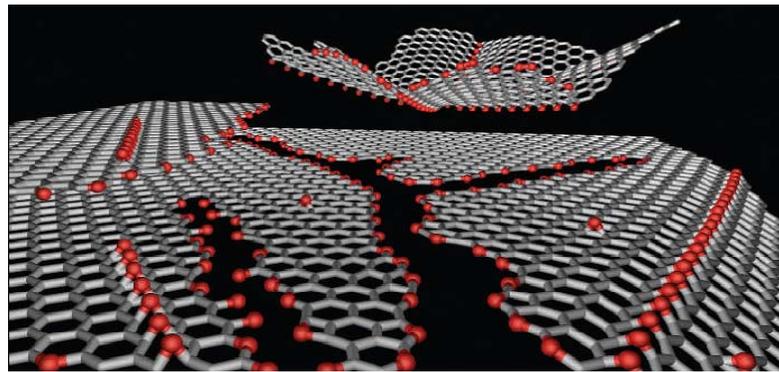


# CHEMICALLY DERIVED GRAPHENE: ELECTRONIC AND MECHANICAL PROPERTIES



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Universidad Autónoma de Madrid

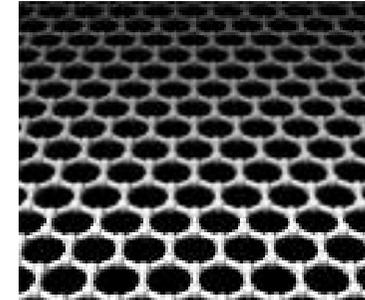
Max-Planck-Institute for Solid State Research



MAX-PLANCK-GESELLSCHAFT

# Why Graphene?

Single layer of graphite



## Extraordinary properties

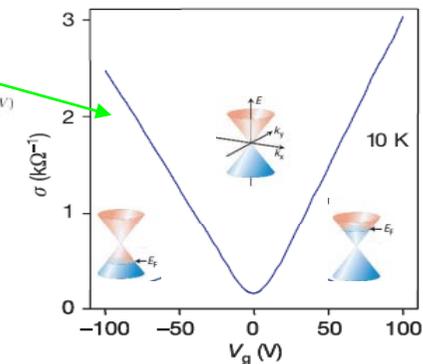
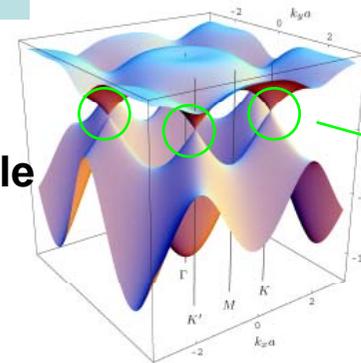
- One atom thick: real 2D material

- Electronic band structure, transport properties

**Semi-metal with field effect**

**High quality: Ballistic transport on micron scale**

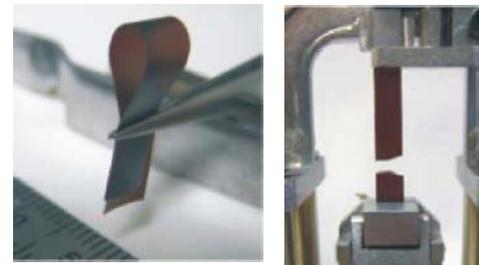
$\mu \sim 100,000 \text{ cm}^2/\text{Vs}$



- Mechanical properties

**High strength of carbon-carbon bond**

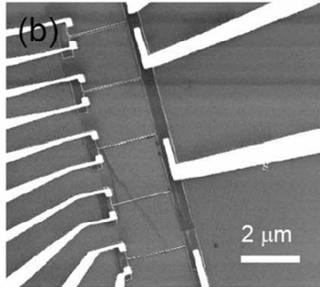
**2D flexible but stiff films**



# Applications: Proof of concept devices

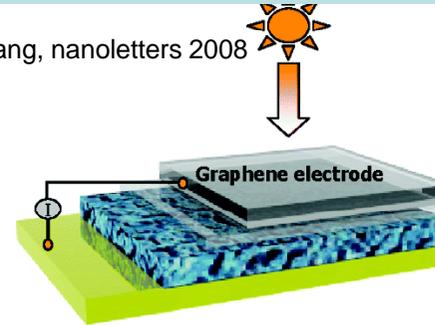
## FET: graphene ribbons

Han, PRL 2007



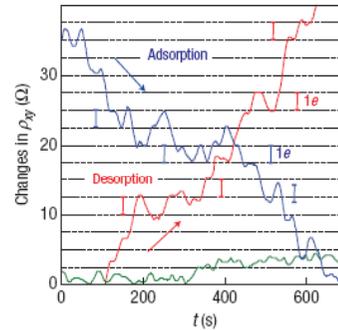
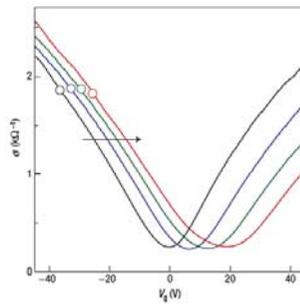
## Transparent electrodes

Wang, nanoletters 2008



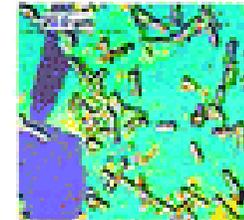
## Gas sensors

Schein, Nature Materials 2007



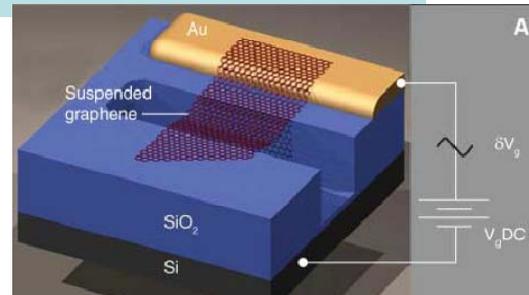
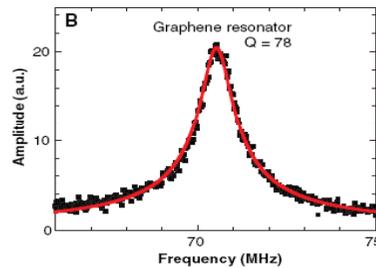
## Bio devices

