Graphene Oxide Transparent Conductors

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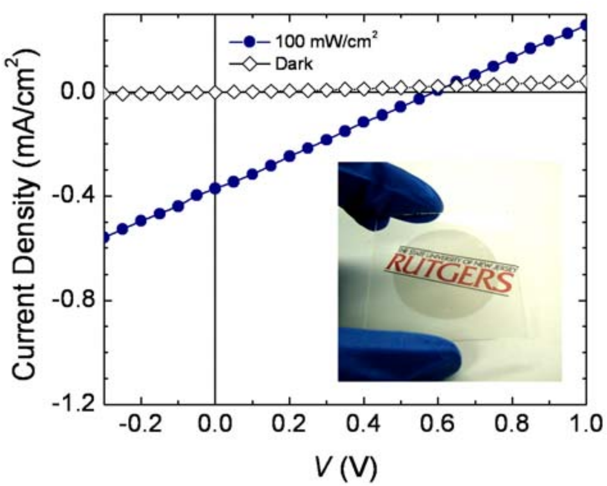
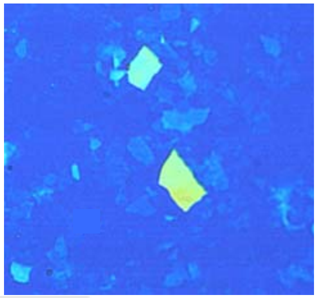
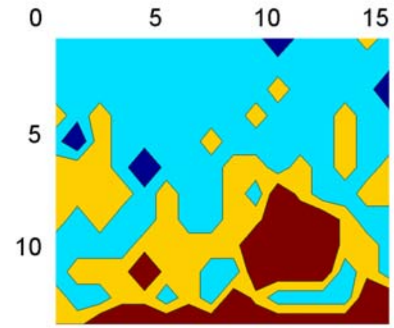
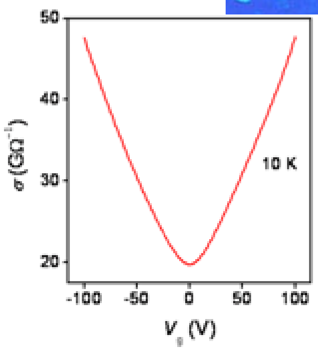
- Opto-electronic properties of solution processed graphene thin films
  - Deposition and Reduction
  - Electrodes for OPVs

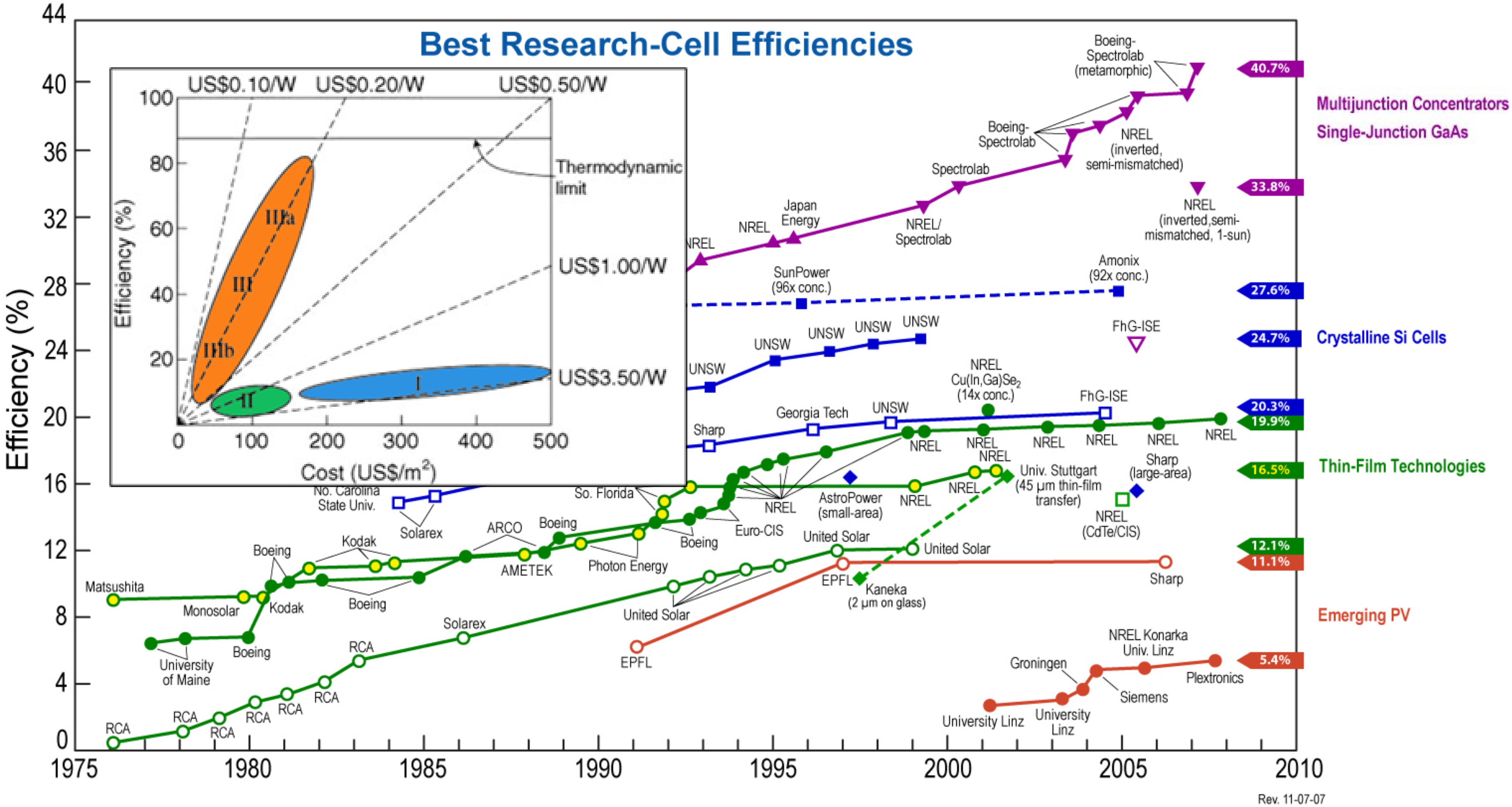








The Current State of Photovoltaics



Kazmerski *et al.* NREL website

Indium Tin Oxide

- The scarcity of Indium and the demand for ITO by the LCD industry drove the price of Indium up 900% from 2002 to 2006.
- ITO is expensive!
- Many of the extensively-used metal oxides are increasingly problematic due to:

    (i) nonuniform transmission across the visible spectrum;

    (ii) limited transparency in the near-infrared region;

    (iii) their chemical instability (e.g, Indium Tin Oxide (ITO) is known to inject oxygen and indium ions into the active media of a device), unstable in the presence of an acid or base;

    (iv) the current leakage, e.g., in Fluorine Tin Oxide (FTO) devices.

The III-V solar cells and even c-Si (HIT, Heterojunction with Intrinsic Thin layer) solar cells extensively use metallic grids as front contacts to collect photocarriers. The expensive process of metallization used to print the front contact grid blocks more than 5%

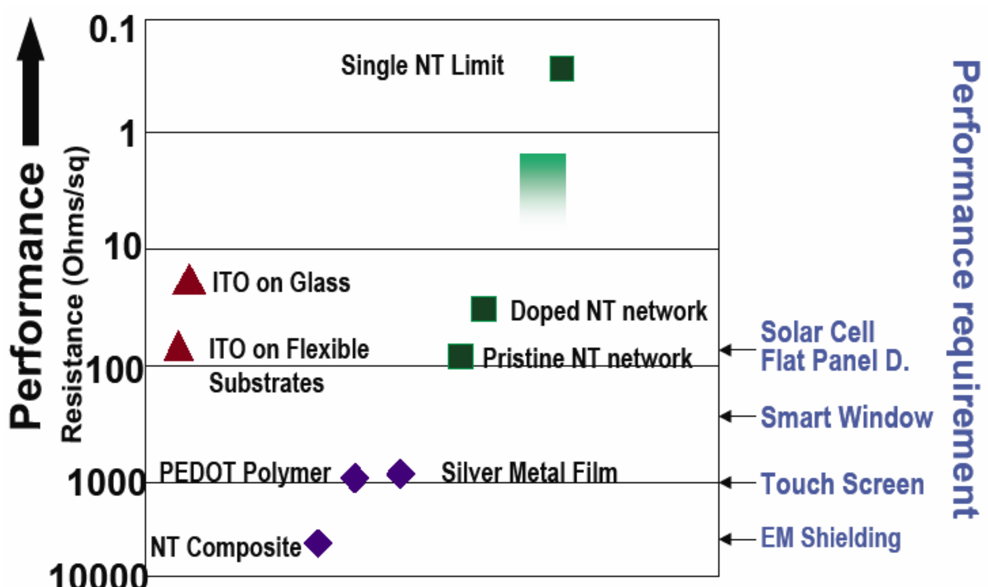
↓

begs for a viable alternative to reduce cost and increase functionality of the device.

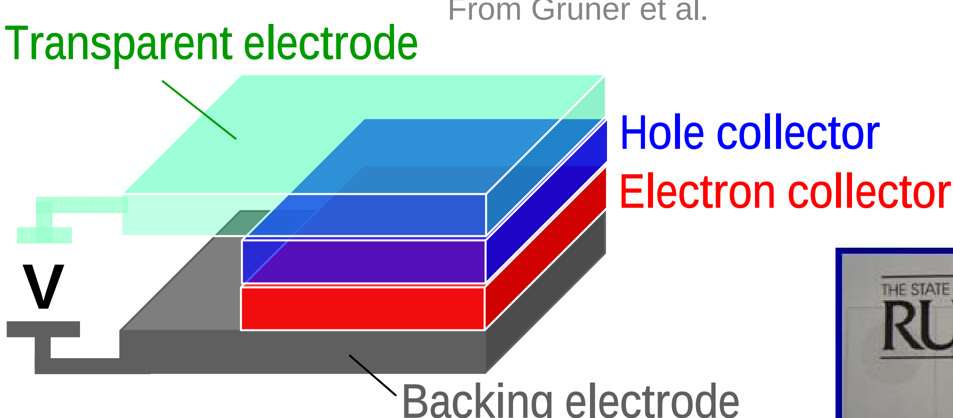
OPVs and TFTs with Graphene Thin Films

- Graphene for plastic electronics:

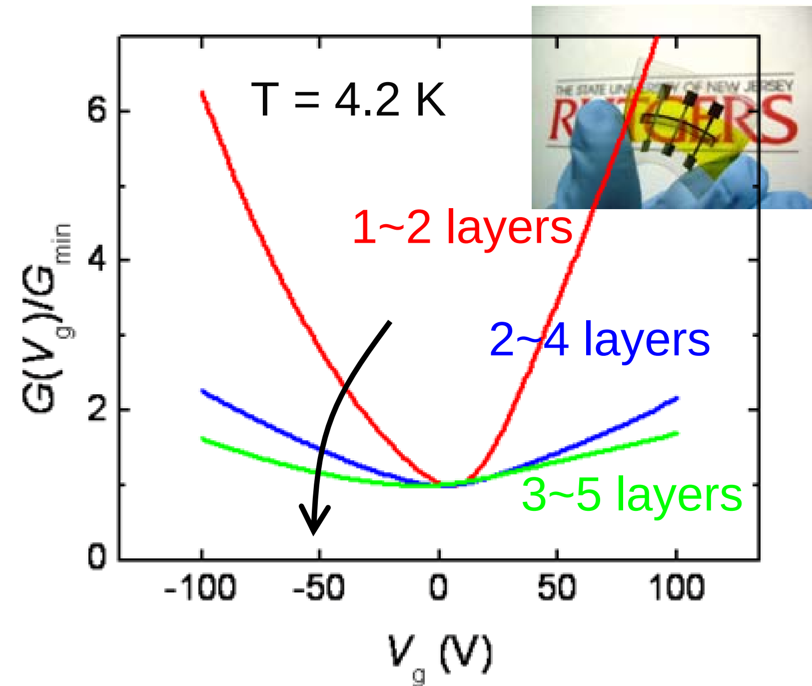
Transparent and Conducting Electrodes

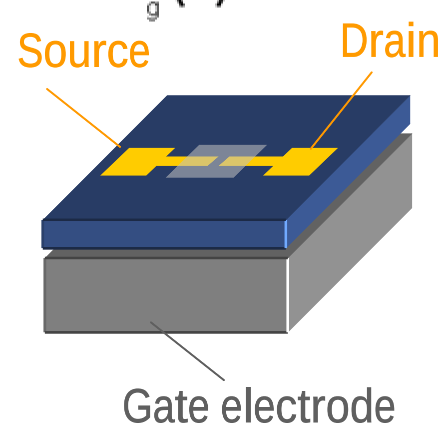


From Gruner et al.



