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Properties of Graphite Oxide, Carbon Nanotubes and their Composite Effect of Irradiation

Viera Skákalová

2001-2011



**Max Planck Institute for Solid State Research
Stuttgart**

2011- ????



University of Vienna

Collaborations



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Sample preparation, characterization:

**Viliam Vretenár
Martin Hulman
Peter Kotrusz
Marcel Meško**

TEM, modelling:

**Jannik Meyer
Franz Eder
Jani Kotakoski**

Max Planck Institute, Stuttgart

Electronic transport:

***Dong Su Lee
Hye Jin Park***

Hungarian Academy of Sciences:

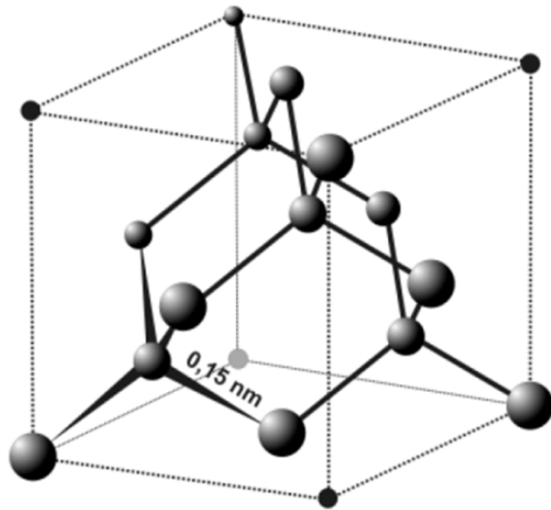
Ion irradiation:

**Zsolt E. Horvath
Laszlo P. Biro**

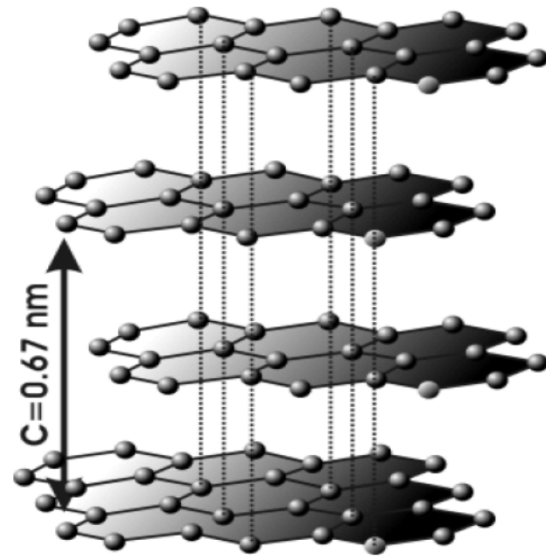
Carbon (${}^6\text{C}=1s^22s^22p^2$, group IV)

$2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals can mix with each other.

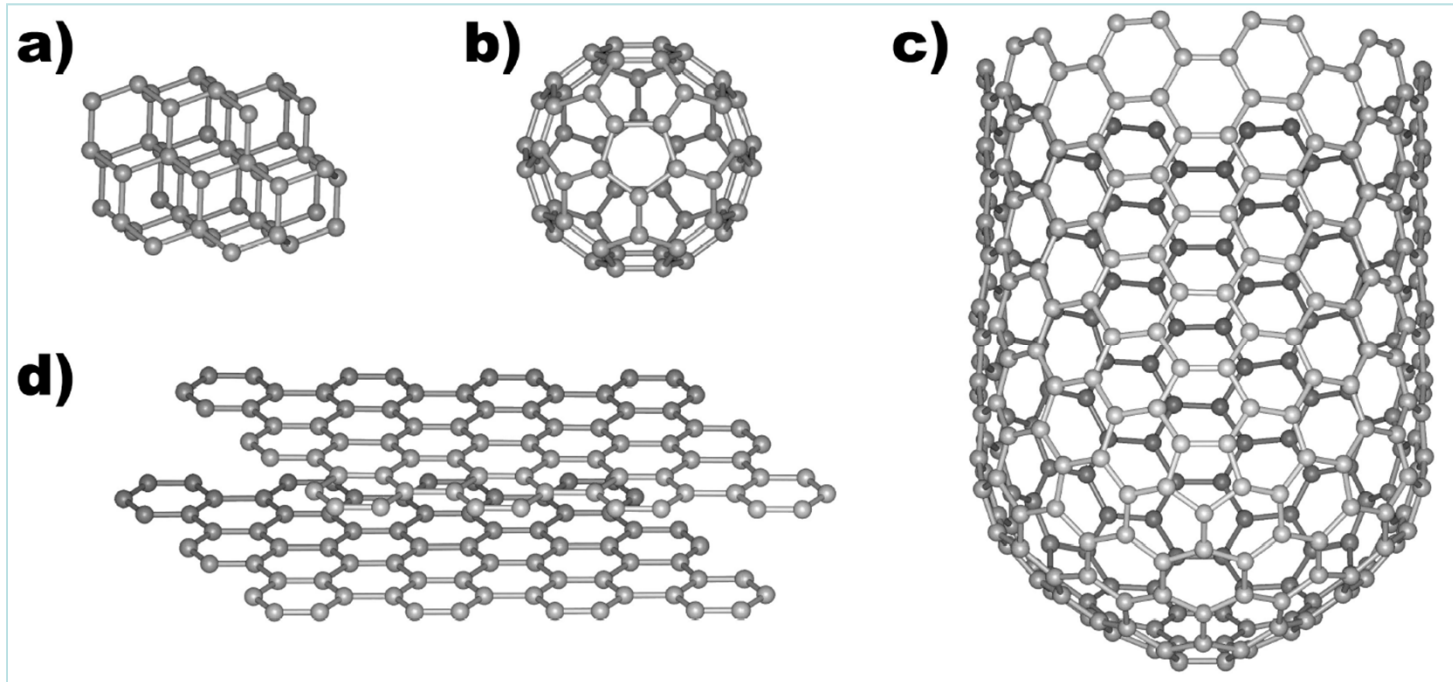
diamond : sp^3



graphite : $sp^2 + p_z$



Different modifications of carbon

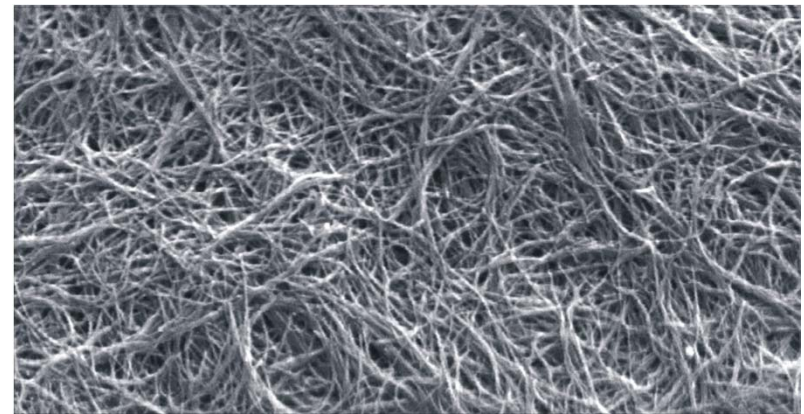




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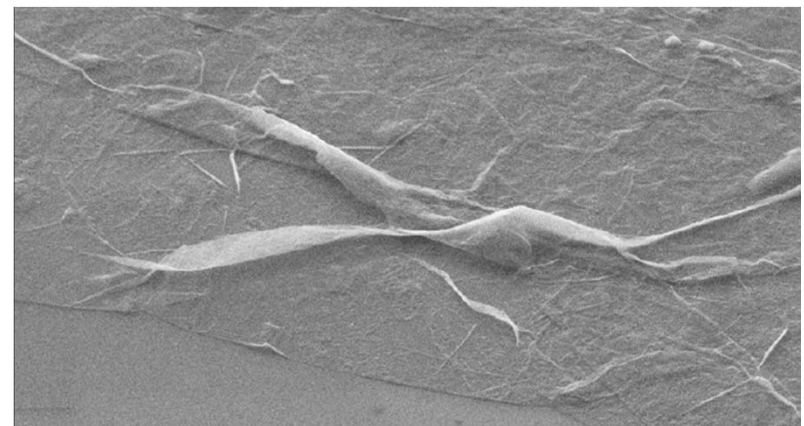
- **Production of Single Wall Carbon Nanotubes**