Mohanty, nanoletters 2008

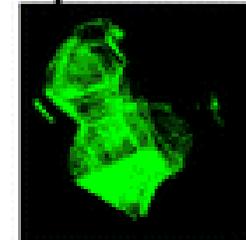


## NEMS: Electromechanical Resonators

Bunch, Science 2007



## Graphene Bacte



## Graphene DNA

# Current ways to obtain Graphene

- **Mechanical exfoliation of graphite.**

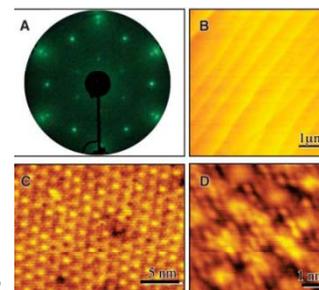
- Very simple method, but:
  - High multilayer/monolayer ratio.
  - Finding monolayers time consuming



Novoselov et al **Nature**, 2005

- **Epitaxial growth on silicon carbide and metals**

- Limited to certain substrates
- Uniformity, size domain?
- UHV, high temperatures



Berger, et al **Science**, 2006  
Land, **Surface Science**, 1992

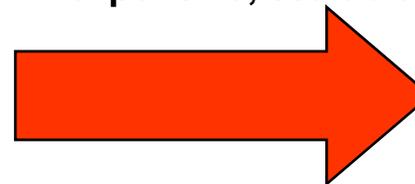
Not applicable  
to technology yet

- **Chemical approach:**

- Via graphite oxide: Graphite oxide, easily layered
  - Mainly monolayers
  - Solution based
  - Reducing graphite oxide on surface?

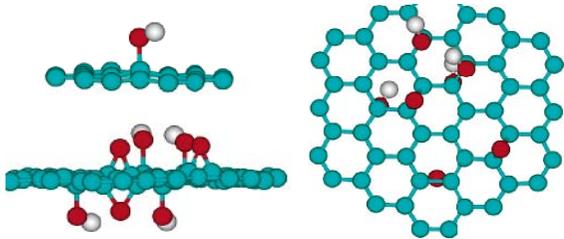
Stanovich et al **Nature**, 2006

Inexpensive, scalable, substrates

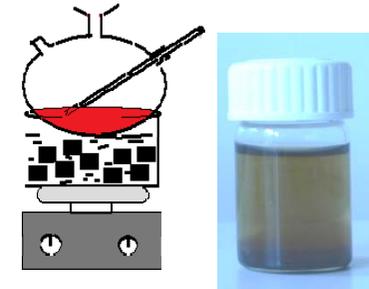


# Initial idea

## 1<sup>st</sup>: Synthesizing graphite oxide

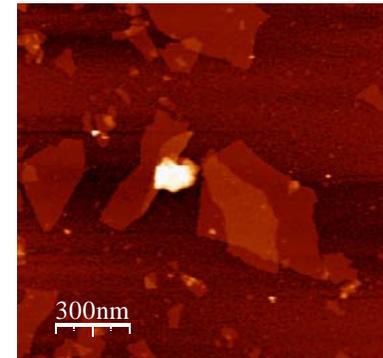


Graphite oxide: graphite functionalized with epoxy C-O-C and hydroxyl C-OH groups in the interlayer and C-OH -COOH groups at the edges of the graphene sheets.

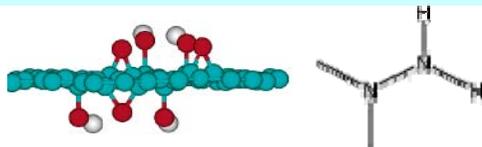


Graphite oxide layers are easy to separate in water...leading to “graphene oxide”  
Solution process

