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THE STATE UNIVERSITY OF NEW JERSEY

Opto-electronic Properties of Graphene Oxide and Partially Oxidized Graphene

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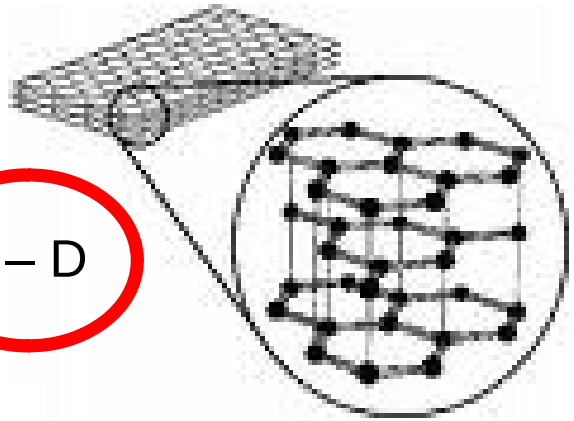
Forms of Carbon

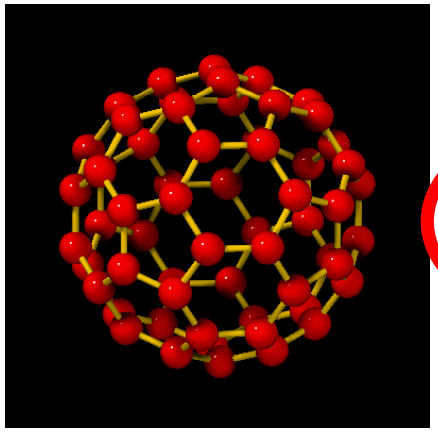
Diamond, circa 4000 BC
In India

Graphite, ~ 1550
Great Britain



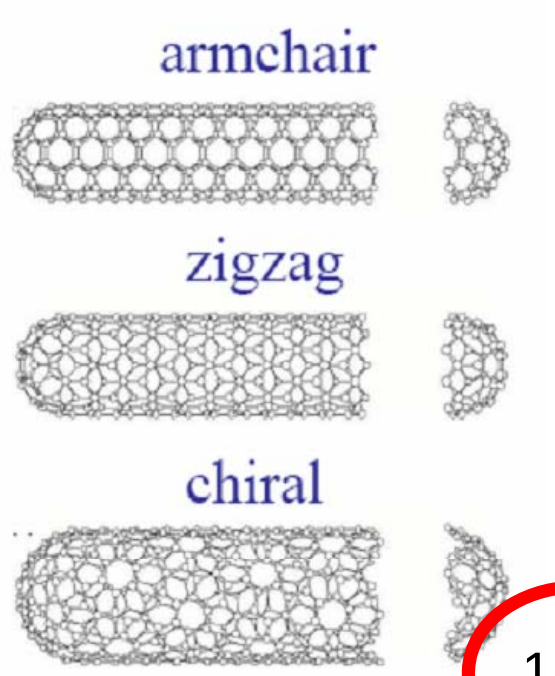
3 – D

C60, 1985



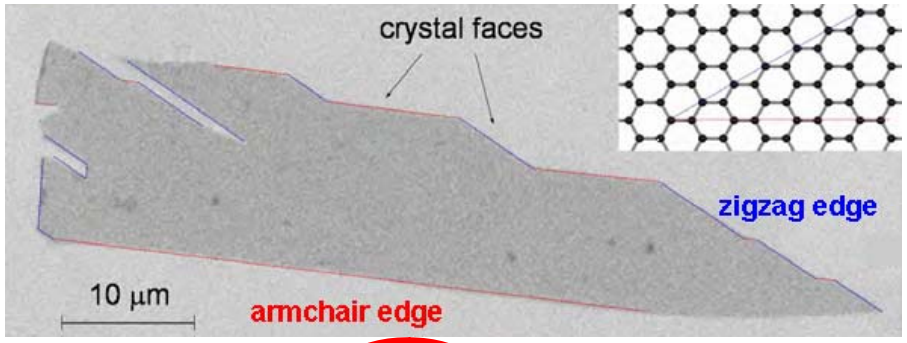
0 - D

SWNTs in 1993



1 - D

Graphene, 2004



2 - D

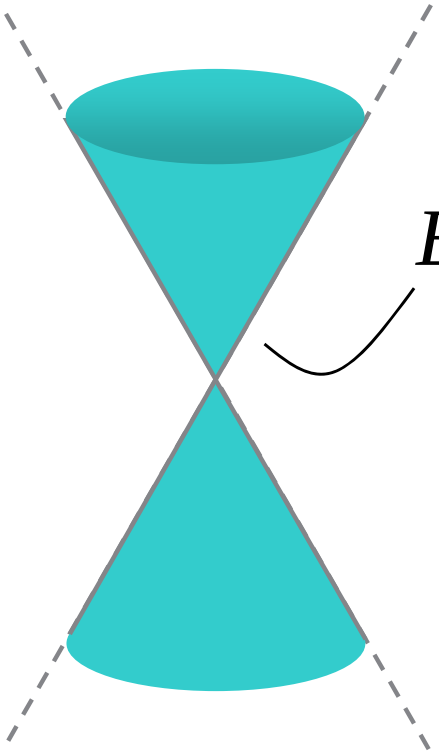
?

Electronic structure of graphene

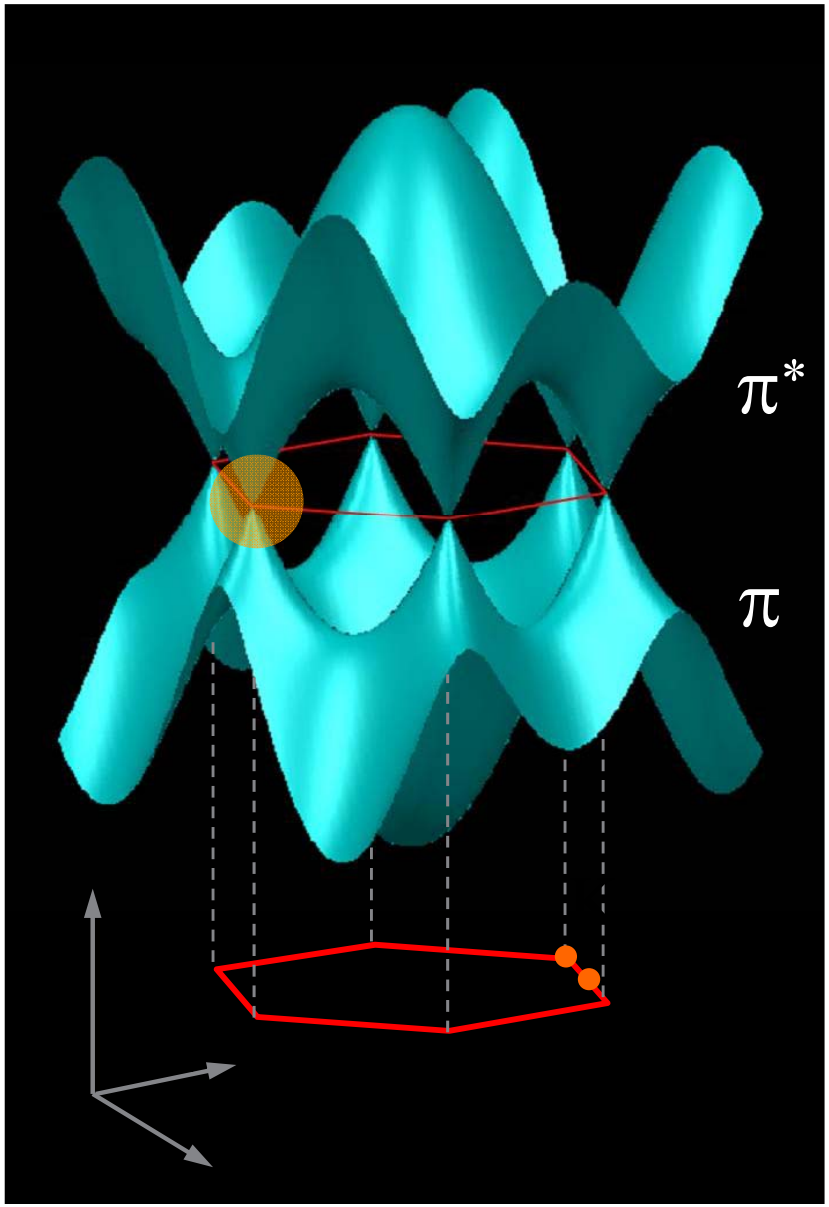
Dispersion relation using Tight Binding:

$$E(k_x, k_y) = \pm\gamma_0\left[1 + 4\cos\left(\frac{\sqrt{3}k_x a_{C-C}}{2}\right)\cos\left(\frac{k_y a_{C-C}}{2}\right) + 4\cos^2\left(\frac{k_y a_{C-C}}{2}\right)\right]^{1/2}$$

Dirac cone

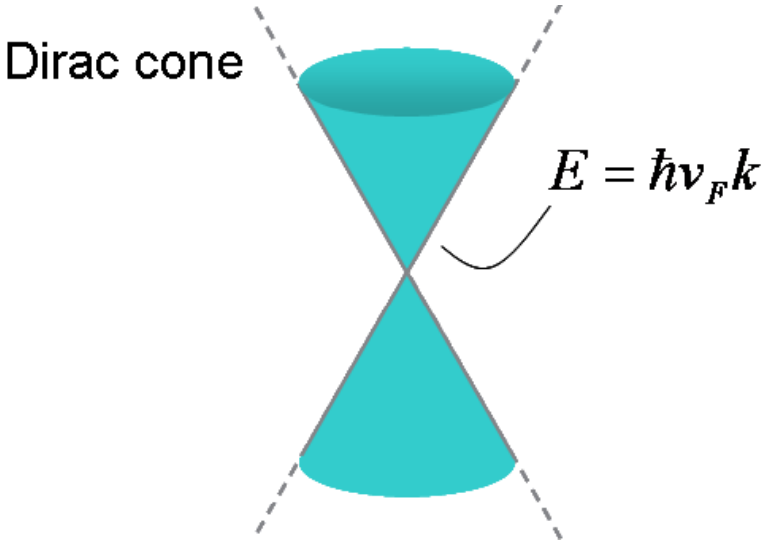


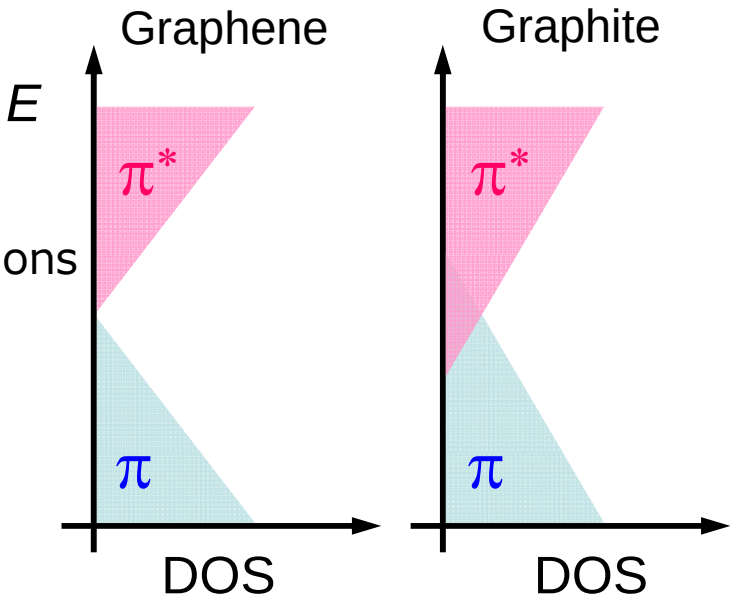
$$E = \hbar v_F k$$



Why Graphene?

- Chemical, mechanical, and thermal stabili
- 0 eV band-gap semiconductor
  - Ambipolar field effect transistors
- Extraordinary mobility
  - Room temperature mobility of ~10,000 cm^2/
- High current carrying capability
  - Electrons and holes up to 10^{13}/cm^2
- Exotic physical properties
  - Relativistic charge carriers – massless Dirac Fermions
  - Unusual quantum Hall effect
  - Ballistic transport





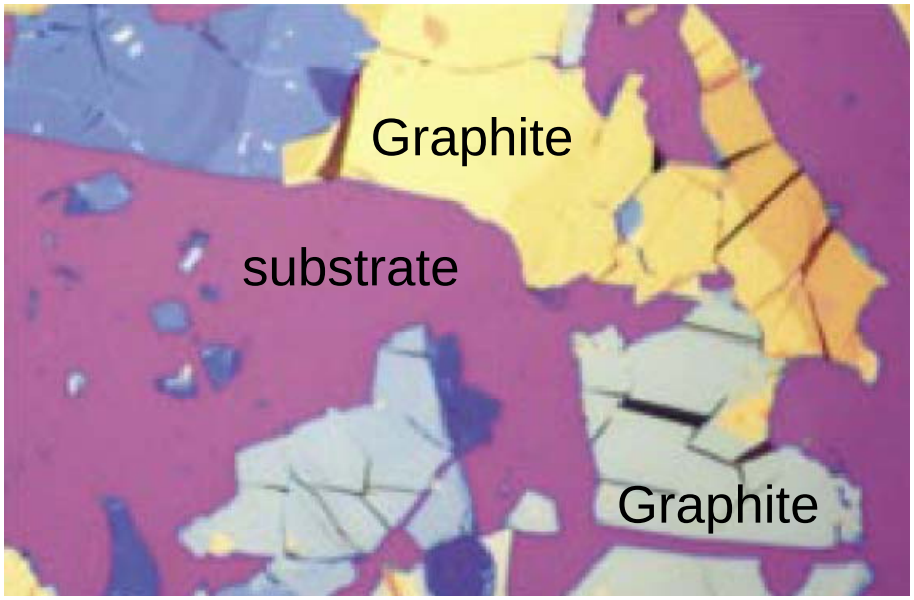
Graphene: Challenges

Graphene science is exciting...

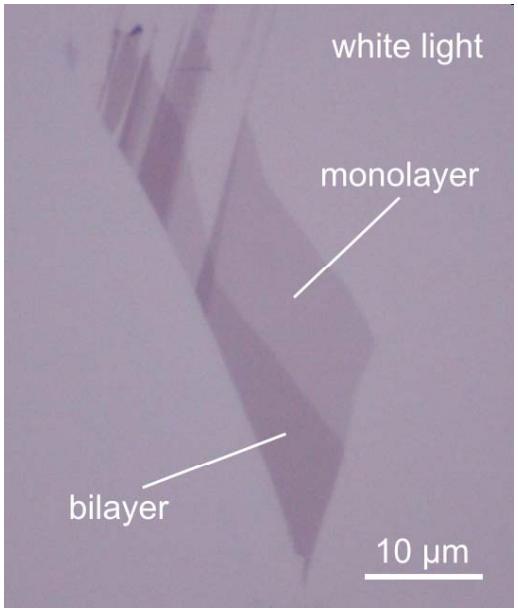
Graphene properties are remarkable...

BUT for technological implementation

- Technologically viable deposition method
- Control over deposition areas
- Choice over substrate
- Control over the number of graphene layers
- Reliable growth method

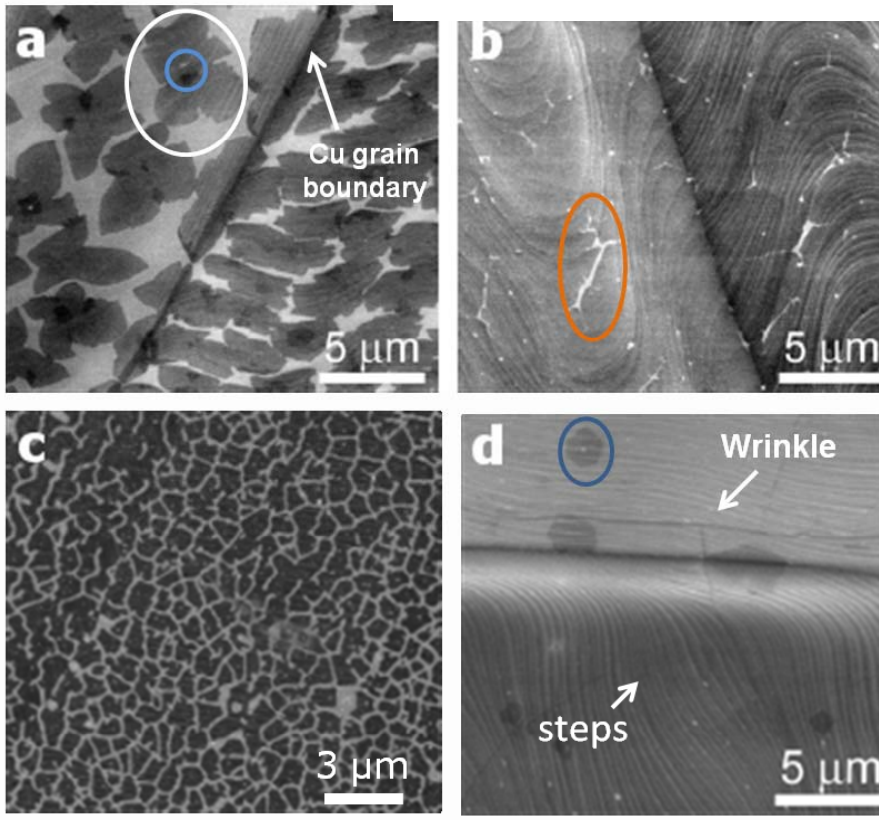


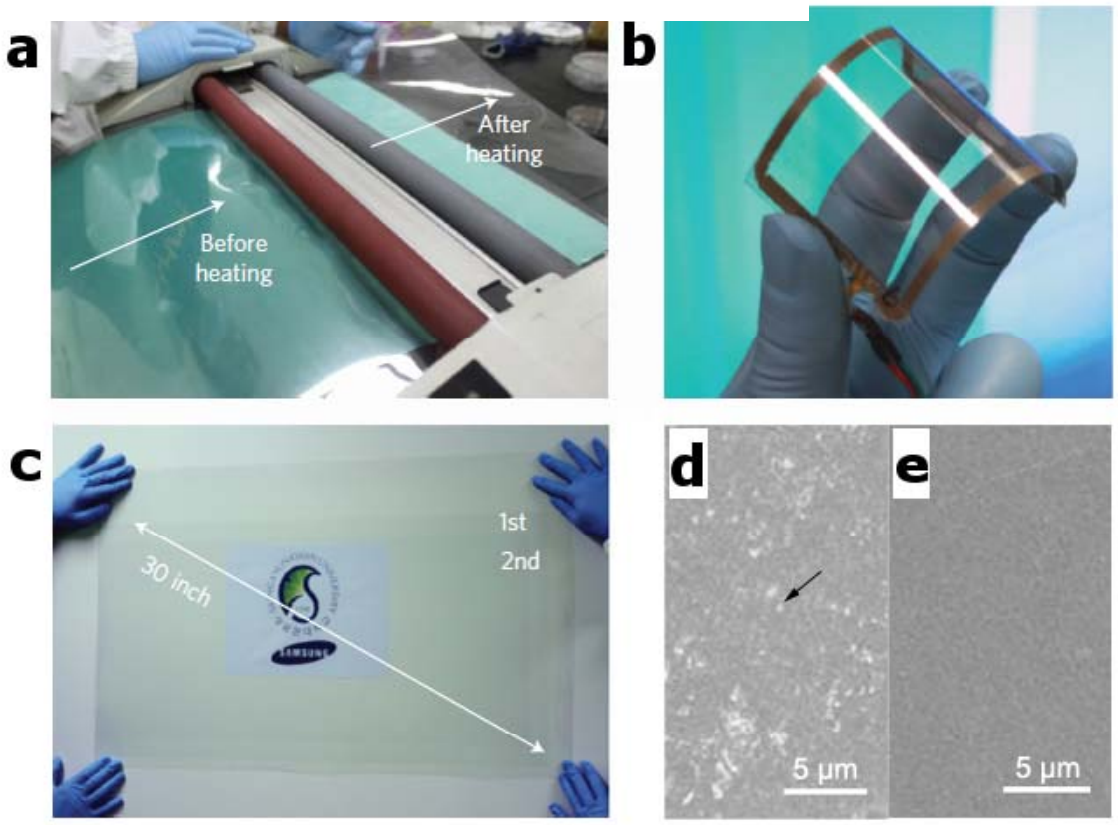
Geim and Kim *Scientific American* (2007)



www.grapheneindustries.com

Graphene on Copper

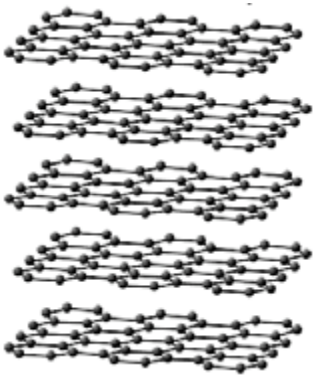




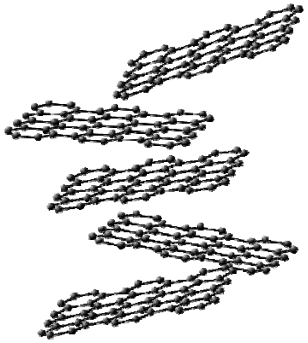
Li et al, Science (2009)

B H Hong Group, Nature Nano (2010)

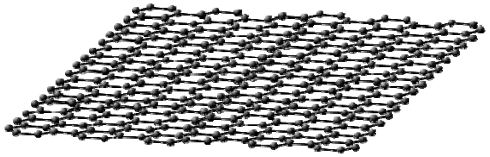
“Graphene Inks?”