- **Research on SWNT**

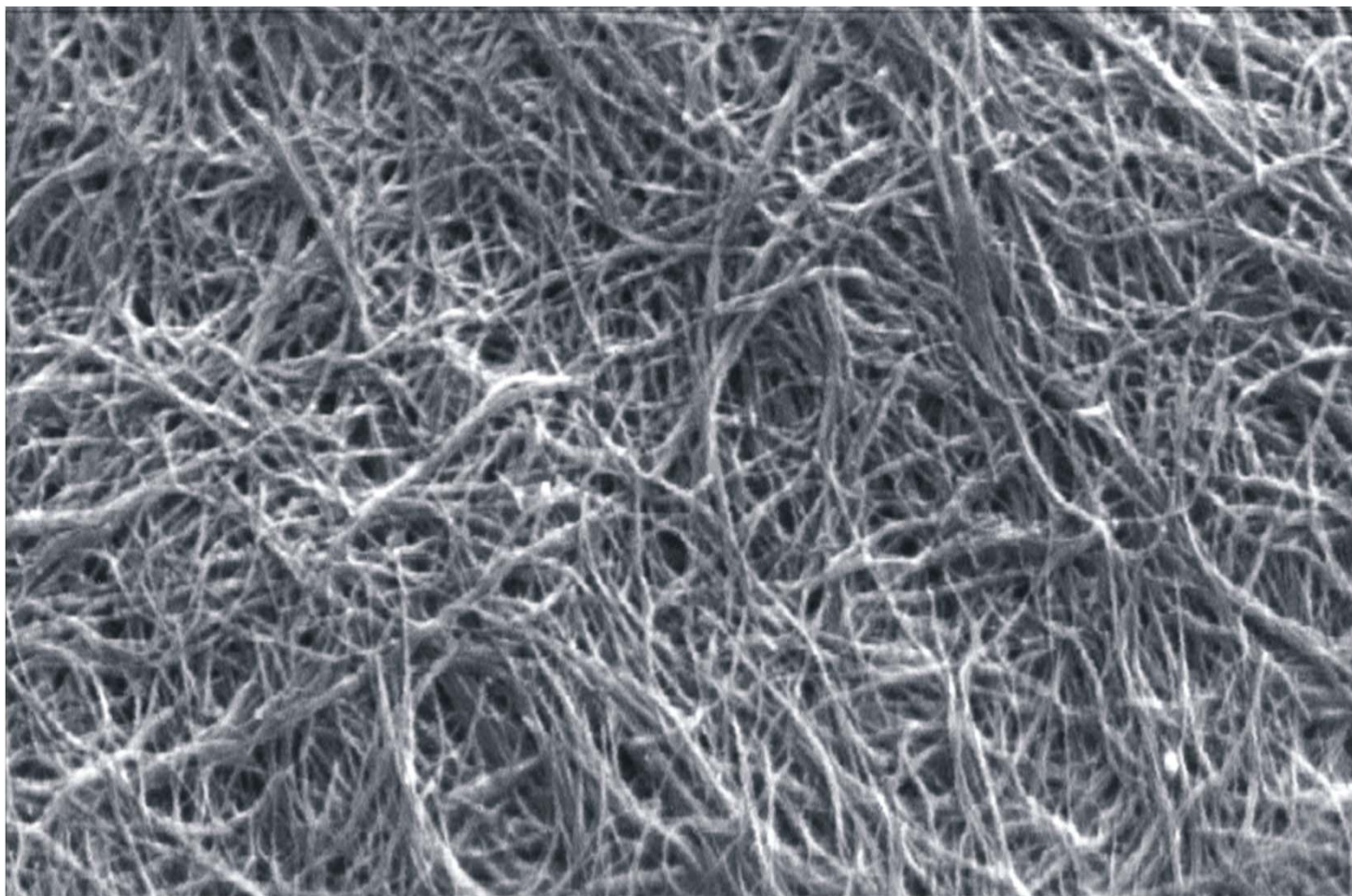


- **Production of Few-Layer Graphene**

- **Research on Graphene**

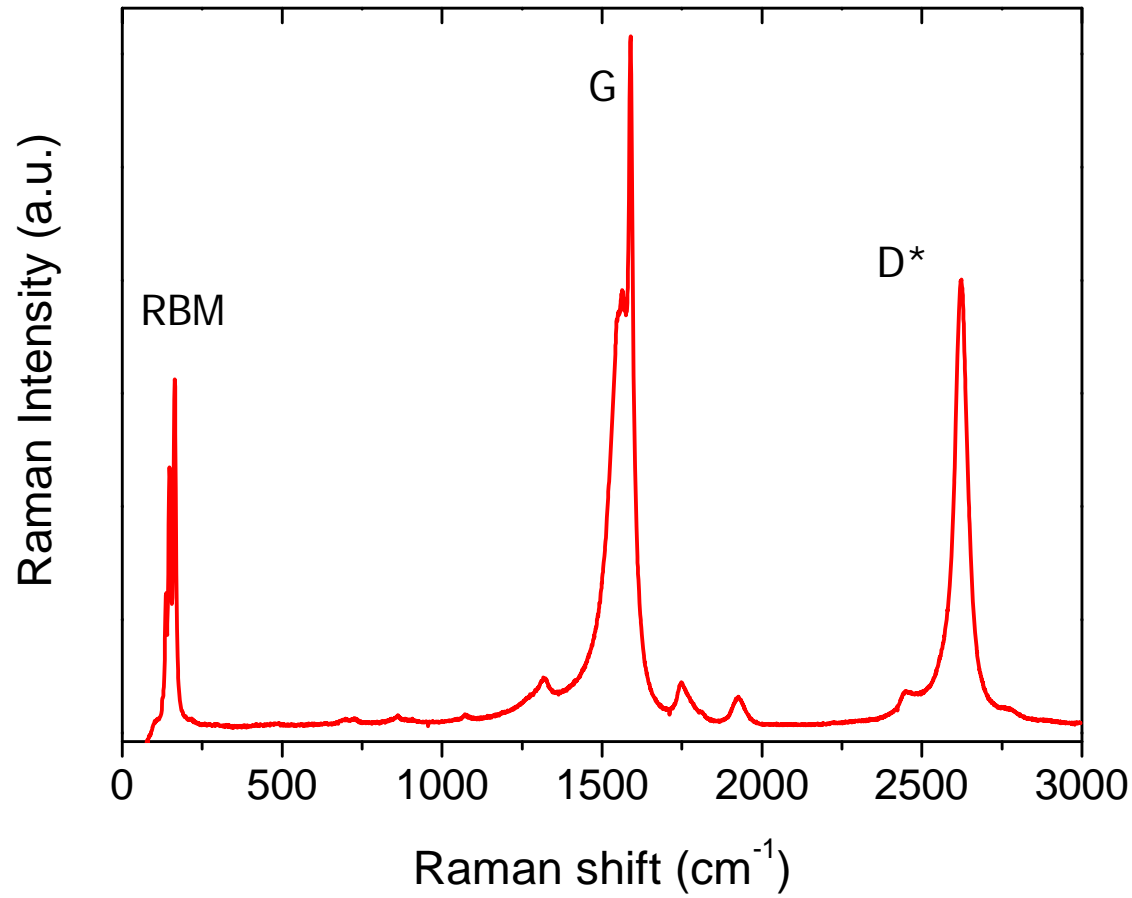


Defects in SWNTs

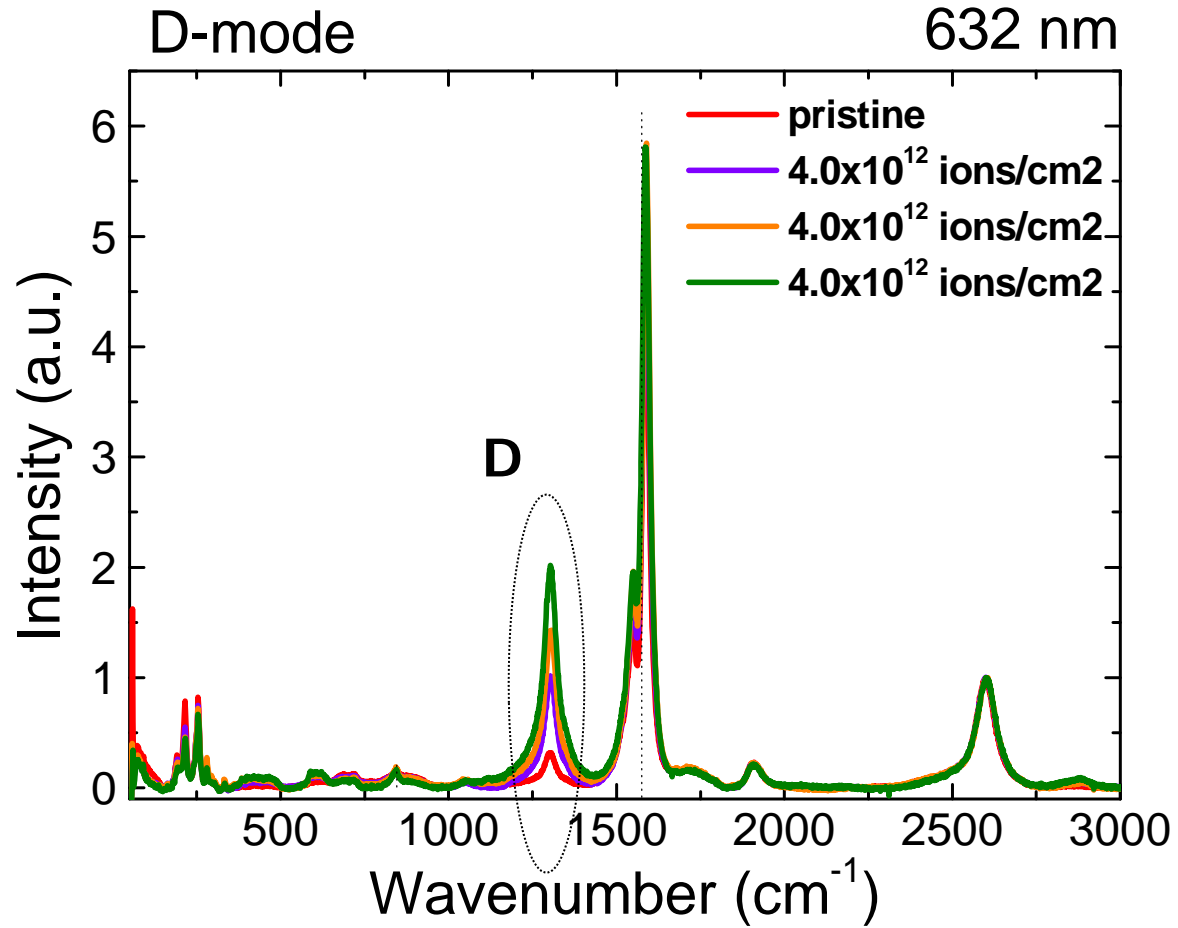


Raman spectroscopy

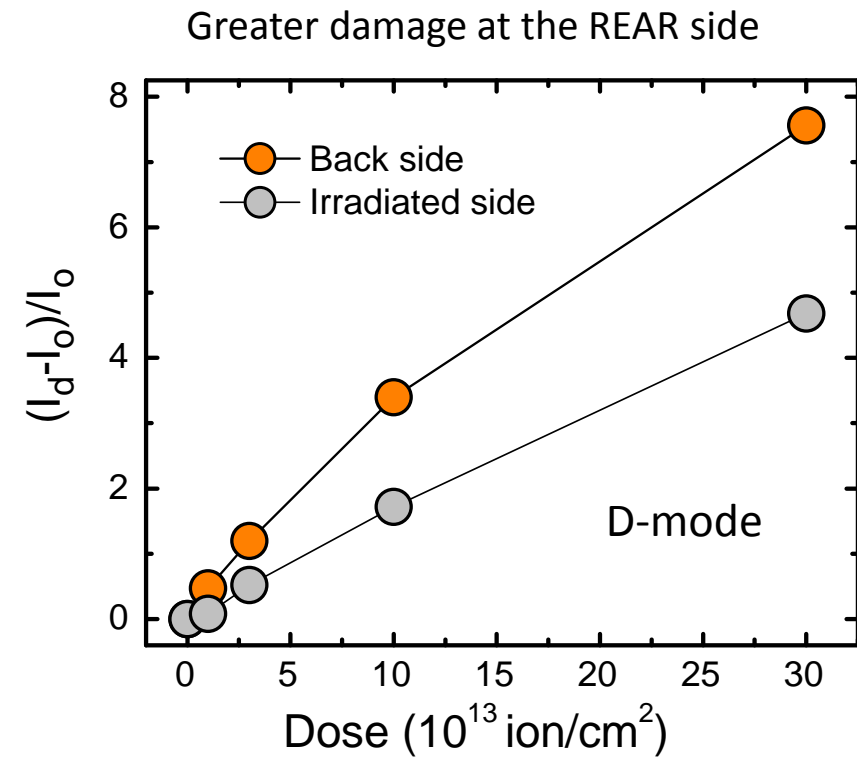