Thin-film transistors

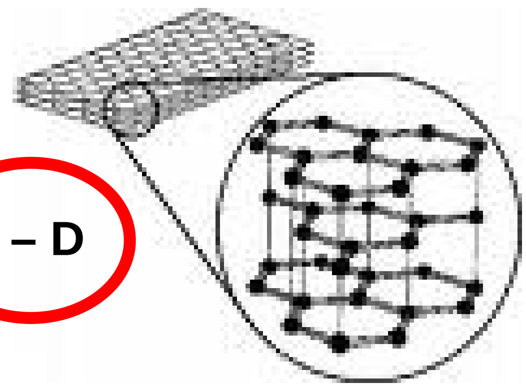




Forms of Carbon

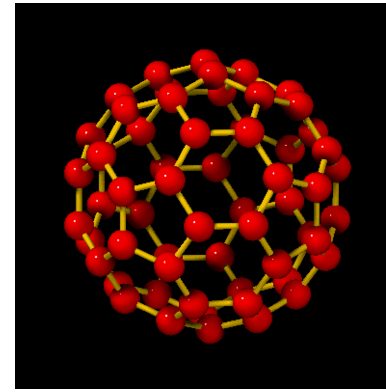
Diamond, circa 4000 BC
In India

Graphite, ~ 1550
Great Britain



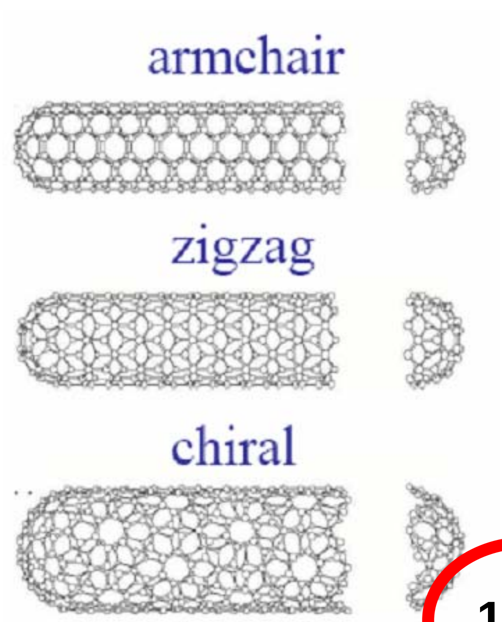
3 – D

C60, 1985



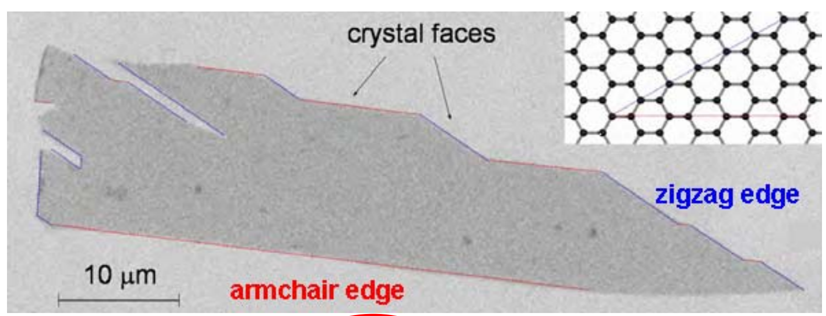
0 - D

SWNTs in 1993



1 - D

Graphene, 2004

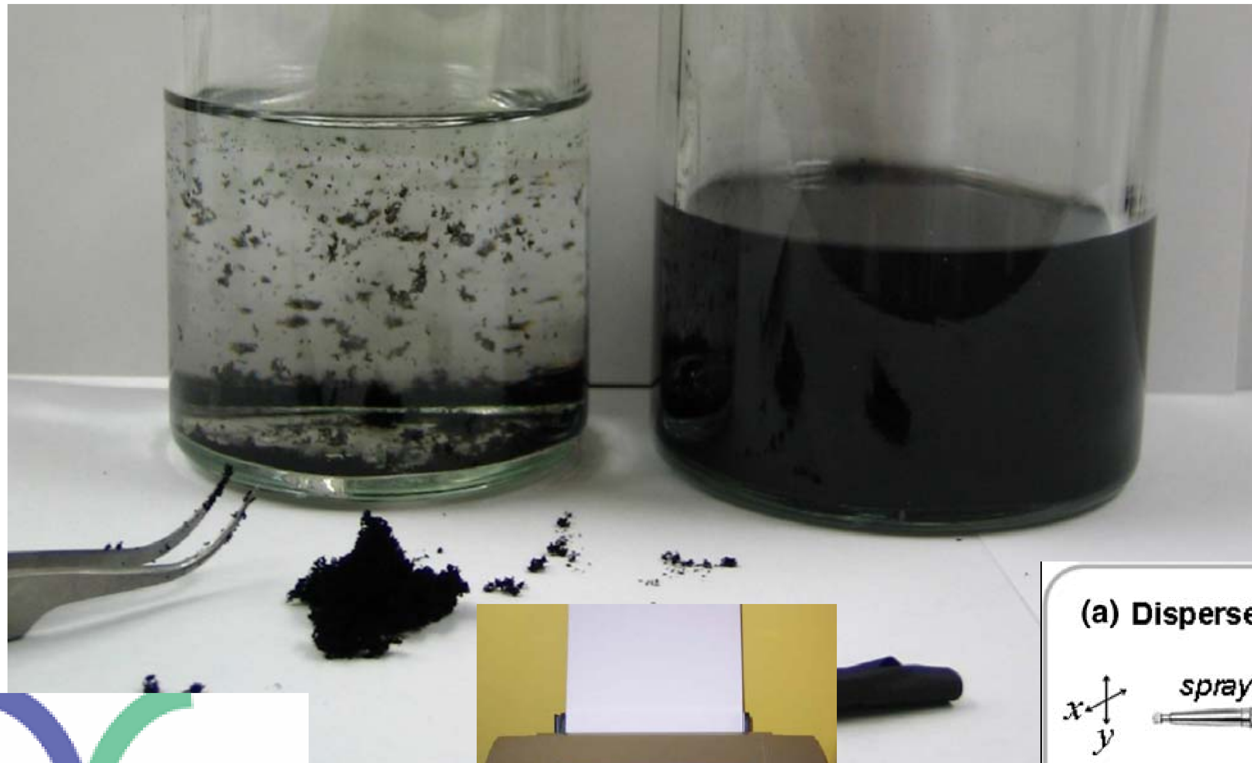


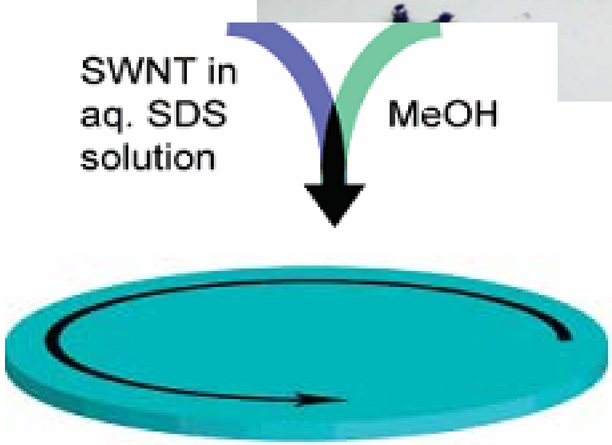
2 - D

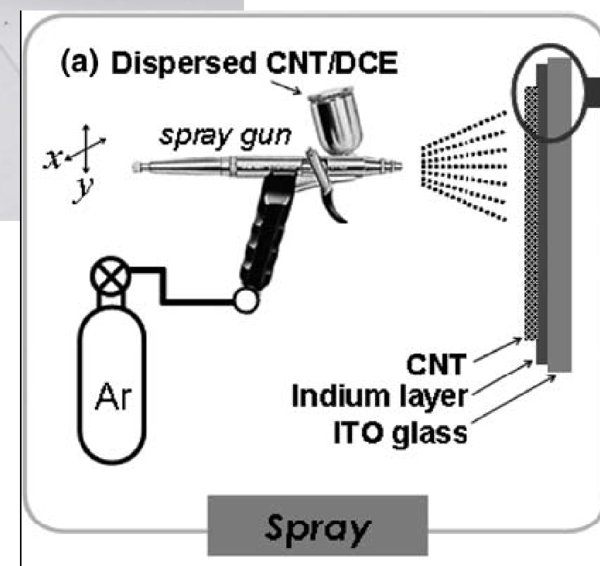
?

Nanomaterials for Electronics

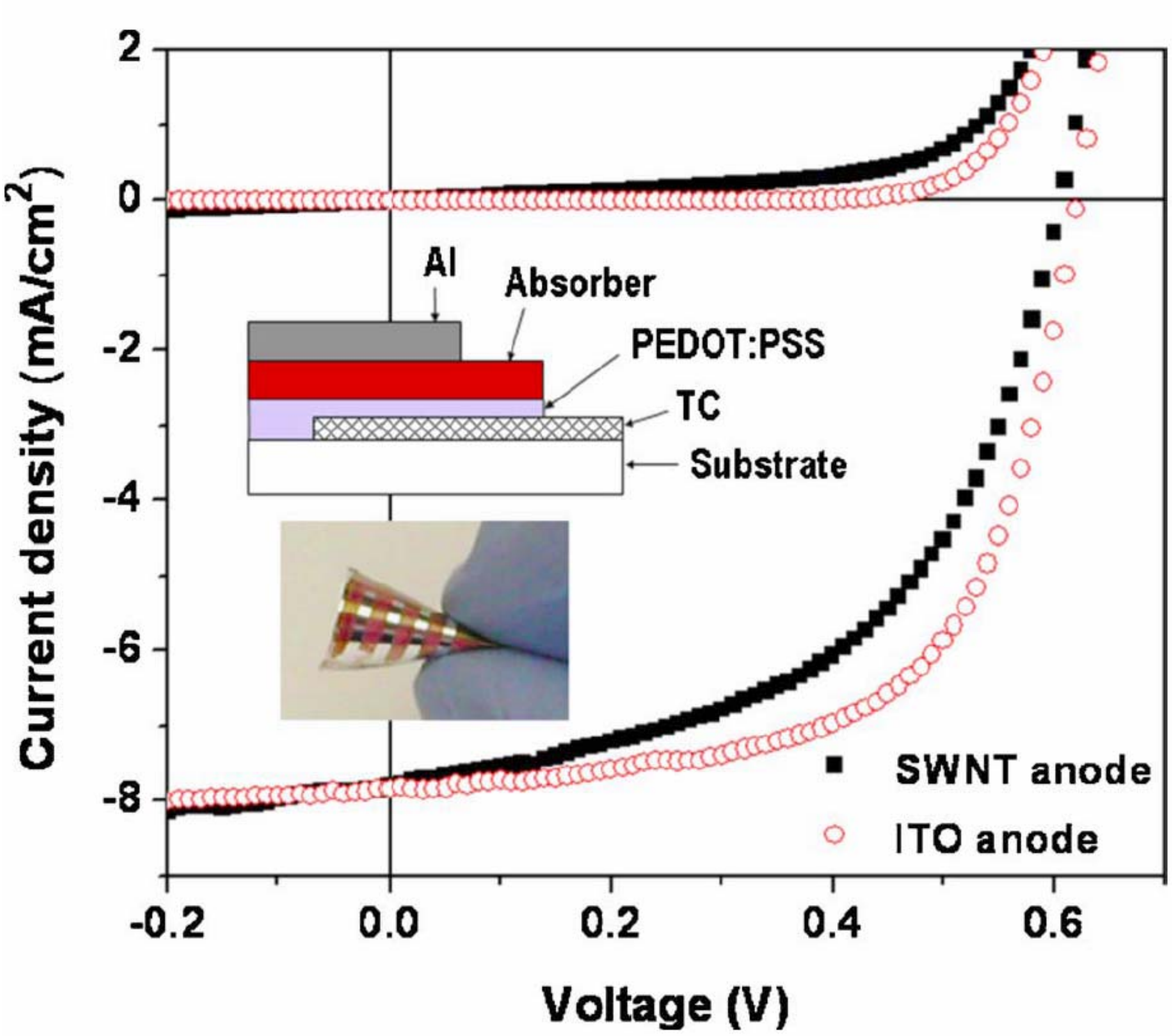
- Disperse nanomaterials to form an “ink” for flexible, printable electronics:







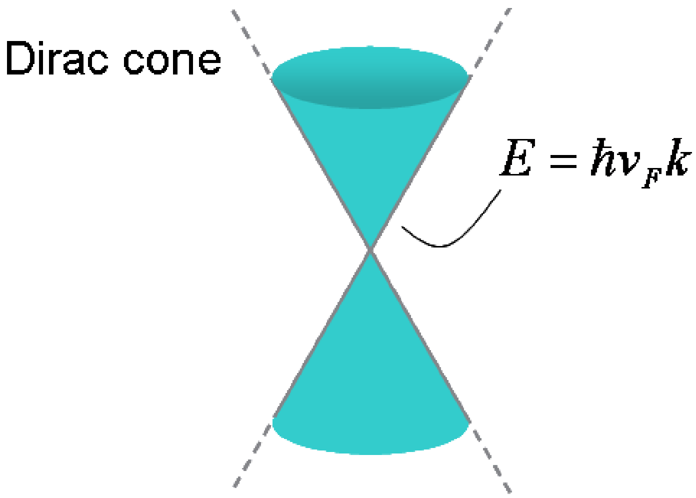
SWNTs vs ITO in OPVs

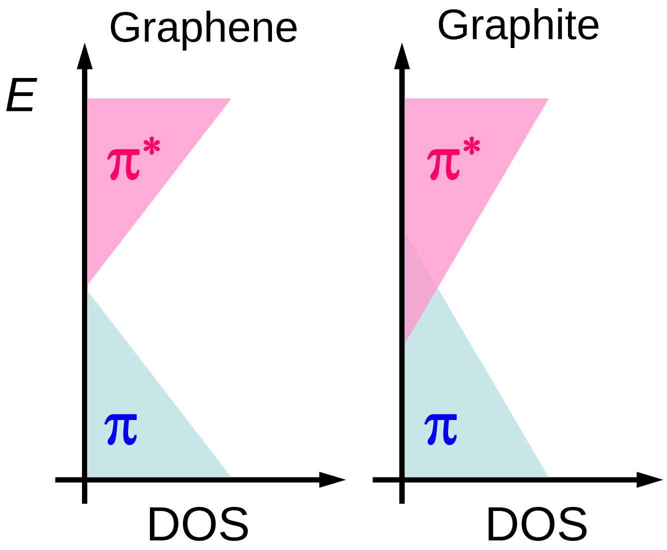


Rowel et al. *APL* 88, 233506 (2006)

Why Graphene?