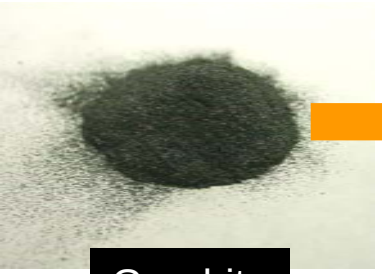
Graphite



Exfoliation

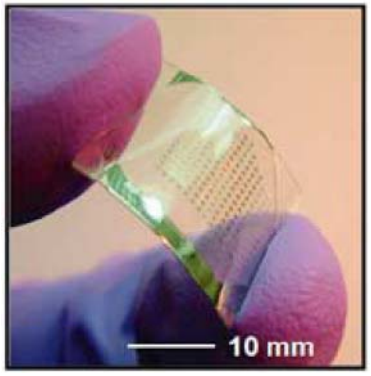


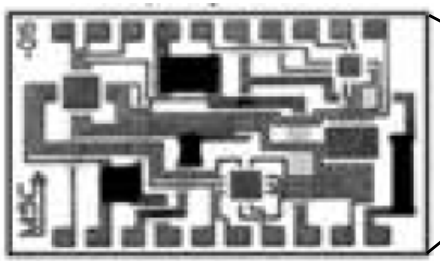
Thin film deposition

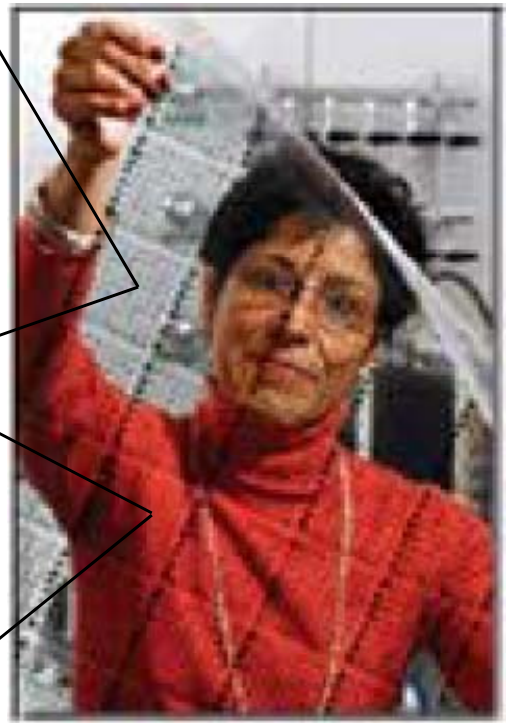


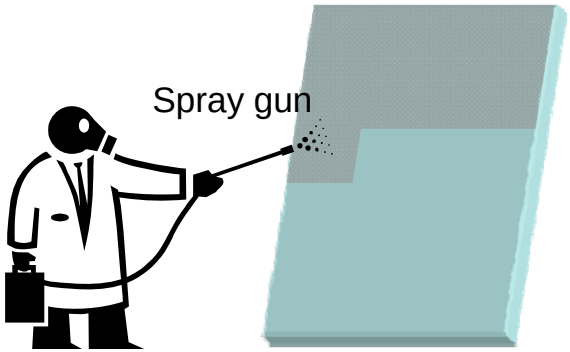
Graphite

“Graphene ink”







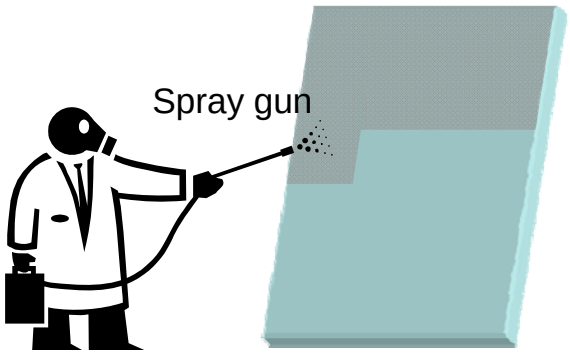


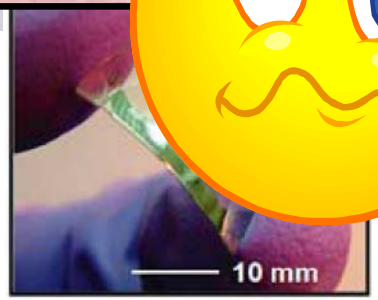
“Solution-based deposition”

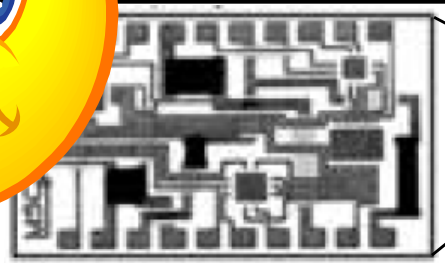
Reuss *et al. Proc IEEE* **93** (2005) 1239

“Graphene Inks?”

Graphite is insoluble!!







“Solution-based deposition”

Reuss *et al. Proc IEEE* **93** (2005) 1239

Graphite oxide

XIII. *On the Atomic Weight of Graphite.* *By* B. C. Brodie, *F.R.S., Professor of Chemistry in the University of Oxford, and President of the Chemical Society.*

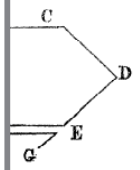
Received May 12,—Read May 12, 1859.

The term Graphite has been indiscriminately applied to many varieties of native carbon of very different properties. The graphite of New Brunswick differs but little in appearance from anthracite coal. The graphite of Greenland is not very dissimilar, but possesses rather more metallic lustre. However, among these varieties of carbon, two may be especially distinguished,—by a superior degree of metallic lustre, by their structure, and other well-defined properties. In the following paper, the term Graphite is limited to these two varieties, which may be further distinguished as "lamellar" and "amorphous."

These crystals, when examined with the microscope, are perfectly transparent, and exhibit beautiful colours by the agency of polarized light. Professor Miller of Cambridge, who was good enough to examine them, has communicated to me the following observations:—"The crystals, though not absolutely too small to be measured, are too thin and too imperfect to admit of measurement with the reflective goniometer. I have examined them under a microscope, for the purpose, if possible, of making out at least the system of crystallization to which they belong. Their system appears to be either

cleavage in that direction. The crystals are so extremely thin in a direction perpendicular to the paper on which the above figure is traced, that it is impossible to obtain any reflexion,

stals appear



except from the faces parallel to the plane of the paper."

Brodie Phil Trans Roy Soc (1859)

What is Graphene Oxide?

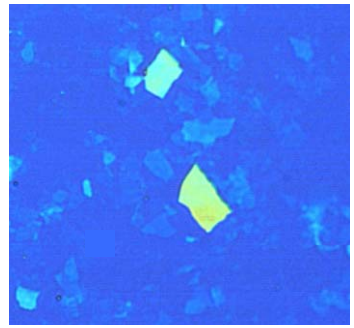
Graphite powder

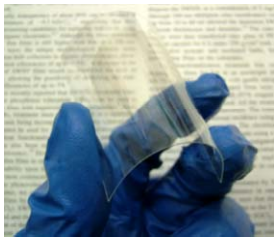
~ $2/kg

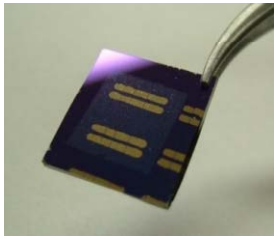
Graphite oxide

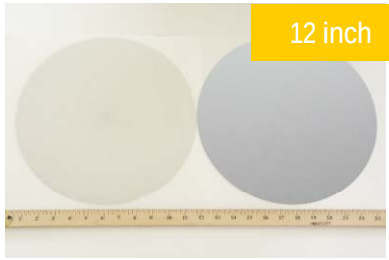
Graphene oxide
Colloidal suspension

GO: thin films









Some of Our Contributions:
Nature Nanotechnology 3, 270 (2008)
Nano Letters 9, 1058 (2009)
Adv Funct Mat 19, 2577 (2009)
ACS Nano 4, 524 (2010)
Nature Chemistry 2, 581 (2010)
Advanced Materials 22, 2392 (2010)
Nature Materials, 9, 840 (2010)
Nature Chemistry, 2, 1015–1024 (2010)
Adv. Mat. DOI:10.1002/adma.201004161. (2011)

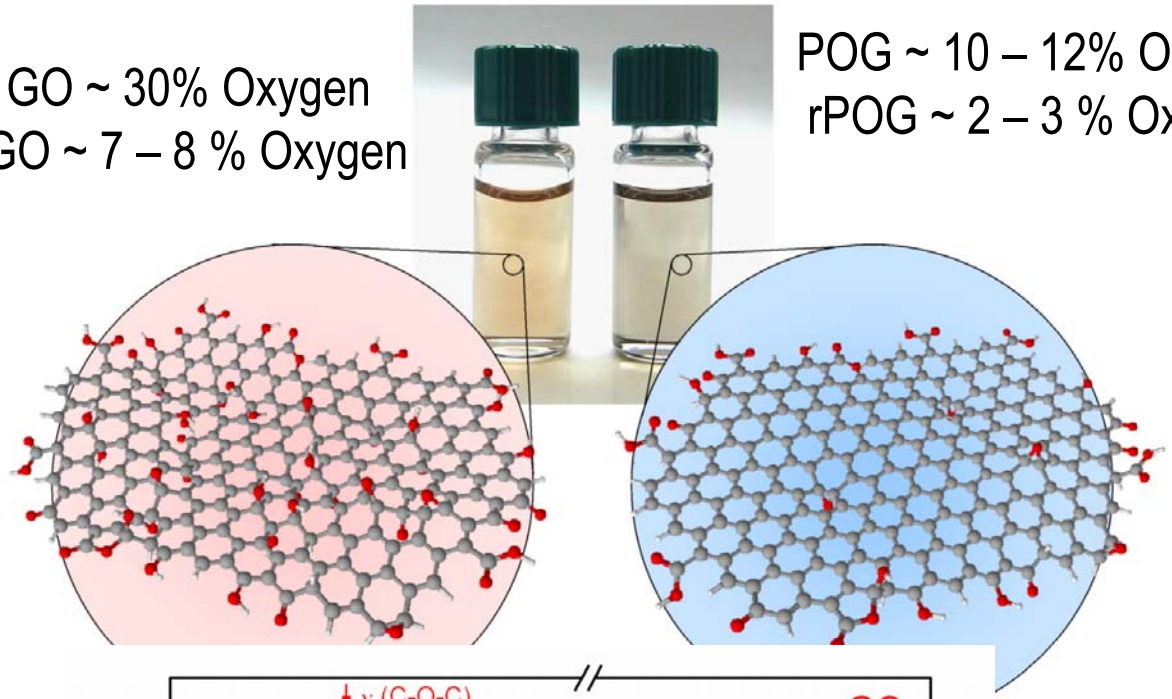
OXIDATION: Hummers-Offeman (1958)
($NaNO_3$, $KMnO_4$, H_2SO_4)

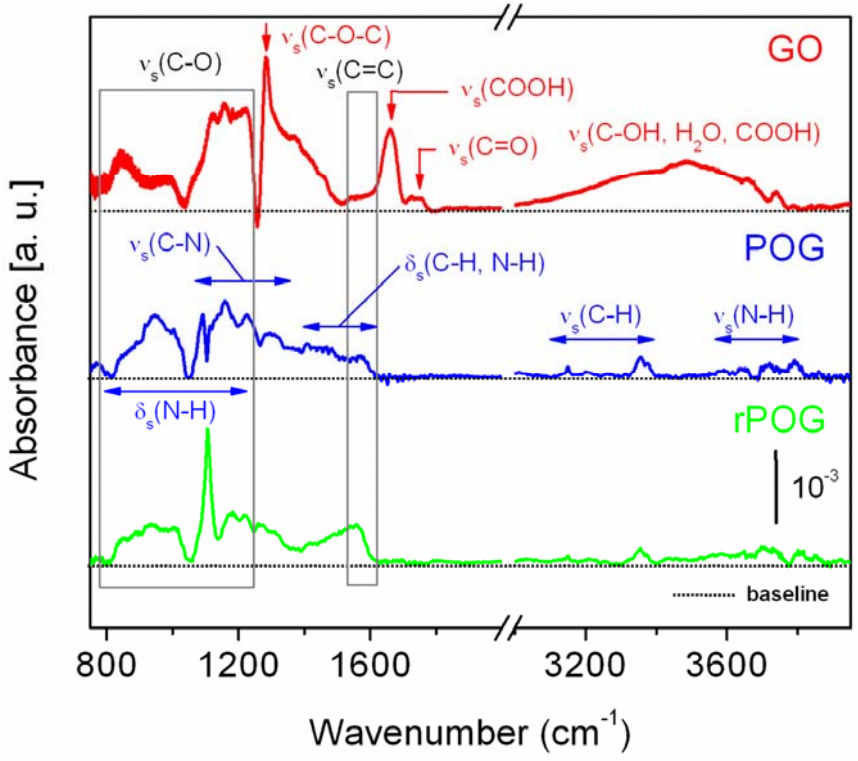
Brodie (1859)
Staudenmier (1898)
Hofmann-Frenzel (1930)
Hofmann-Konig (1937)
Ruoff et al. (2006)

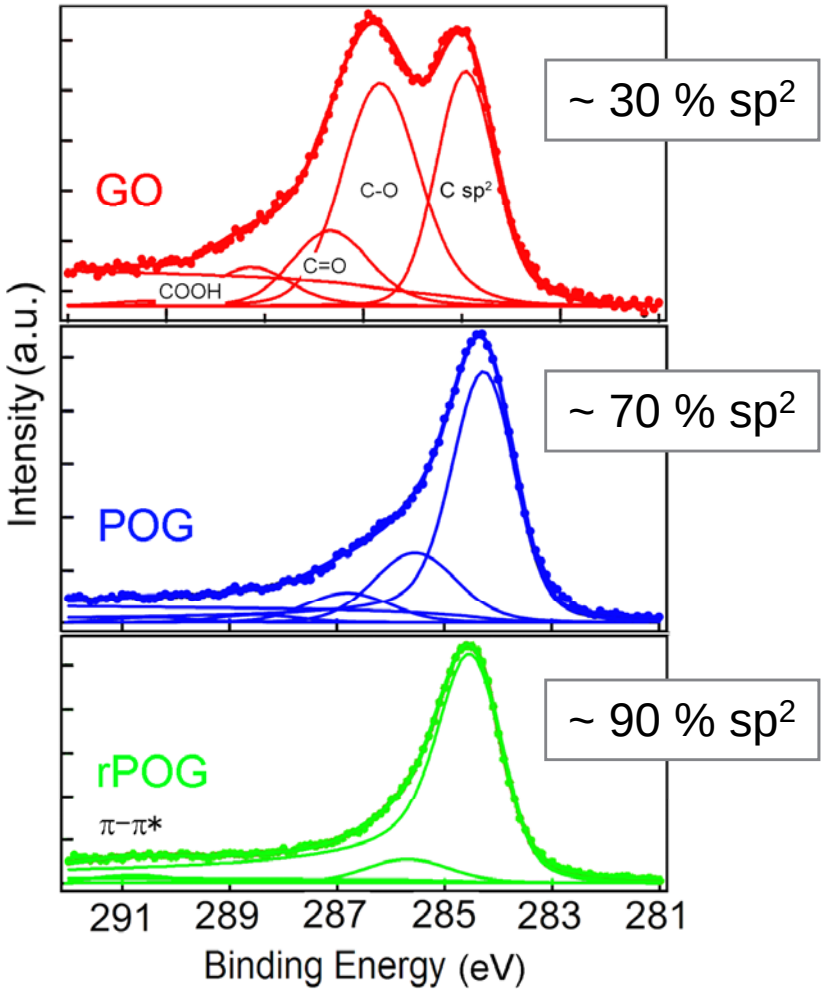
Variable Oxidation

GO ~ 30% Oxygen
rGO ~ 7 – 8 % Oxygen

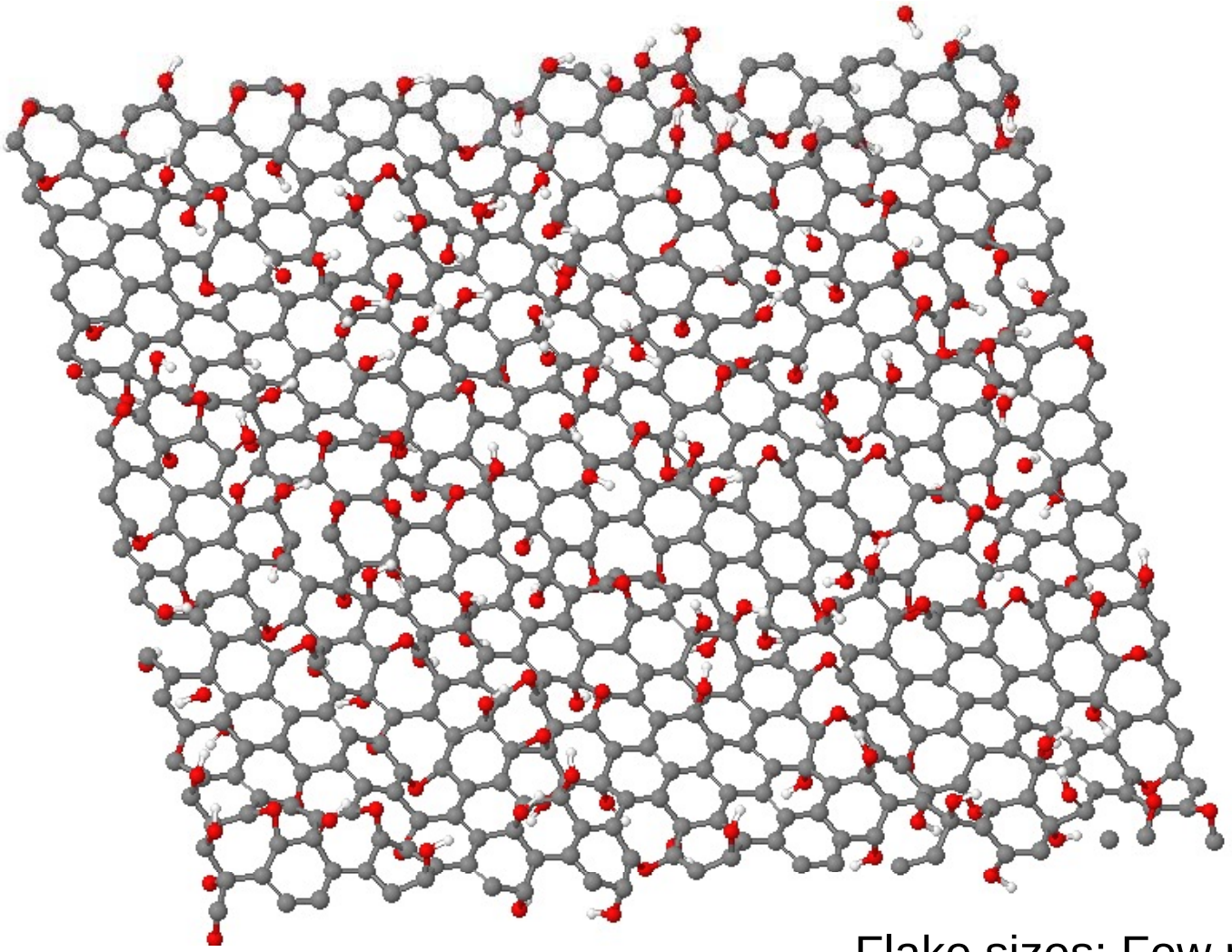
POG ~ 10 – 12% Oxygen
rPOG ~ 2 – 3 % Oxygen

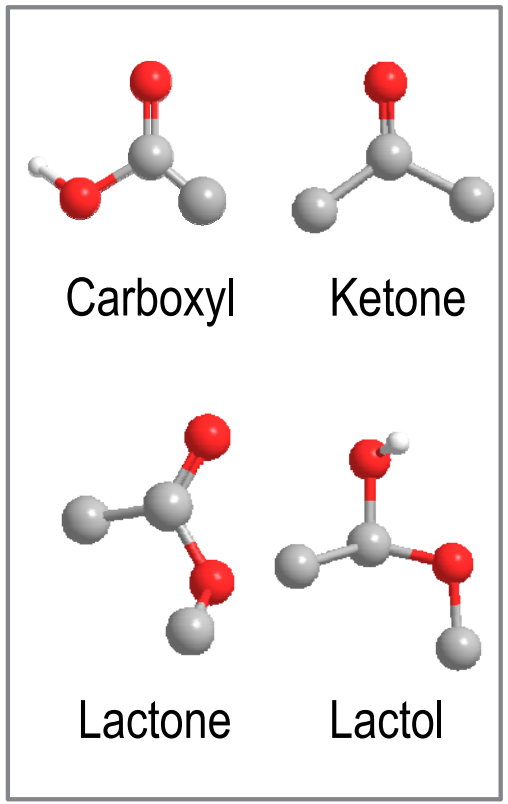






Graphene Oxide





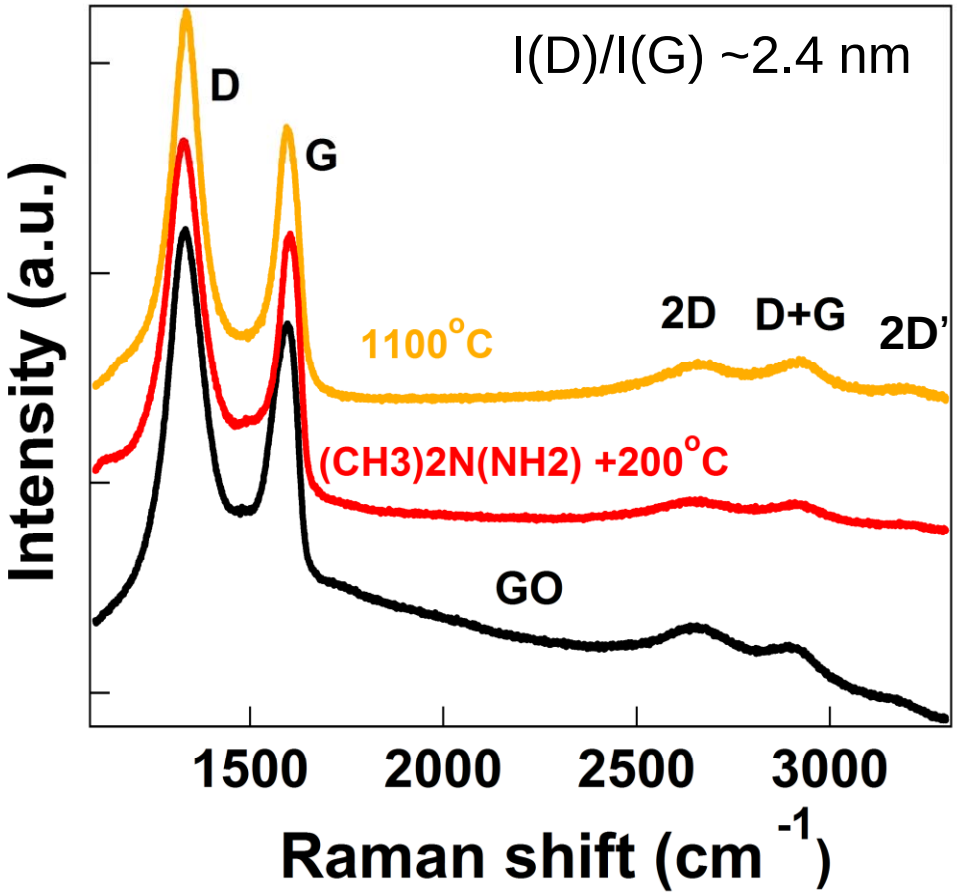
Flake sizes: Few microns up to 100μm.