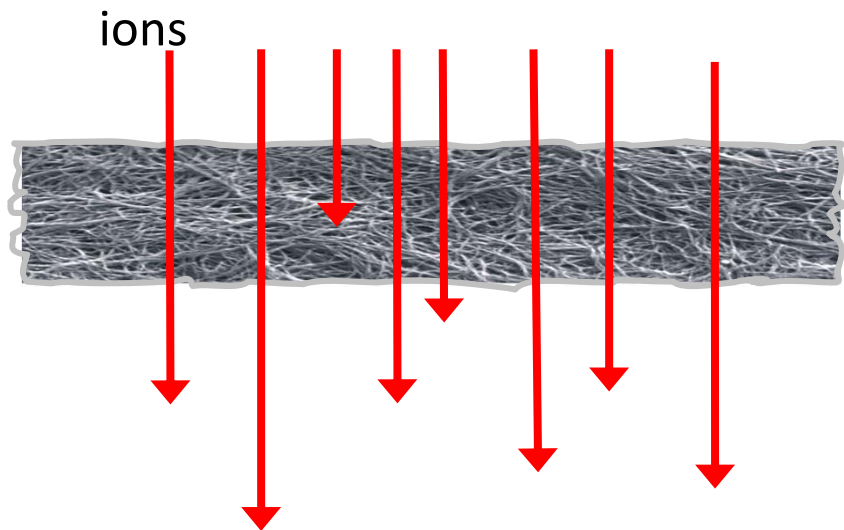
- inelastic photon scattering



D-mode of Raman spectra increases with the Dose of Ar⁺ ions

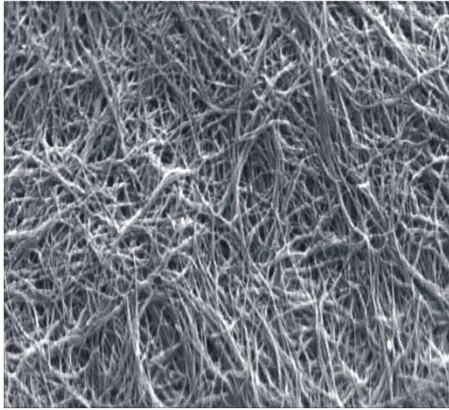


SWNT paper irradiated by 23 MeV C⁴⁺ ions

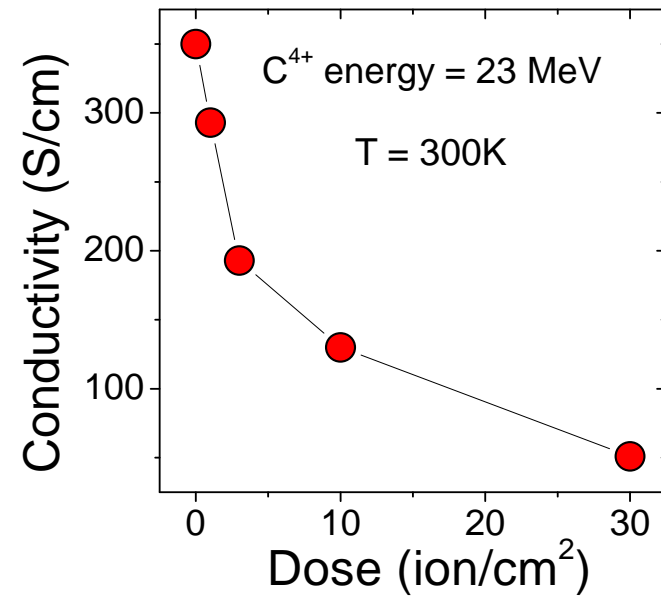
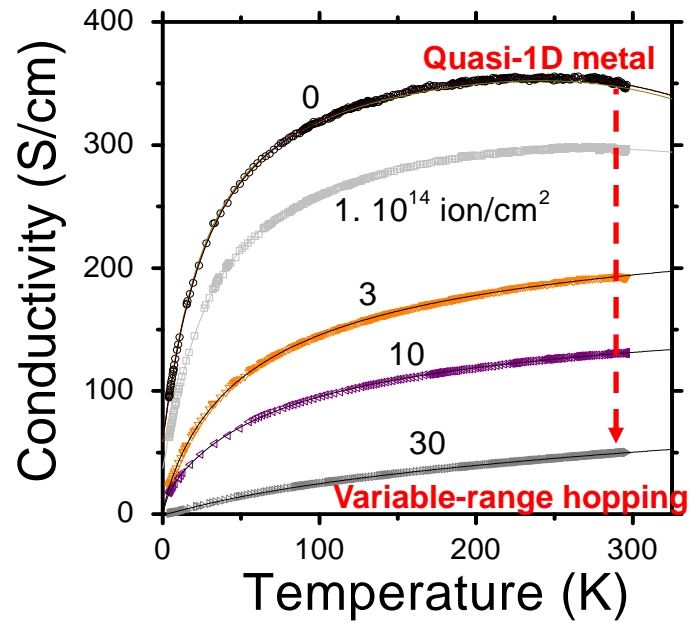


C⁴⁺-irradiation of SWNT paper:

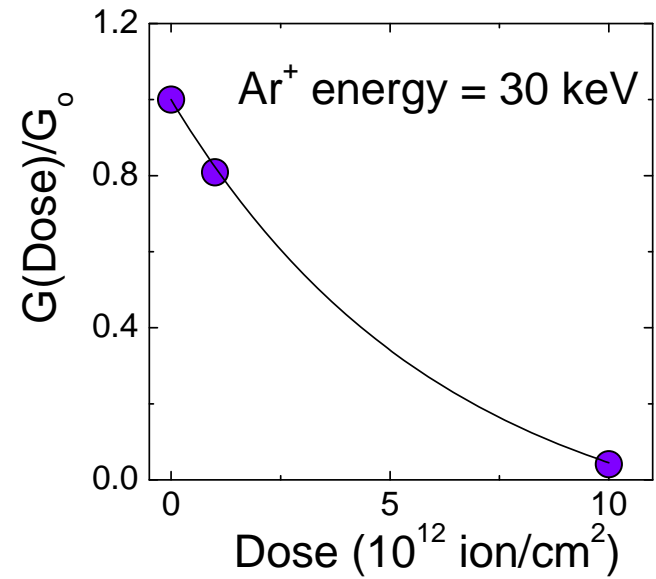
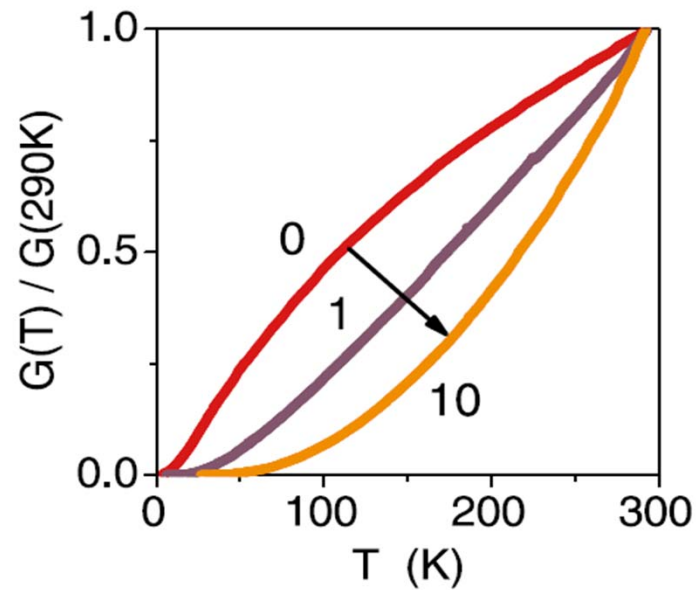
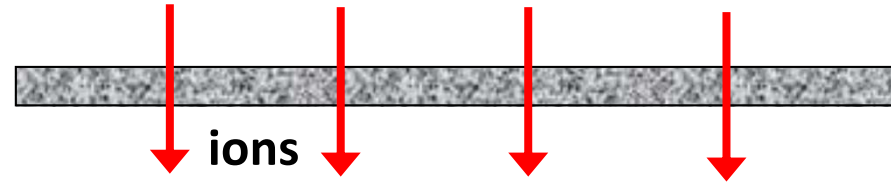
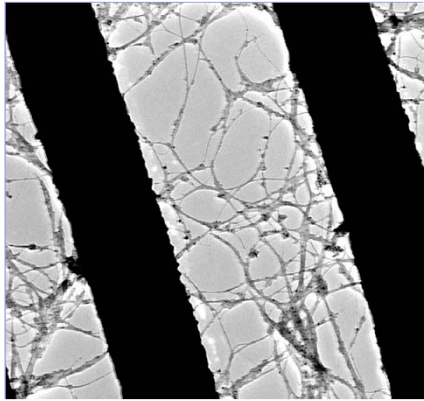
Electrical conductivity



C⁴⁺-energy = 23 MeV



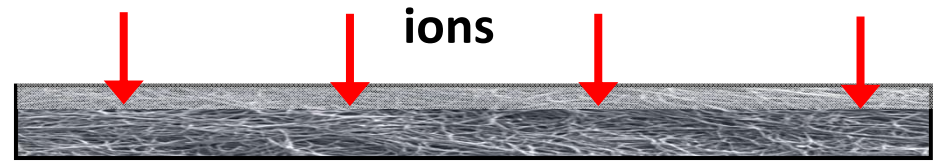
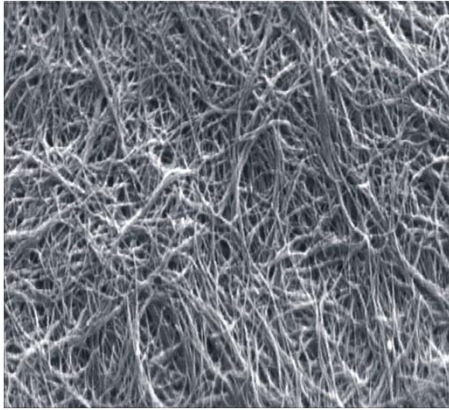
Electrical conductance of Ar⁺ irradiated thin SWNT networks



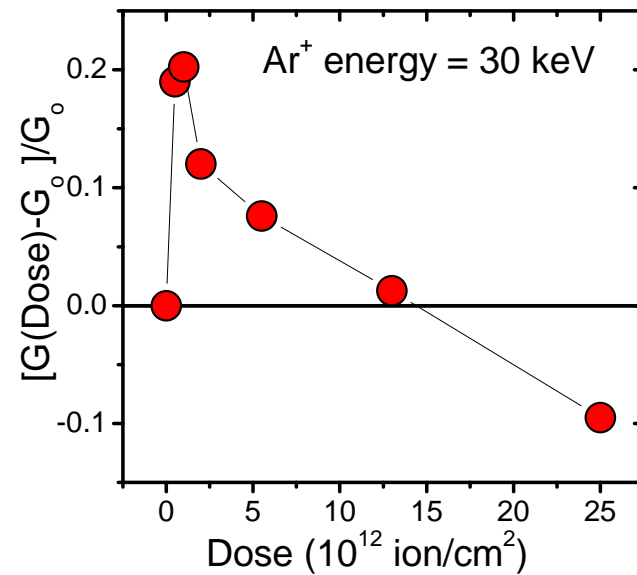
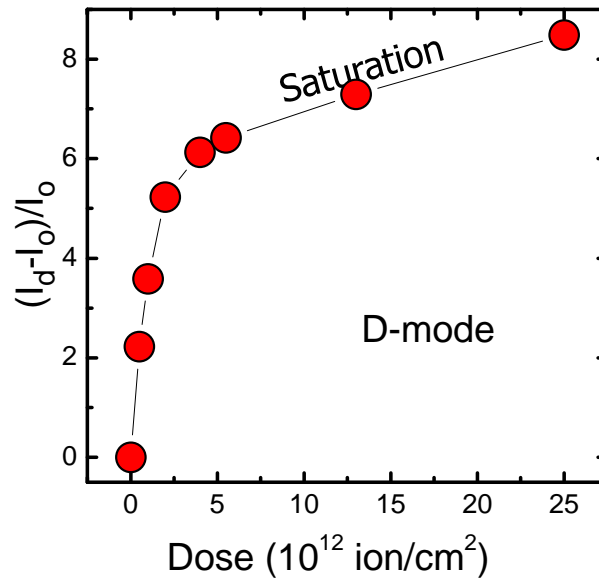
Variable-Range Hopping:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/(1+d)} \right]$$