## 2<sup>nd</sup>: Adsorption of single GO layers on surface



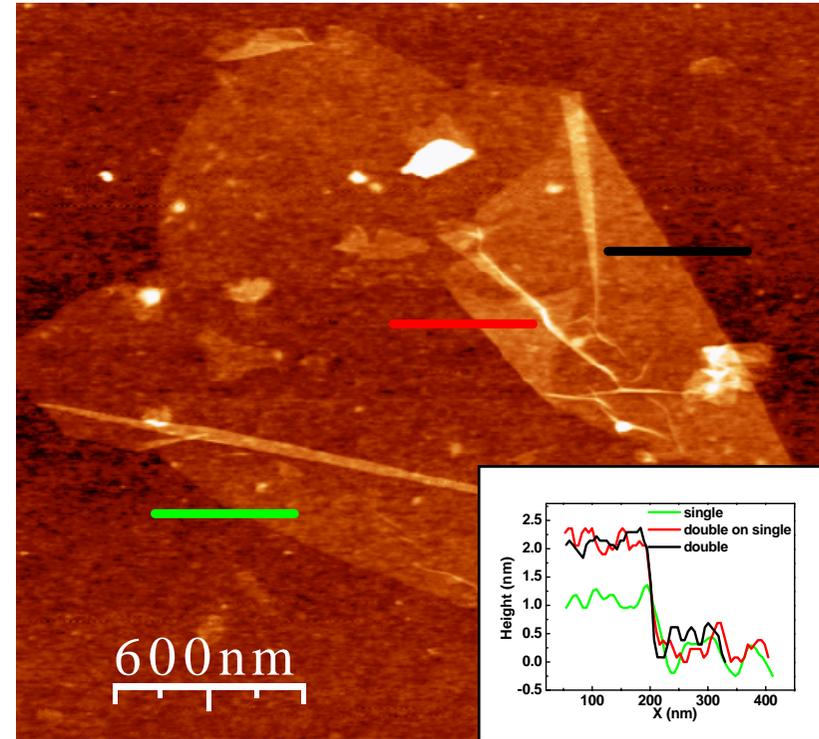
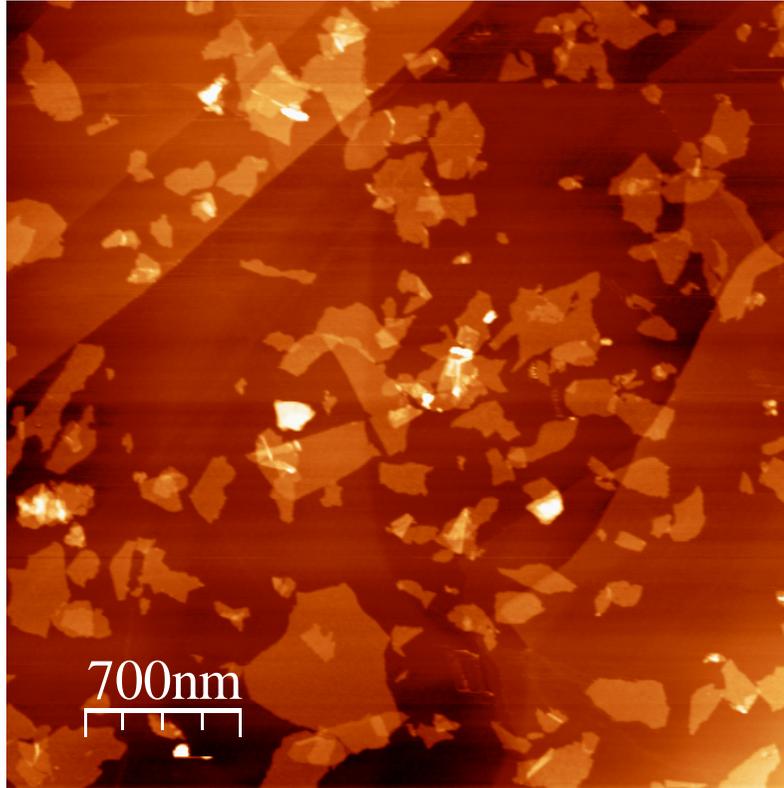
## 3<sup>rd</sup>: Reducing GO by chemical procedures on surface



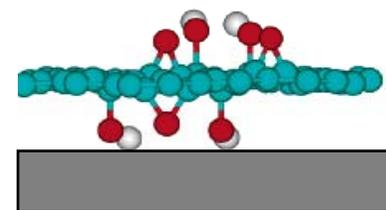
Hydrazine or hydrogen plasma

**Quality and properties of graphene obtained through this route?**

# AFM imaging of GO



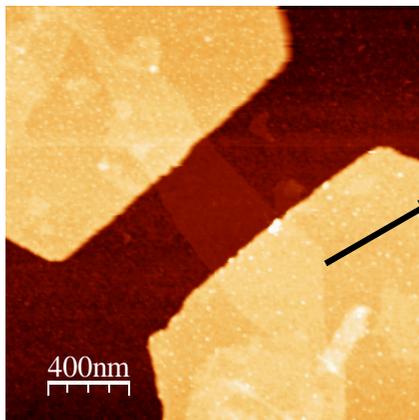
Very high mono\multilayer ratio



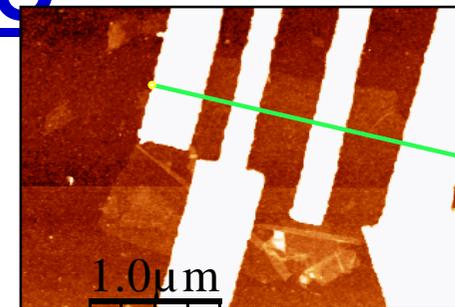
1 st layer  $h \sim 1.0 \pm 0,1 \text{ nm}$   
2nd layer  $h \sim 0,8 \pm 0,1 \text{ nm}$