1. As- Synthesized GO: sp^3 = 60%
2. Solution Processable
3. Can be produced in ton quantities

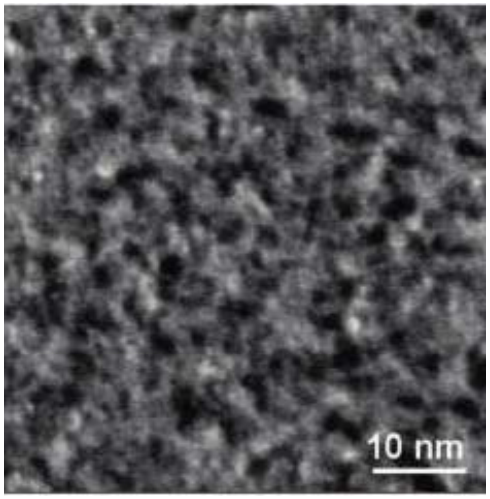
Nature Chemistry 2, 581 (2010)

Structure of GO

Distribution of oxygen in GO is highly non-uniform, with approximately 2-3 nm domain of very high oxidation and sparse oxidation

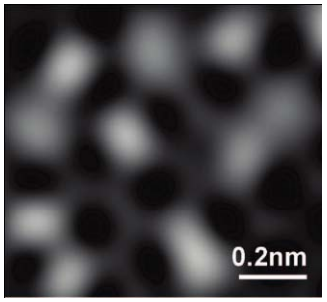


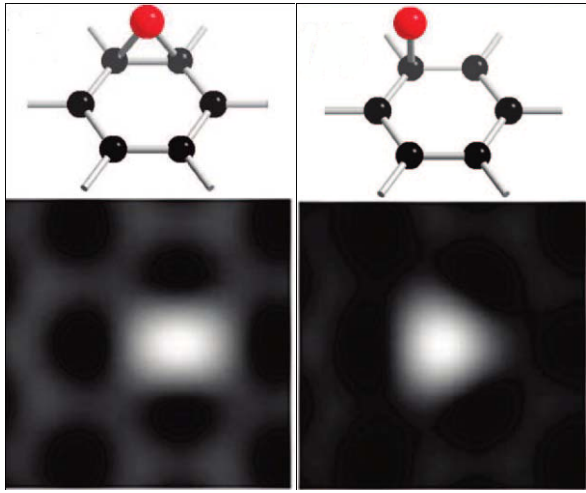
Mattevi, C. *et al. Adv. Funct. Mater.* 19, 2577-2583 (2009)



High-magnification Annular Dark Field image of monolayer GO

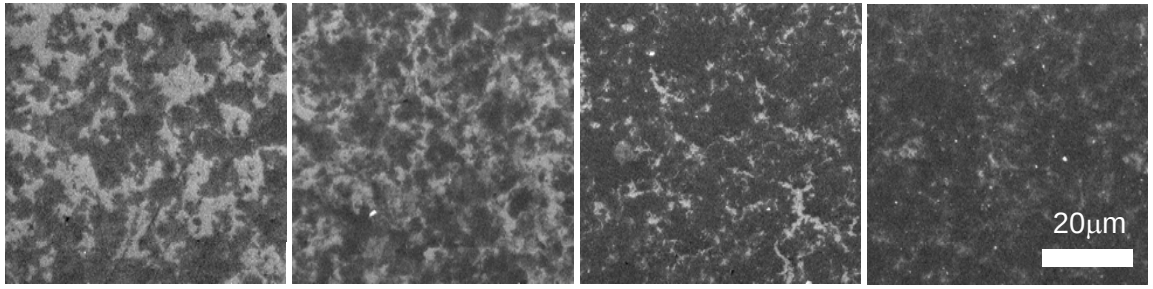
Simulation by multislice computational method



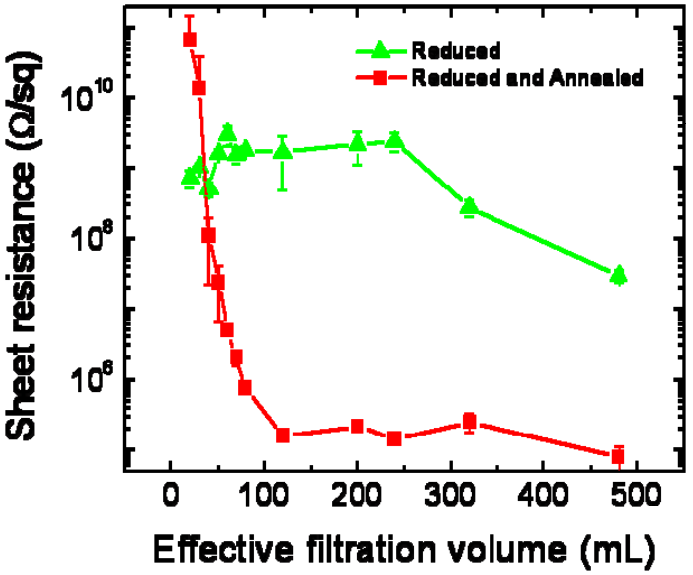


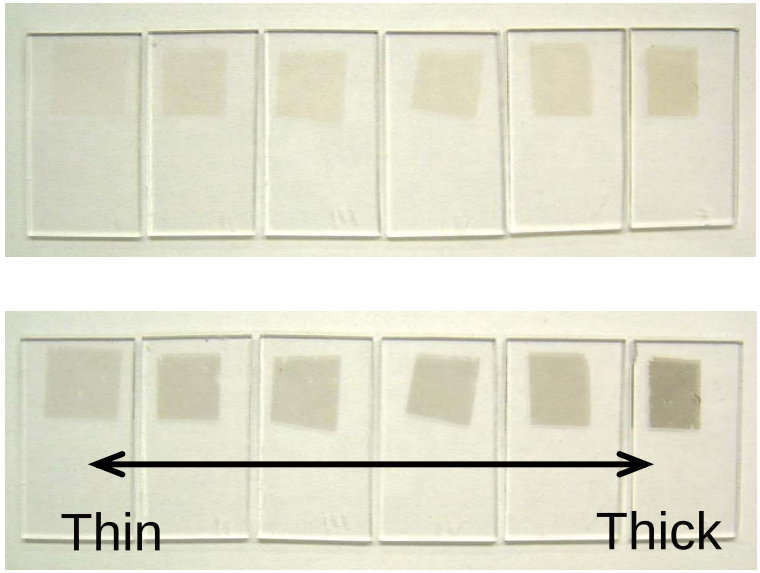
Mkhoyan, K. A. *et al. Nano Lett.* 9, 1058-1063 (2009).

“Tunable” opto-electronic properties

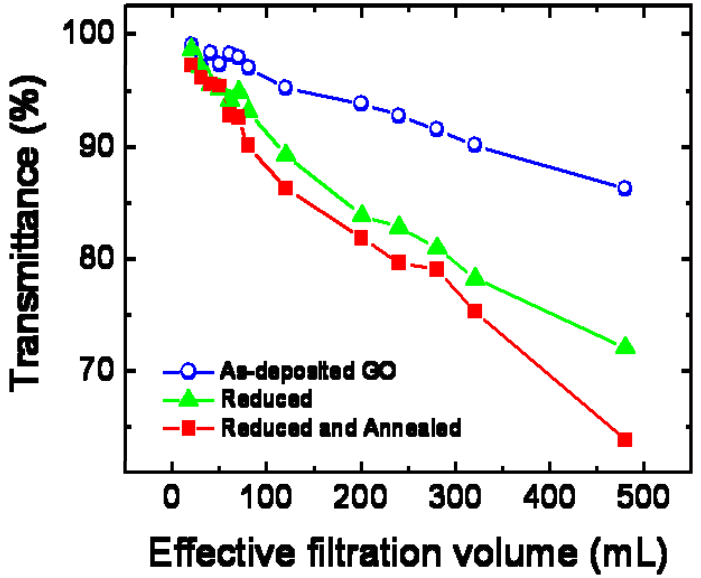


Increasing filtration volume



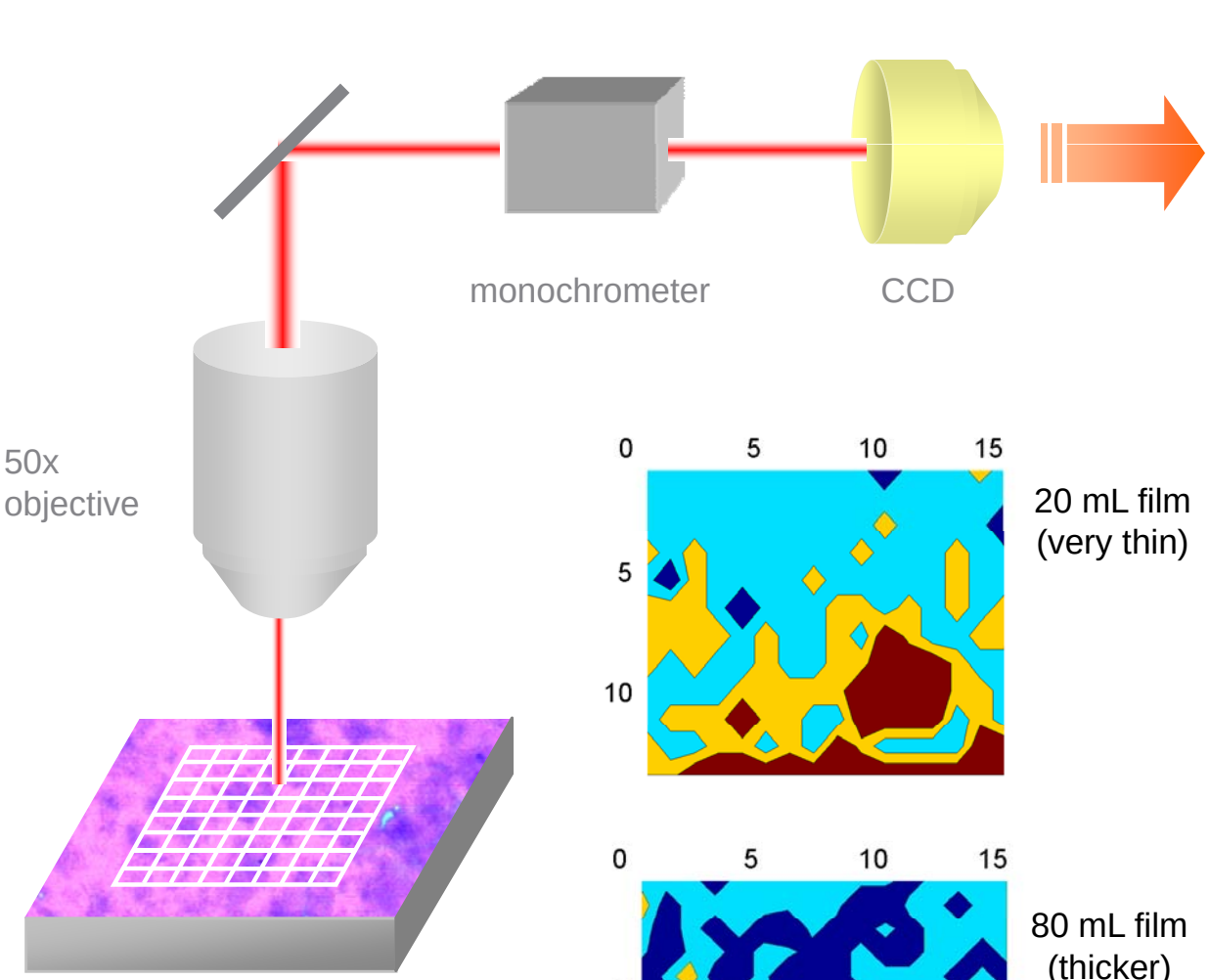


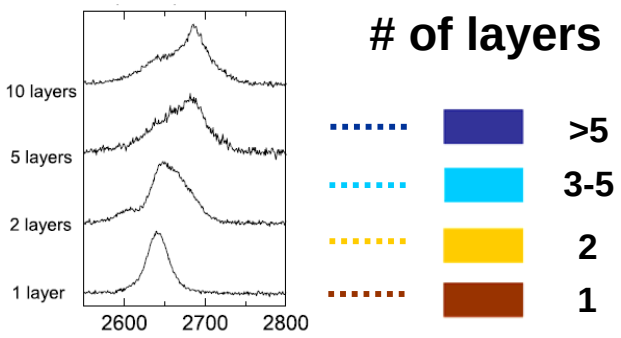
Reduce



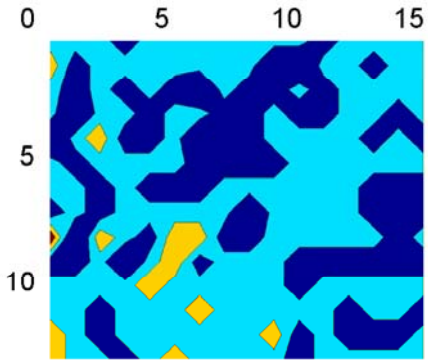
Nature Nanotechnology 3, *270 - 274 (2008)*

Raman mapping

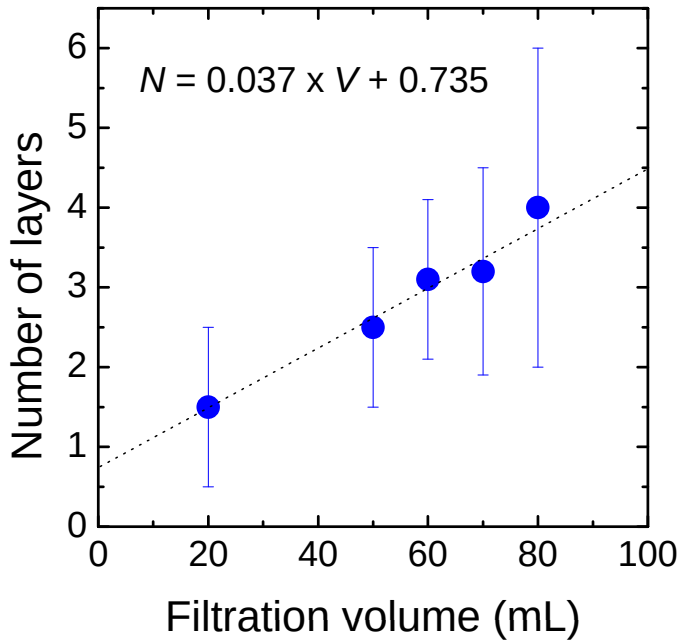




20 mL film
(very thin)

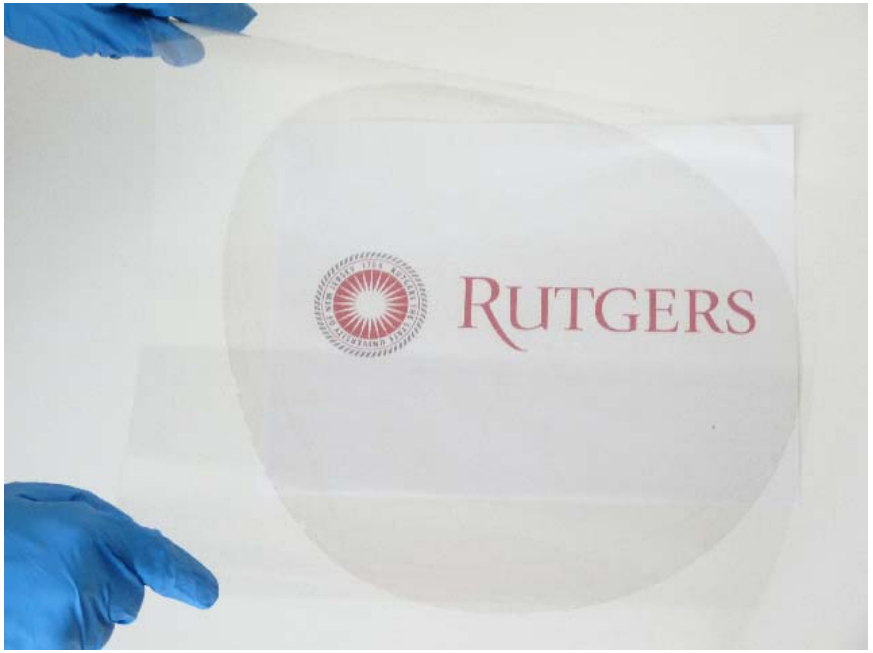


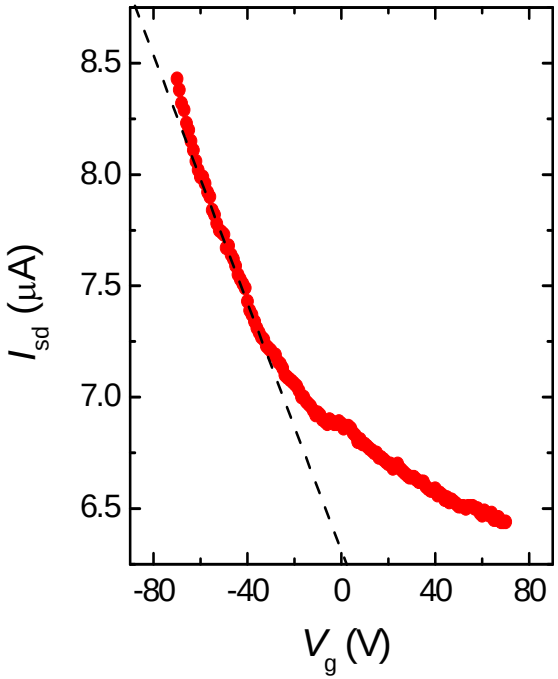
80 mL film
(thicker)



Eda *et al*. *Nature Nanotech.* 3 270-274 (2008)

12 in. (300mm) Wafer Scale Deposition

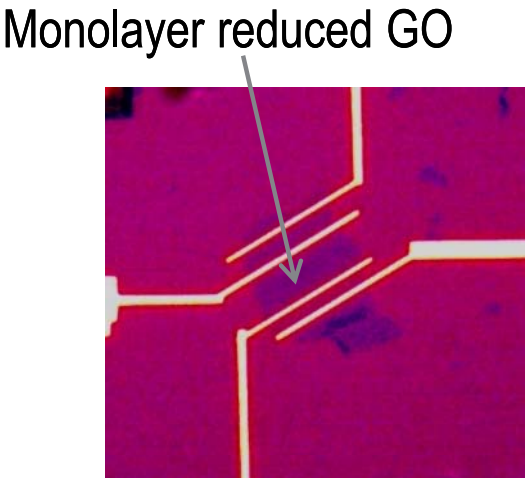




μ> 10 cm²/V-s
up to 300 cm²/V-s

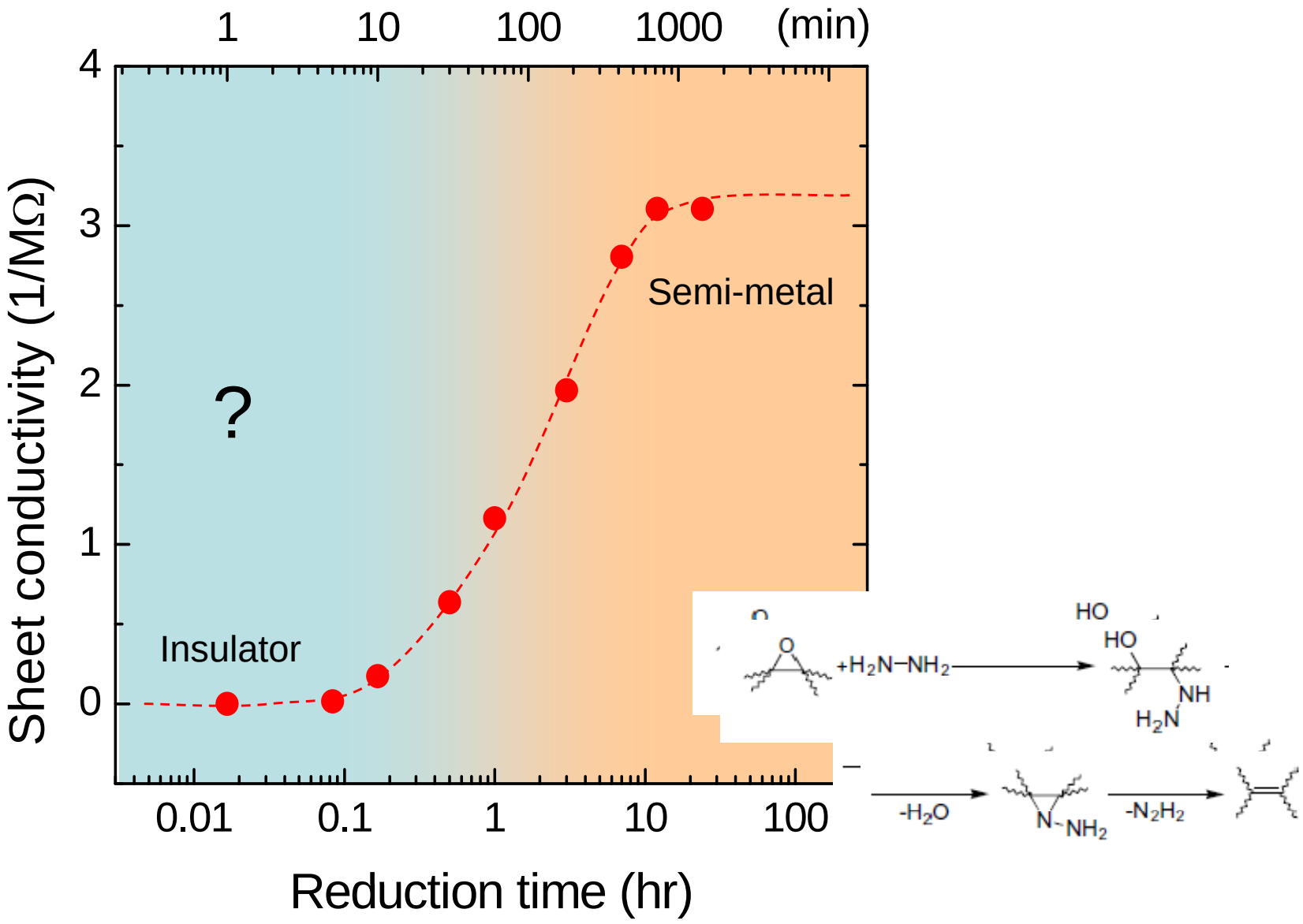
Reduced GO: open questions

- How does the GO structure (chemical, atomic, electronic) evolve upon reduction?
- How do the properties (optical, electrical) evolve upon reduction?
- What are the limiting factors for mobility and conductivity of rGO?
  - How much oxygen can be removed ? In which form is the residual oxygen present ?