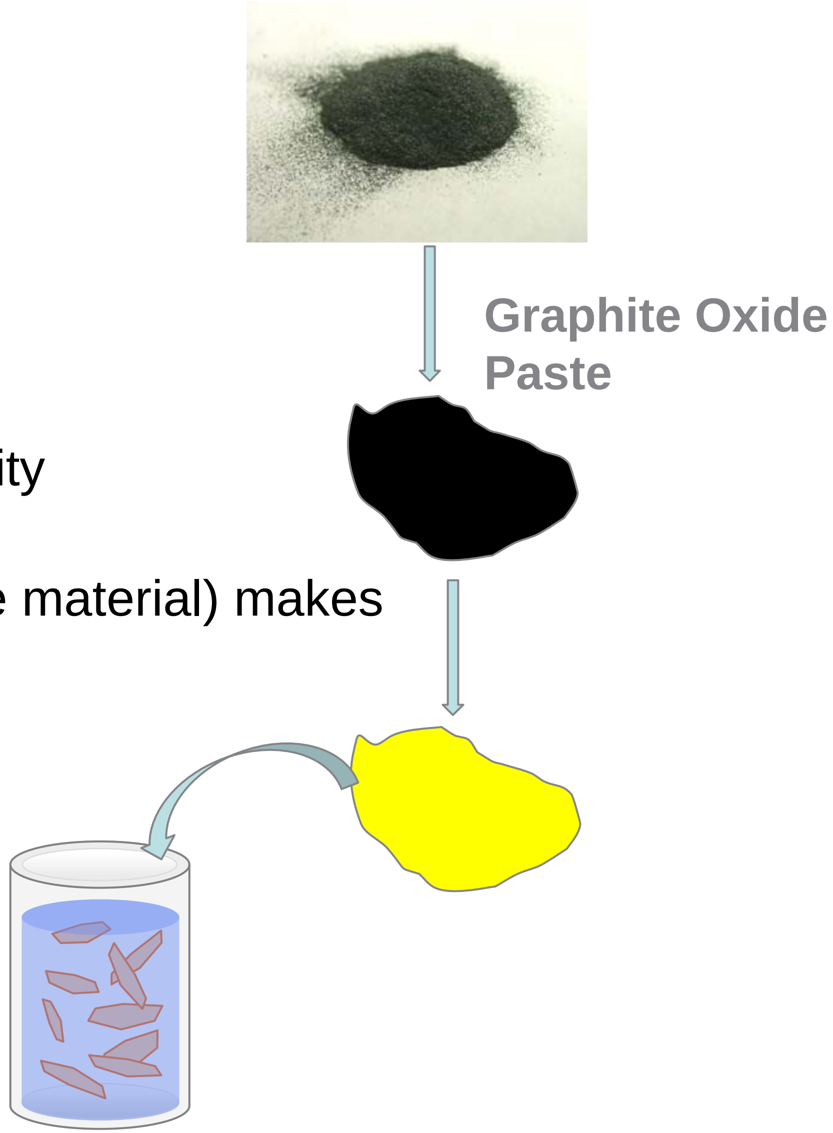
- Chemical, mechanical, and thermal stability
- 0 eV band-gap semiconductor
  - Ambipolar field effect transistors
- Extraordinary mobility
  - Room temperature mobility of ~10,000 cm^2/Vs
- High current carrying capability
  - Electrons and holes up to $10^{13}/cm^2$
- Exotic physical properties
  -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

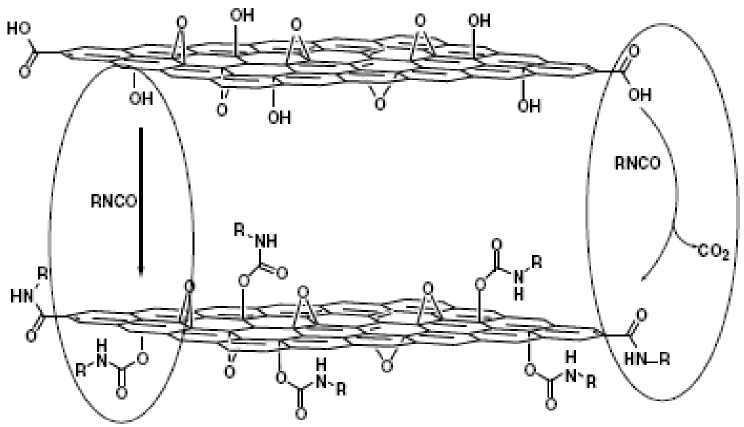




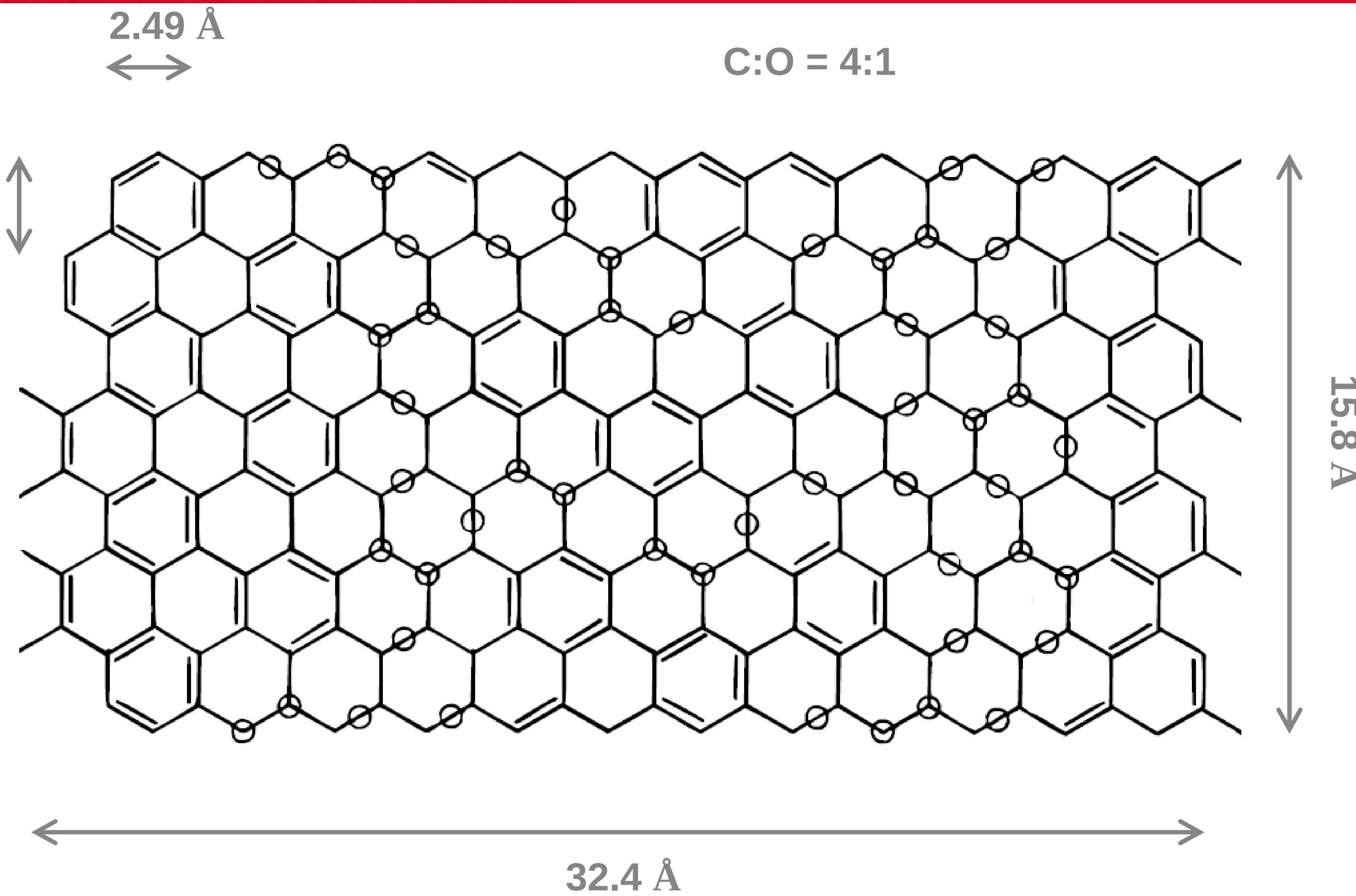
Why Graphene Oxide?

- Cheap transparent conductor
- Solution processing
- Mechanically robust and flexible
- Potentially high current carrying capability
- Reducing to graphene (or graphene-like material) makes for interesting science/engineering
- Did I mention it is really cheap?