h in agreement with theoretical expectation

# Electronic transport GO



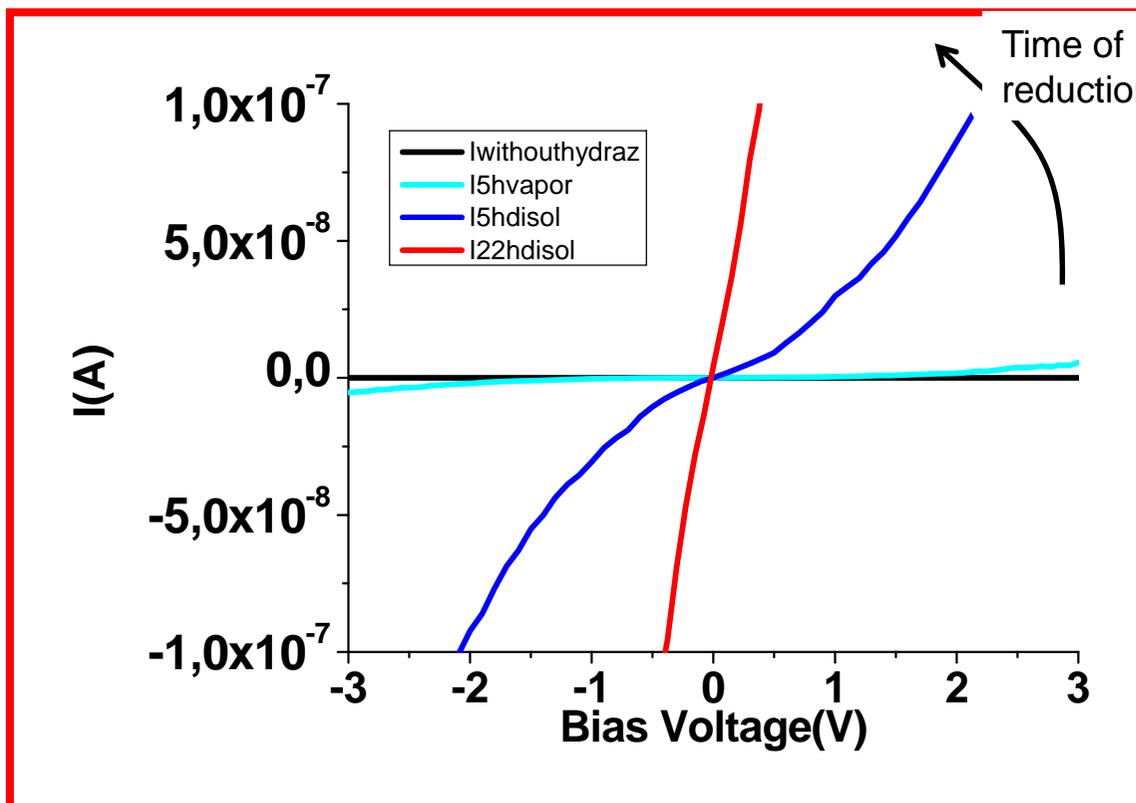
Electrodes by e-beam lithography



## IV curves as a function of reduction time with hydrazine

Before reduction  
good insulator

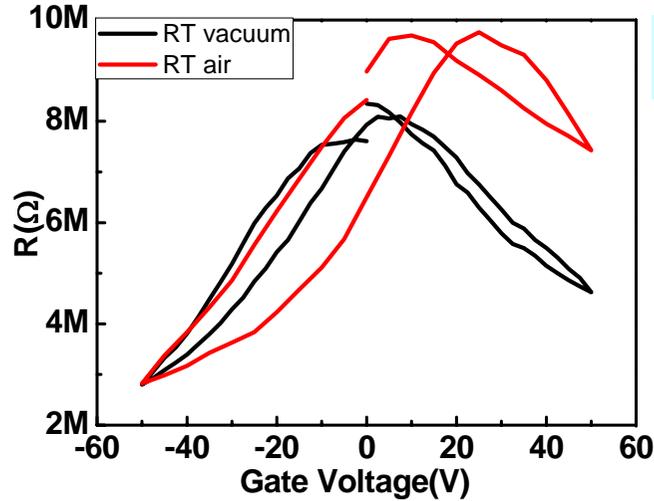
Reduction improves  
conductivity 3 orders  
of magnitude



Maximum in conductivity after 24h of NH or 5 sec H plasma

Fixed channel length

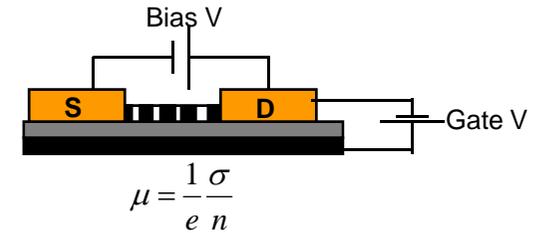
# Electronic transport reduced GO



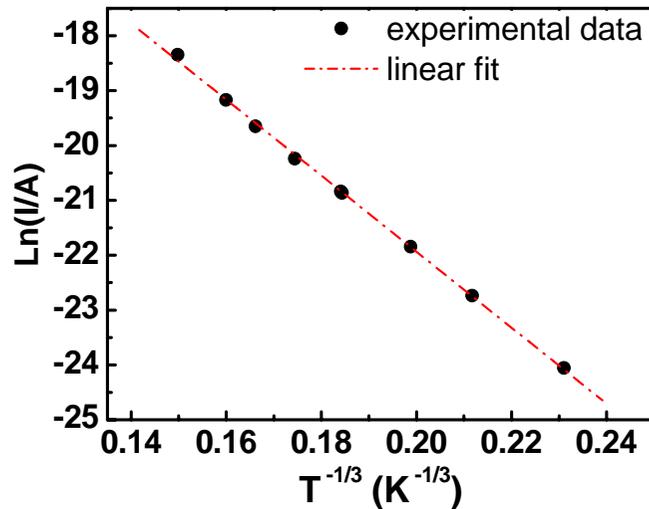
Ambipolar behaviour similar to pristine graphene

Conductivity:  $\sigma=0.1-1$  S/cm

Mobility:  $\mu=-0.1-1$  cm<sup>2</sup>/Vs

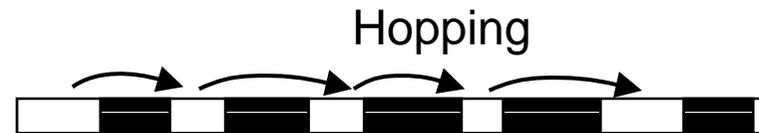


For high quality graphene  $\mu=1.000-100.000$  cm<sup>2</sup>/Vs



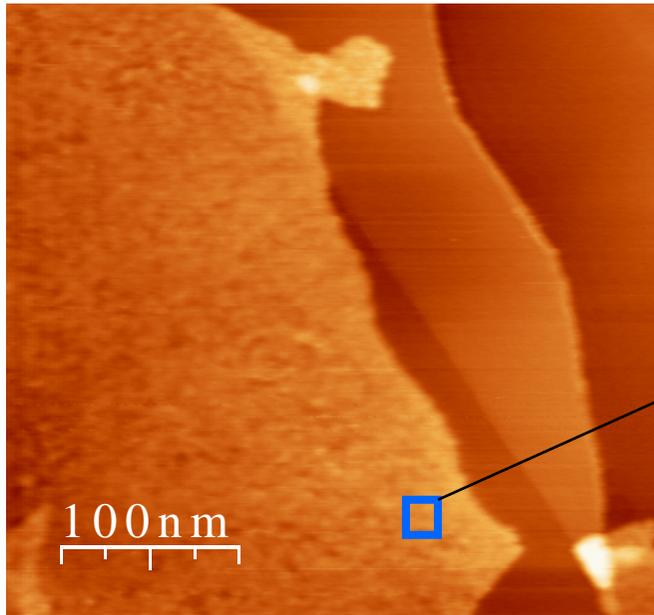
Temperature dependence indicates a hopping transport mechanism

