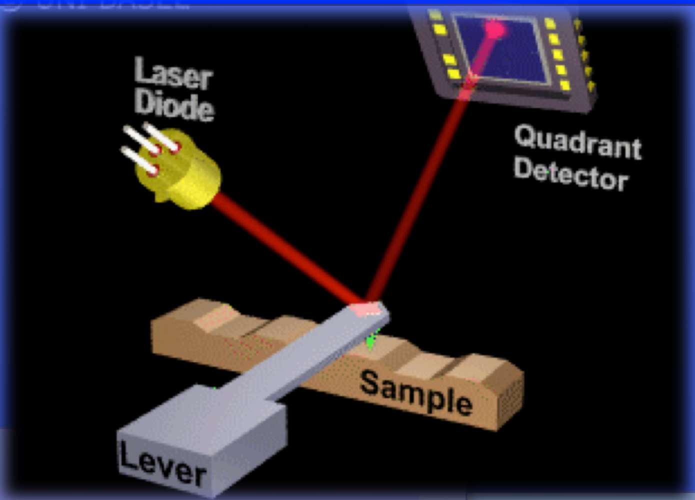


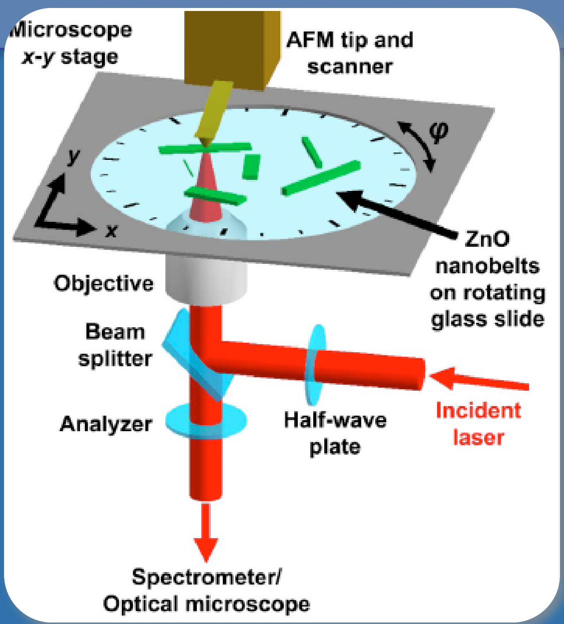


Nature Materials **11**, 544 (2012)
J. Phys. Chem. C **117**, 6267 (2013)

Experimental methods

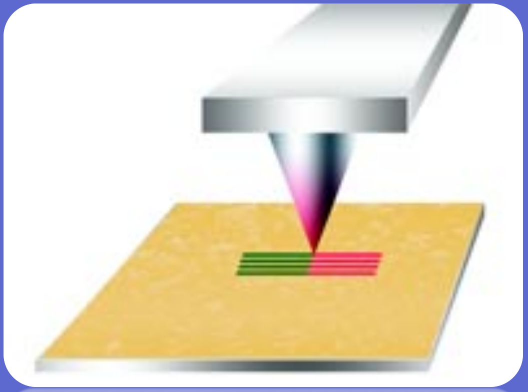
Atomic Force Microscopy (AFM):
- Topography
- Local electronic and magnetic properties
- Nanoscale Friction
- Nano-elasticity
- Nanoconfined Fluids





Combined AFM-Optical Spectroscopy

SPM-Based Nanofabrication



Facilities:
- XPS
- IR
- X-Rays
- Etc…