C:O = 4:1



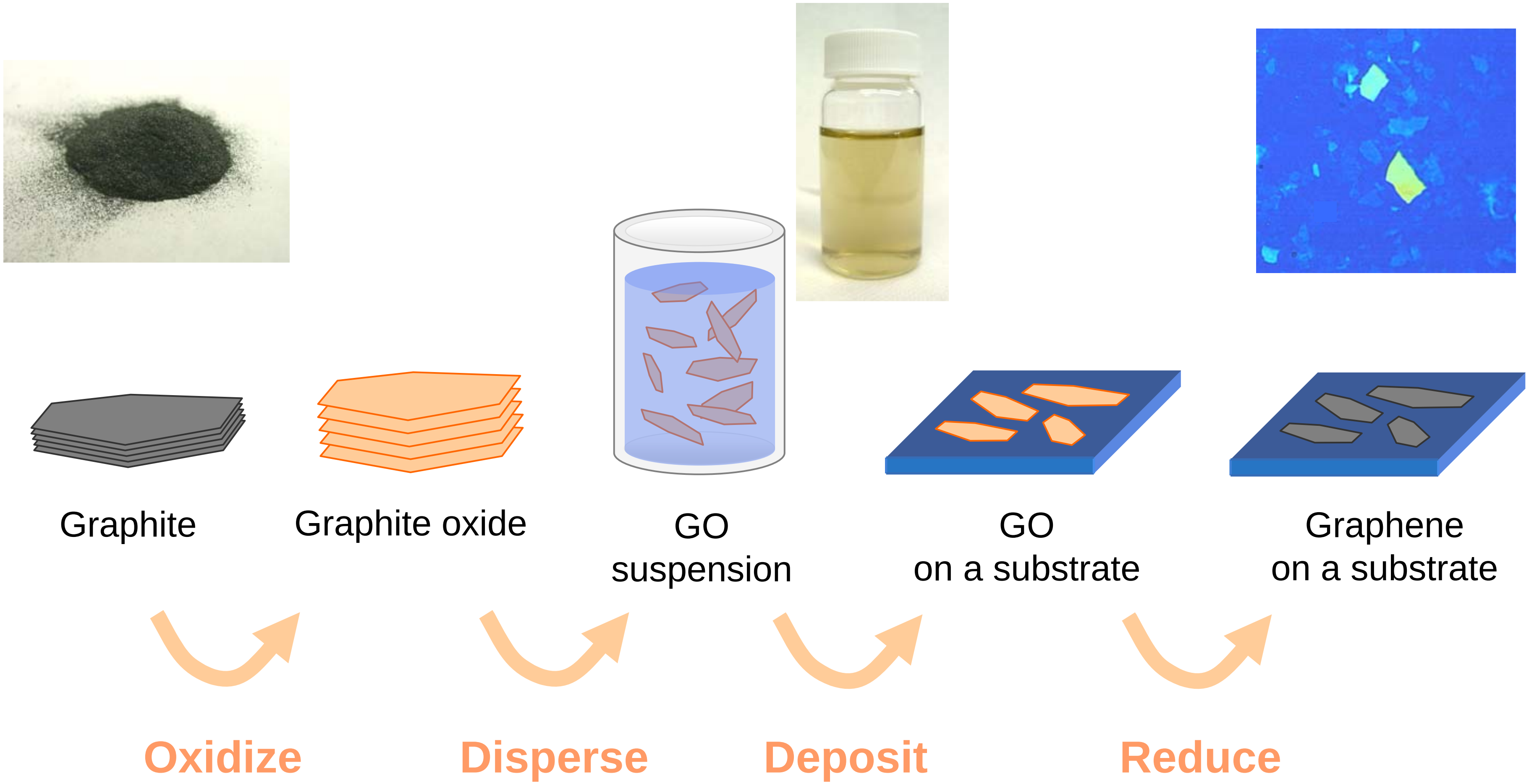
28% coverage of O

50 O, (19 –OH, 31 C-O-C)

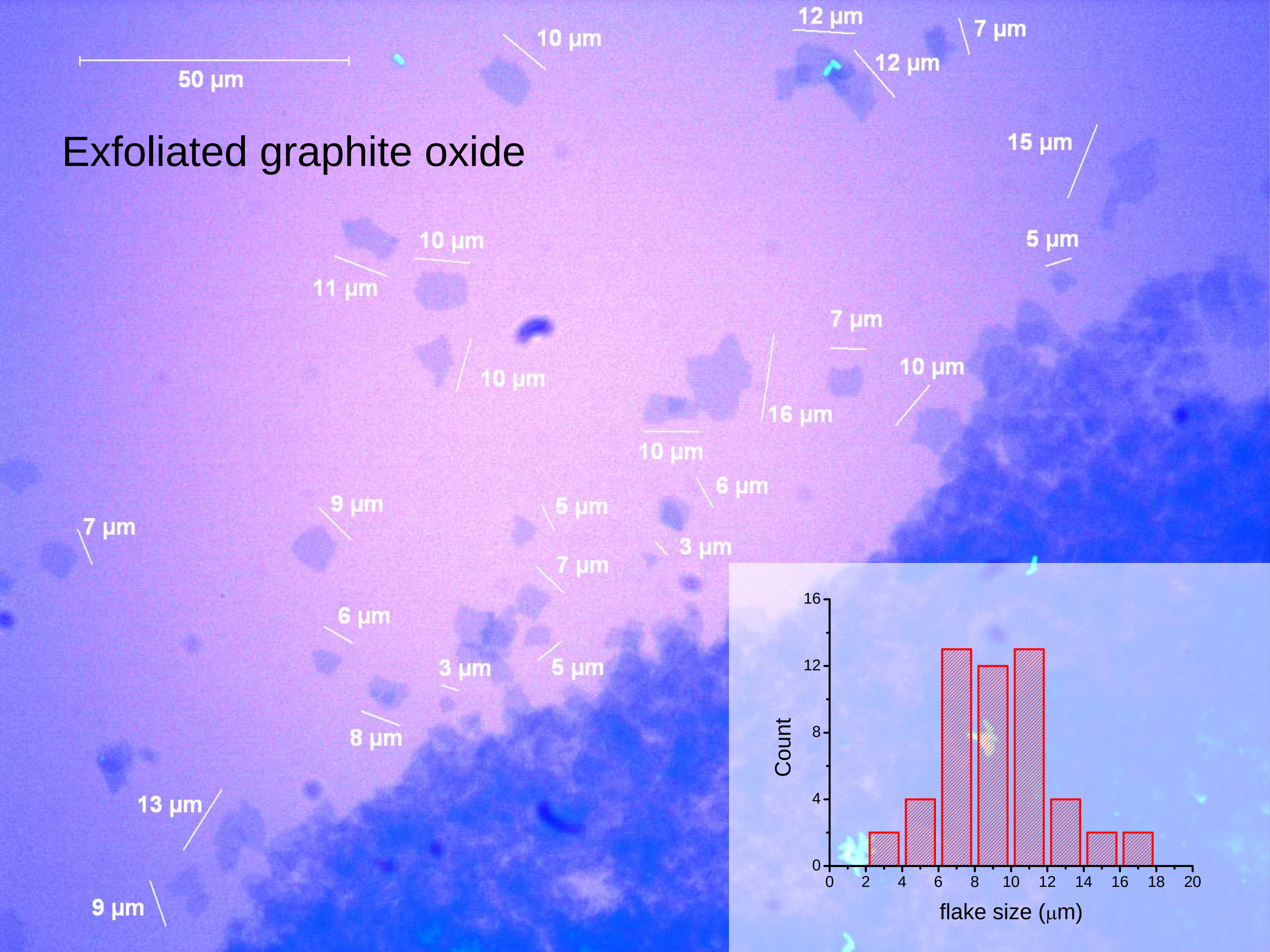
206 C

54 oxidized C

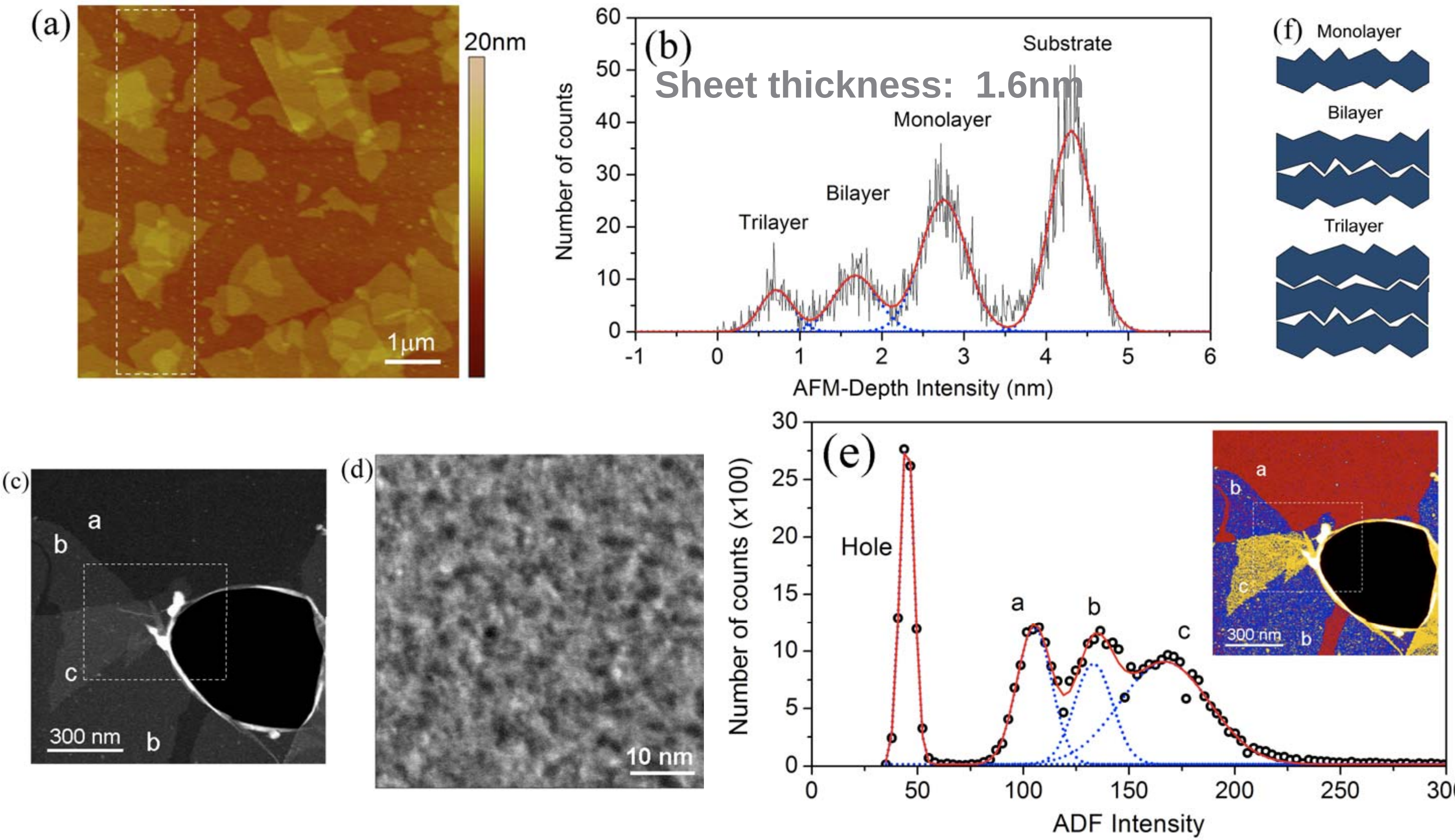
A Chemical Route to Graphene



Exfoliated graphite oxide

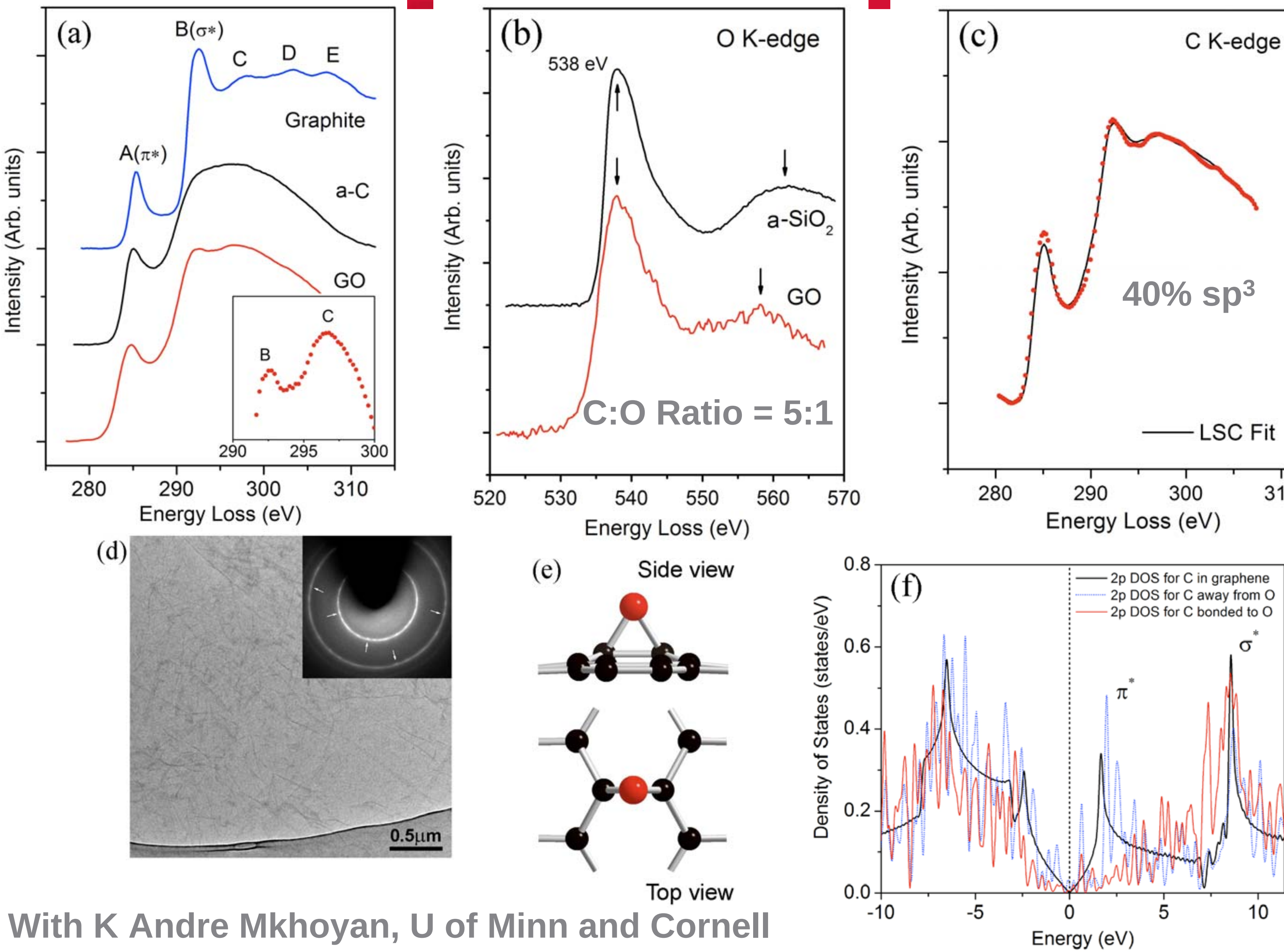


Structure of GO



With K Andre Mkhoyan, U of Minn and Cornell

Structure of GO

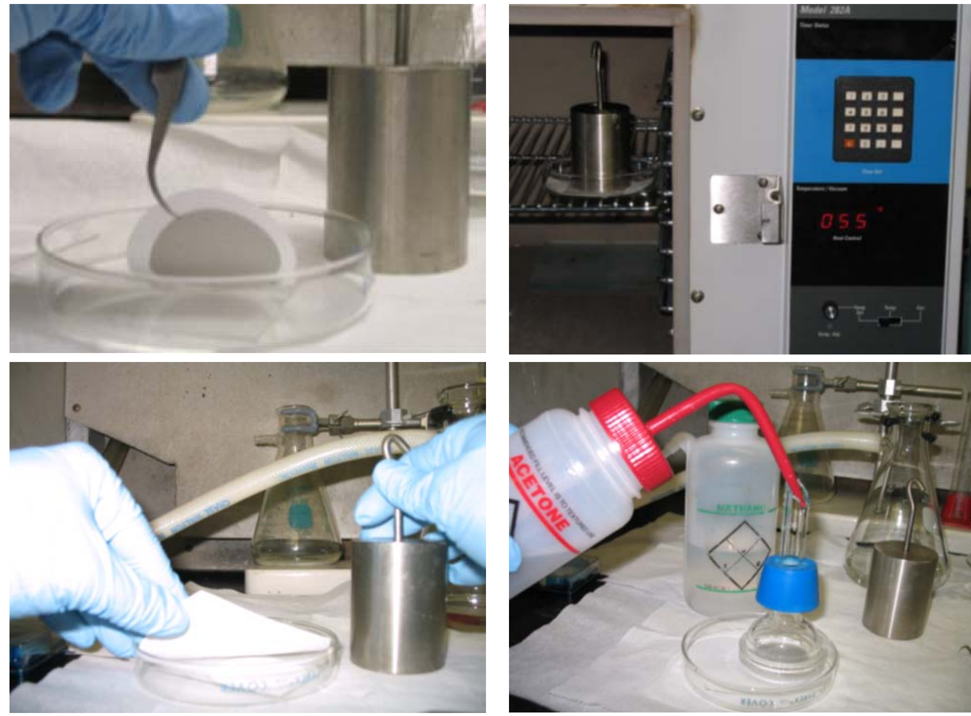


With K Andre Mkhoyan, U of Minn and Cornell

Preparation of Graphene Thin Films

Pristine **Suspensions**