Surface penetration by 30 keV Ar⁺ ions

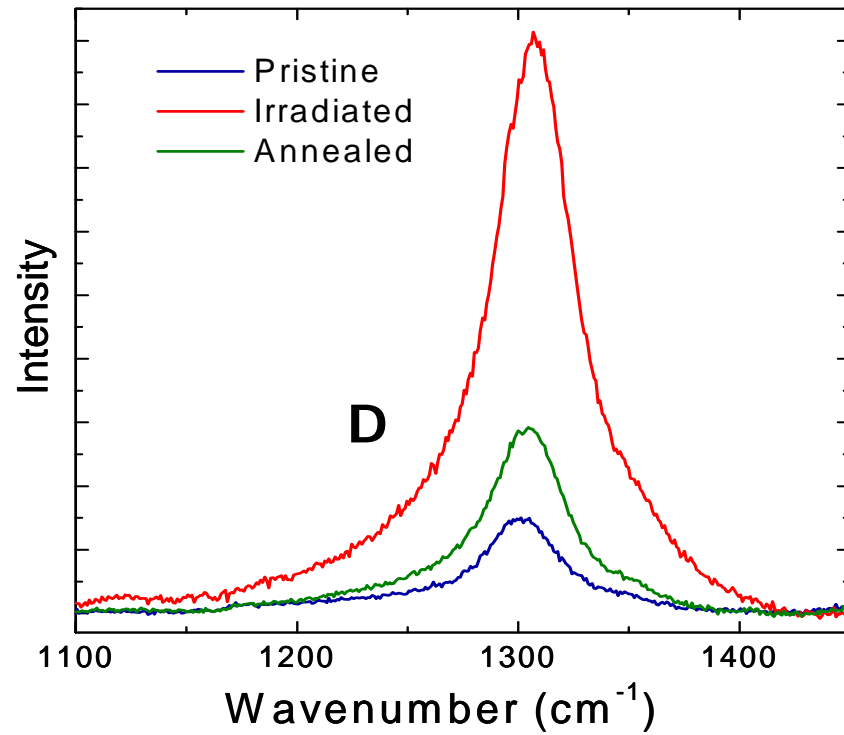


Dose effects of 30 keV Ar⁺ ions

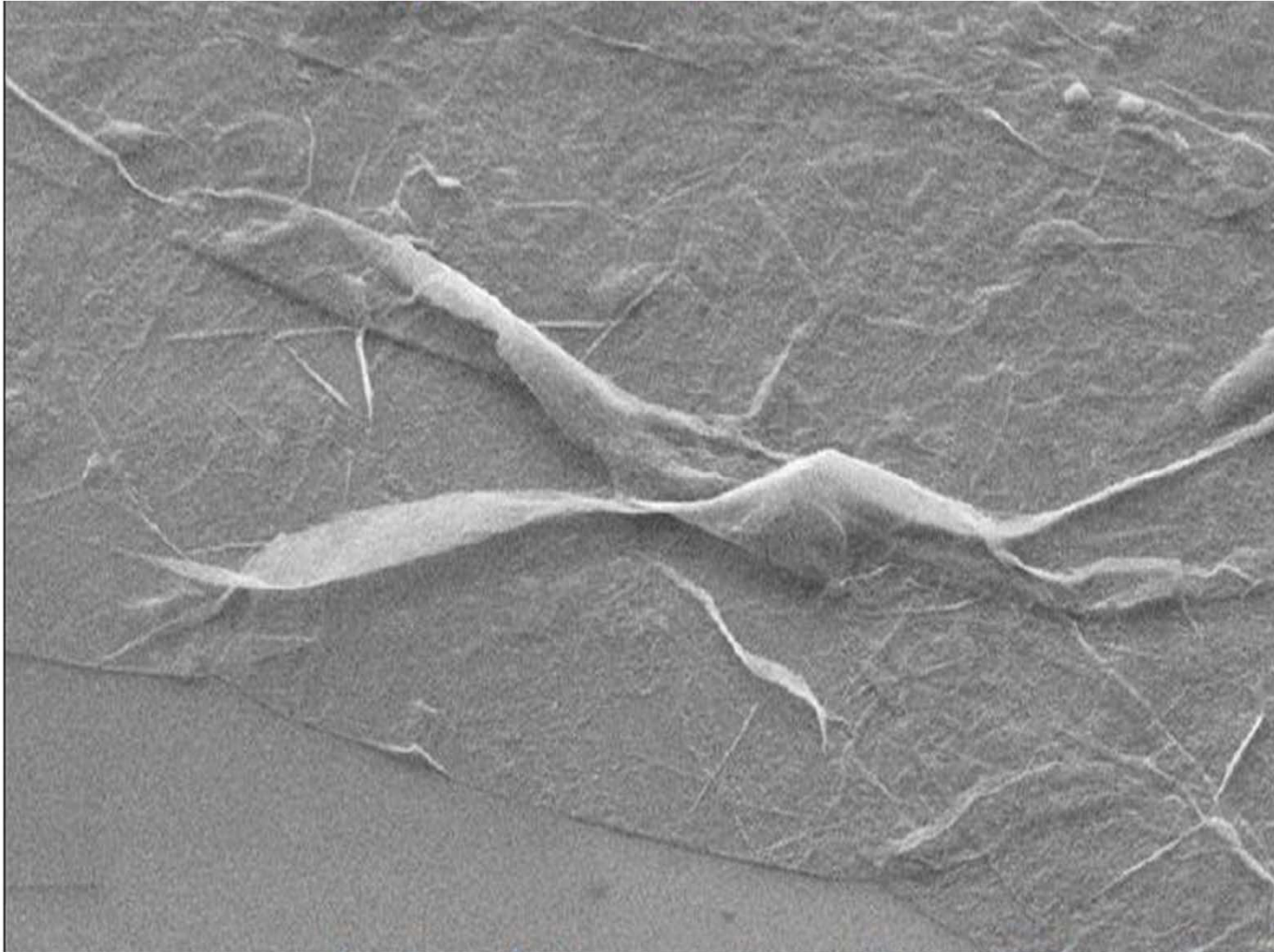


Effect of thermal annealing:

Recovering structure of SWNTs



Defects in Graphene



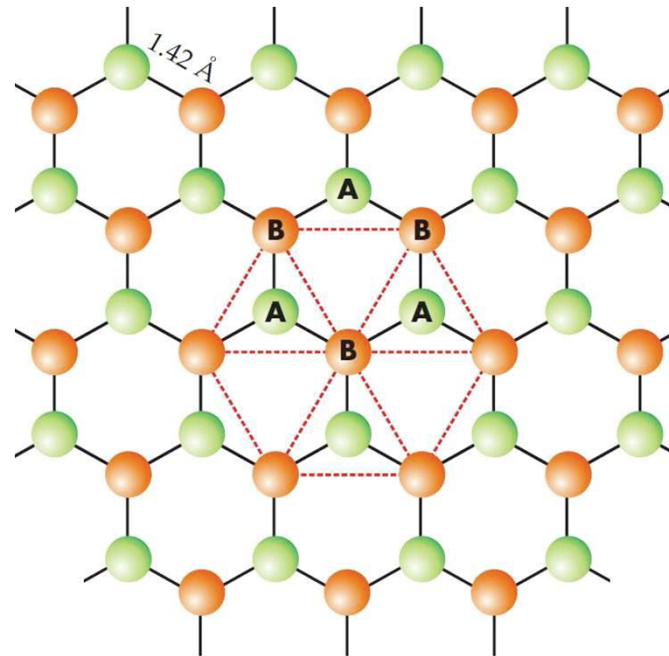
The Band Theory of Graphite

P. R. WALLACE*

National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario

(Received December 19, 1946)

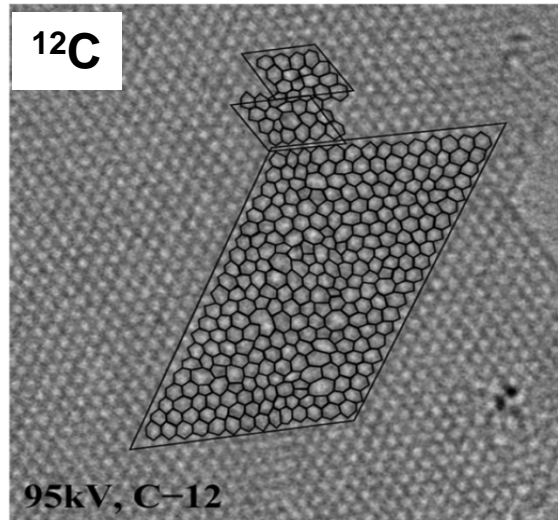
Hexagonal crystal structure of graphene



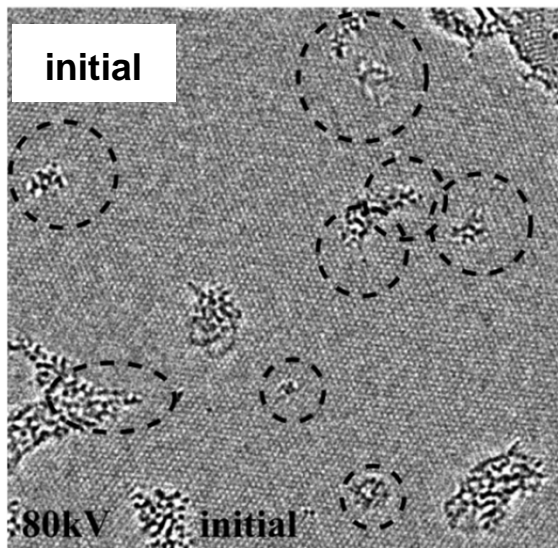
Two equivalent sub-lattices A and B

TEM study of electron irradiation: ^{12}C vs ^{13}C

Direct knock-on damage: Energy = 95 keV, Dose of 1.4×10^9 e/nm²

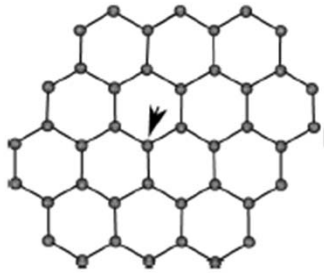


Damage induced by contamination



Jannik C. Meyer, et al. , PHYSICAL REVIEW LETTER 108, 196102 (2012)

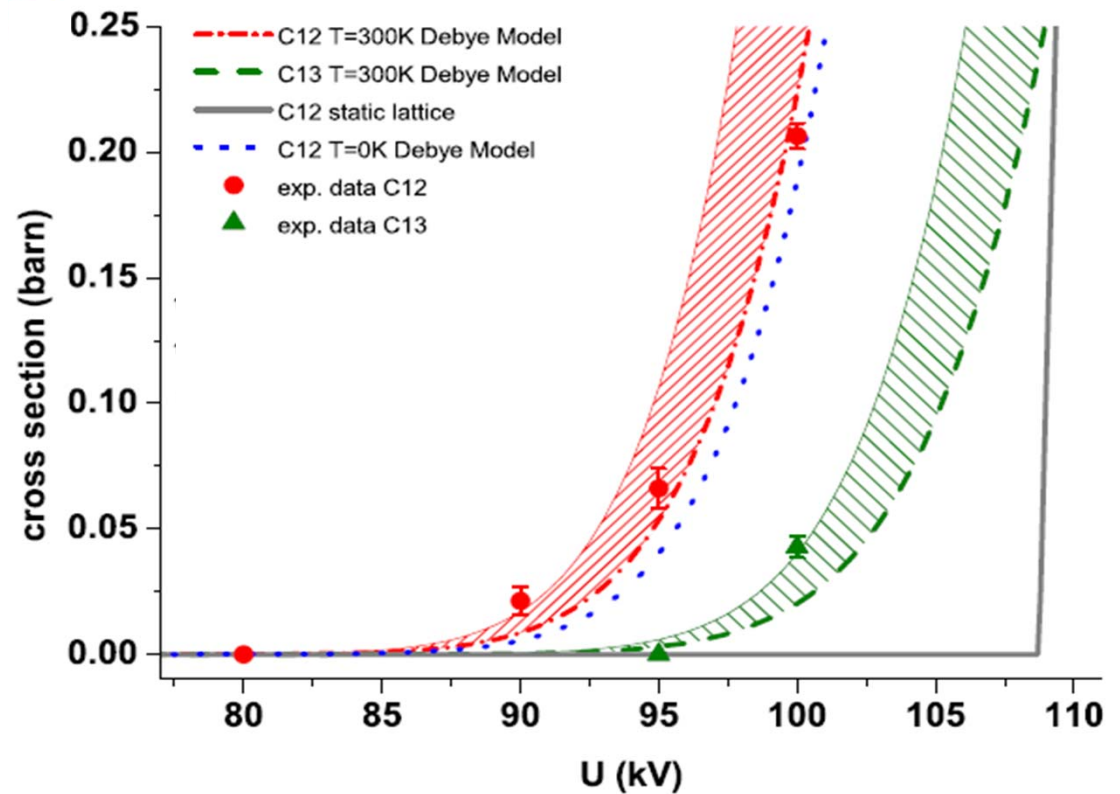
Measured and calculated knock-on displacement cross sections.