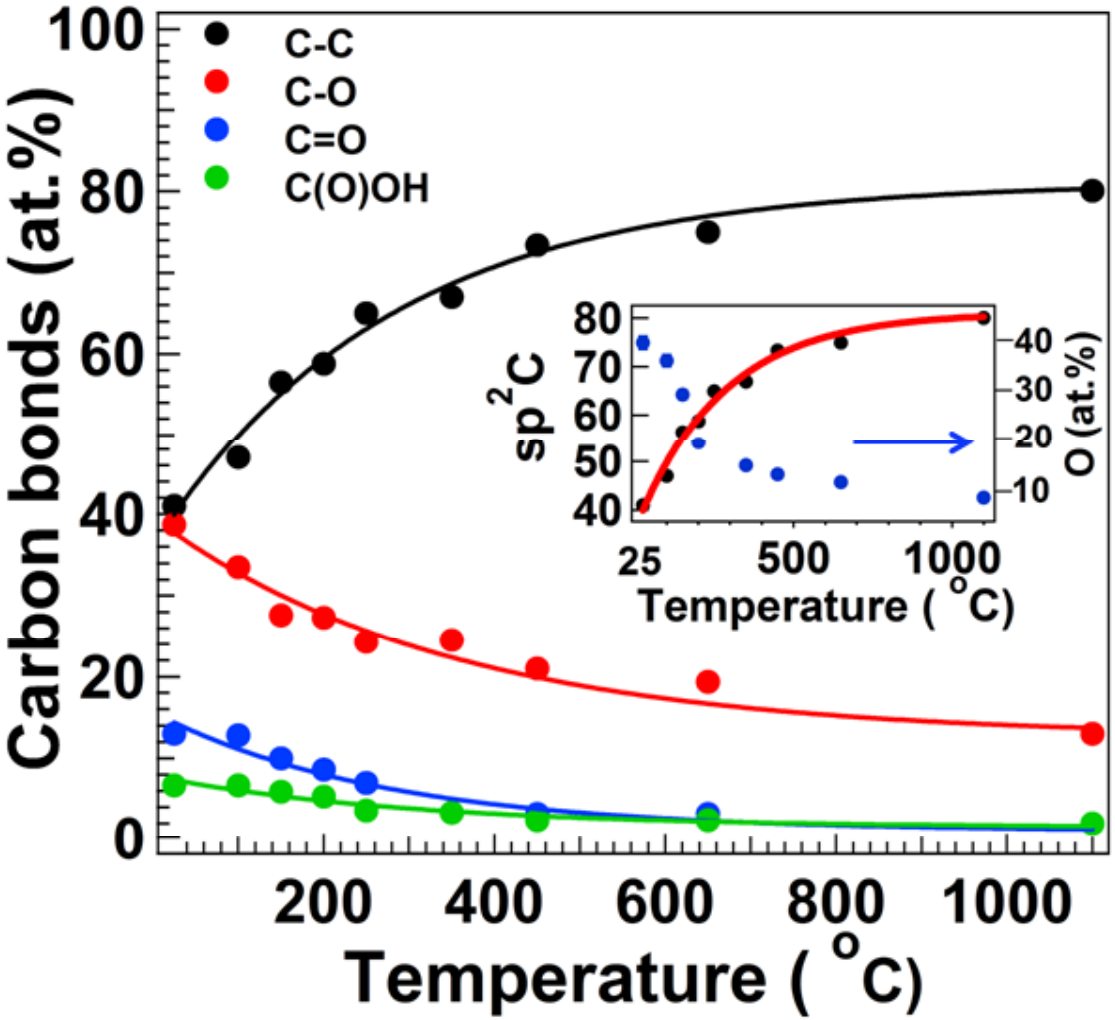


- **mobility**: Up to 100 – 300 cm^2/Vs
- **on/off ratio**: 2~100
- **sheet resistance**: ~ 1 kΩ/sq

Evolution in electronic structure



Rate of oxygen release



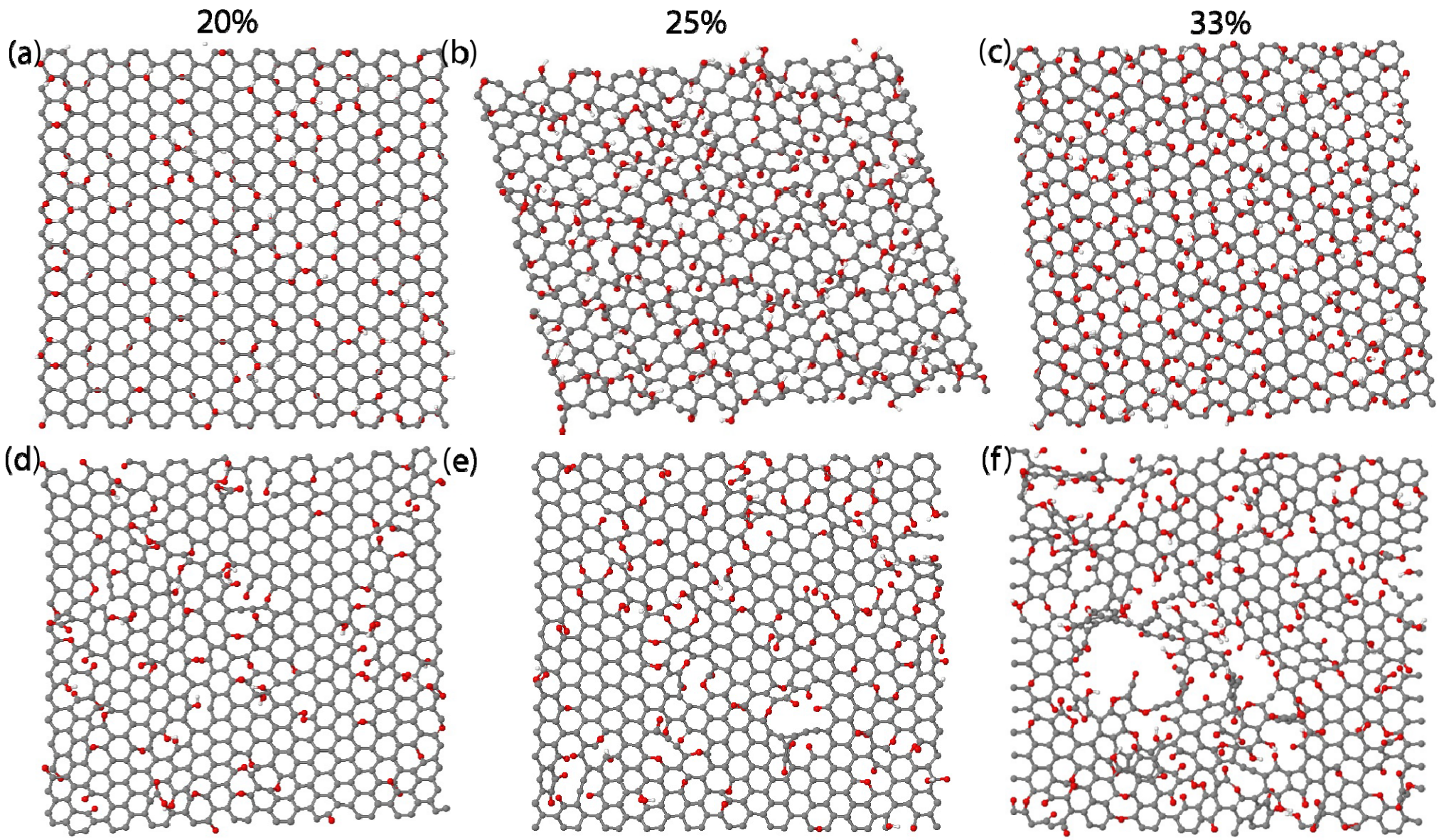
Initial Oxygen 40 at.%

150 °C Oxygen 27 at.%

Final Oxygen 8 at.%

Advanced Functional Materials 19, 2577-2583 (2009)

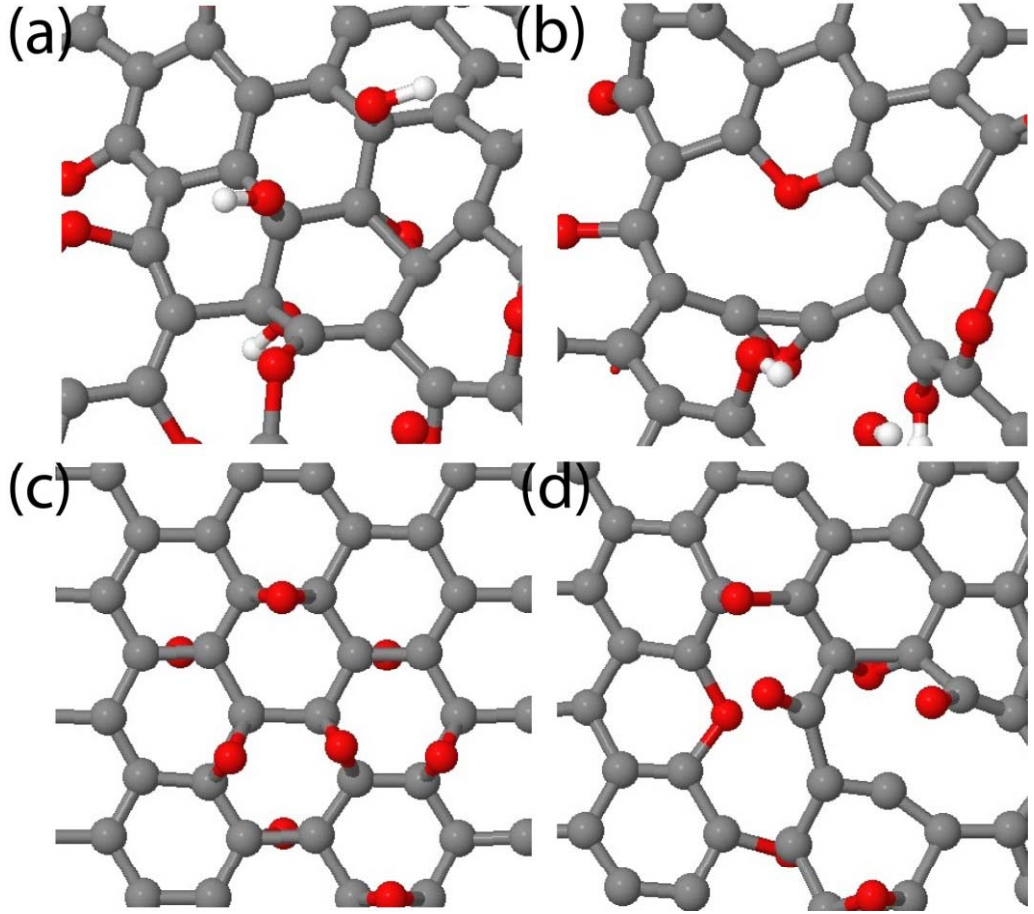
Evolution of structure with reduction



Pyran formation

Hydroxyls-epoxies

epoxy-epoxy



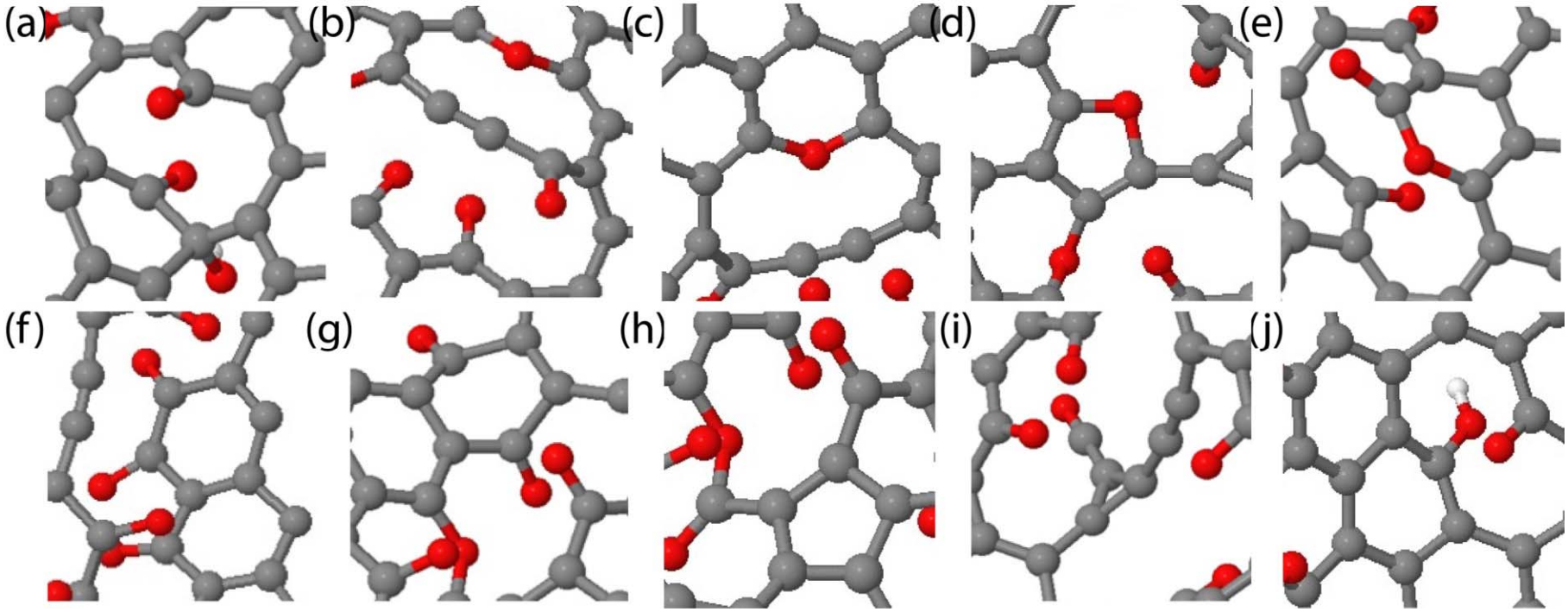
Loss of CO_2

Loss of CO

Nature Chemistry 2, 581 (2010)

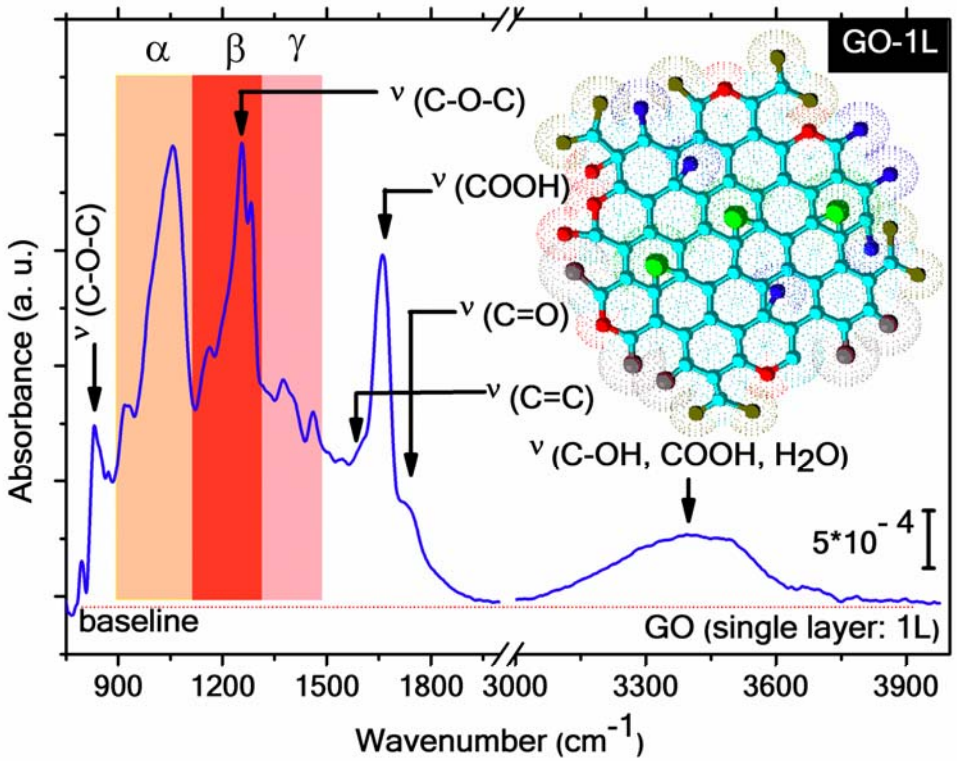
Hydroxyl - Epoxy interplay lead to…

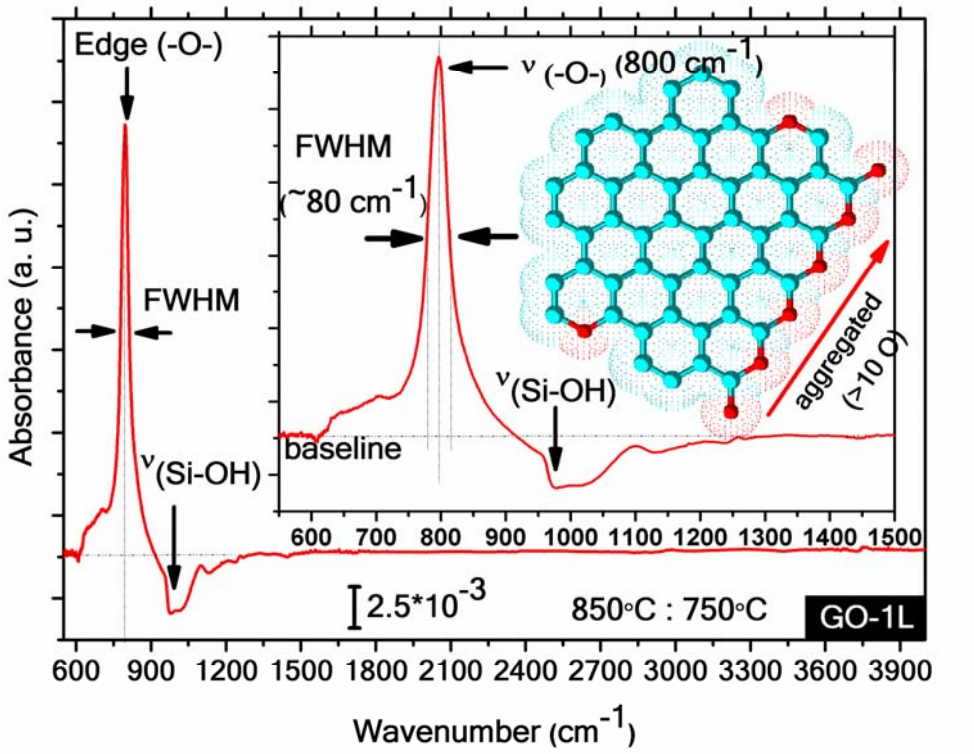
Oxygen functional groups and carbon arrangements after annealing

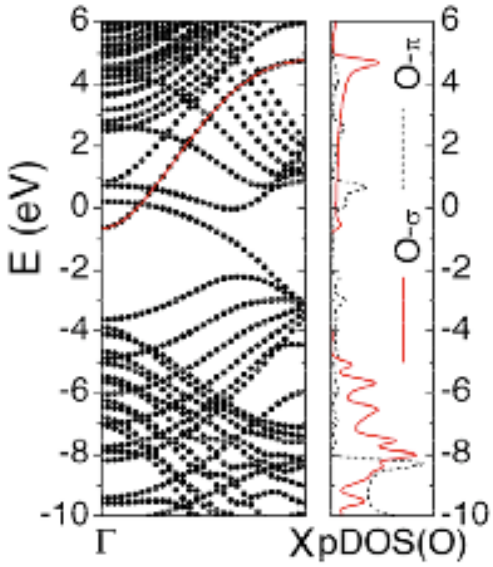


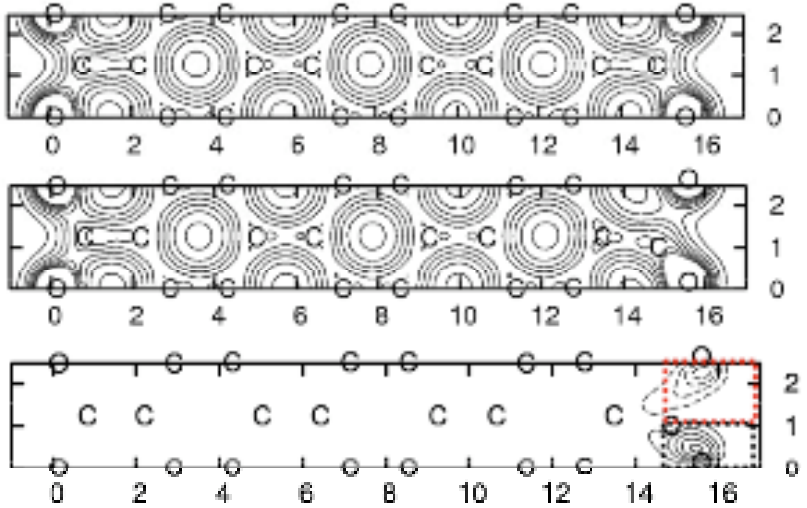
(a) pair of carbonyls, (b) carbon chain, (c) pyran, (d) furan, (e) pyrone, (f) 1,2-quinone, (g) 1,4-quinone, (h) carbon pentagon, (i) carbon triangle, (j) phenol. Carbon, oxygen and hydrogen atoms are color-coded as gray, red and white, respectively.

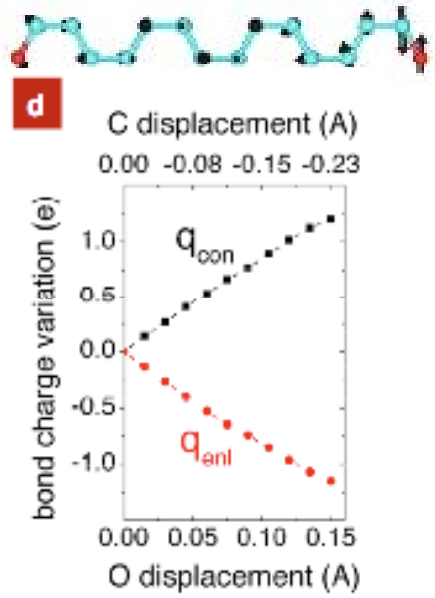
Giant IR Effects in rGO





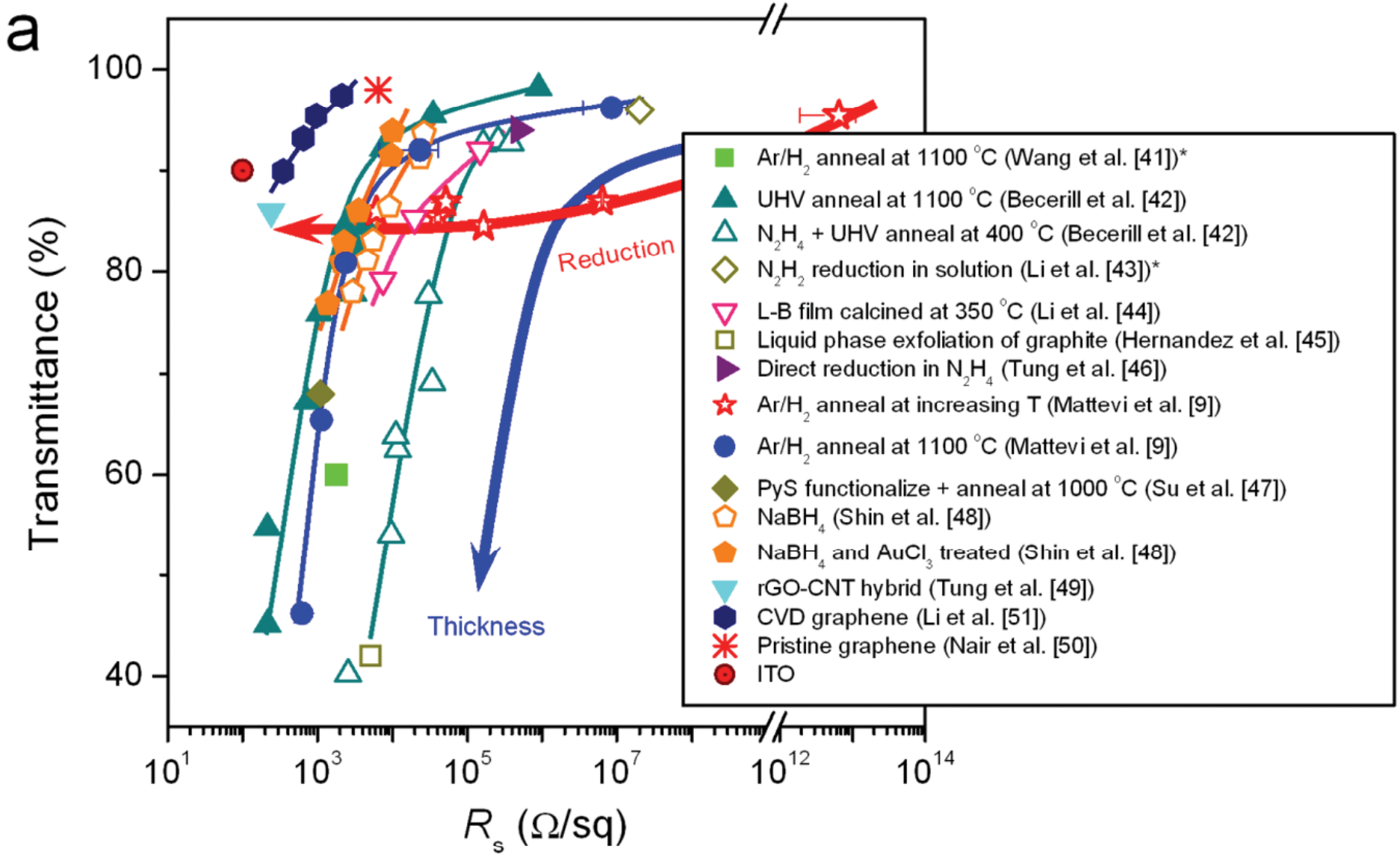






In collaboration with Muge Acik and Yves Chabal at UT – Dallas (Nature Materials, 9, 840 2010)