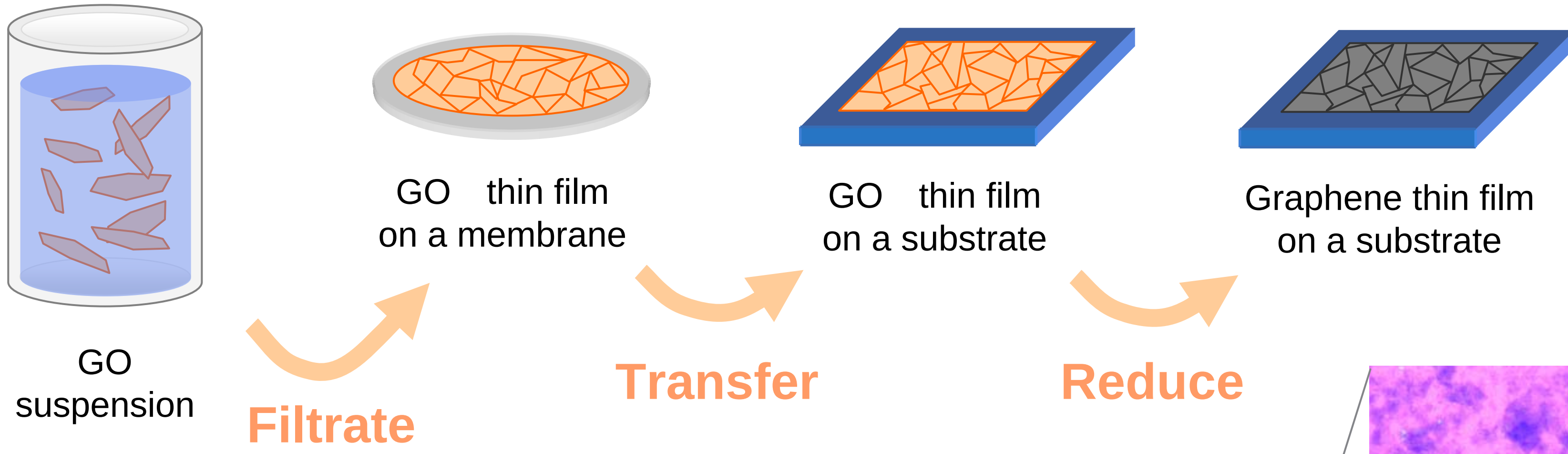
Filtering

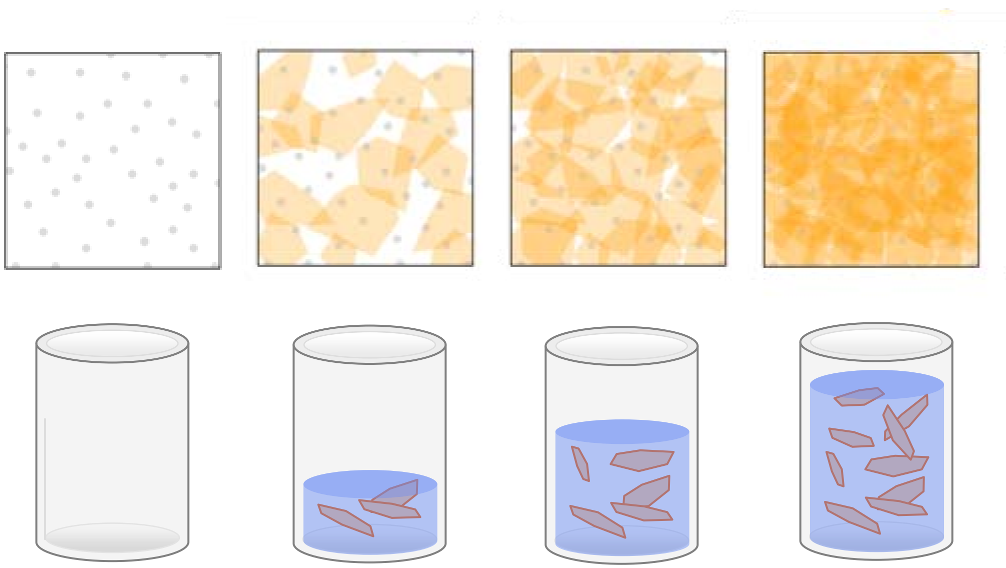


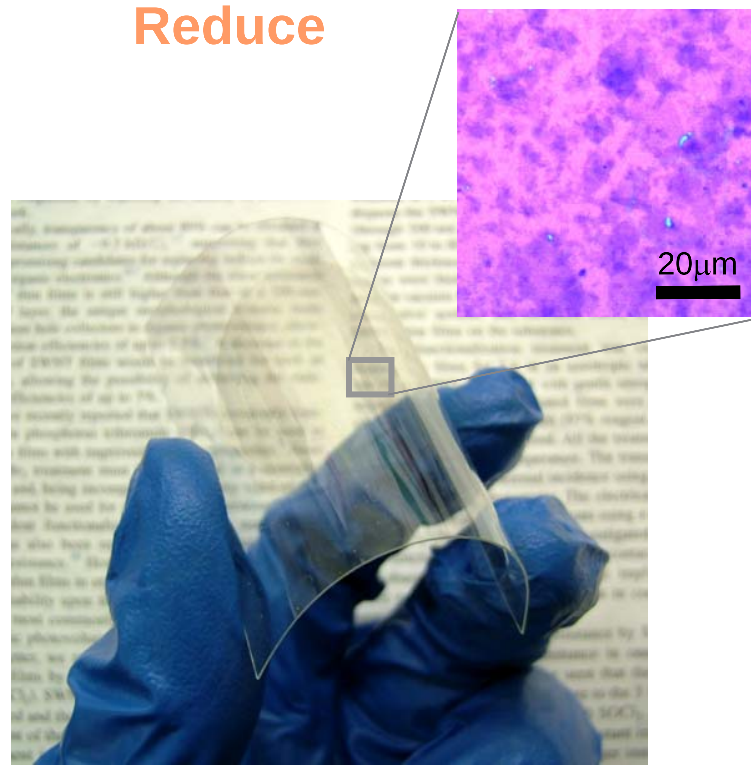
Deposition

After Rinzler et al., Science 2004

Graphene thin film via vacuum filtration

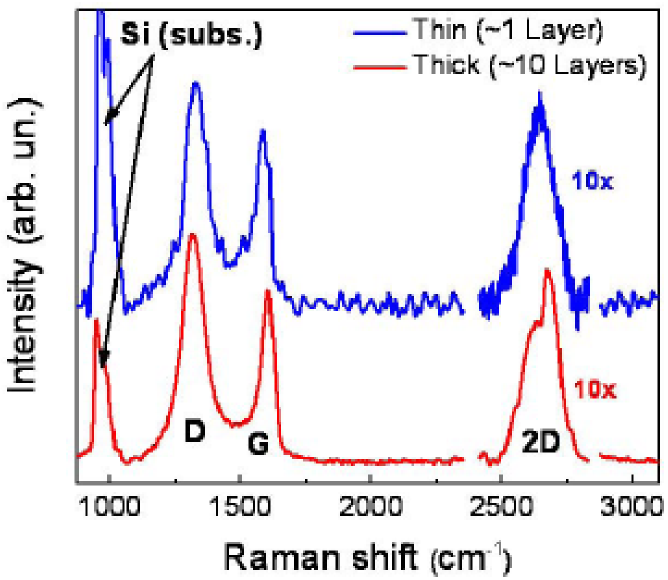


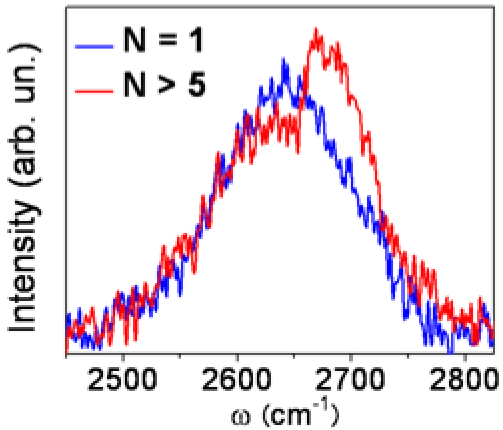




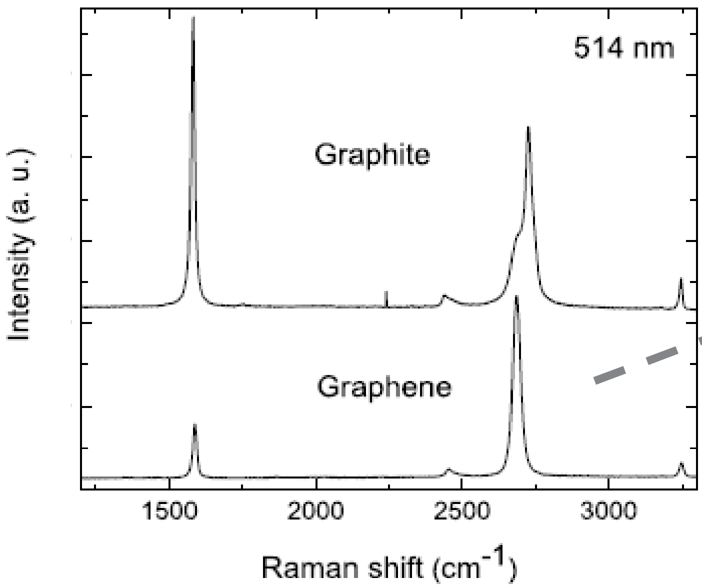
Counting Graphene Layers

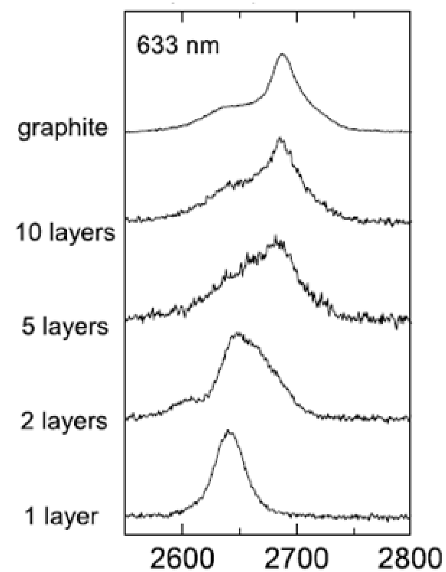
Reduced GO
thin film





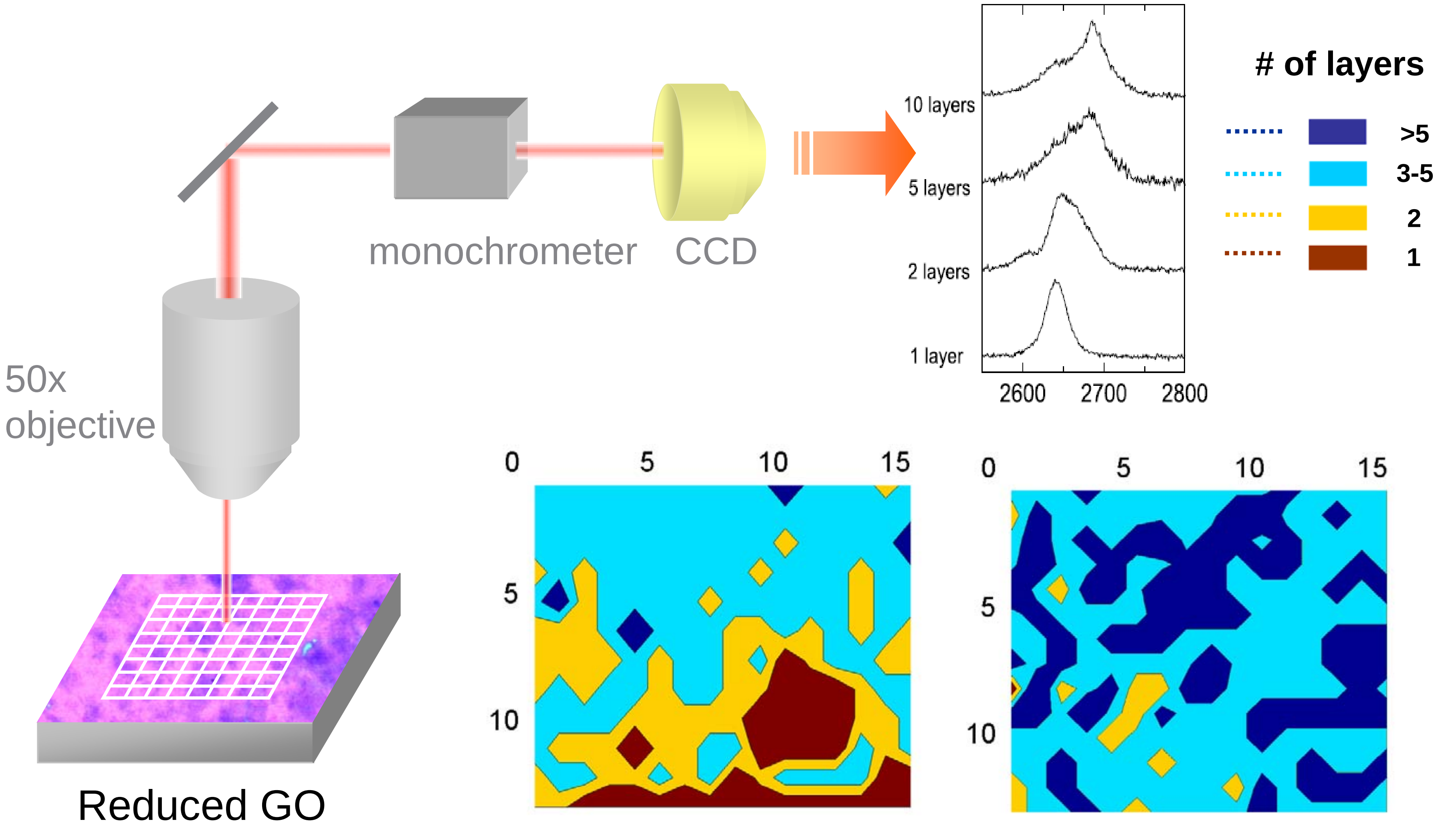
Graphite
&
Graphene





Ferrari *et al.* *PRL* **97** (2006) 187401.