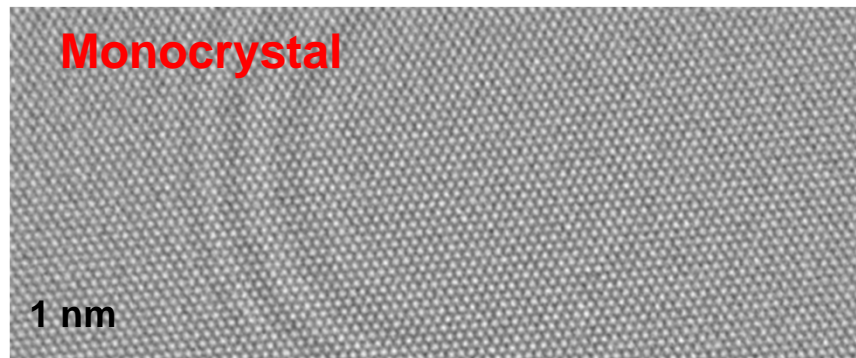
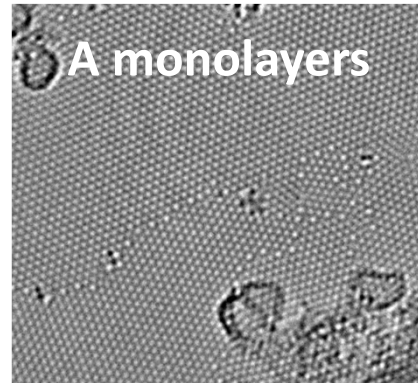
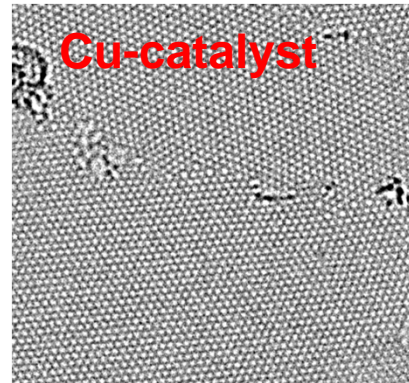
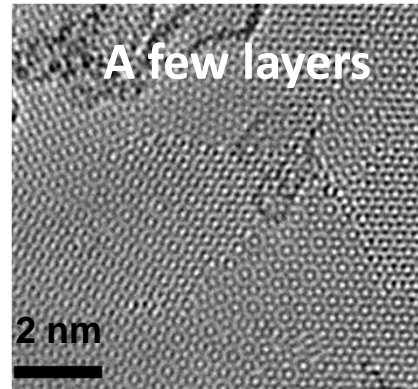
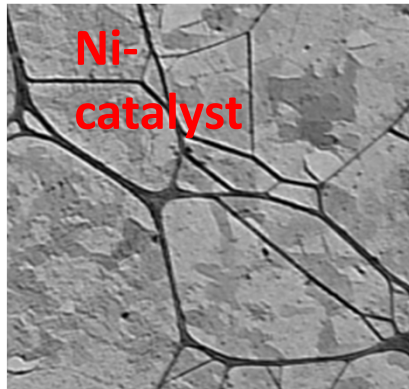
Monovacancy: dangling bond with a much lower emission threshold. Subsequent sputtering of this atom may double the cross section.

The lower boundary of the shaded areas correspond to the calculated cross section.

The upper boundary is twice the calculated value (expected for correlated sputtering).

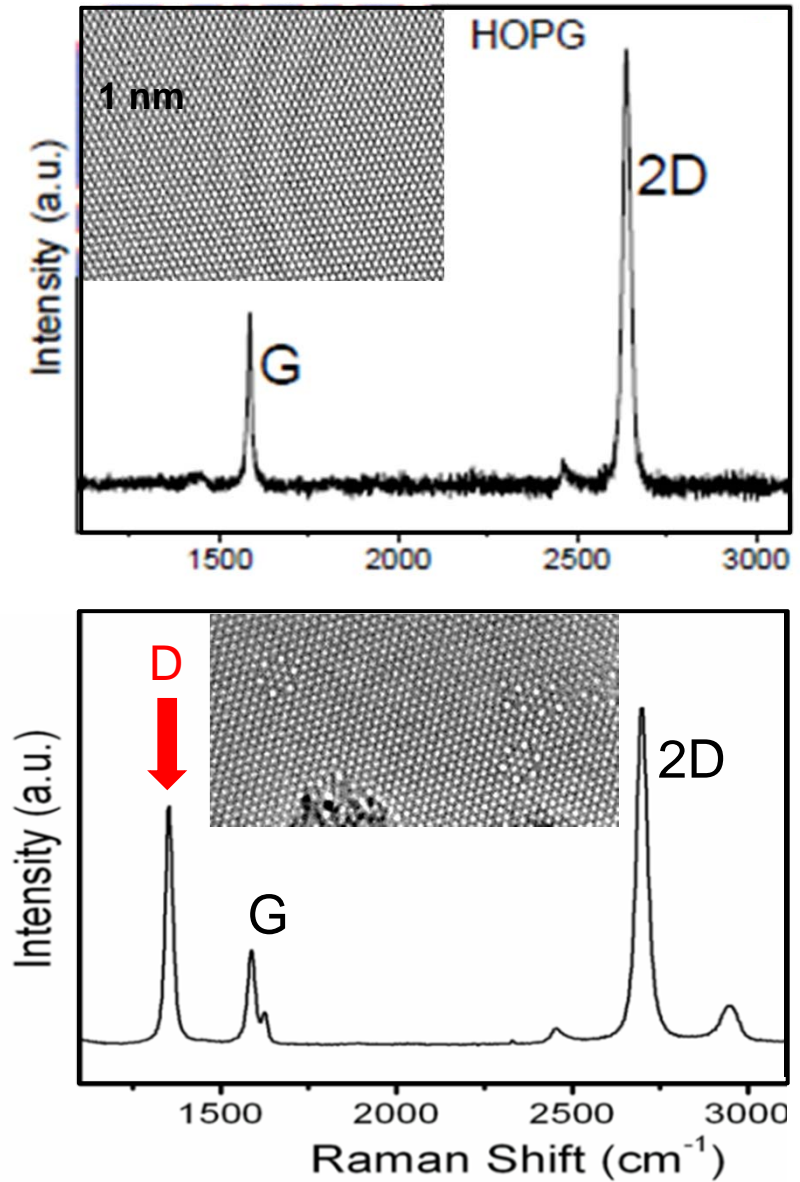
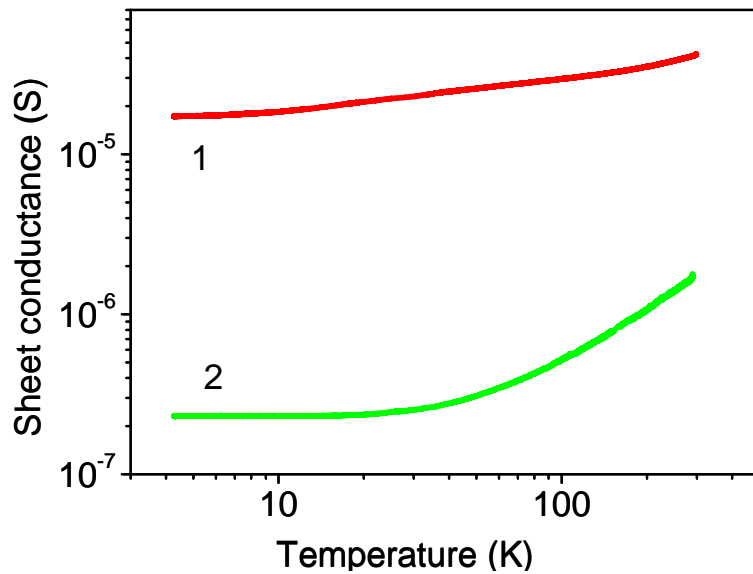


Temperature dependences of conductance



Defects formed in presence of ammonia

1. **pristine** CVD-monolayer
2. **N-doped** CVD-monolayer



Chemical Oxidation-Reduction of Graphite

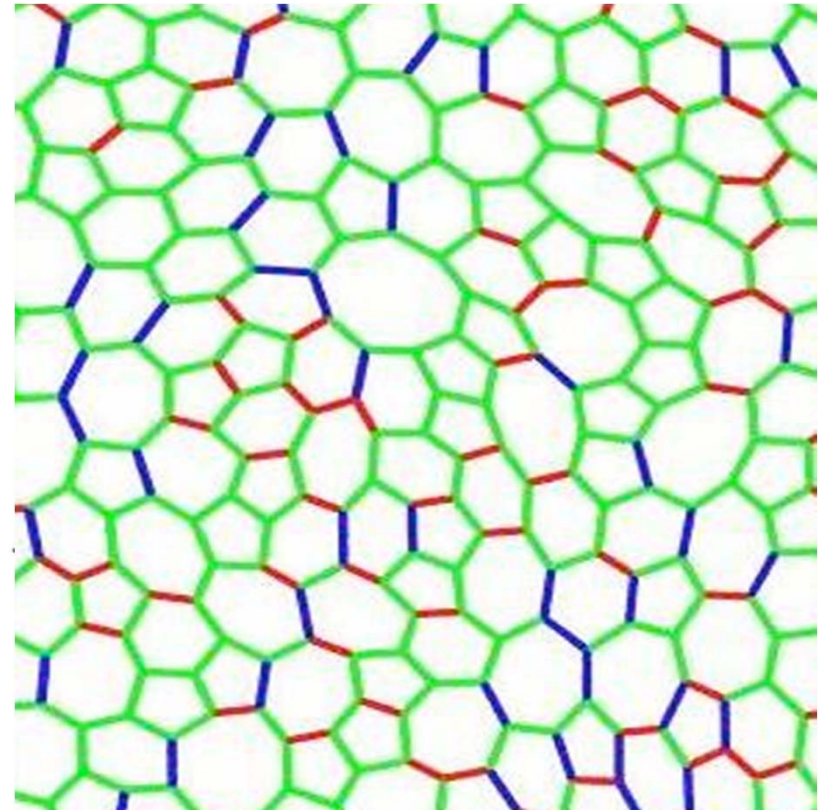
Graphite oxide was first prepared by Oxford chemist Benjamin C. Brodie in 1859