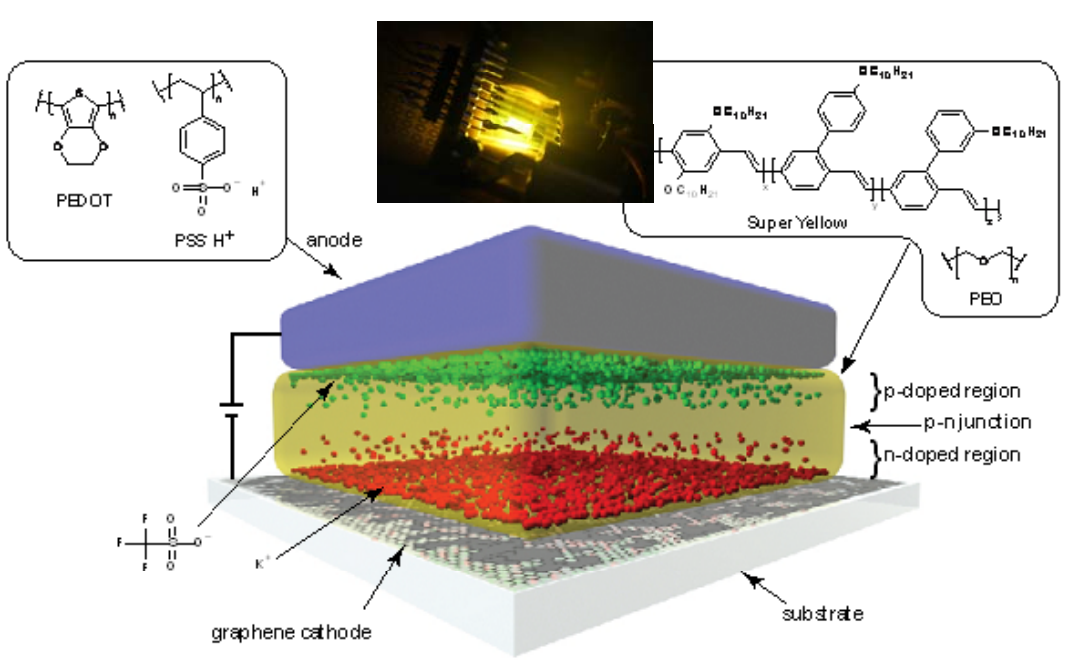
“Tunable” Opto-electronic Properties



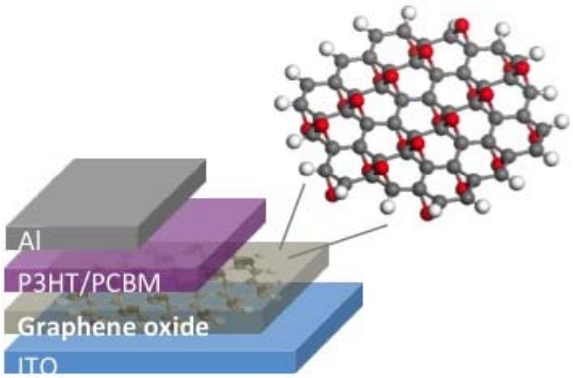
Advanced Functional Materials 19, 2577-2583 (2009)
Nature Chemistry, 2, 1015–1024 (2010)

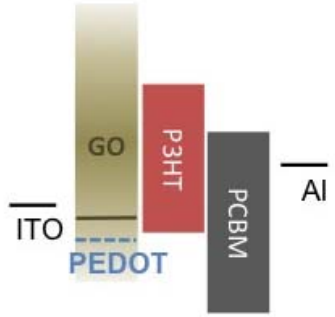
GO for organic electronics

ACS Nano 4, 637 (2010)

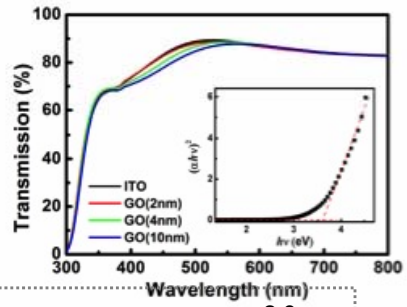


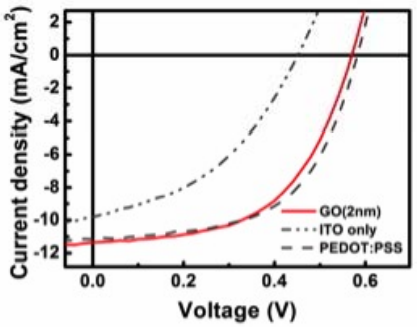
ACS Nano 4, 3169 (2010)

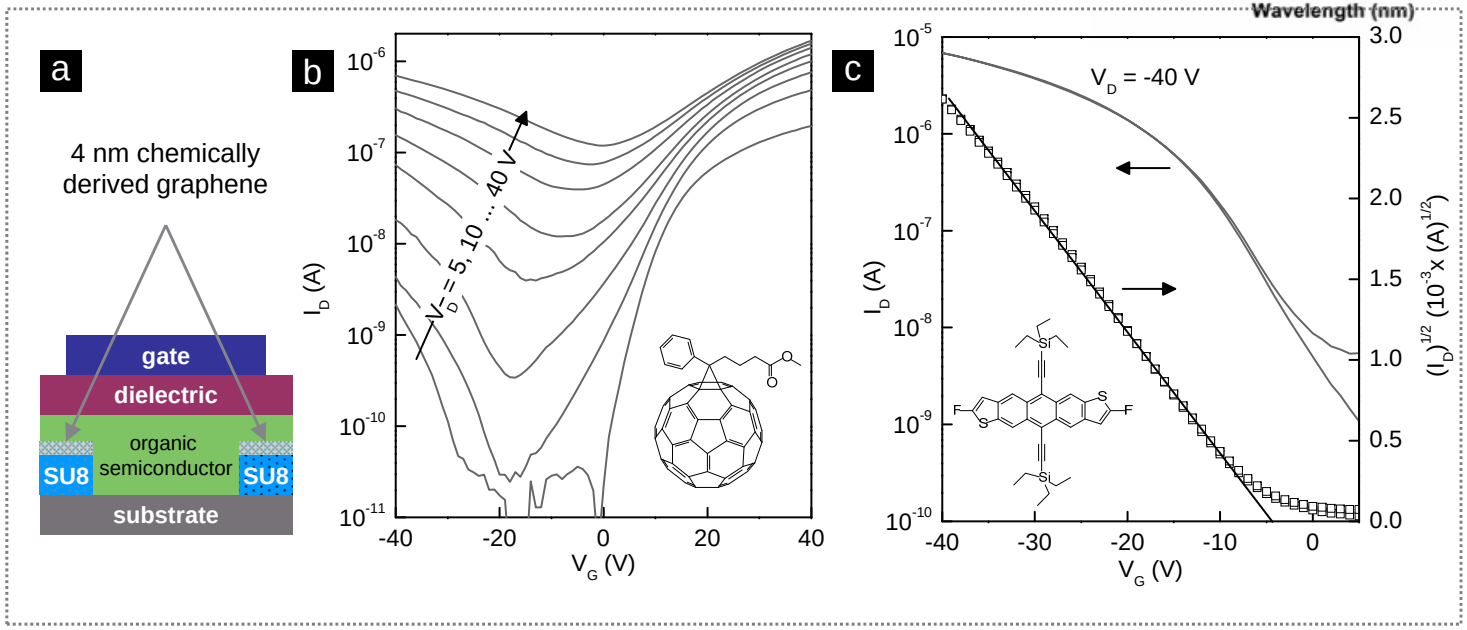




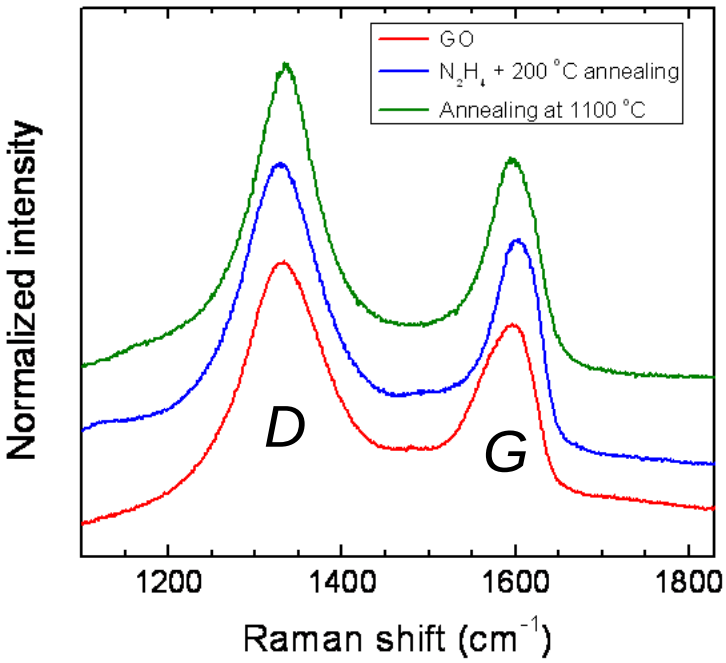
http://www.economist.com/sciencetechnology/displayStory.cfm?story_id=15543667

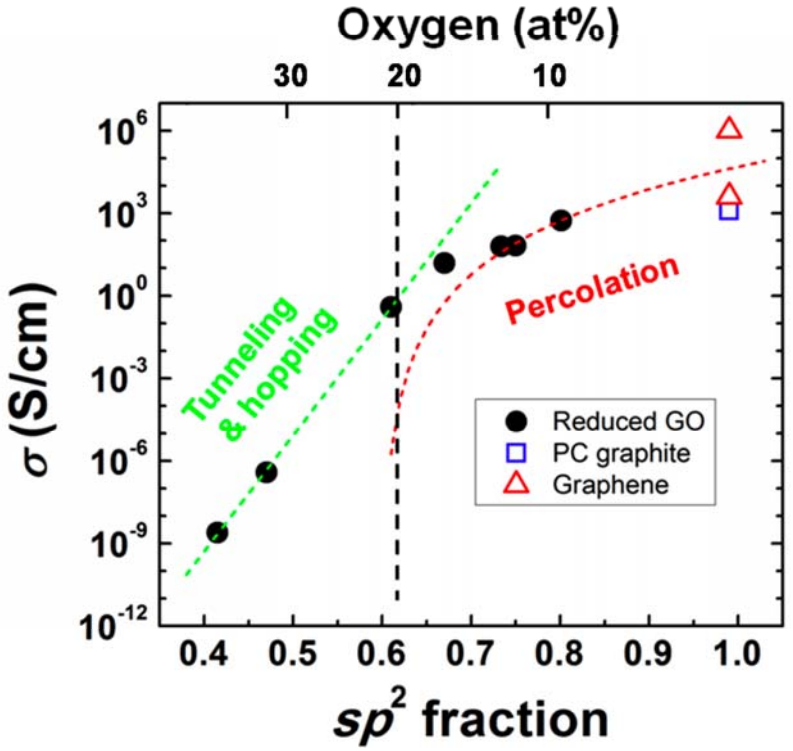






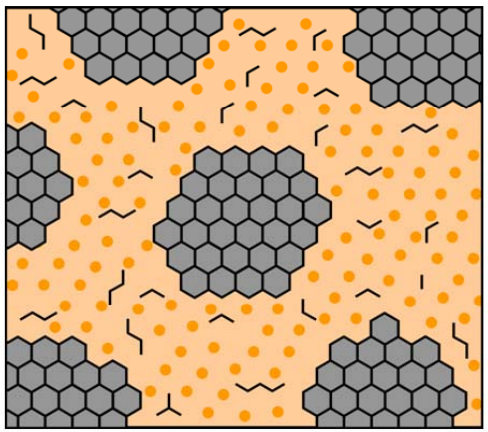
Structure of GO

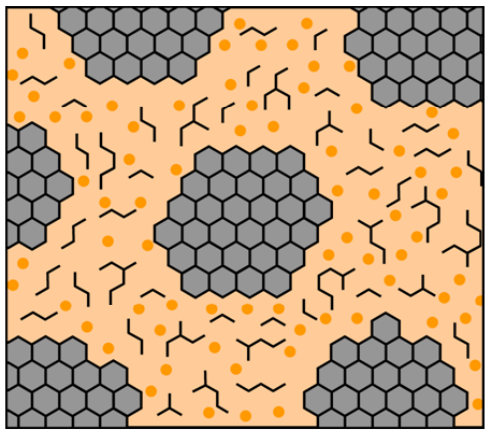


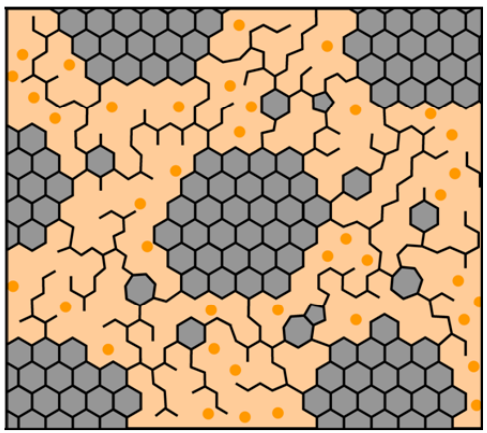


$$L_a = \left[2.4 \times 10^{-10}\,\mathrm{nm}^{-3}\right] \lambda^4 \left(\frac{I_D}{I_G}\right)^{-1} \Longrightarrow \quad L_a \sim 2\ \mathrm{nm}$$

"Domain size"