12 x 15 μm Raman mapping



Reduced GO thin film

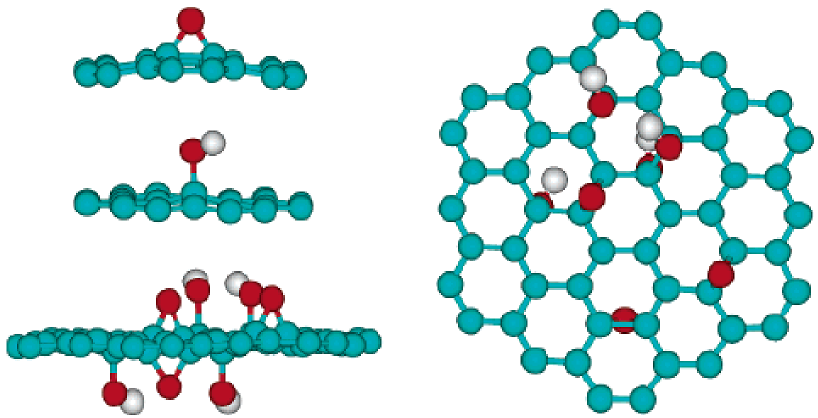
20 mL film (very thin)

80 mL film (thicker)

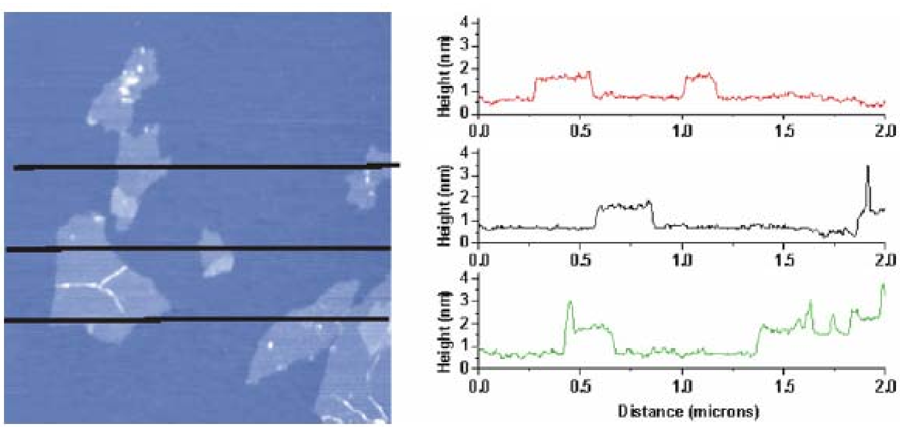
Nature Nanotechnology 3, 270 - 274 (2008)

Graphene oxide (GO)

GO = Graphene + epoxide + hydroxide + ...

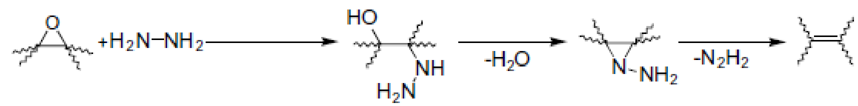


Schniepp *et al. J Phys Chem B* **110** (2005) 8535.



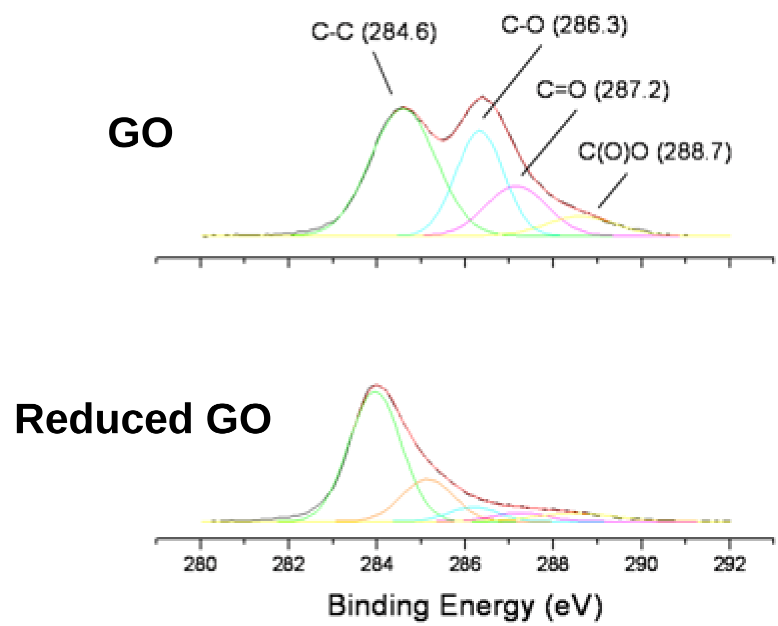
Stankovich *et al. Carbon* **45** (2007) 1558.

Chemical reduction of GO



Stankovich *et al. Carbon* **45** (2007) 1558.

XPS – C1s



In-situ monitoring of GO reduction by XPS

4:1 (C:O)

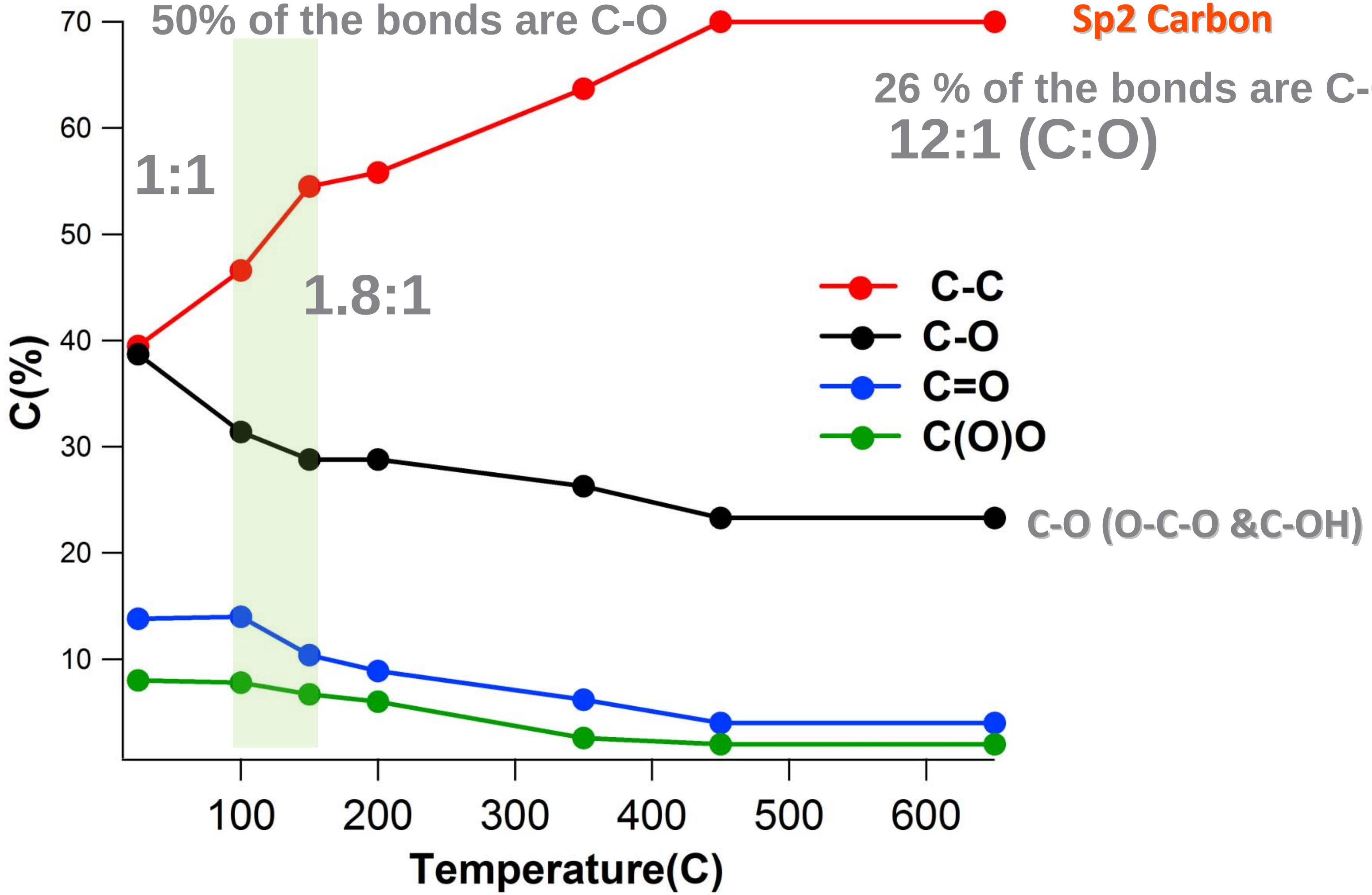
7:2.5 (2.8:1)

50% of the bonds are C-O

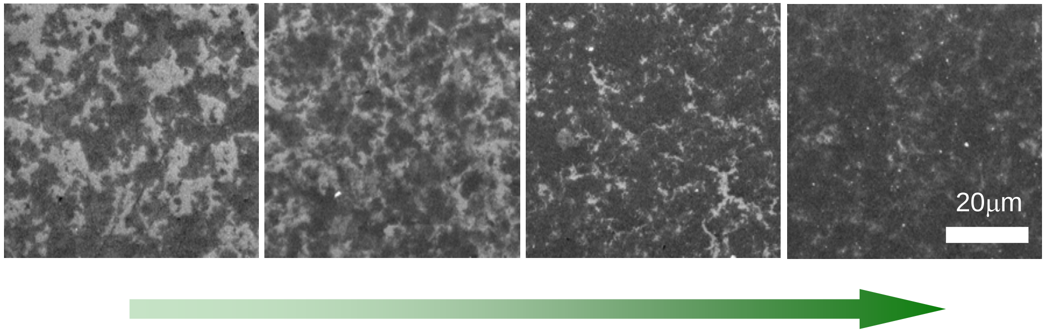
Sp2 Carbon

26 % of the bonds are C-O

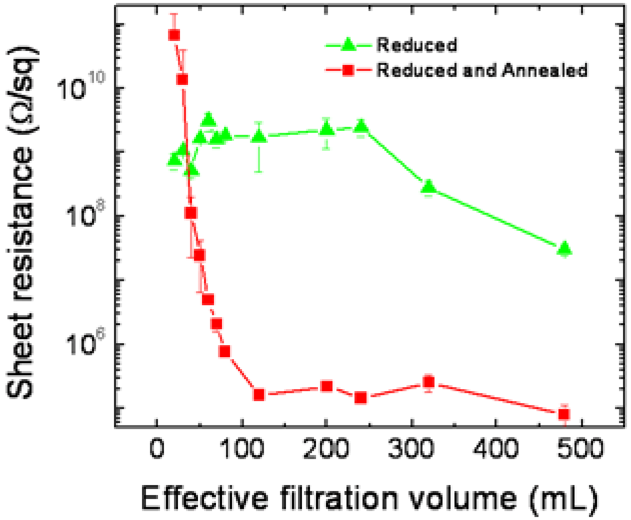
12:1 (C:O)