Oxidation introduces functional groups:

A: Epoxy bridges

B: Hydroxyl groups

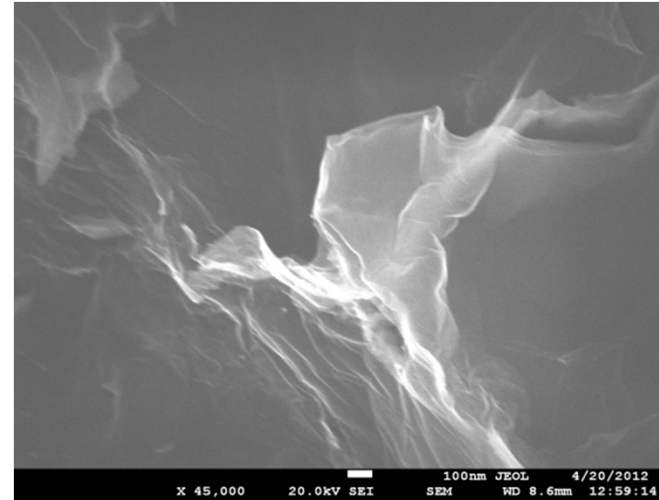
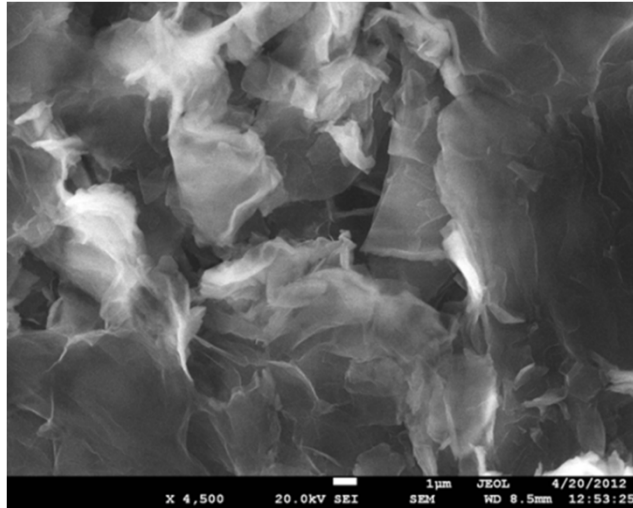
C: Pairwise carboxyl groups



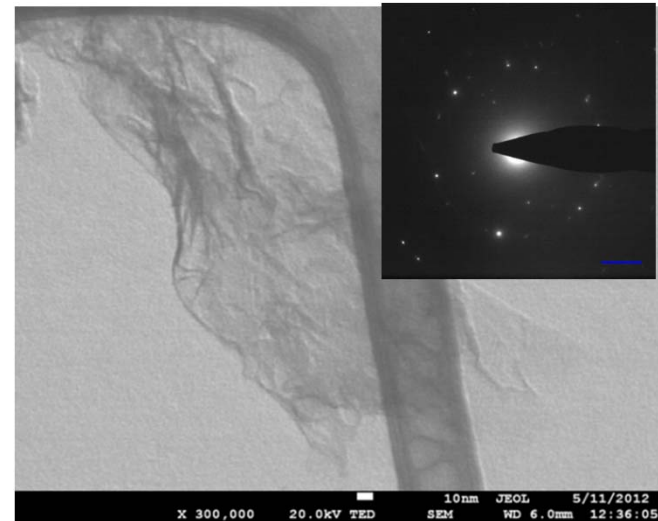
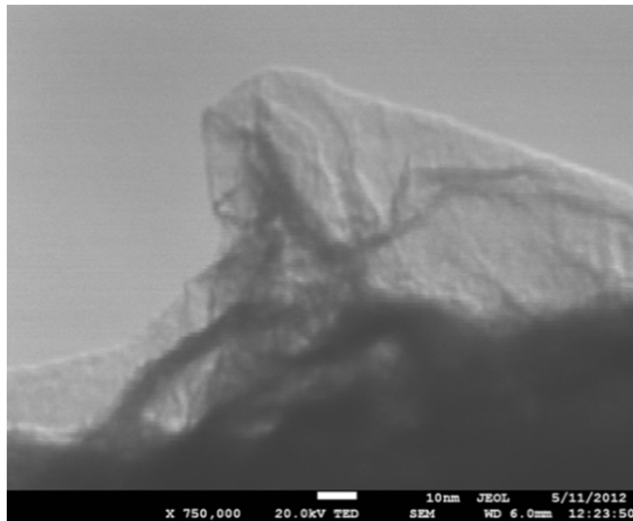
Reduction removes functional groups

- Restores sp^2 orbitals
- Leaves many structural defects

Microscopic characterization of thermally reduced Graphite Oxide (rGO)



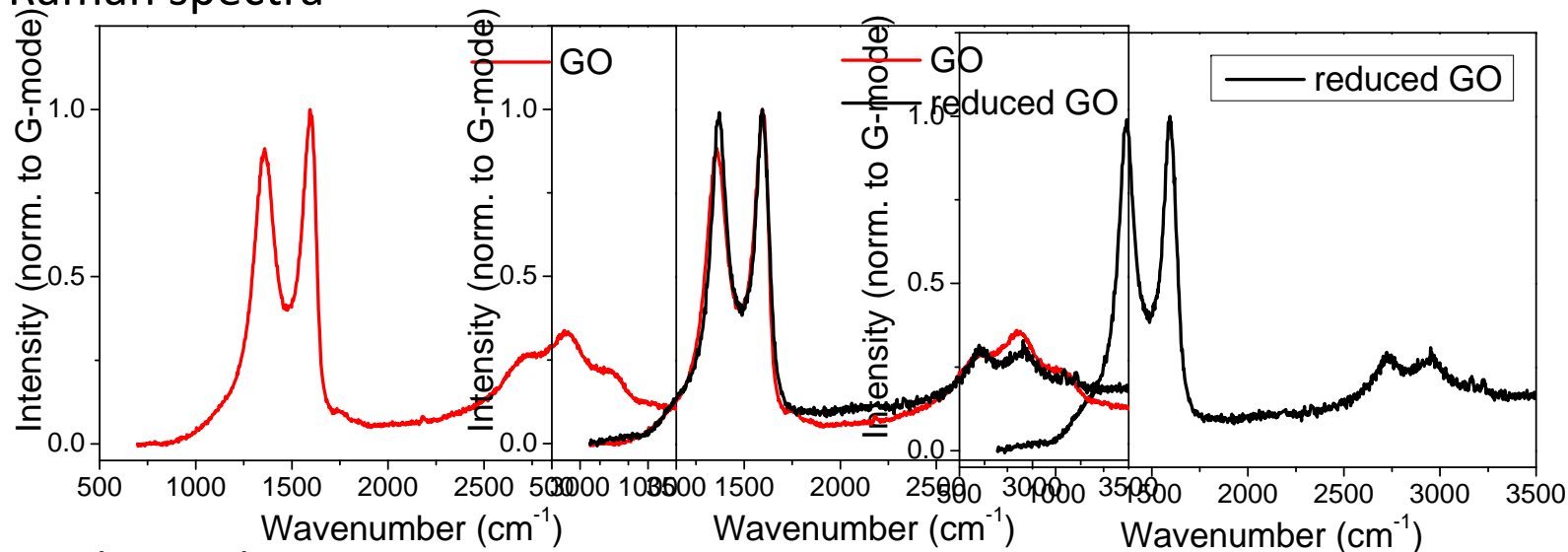
SEM of GO flakes (Hummers)



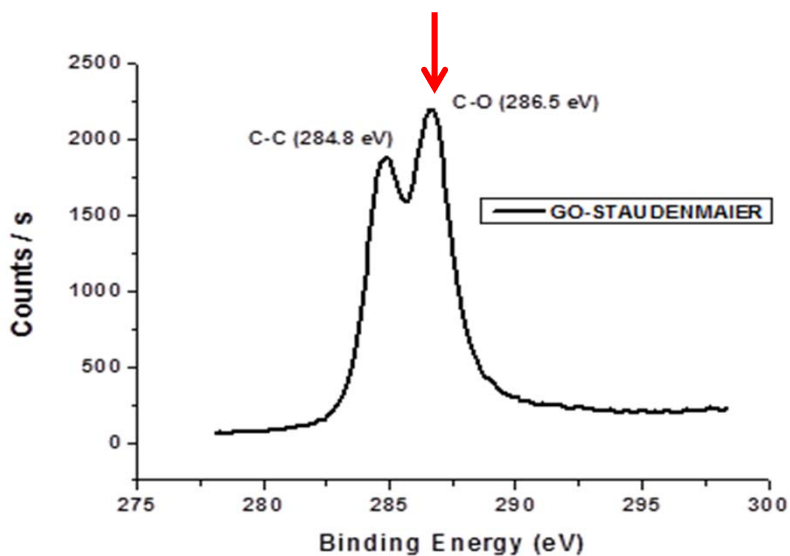
STEM of reduced GO

Spectroscopic characterization of thermally reduced Graphite Oxide (rGO)