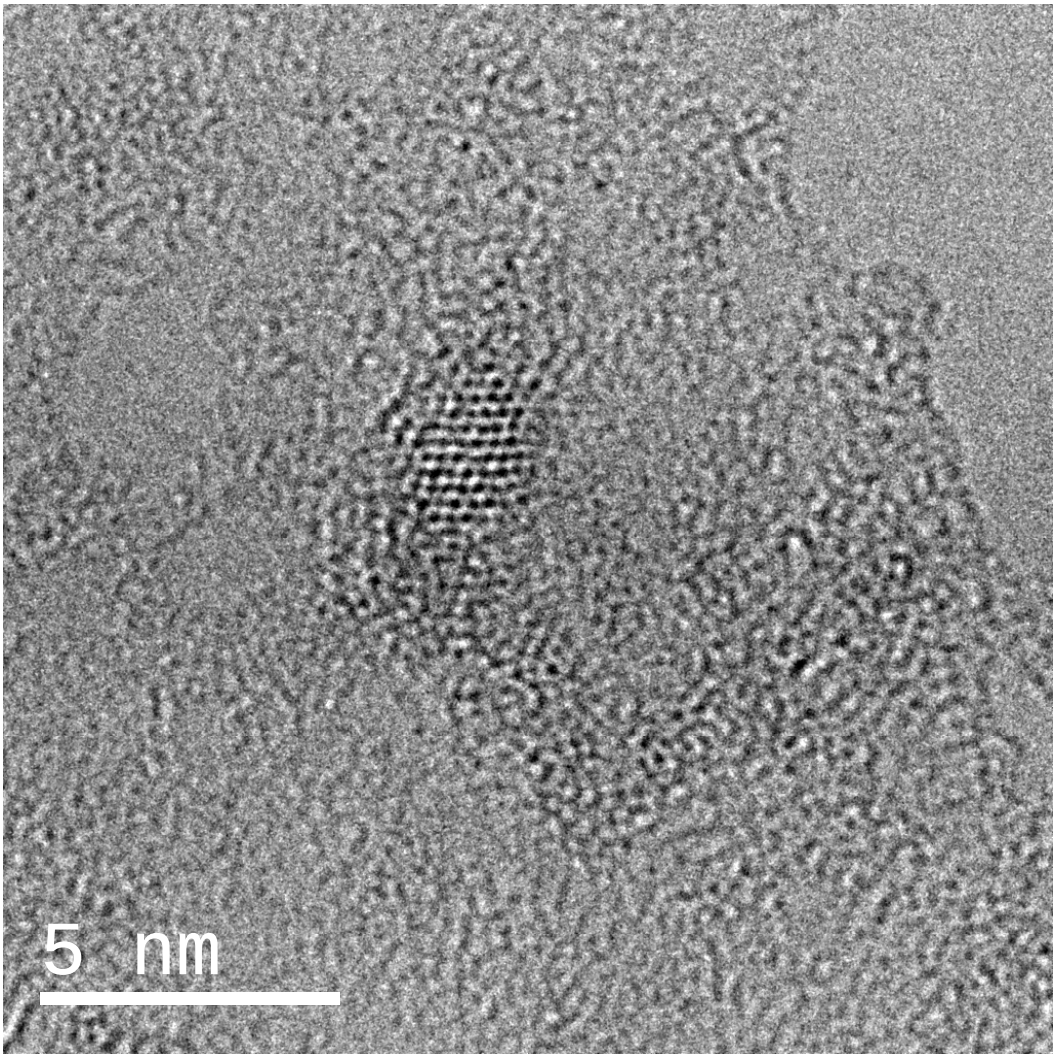


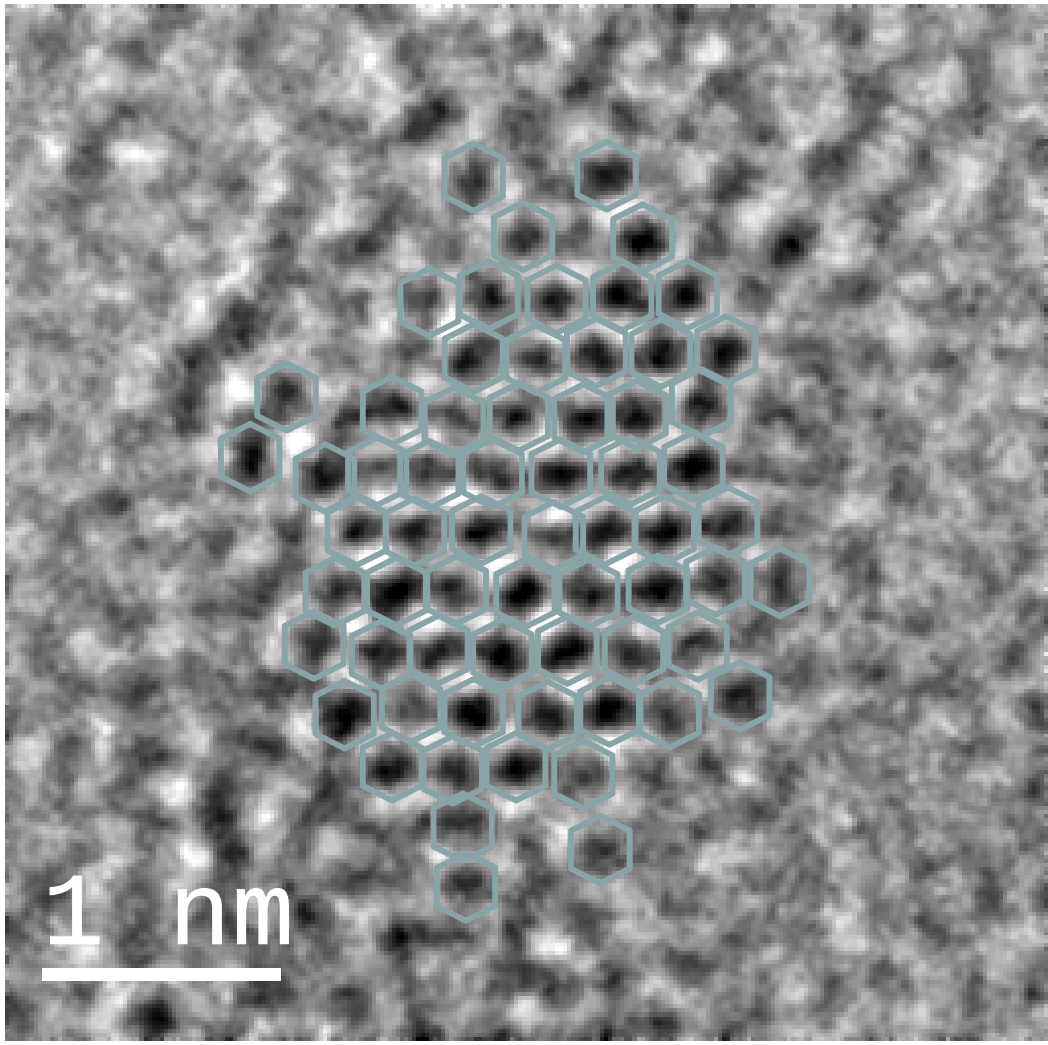




Direct observation of sp2 clusters

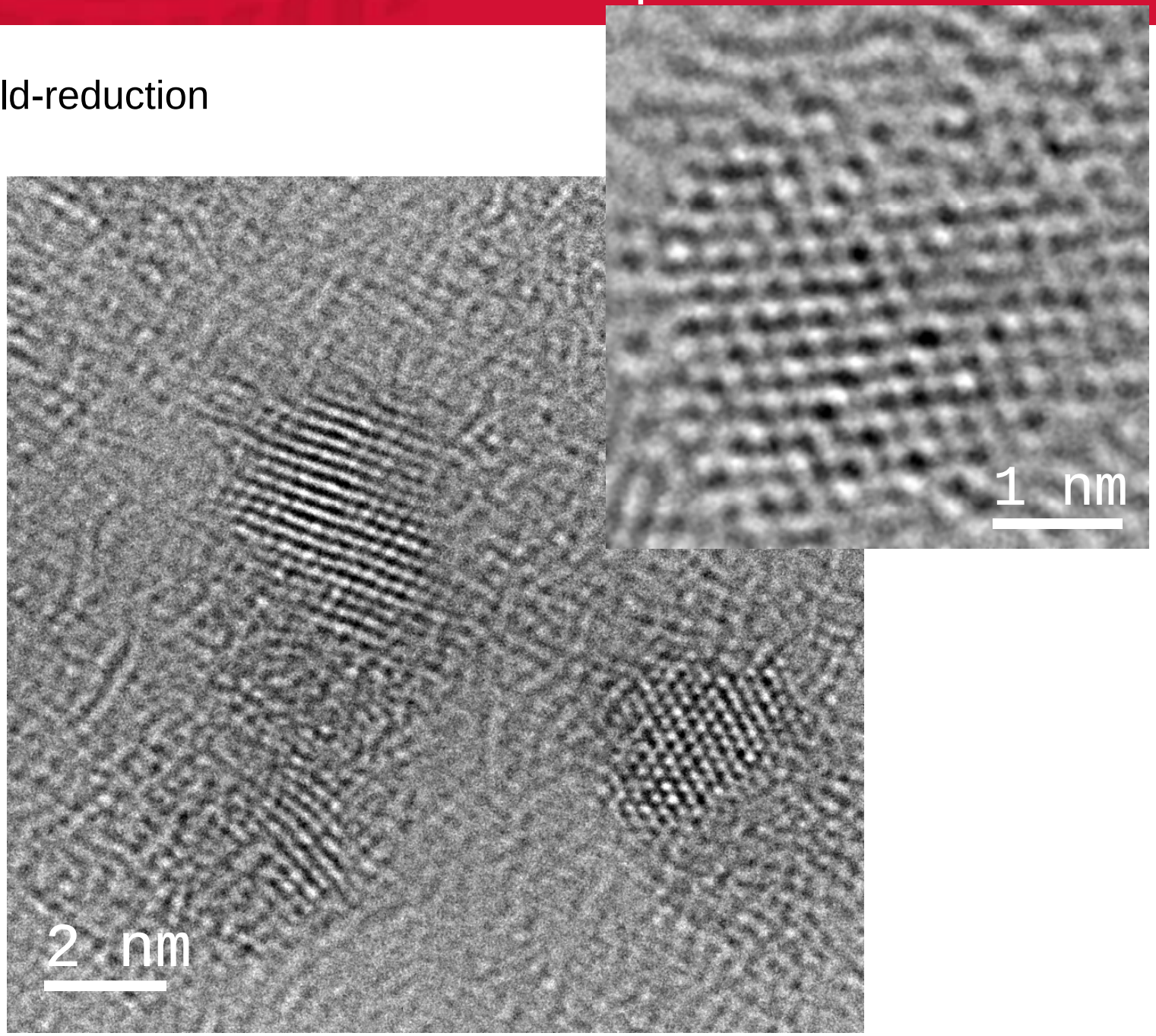
As-synthesized GO



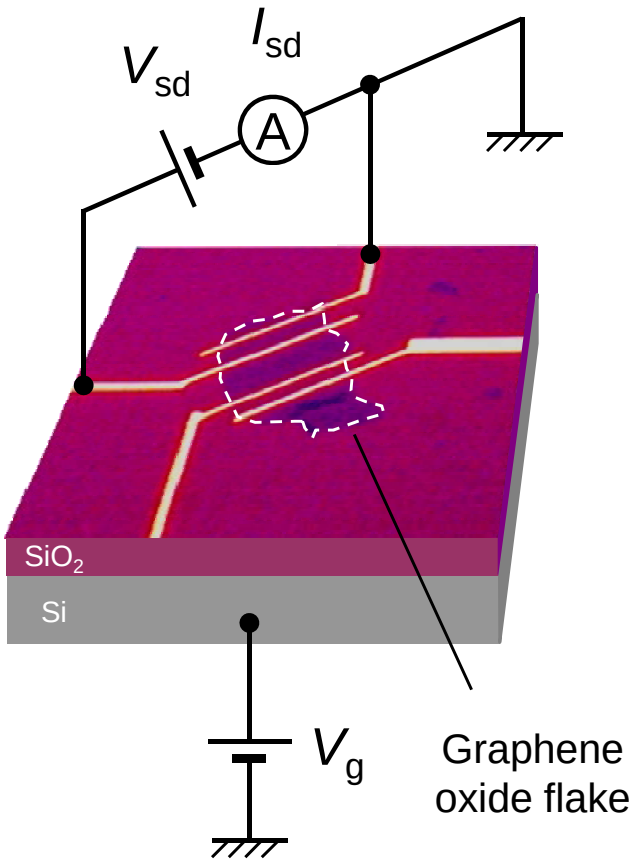


Direct observation of sp2 clusters

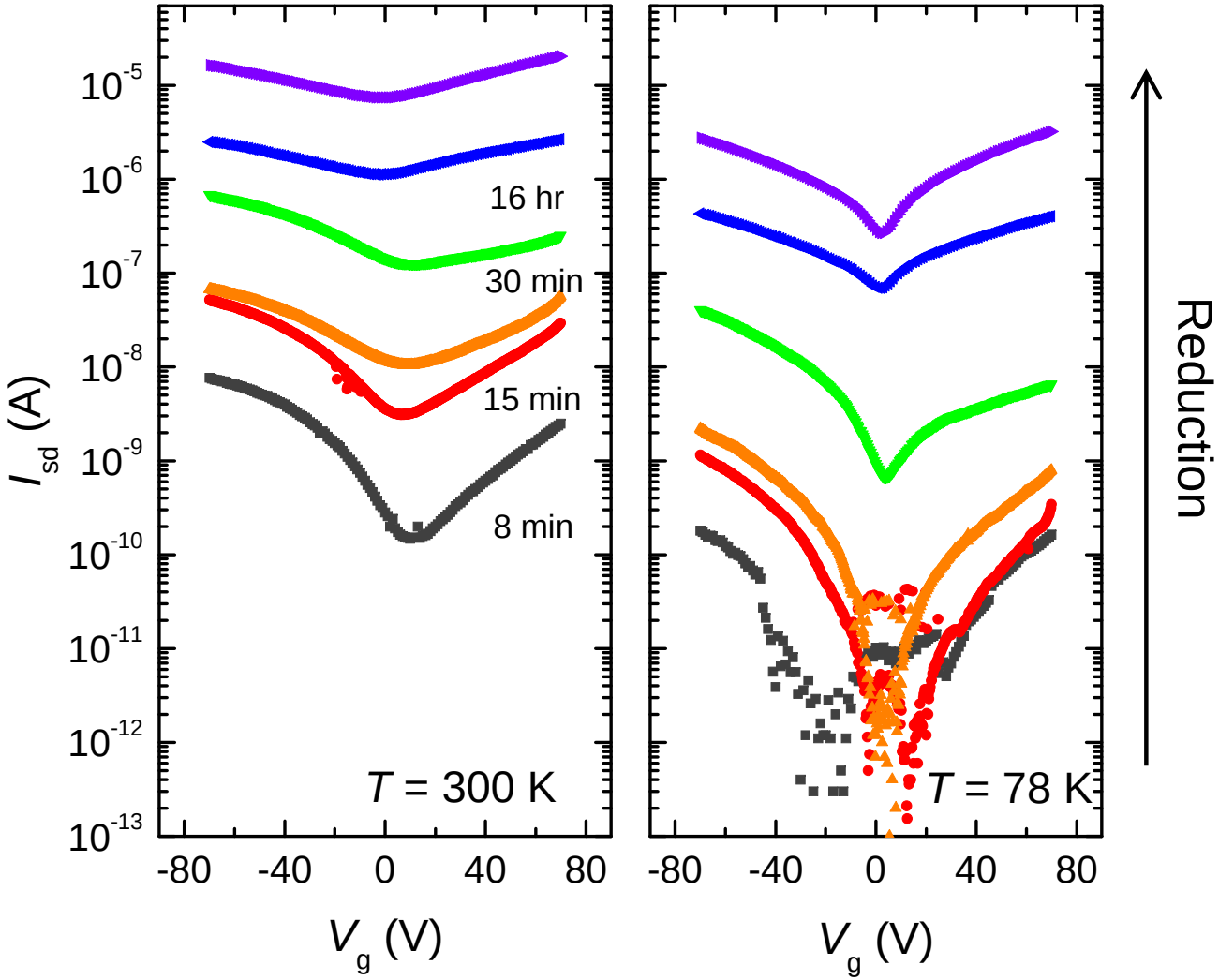
After mild-reduction



Progressive reduction



Transfer characteristics



J. Phys. Chem. C (2009).

Carrier transport via hopping

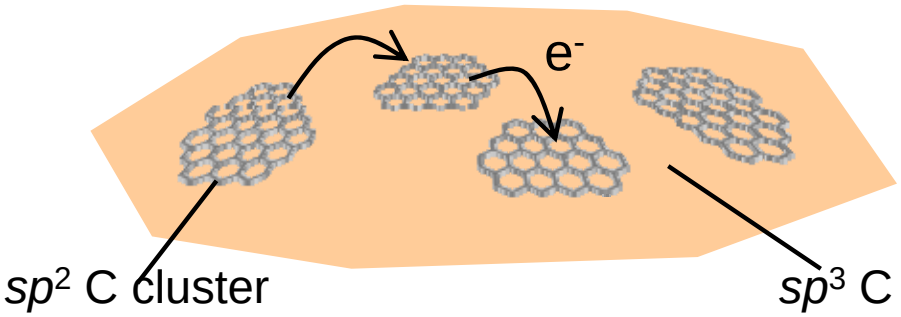
In 2D system, VRH is described by:

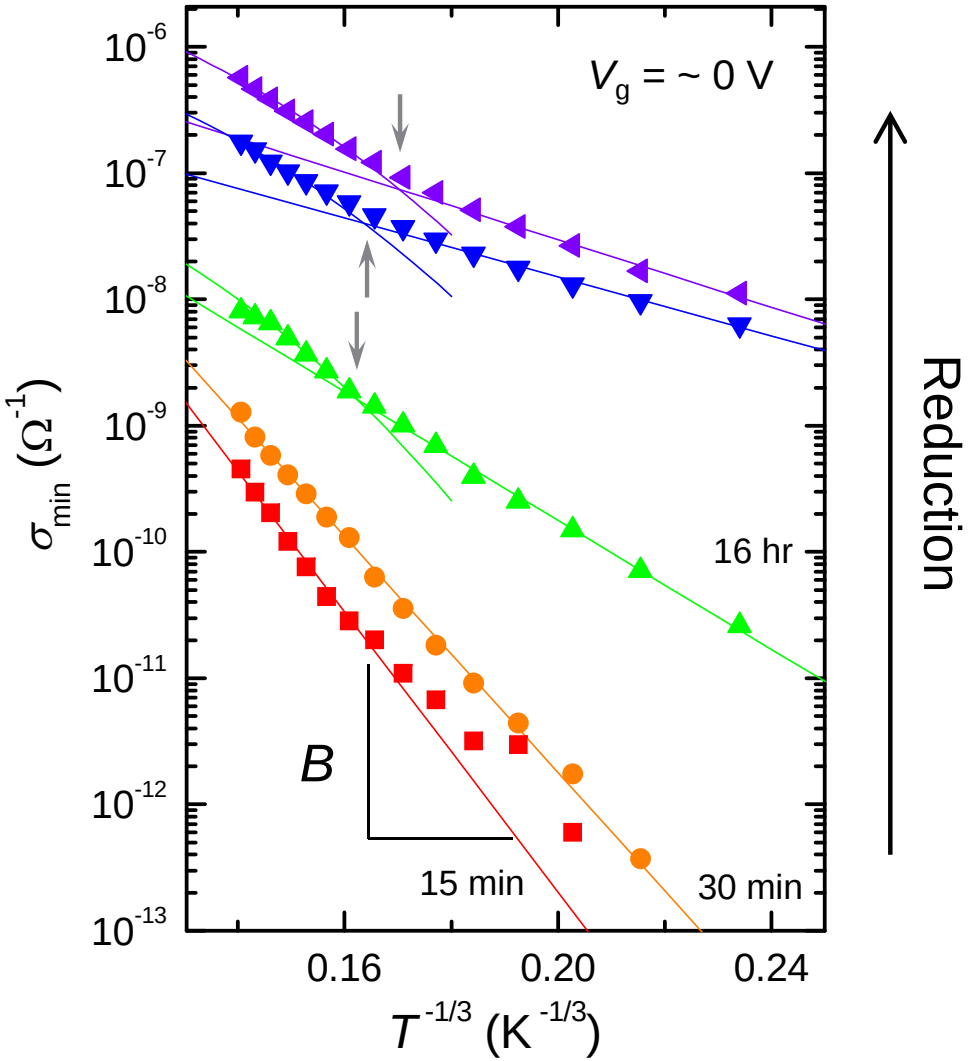
$$\sigma = A\exp\left(-\frac{B}{T^{1/3}}\right)$$

$$A = \frac{eR_0^2\nu_{ph}}{k_B}$$

$$B = \left(\frac{3}{N(E_F)L_l{}^2 k_B}\right)^{1/3}$$

DOS at E_F Localization length





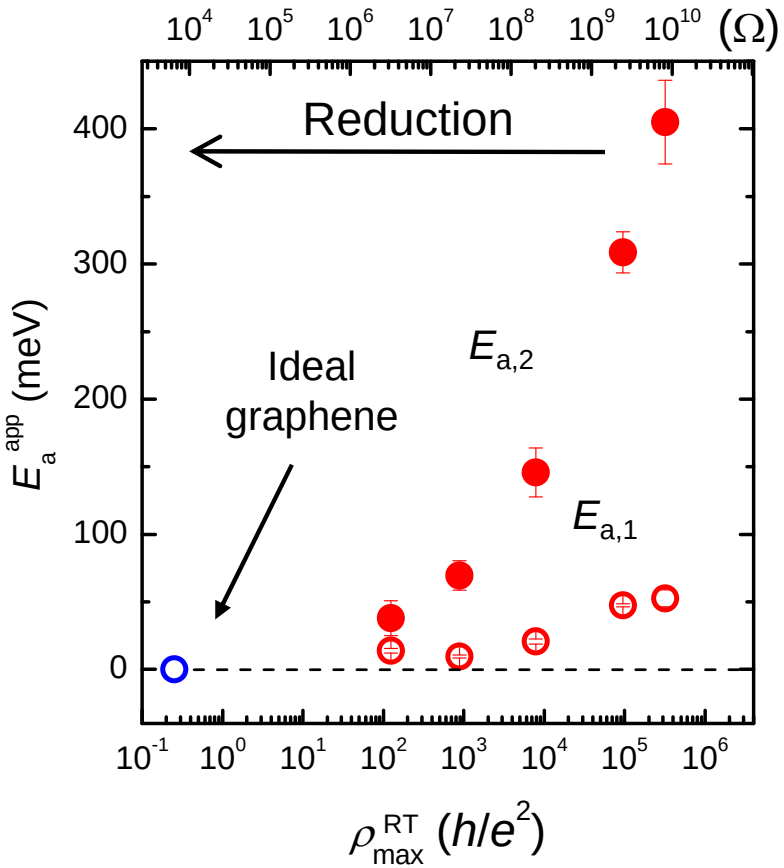
J. Phys. Chem. C (2009).

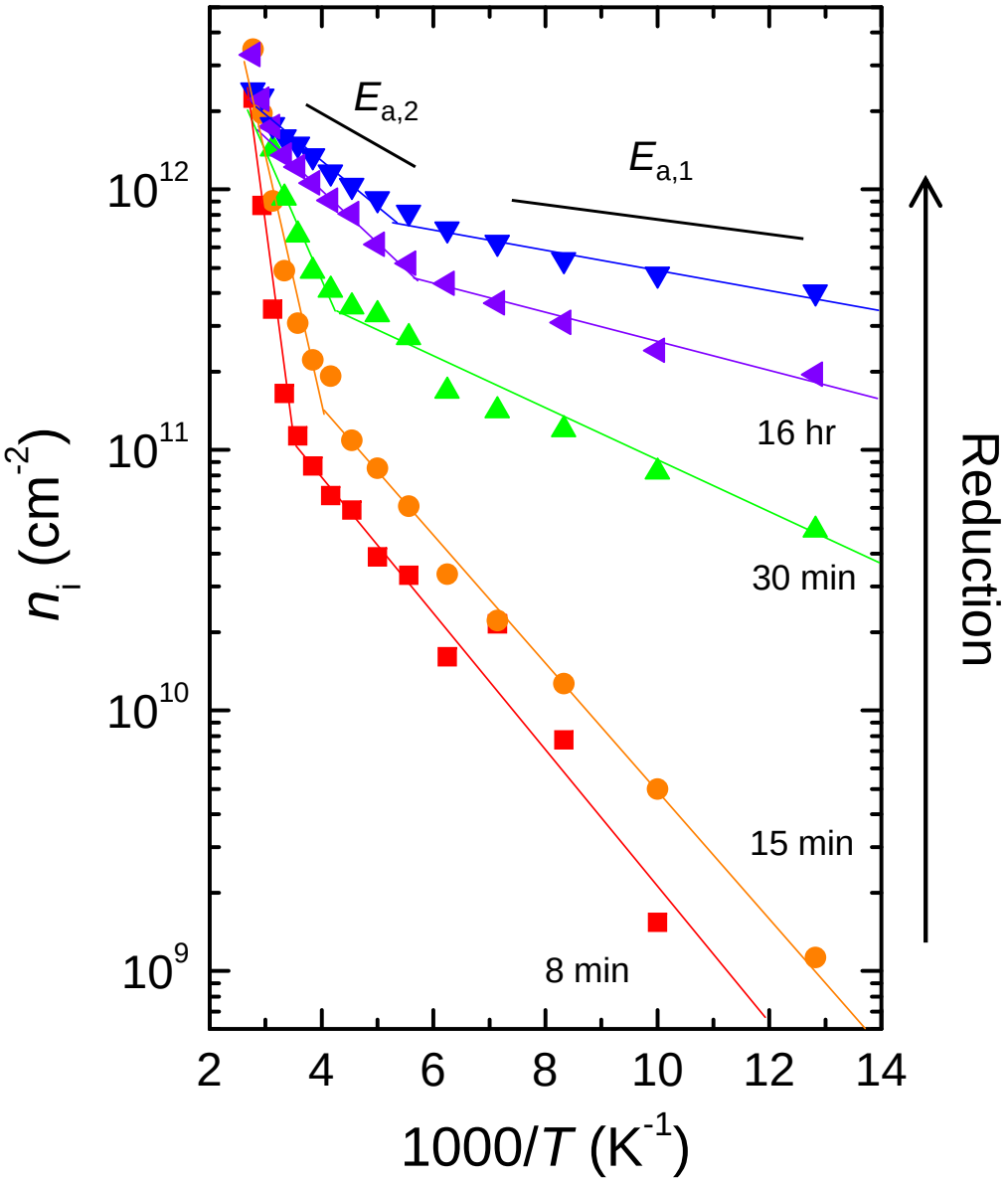
Apparent band gap of reduced GO

At the charge neutrality point,

$$n_e = n_h = n_i$$

$$\sigma_{min} = e n_i (\mu_e + \mu_h)$$

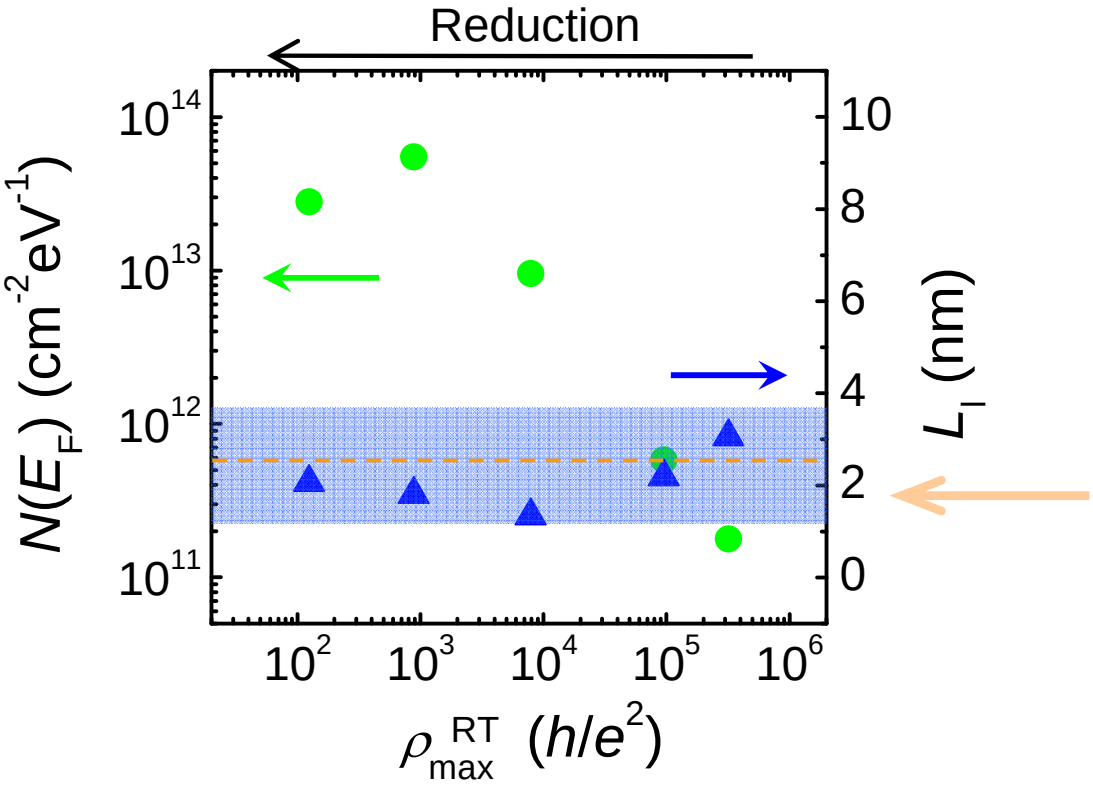


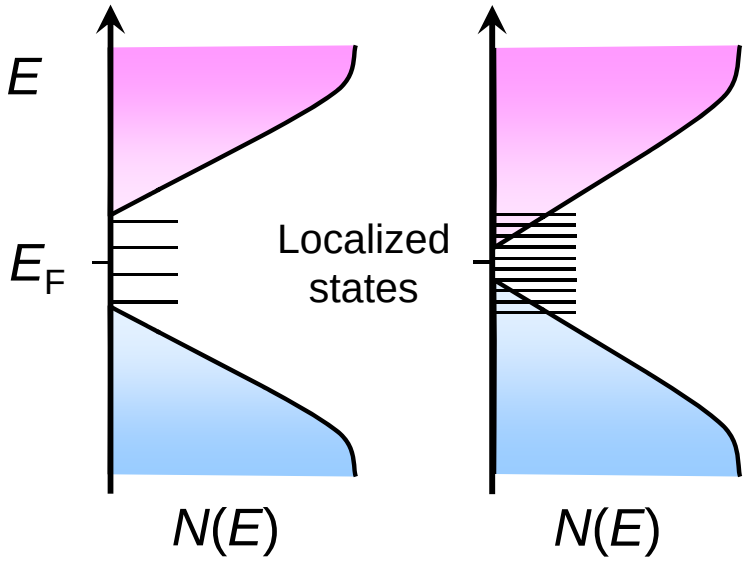


Evolution of the electronic structure

At low T, $\frac{\partial n_i}{\partial T} = N(E_F)k_B$

$B = \left(\frac{3}{N(E_F)L_l^{\,2}k_B} \right)^{1/3}$ → Obtain $N(E_F)$ and L_l





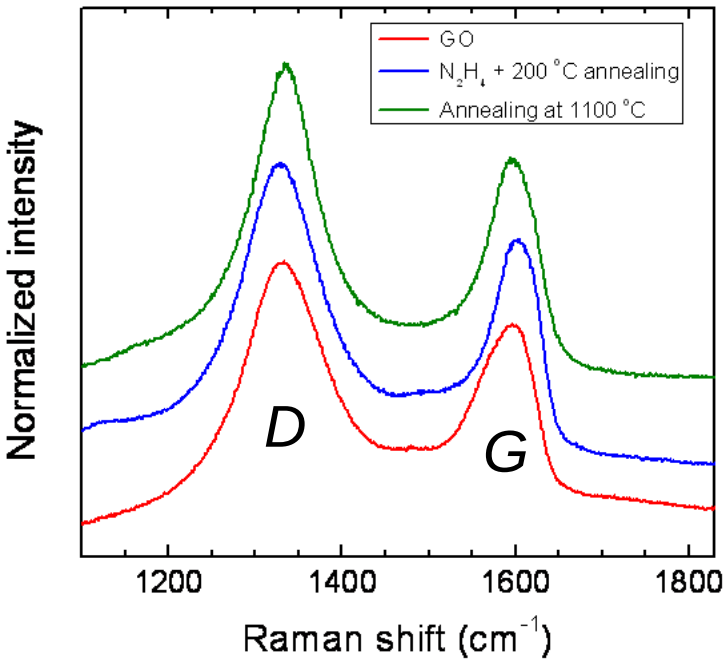
Before reduction

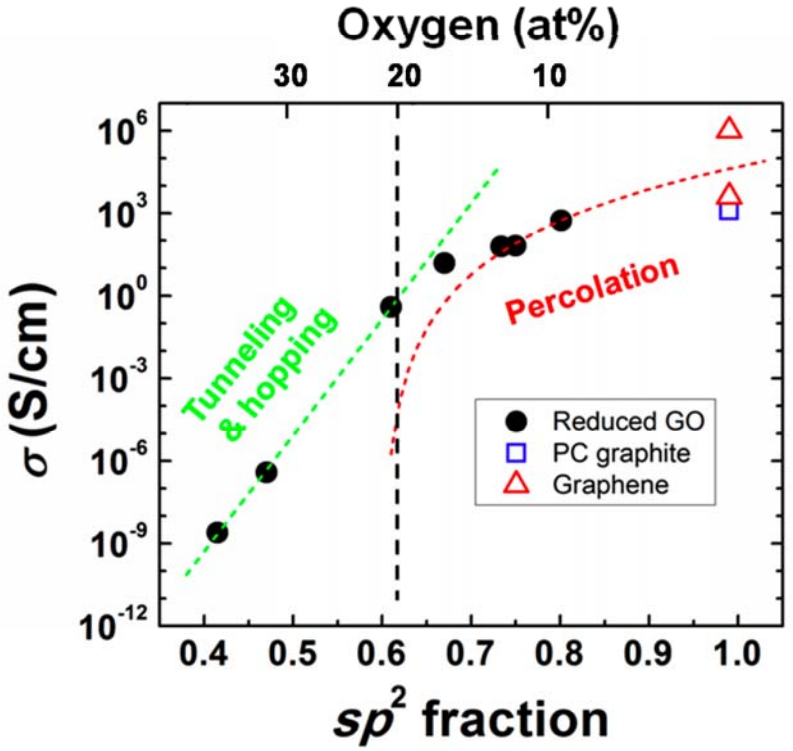
After reduction

Coherence length (sp^2 cluster size) estimated from Raman analysis.