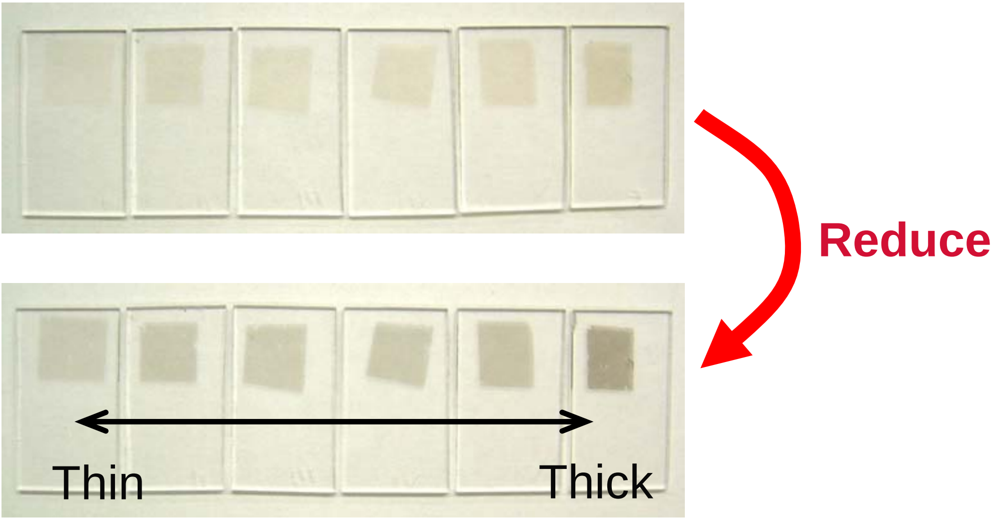


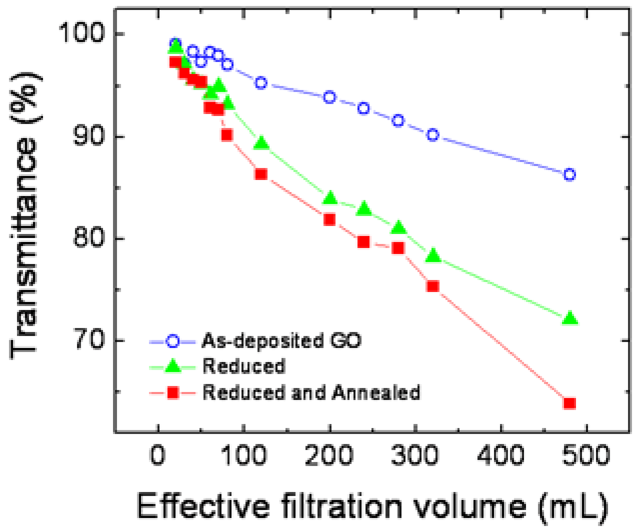
"Tunable" opto-electronic properties



Increasing filtration volume

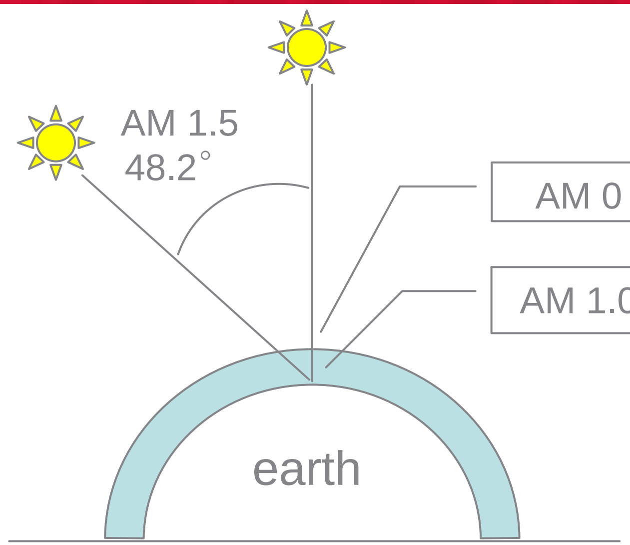


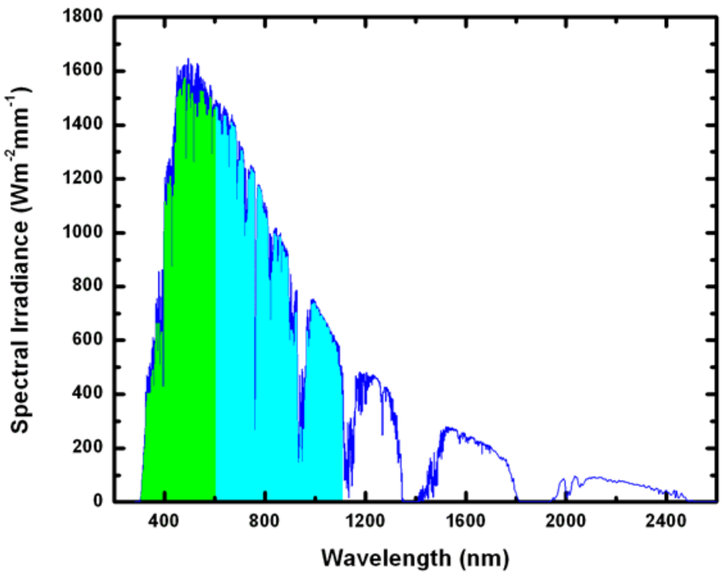


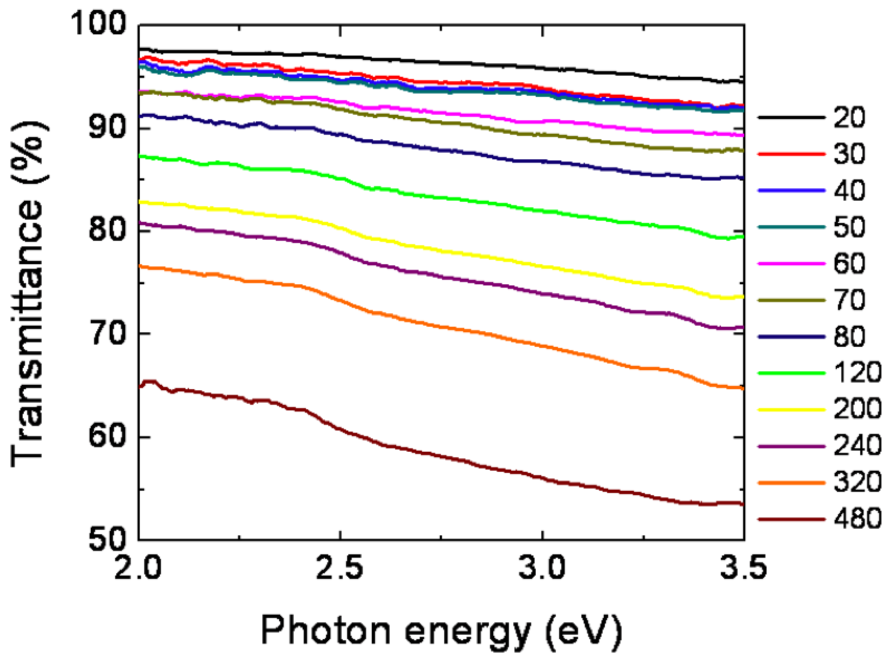


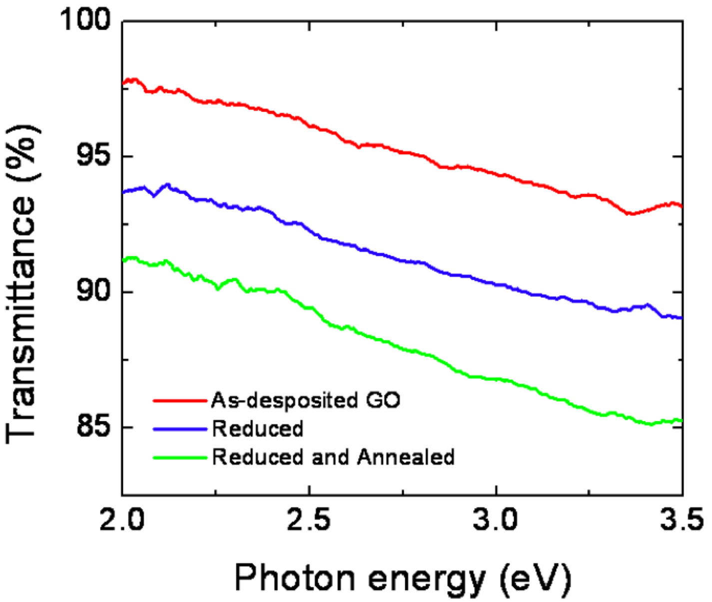
Nature Nanotechnology 3, 270 - 274 (2008)

AM 1.5 Solar Spectrum



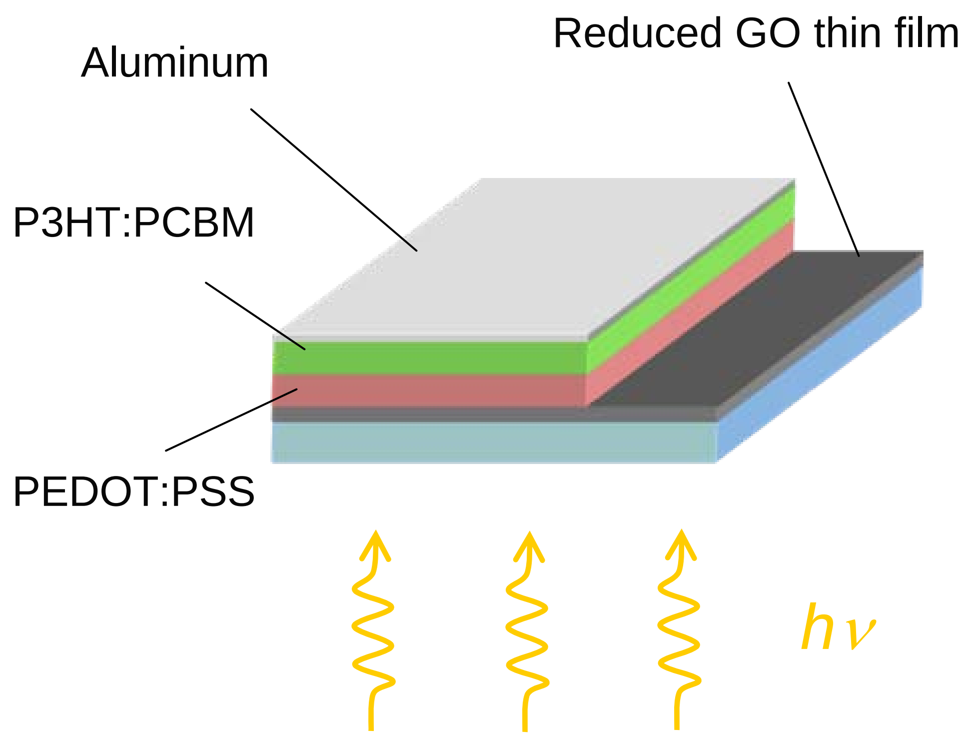


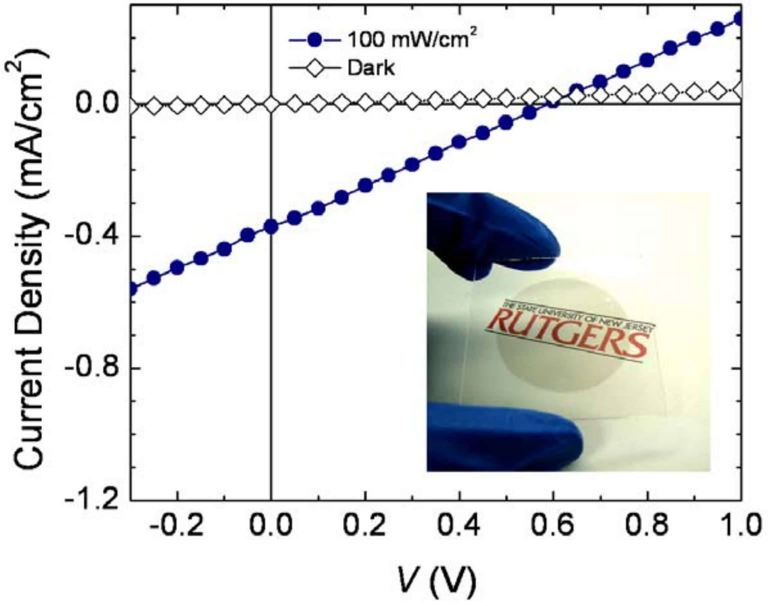




Transparent and Conducting Electrode

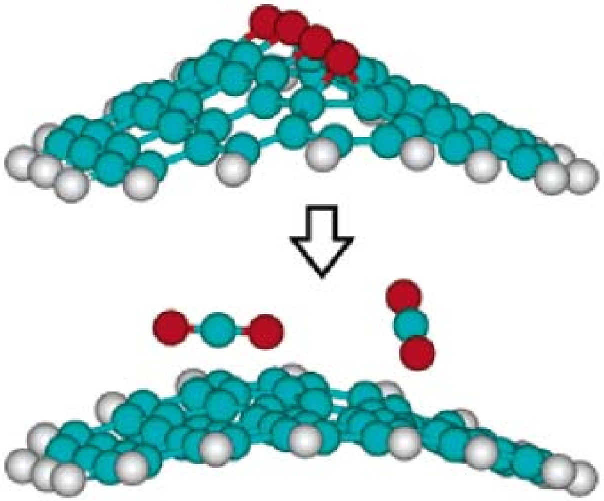
OPVs with reduced GO thin film
as the hole collecting electrode

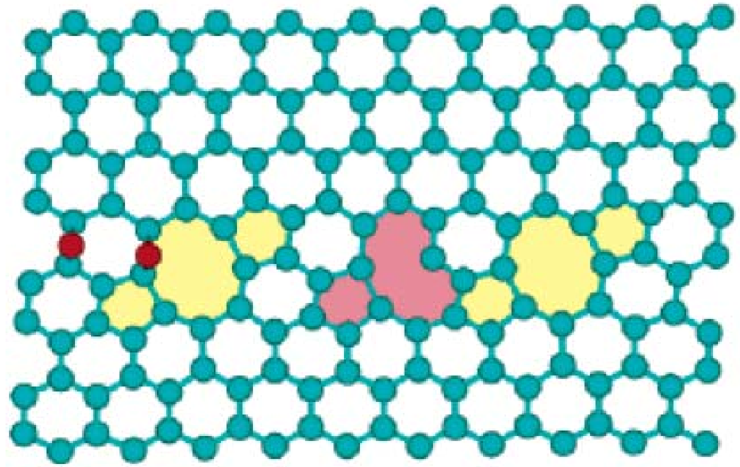




Appl. Phys. Lett. **92**, 233305 (2008)