$$I = I_0 e^{\left(\frac{T_0}{T}\right)^{1/n}}$$

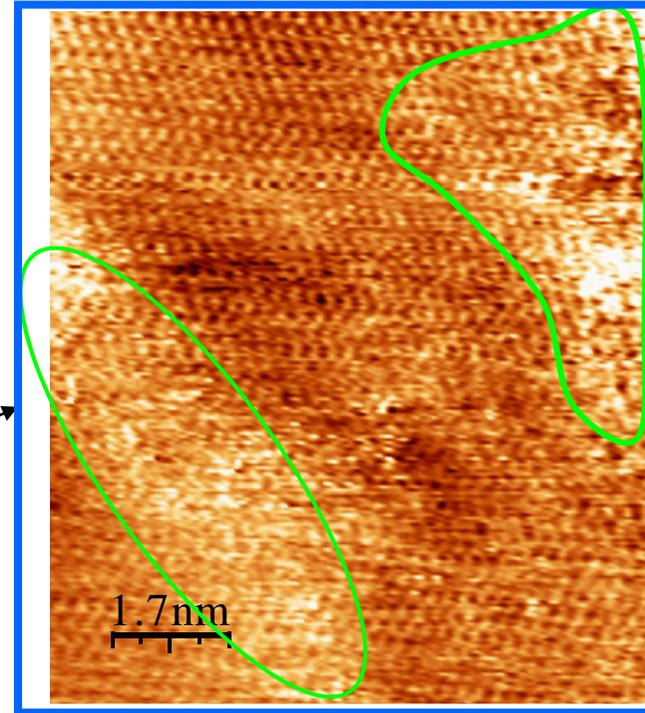


# High resolution imaging of GO

GO on HOPG

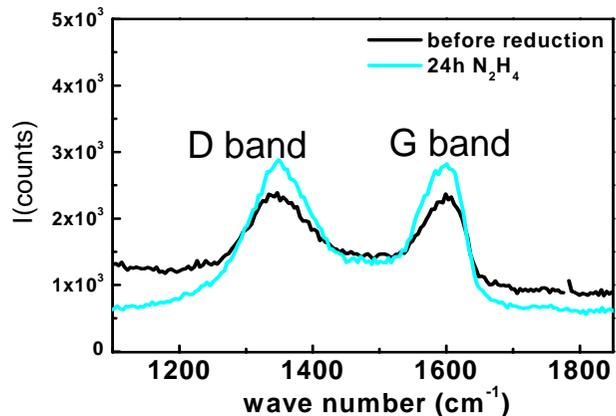


**AFM: wrinkling**



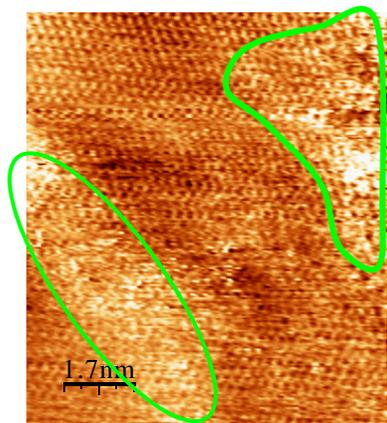
**STM: ordered\disordered regions**

# Raman spectroscopy: GO

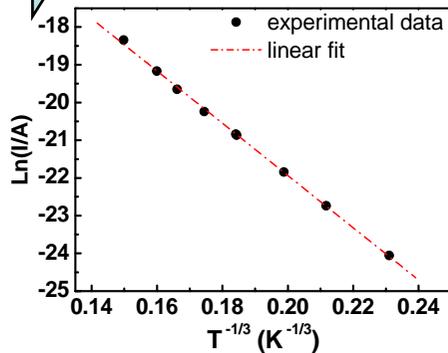


G/D ratio:  
sp<sup>2</sup> carbon domain size of ~ 5-6 nm

Ferrari et al. *Phys Rev B* 2000  
Tuinstra et al. *J Chem Phys* 1970

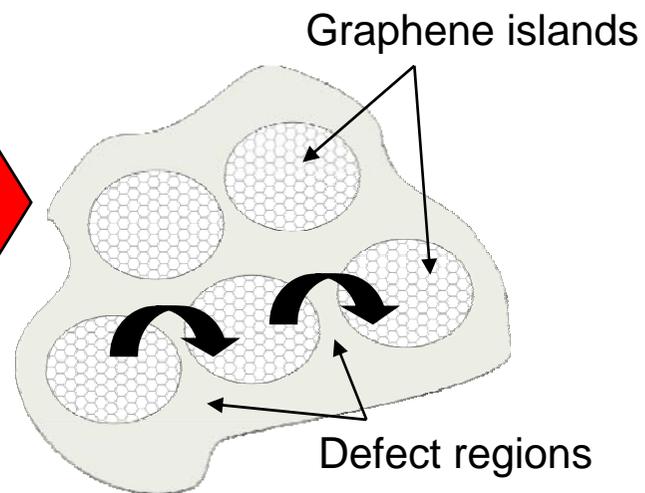


STM

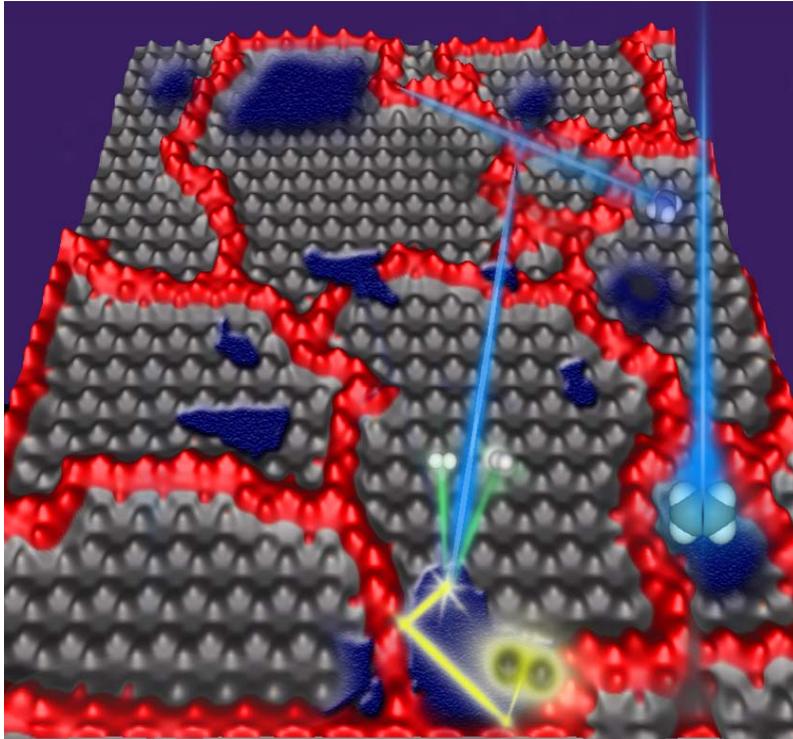