J. Phys. Chem. C (2009).

Structure of GO





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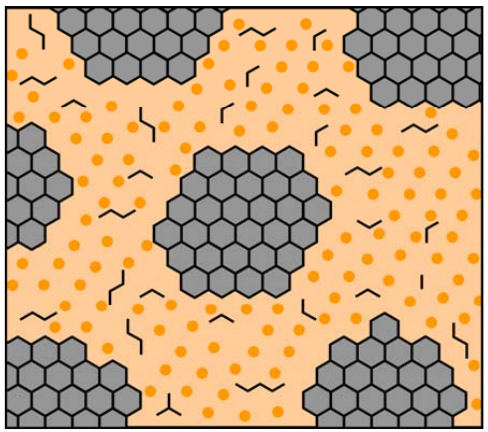
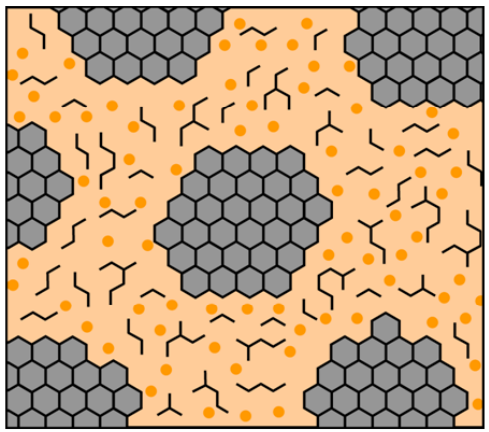
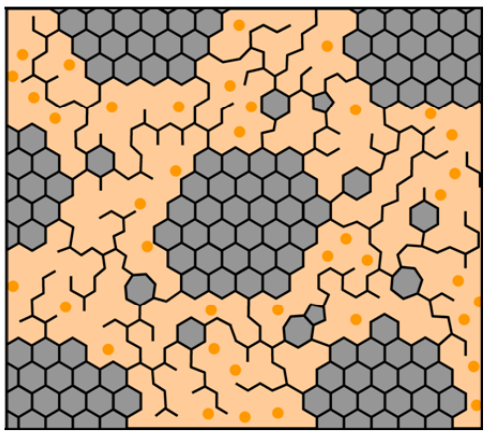
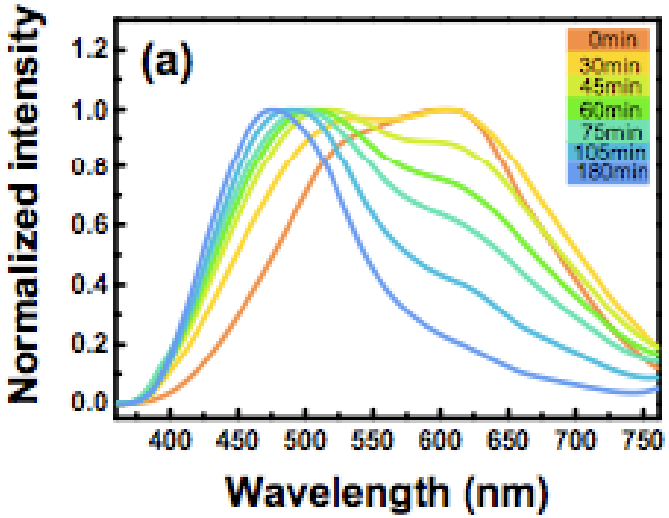
"Domain size"

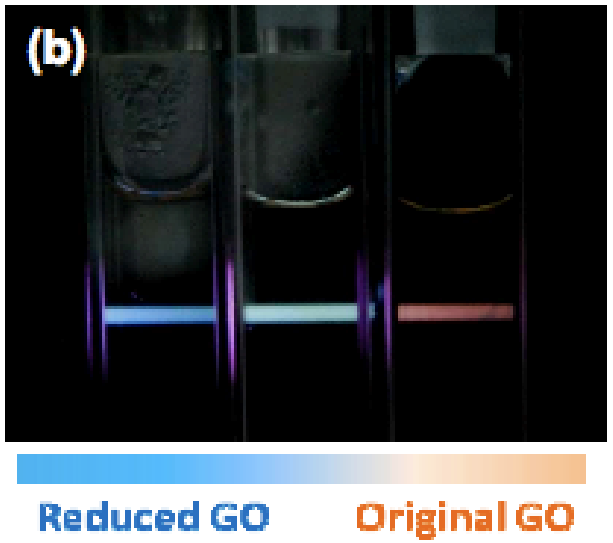


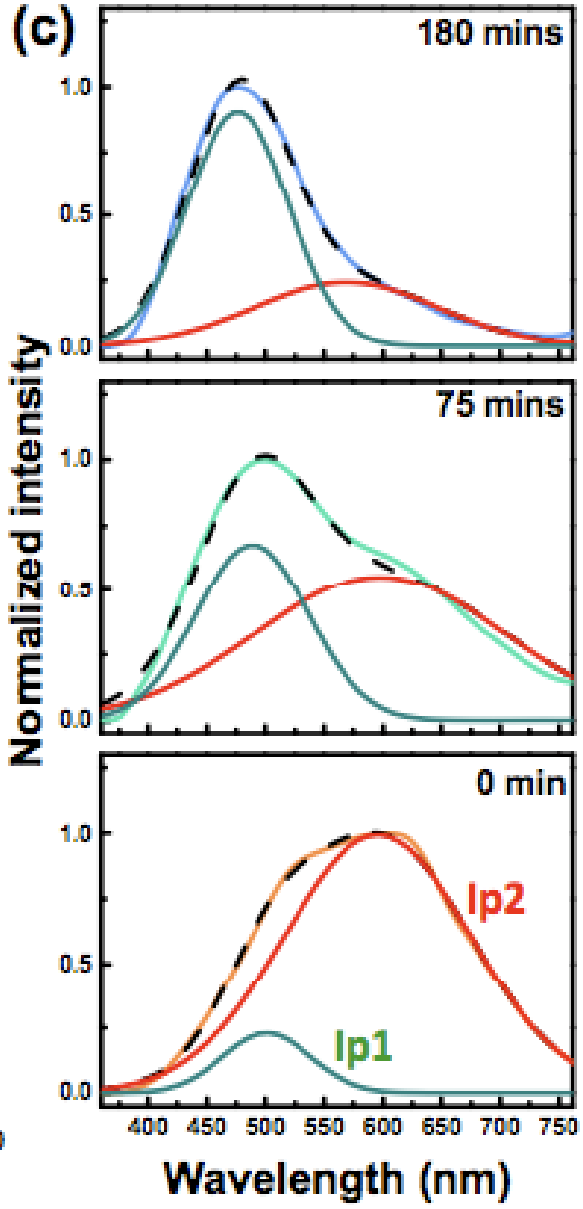


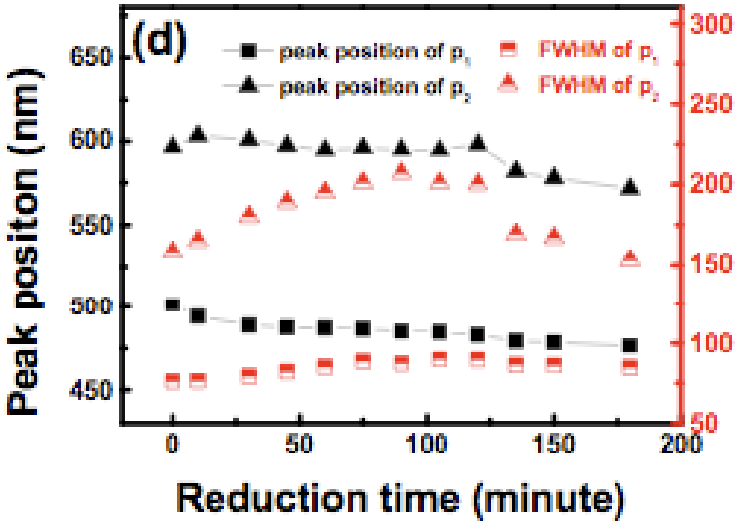


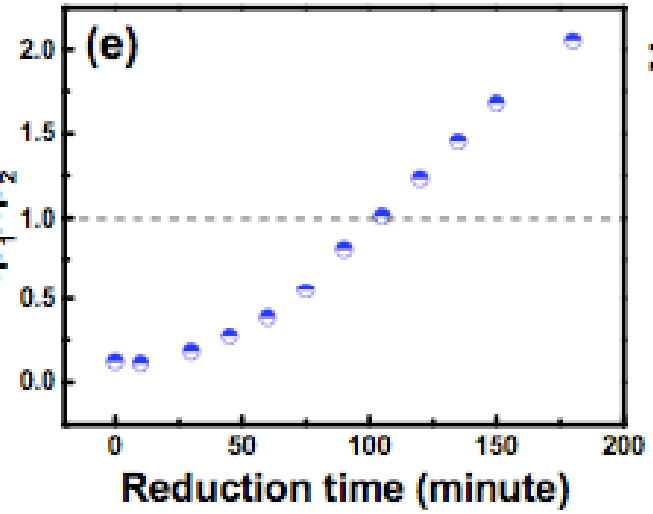
Tunable fluorescence





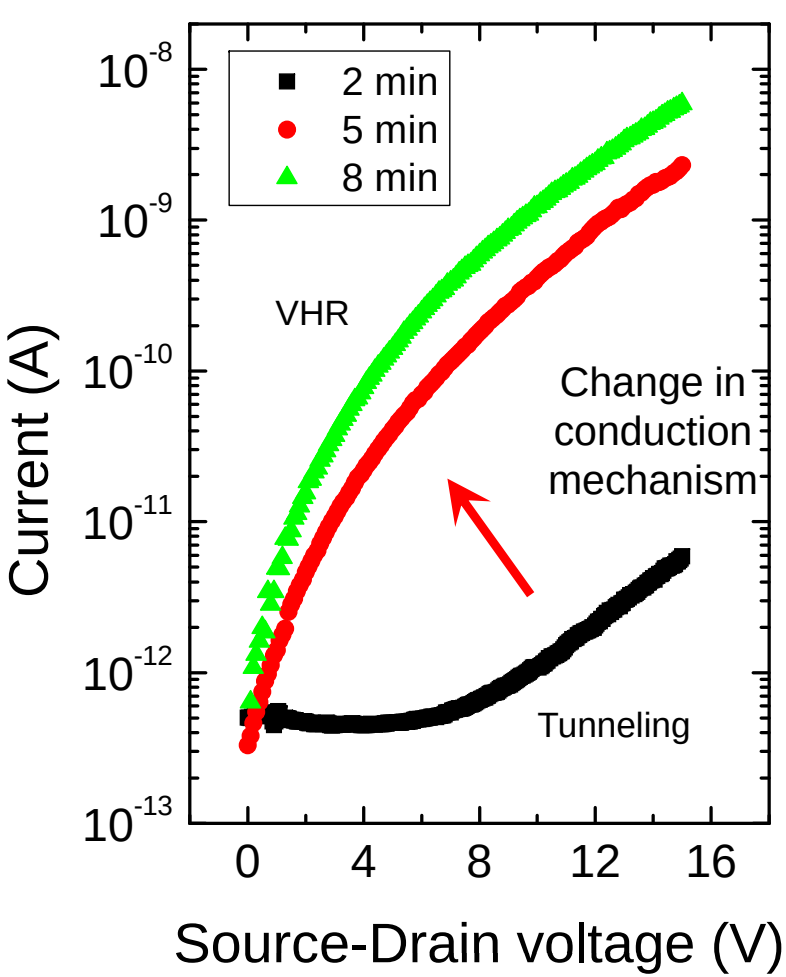


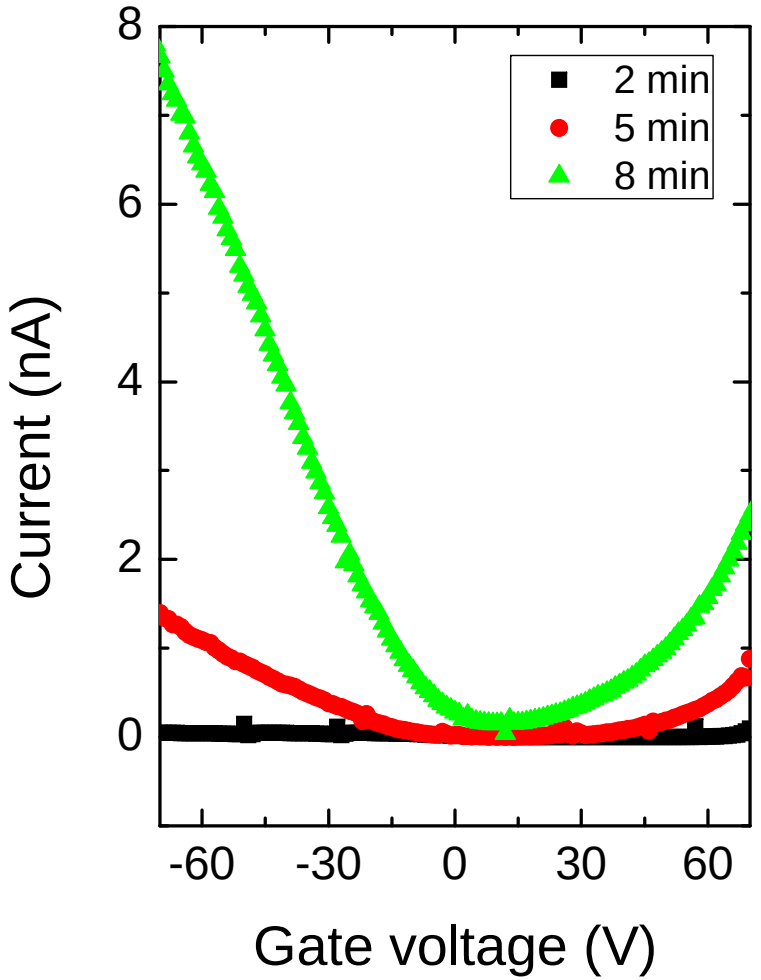




Advanced Materials 22, 505 (2010)

Progressive reduction

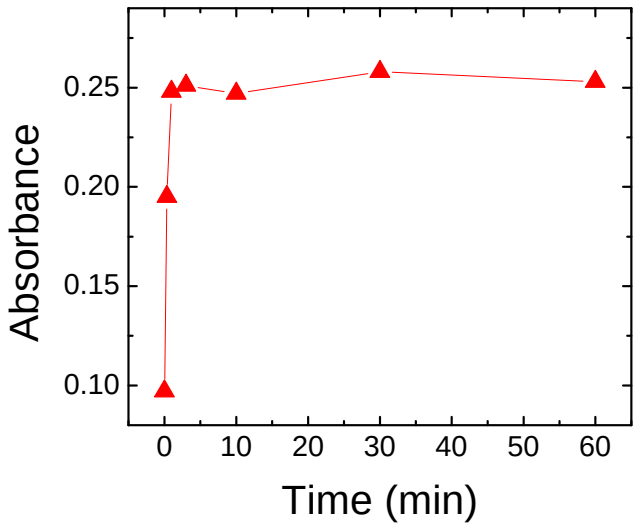


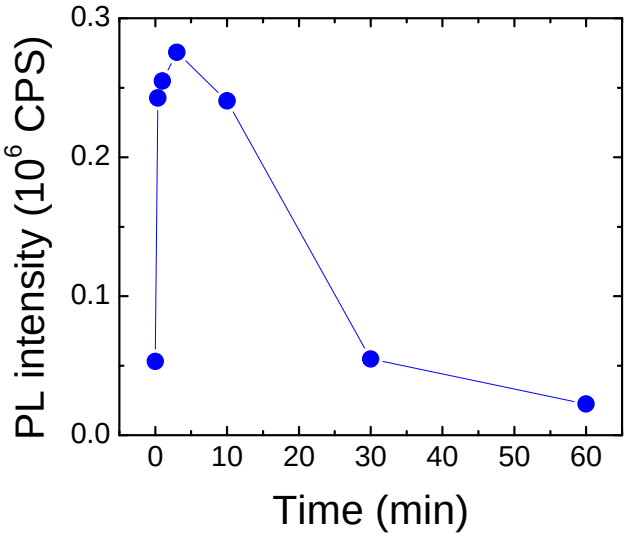


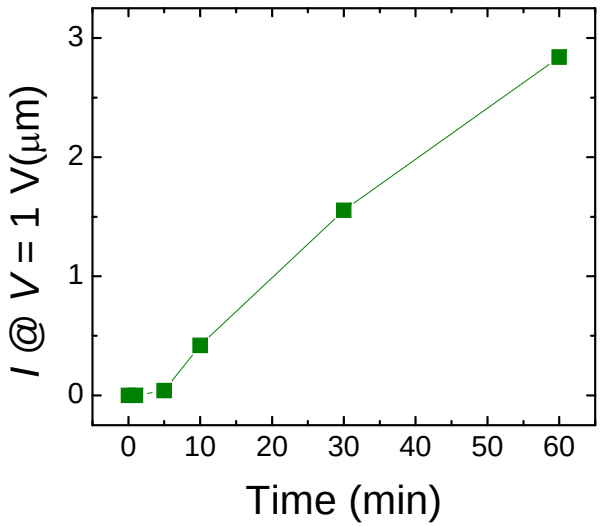
Percolation

No percolation

Optical and electrical property correlation







Absorbance

PL intensity

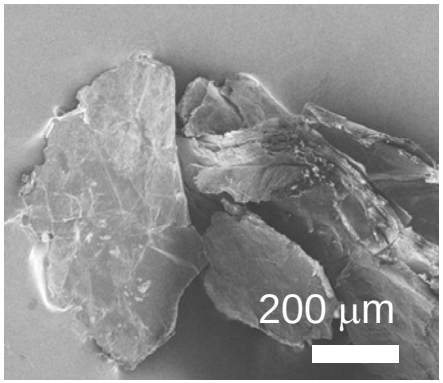
Conductivity

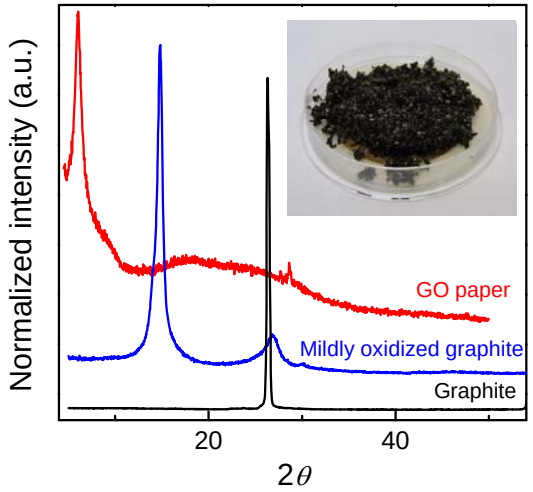
The sp^2 phase of GO becomes percolating after ~ 10 min of exposure to hydrazine

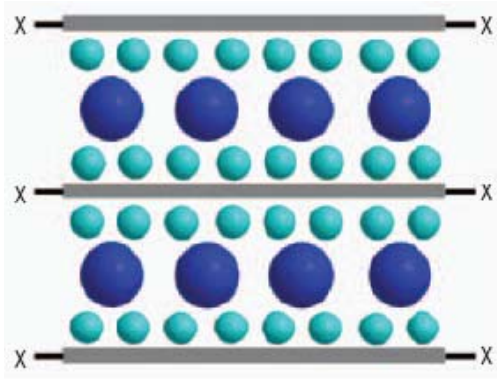
Mild oxidation, intercalation, and exfoliation of graphite

Brodie's method

Graphite + HNO_3 + $KClO_4$



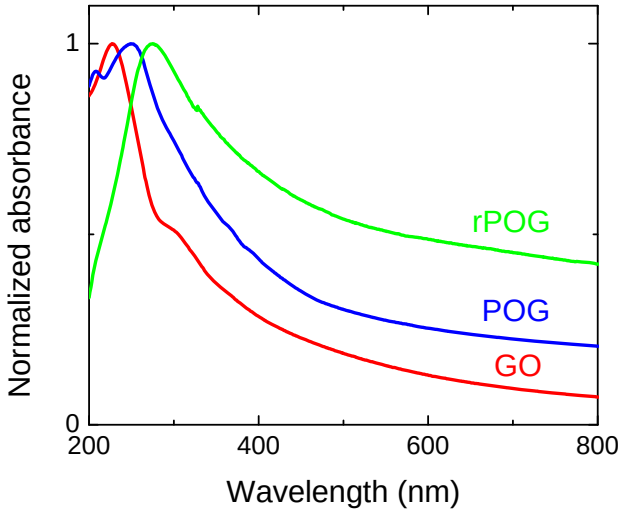


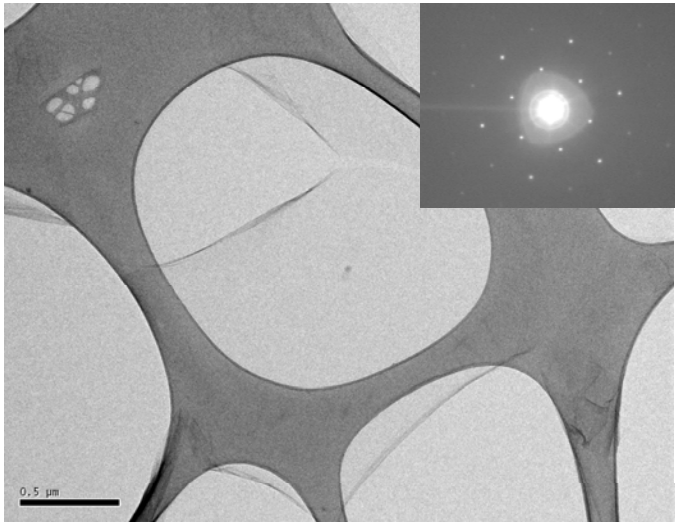


Li et al. Nature Nanotech. (2008)

GO POG

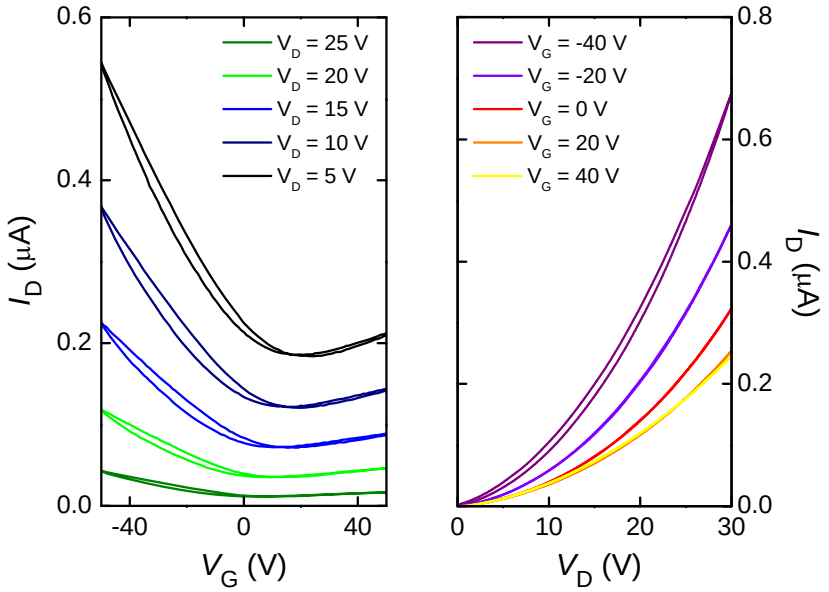
(Partially oxidized graphene)