FTIR on reduced GO





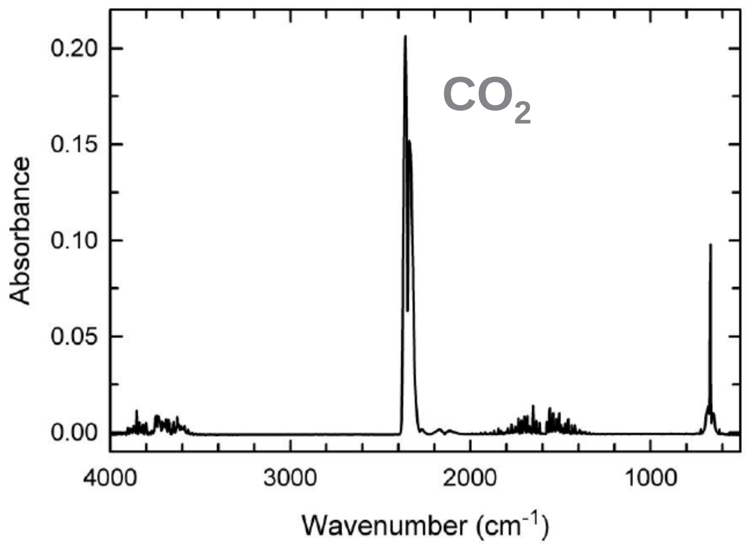


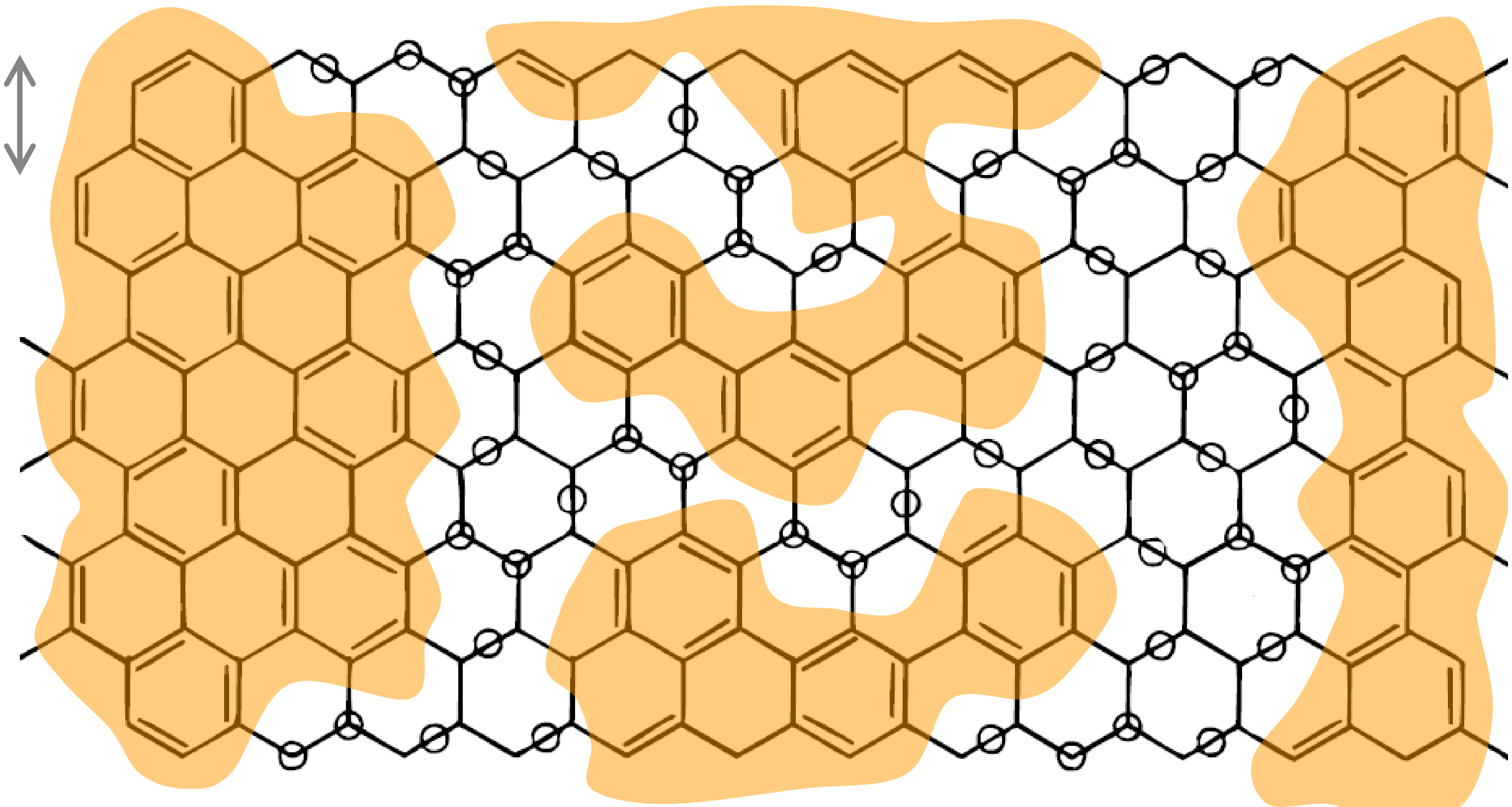
Figure SI1-2. FTIR absorbance data of evolved gas. This scan is acquired at a furnace temperature of 220°C, when the vapor generation rate is greatest. The CO_2 peaks are clearly visible at 2350 cm^{-1} and 670 cm^{-1}. The regions from 1400-1800 cm^{-1} and 3500-3900 cm^{-1} correspond to water vapor.

Schniepp et al. 2006

2.49 Å

C:O = 4:1

2.88 Å



15.8 Å

32.4 Å

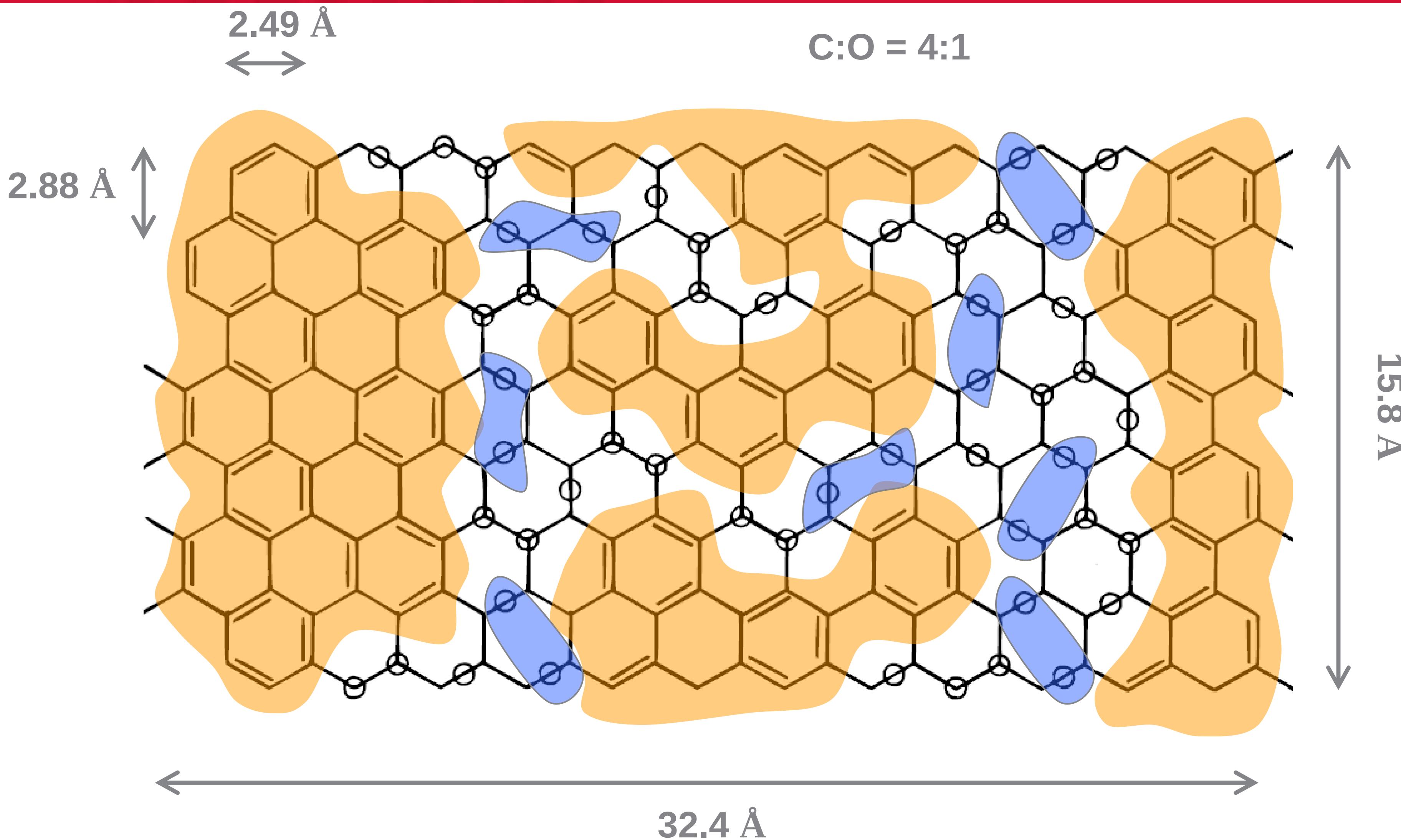
28% coverage of O

50 O, (19 –OH, 31 C-O-C)

206 C

54 oxidized C

C:O = 4:1



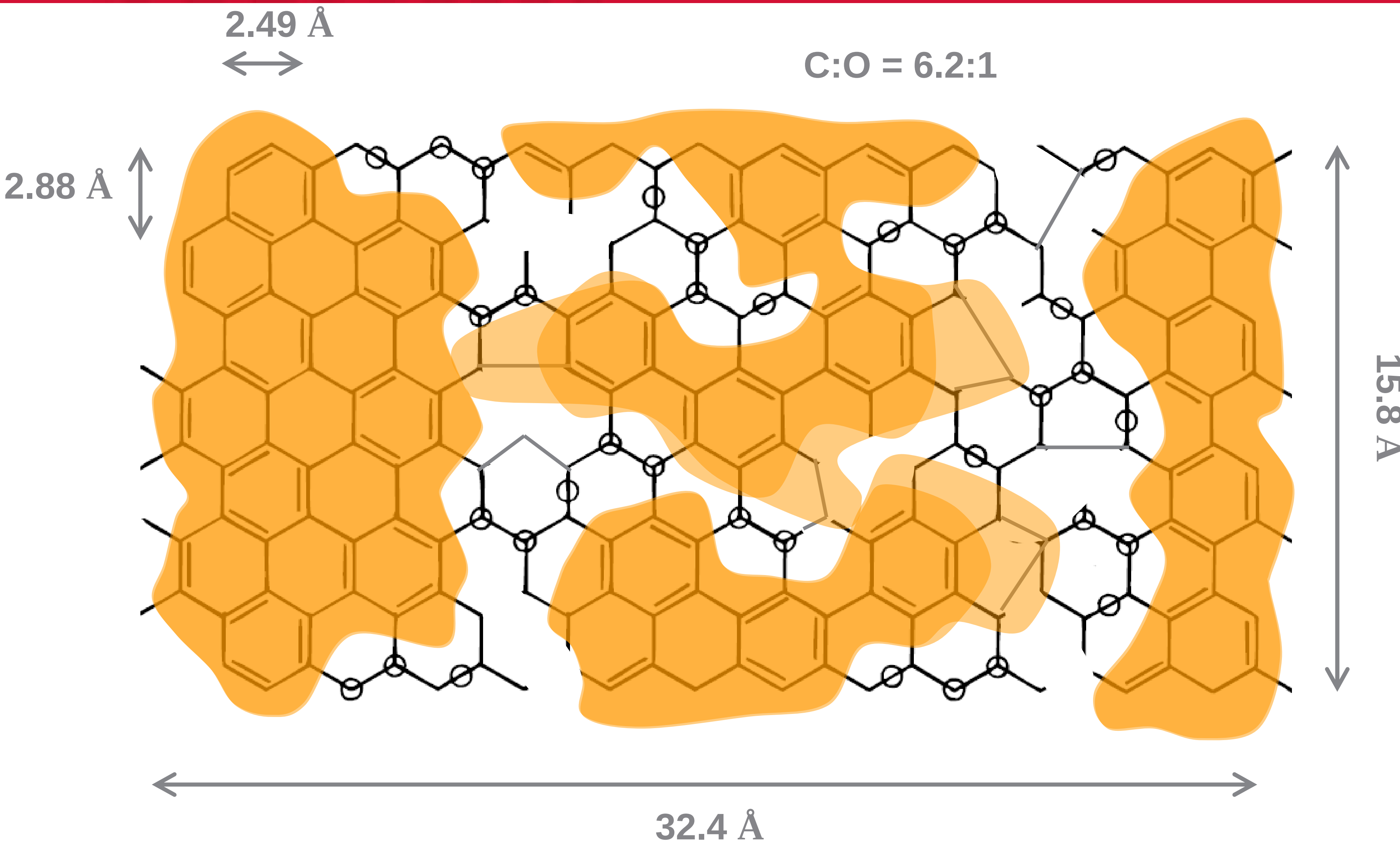
28% coverage of O

50 O, (19 –OH, 31 C-O-C)

206 C

54 oxidized C

Reduced GO is highly defective



20% coverage of O

34 O, (19 –OH, 15 C-O-C)

198 C

X oxidized C

Summary

- Chemically exfoliated graphite can be solution processed into graphene-like thin films.

- Vacuum filtration allows controlled deposition of uniform graphene thin films over large areas.

- Few-layered thin films are graphene-like semiconductors whereas multi-layered thin films are graphite-like semimetals.