Hopping conduction

Model



## 2nd step: Chemical Vapor Deposition of ethylene

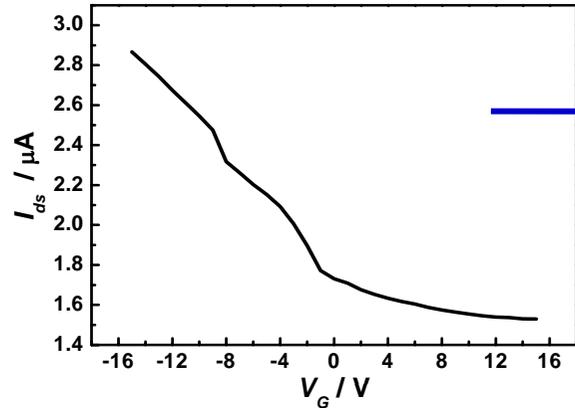


- High T
- Decomposition of C<sub>2</sub>H<sub>4</sub>
- obtaining atomic C  
to be incorporated in vacancies
- High T facilitates healing

Flow ethylene for 3 min at 800 °C

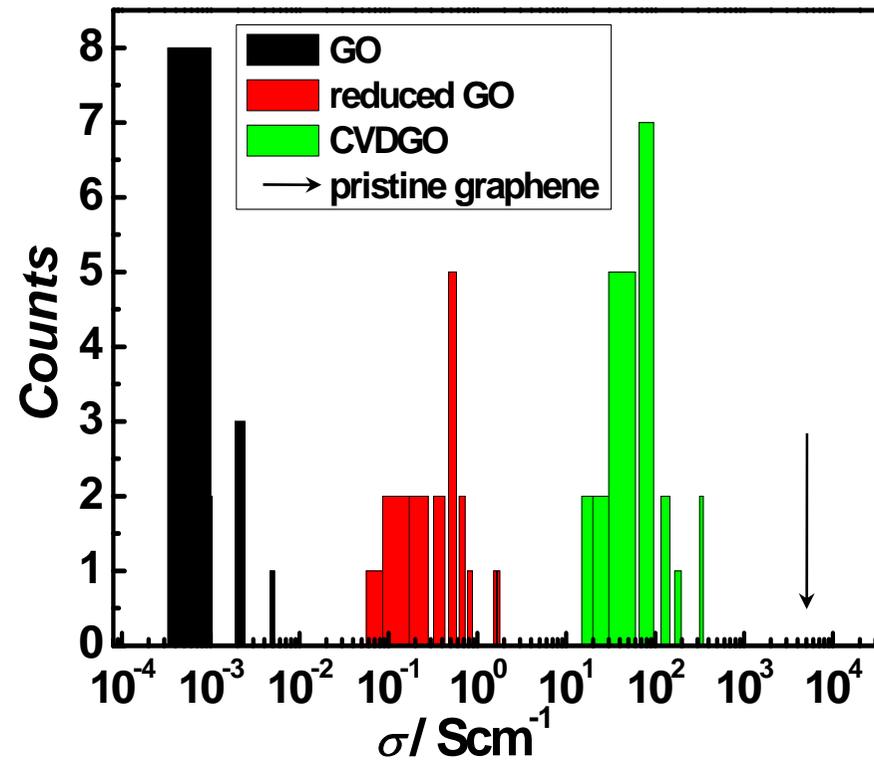
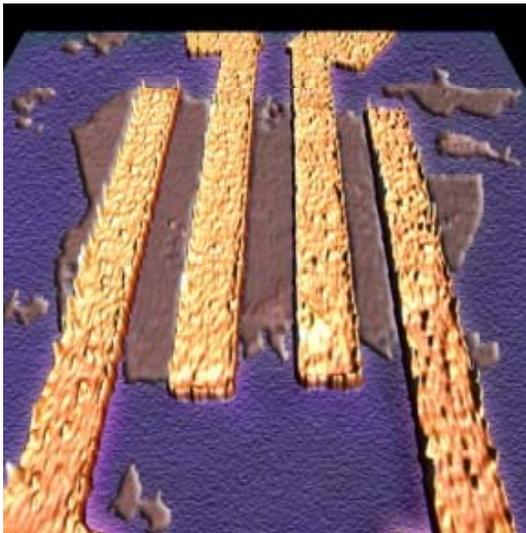
# CVD treated GO: improved conductivity

After CVD conductivity increases two orders of magnitude



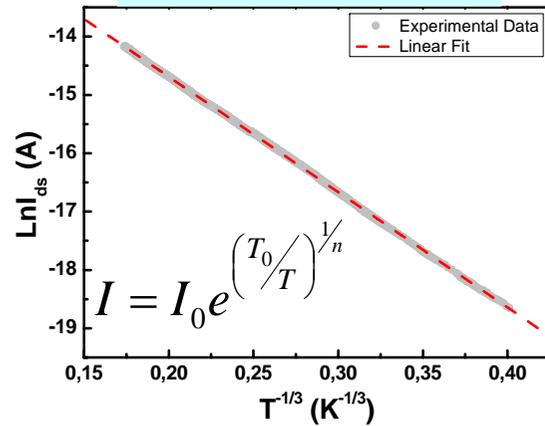
Conductivity:  $\sigma=20\text{-}200\text{ S/cm}$