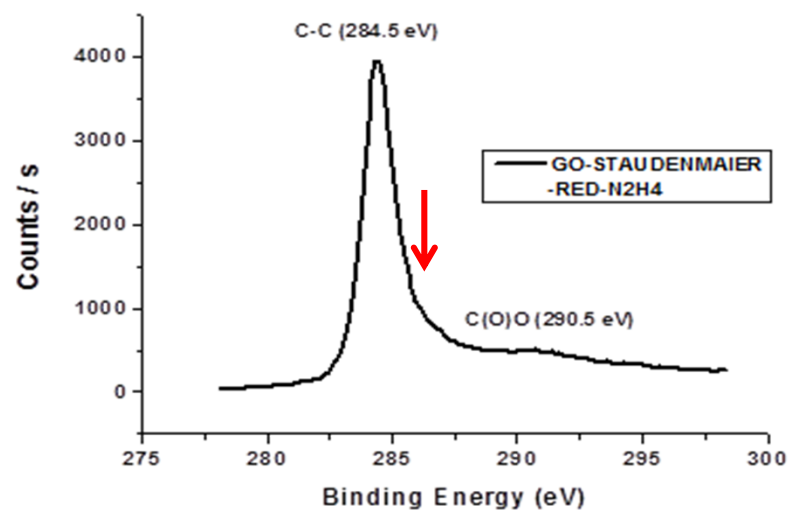
Raman spectra



X-ray Photo-electron Spectra

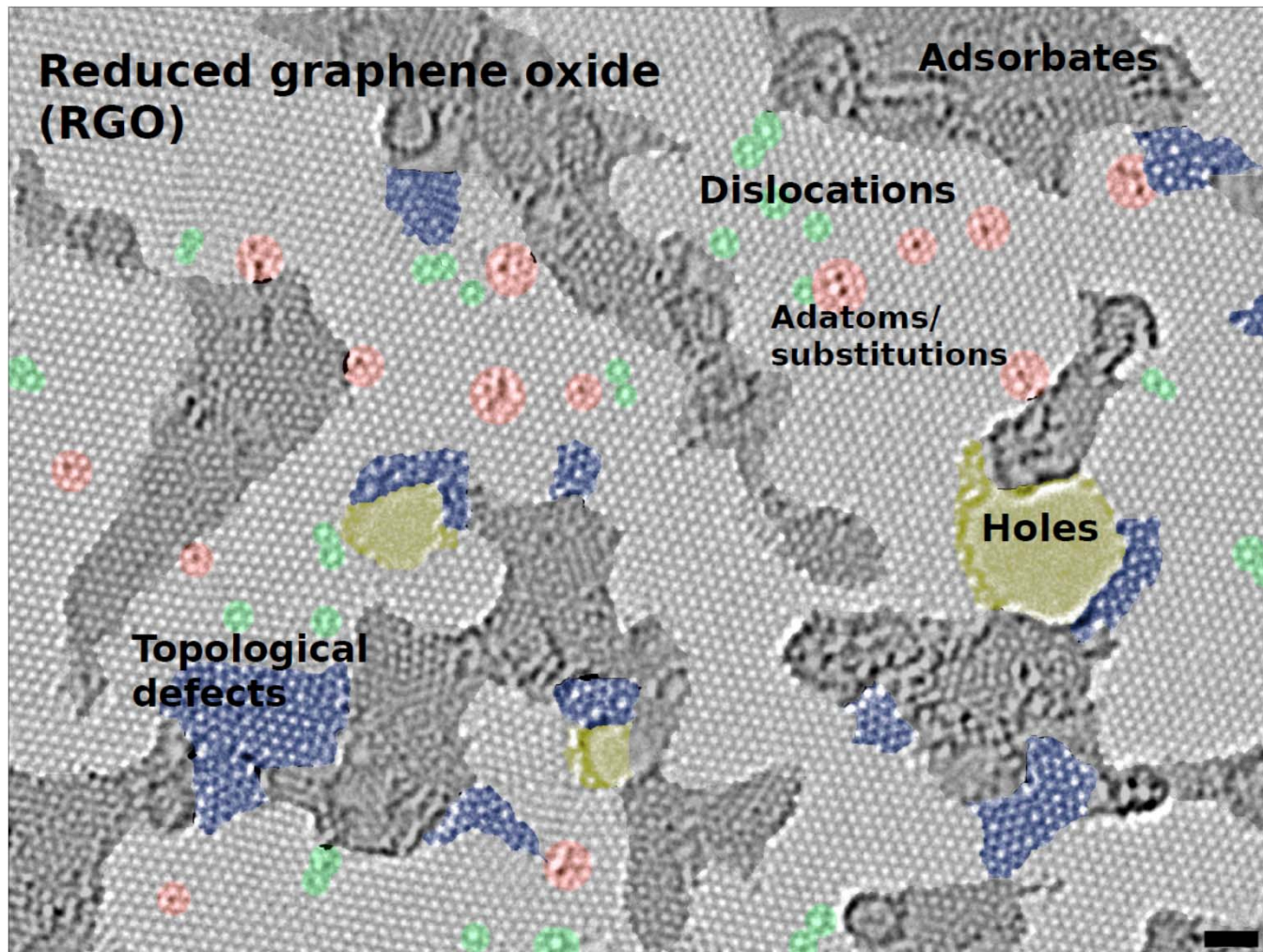


Thorough removal of oxide groups



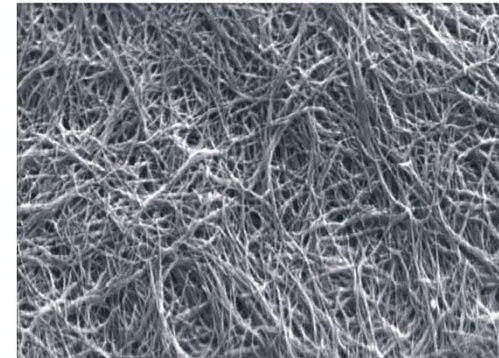
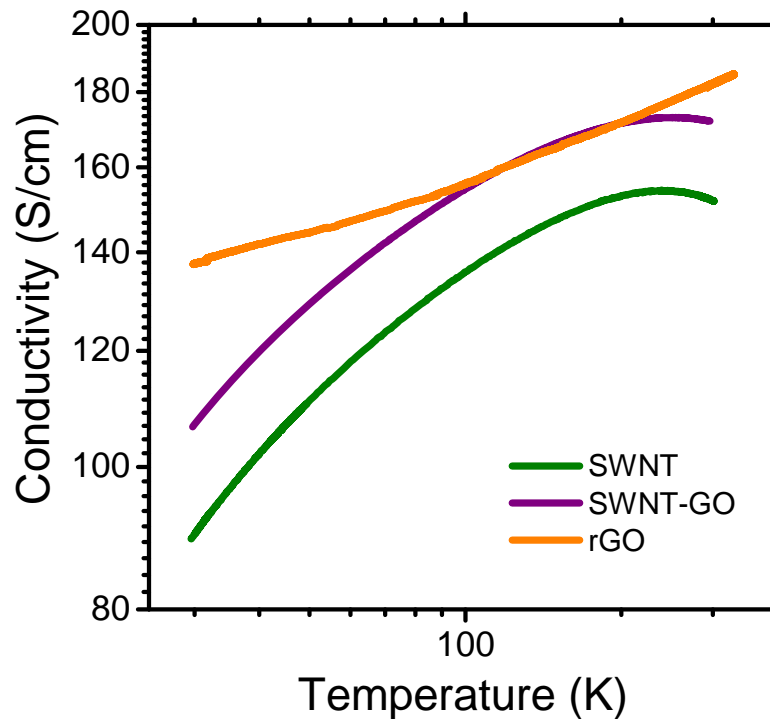
Microscopic characterization of thermally reduced Graphite Oxide (rGO)

HR TEM: Jannik Meyer, Uni Ulm



Electrical conductivity of thermally reduced Graphite Oxide (rGO)

In comparison with SWNT and SWNT-GO composite



- The electrical conductivity of SWNT-GO composite higher than that of SWNT
- Identical electron transport mechanism (Fluctuation Assisted Tunnelling) in SWNT-GO composite and SWNT paper
- Very high electrical conductivity in rGO film with metallic electron transport

Summary

SWNT networks:

- Ion irradiation damages the structure and lowers electrical conductivity
- Thermal annealing removes defects in the SWNT structure

Graphene:

A structural damage affects severely electronic transport

Graphite oxide:

Non conductive and transparent. Electrical and optical properties tunable by reduction of the oxide groups.

Reduced graphite oxide:

Metallic character of electron transport

Composite SWNT-GO:

The same mechanism of electron transport like in SWNT film

Composite SWNT-reduced GO:

???????????????? Under investigation.

Aknowledgment

The results have been acquired within several years of collaboration between



Max Planck Institute in Stuttgart



Danubia NanoTech (SME) in Bratislava

and



University of Vienna

Thanks for attention 😊

SWNT networks