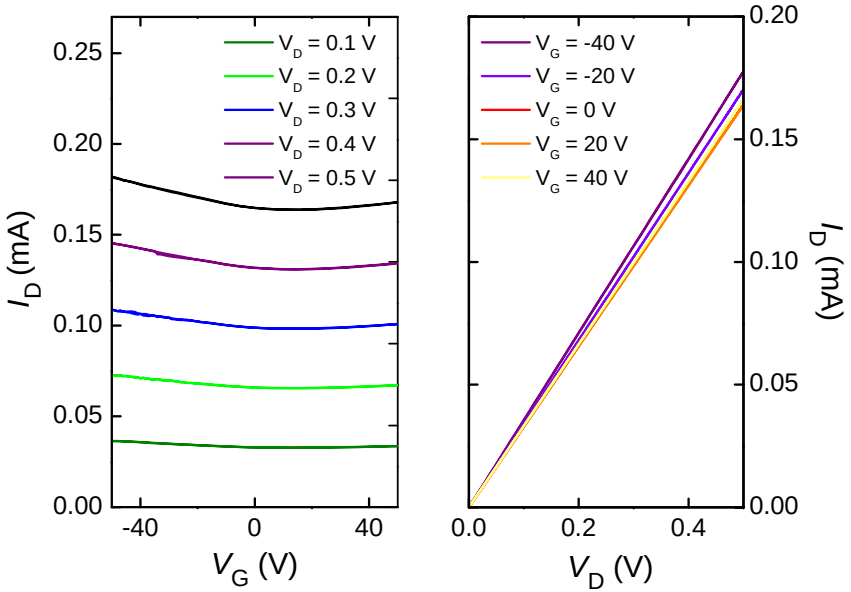


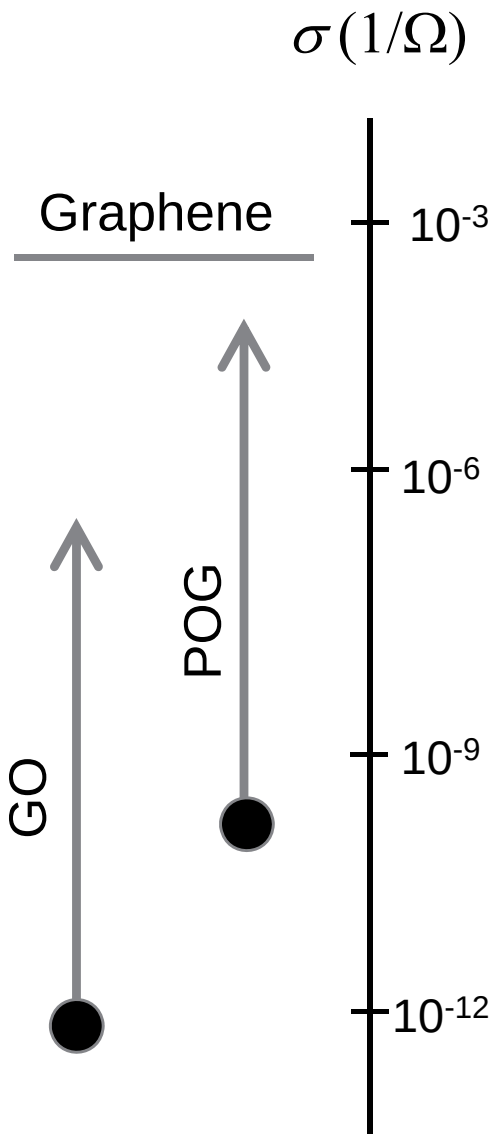
Electrical properties

As-synthesized POG

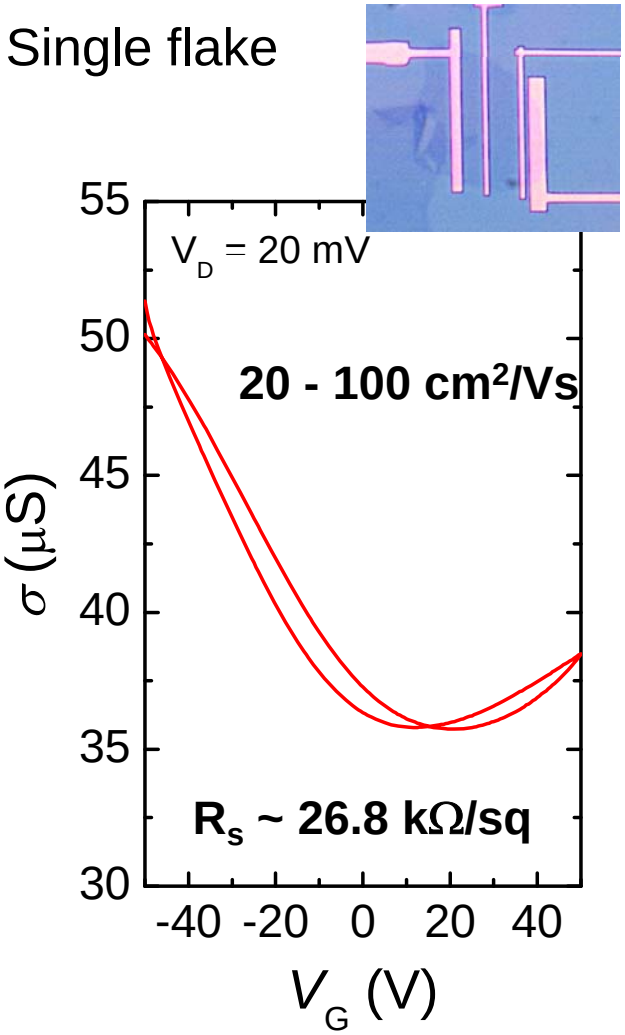


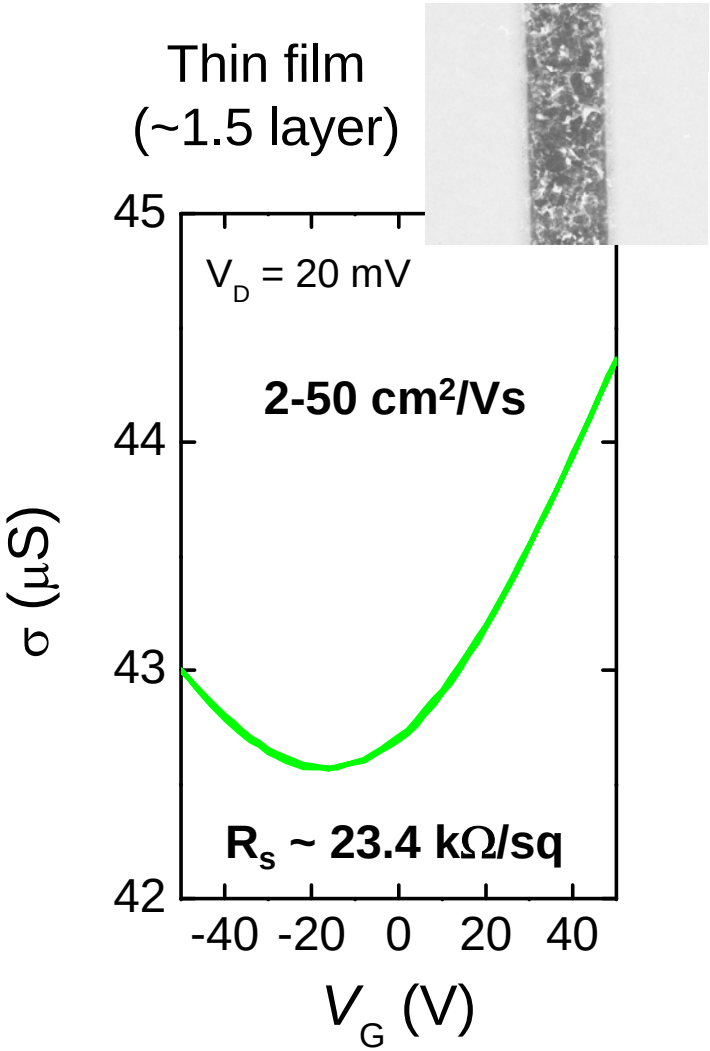
Reduced POG



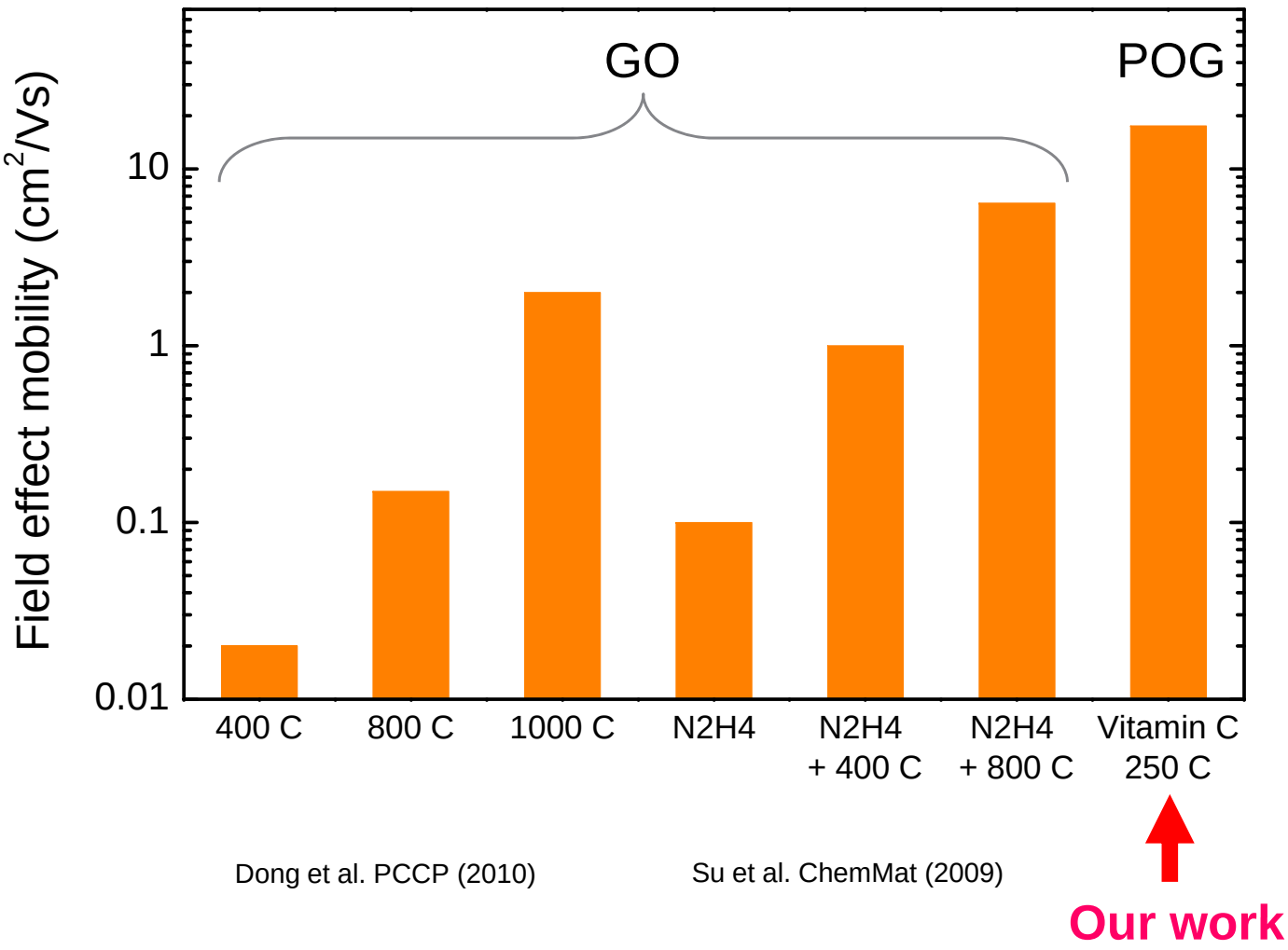


Single flake vs “poly-flake” thin film



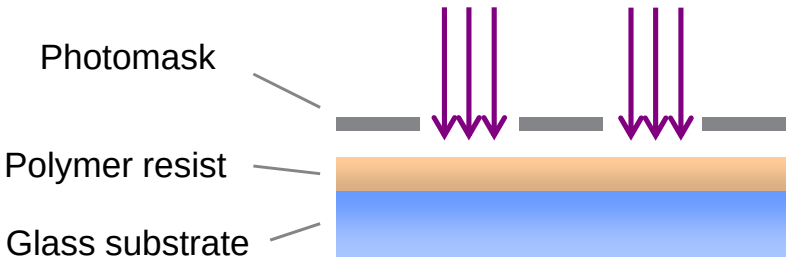


Field effect mobility (individual sheet)

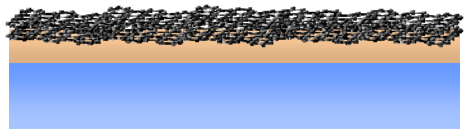


Patterning of graphene films

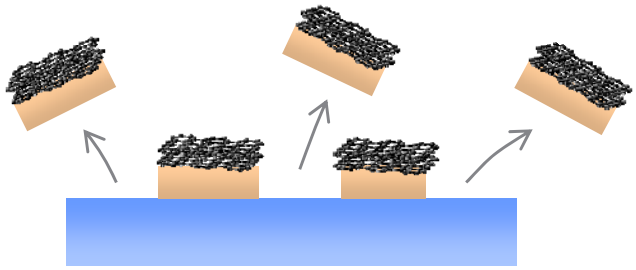
I. UV exposure

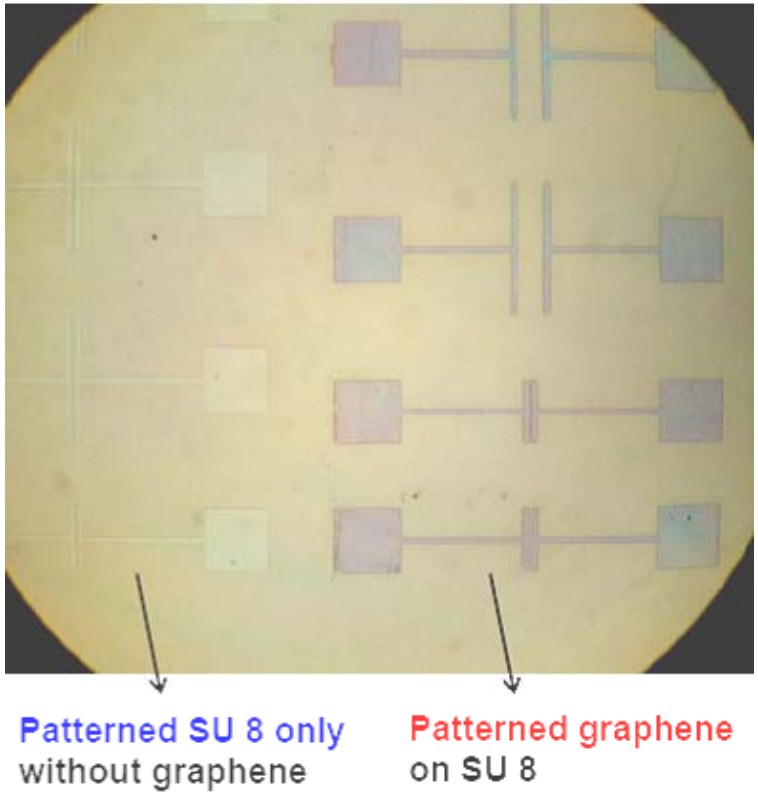


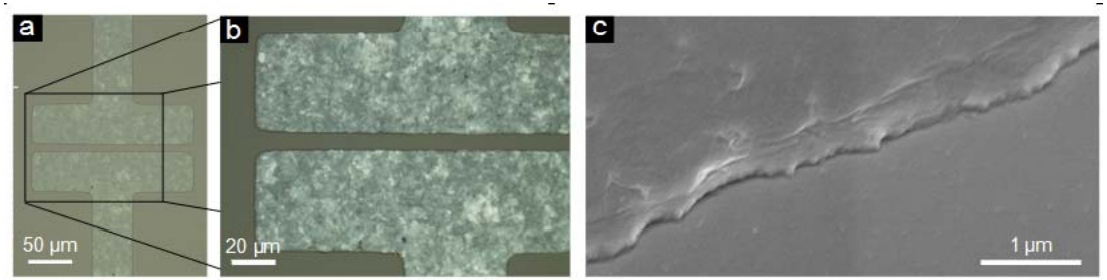
II. Graphene deposition



II. Develop resist/lift-off







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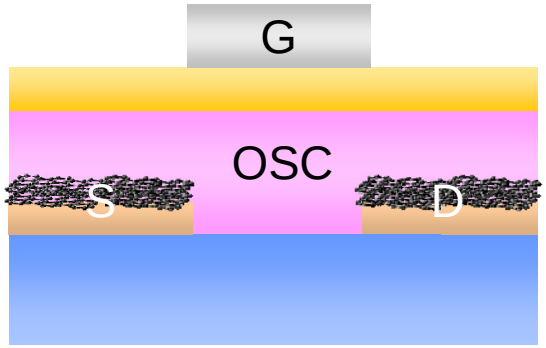
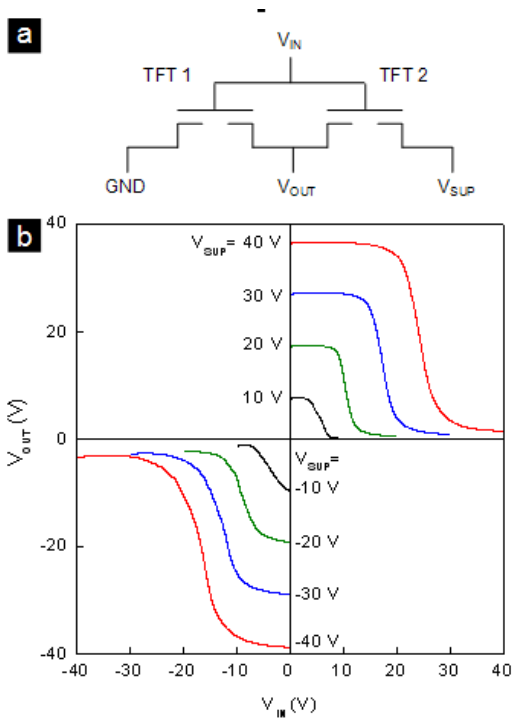
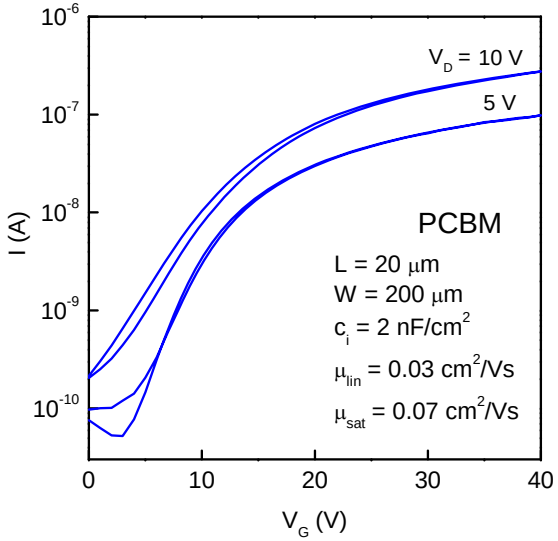
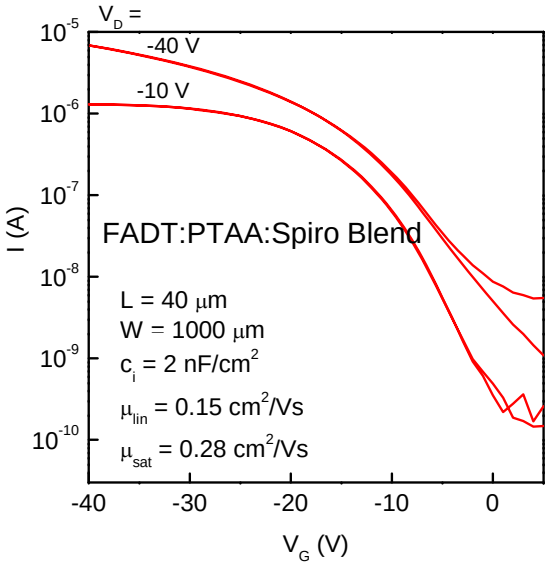
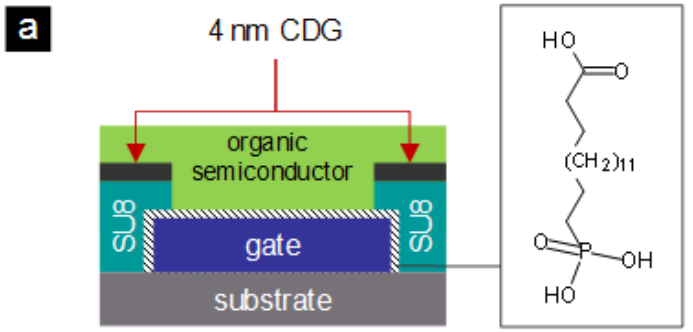
OTFT with graphene electrodes

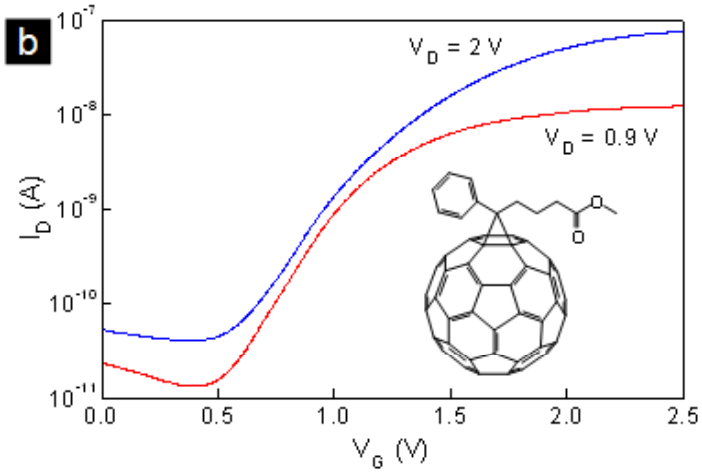












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Conclusions

- Graphene oxide is an interesting and chemically versatile material that allows for obtaining tunable optical and electrical properties.

- The opto-electronic properties of GO is largely determined by sp^2 phase present as nanometer clusters and smaller molecular configurations

- Electrical conduction in reduced GO occurs via tunneling or hopping of carriers among the sp^2 phase.

- Reduction does not lead to growth of the sp^2 clusters but to increased concentration. Hopping transport is thus facilitated with reduction.

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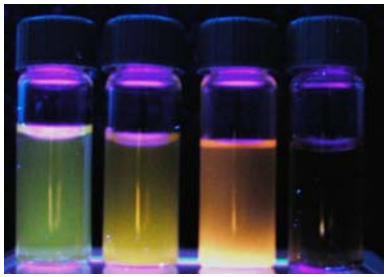

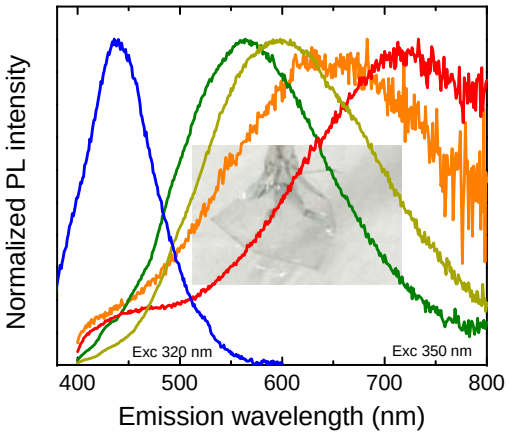

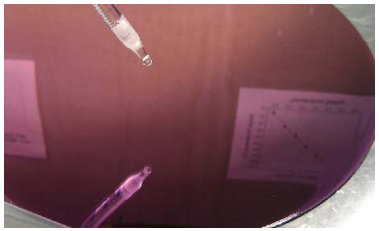

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