Mobility:  $\mu\sim 50\text{-}100\text{ cm}^2/\text{Vs}$

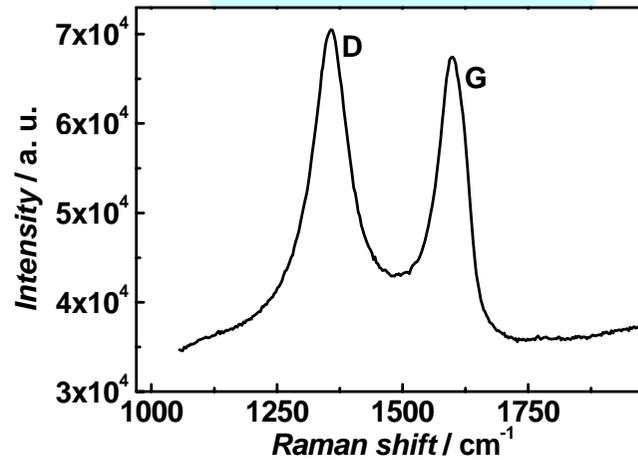


# CVD treated GO: Raman and conductivity

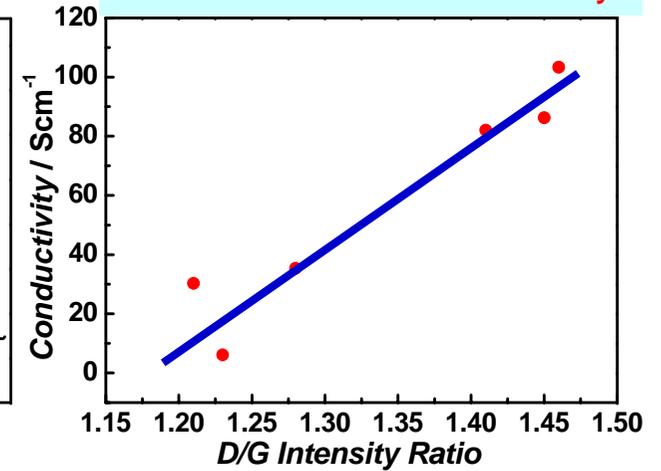
hopping transport



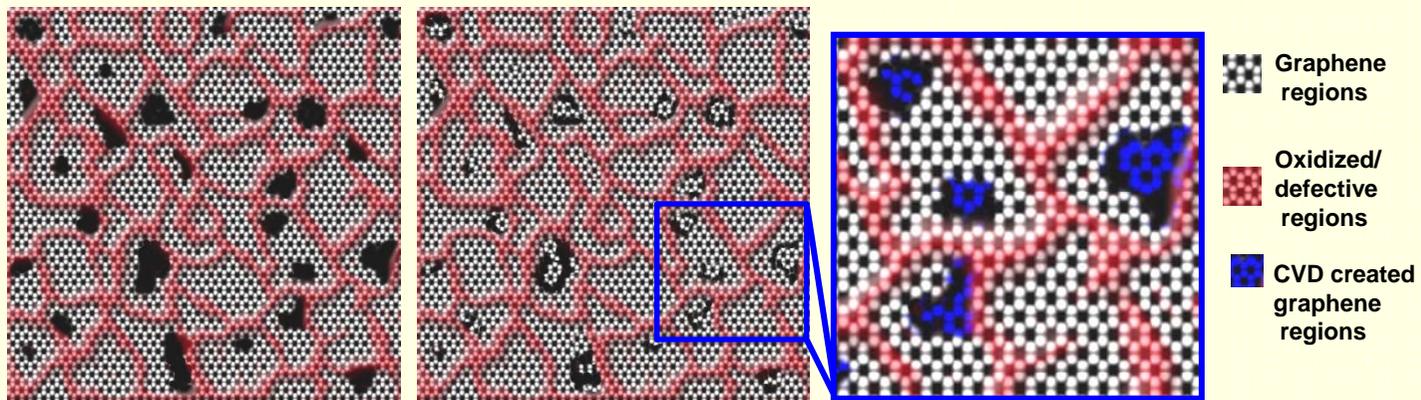
High D/G ratio



Correlation D/G conductivity



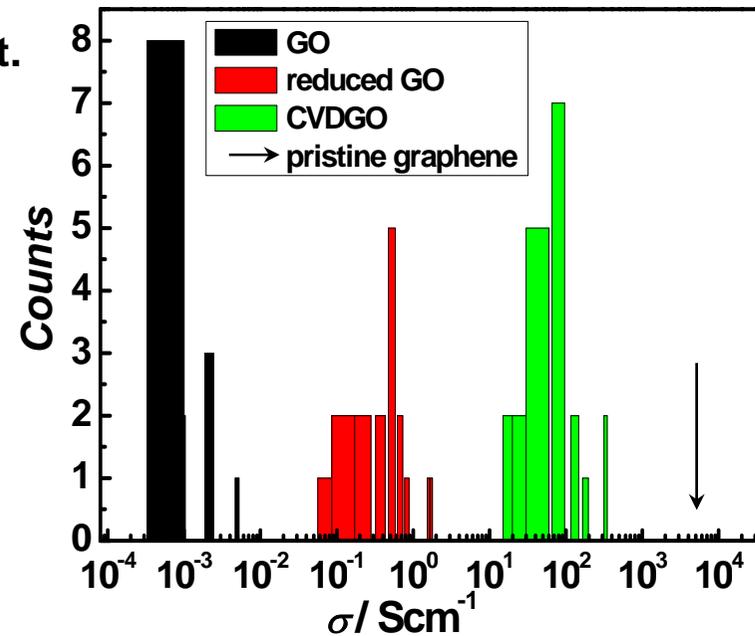
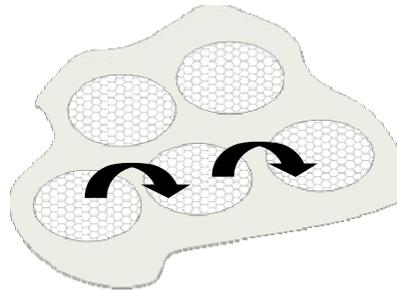
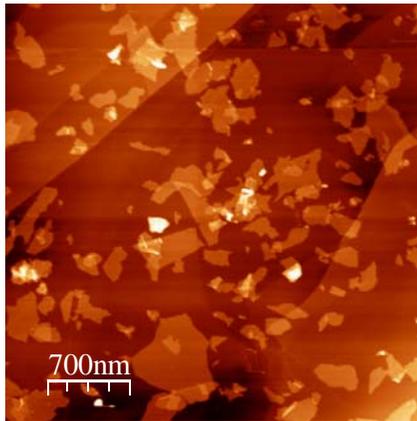
## New smaller graphene regions



RGO → CVD GO

# Conclusions on electrical transport

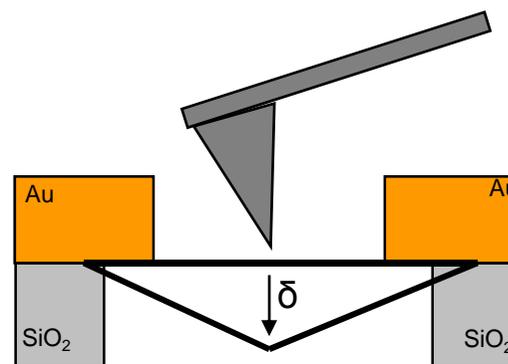
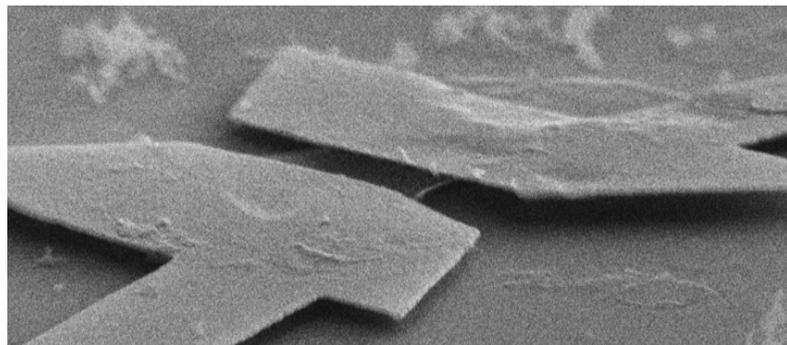
- GO routes provides access to a large scale production of graphene monolayers.
- Reduction improves conductivity in 3 orders of magnitude
- CVD of ethylene increases conductivity in 2 orders of magnitude.
- CVDGO still contains a considerable amount of defects.
- Large range of conditions for improvement.



Gomez-Navarro et al. *Nanoletters* 2007

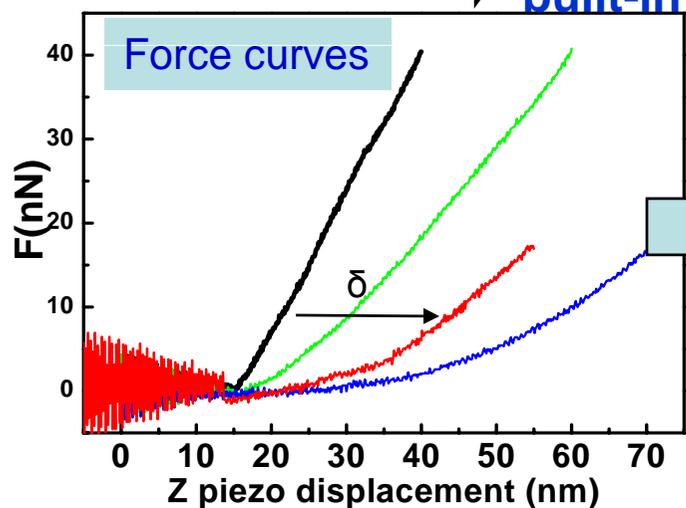
Lopez et al. *Advanced Materials* 2009

# GO: mechanical properties



$$K_{eff} = 32Ew(t/l)^3 + 17T/l$$

Force Constant  $\rightarrow$  Young modulus, built-in tensions

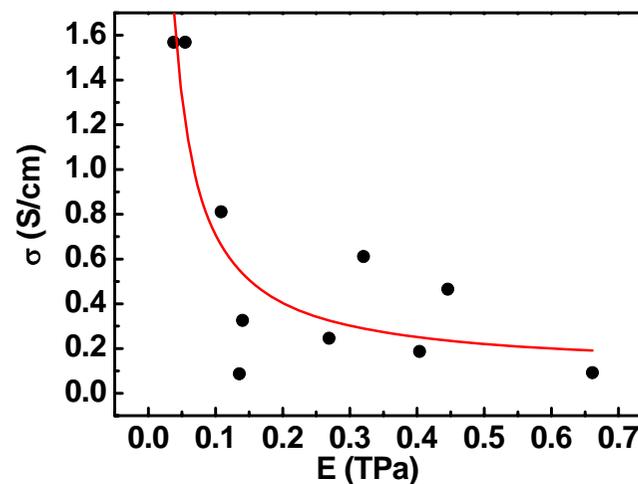


**E=0.3 TPa**

**T=4 nN**

$K_1, K_2, K_3 \dots$

Correlation between conductivity and elastic modulus



Gomez-Navarro et al. *Nanoletters* 2008

# Acknowledgments

## *Max-Planck-Institut fuer Festkoerperforschung*

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- Alf Mews



## *Nanotec Electronica*



**Thank you for your attention!**