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Danubia NanoTech, s.r.o.
Research in science and technology

Electronic Transport in C-C composites

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Need for Graphene mass production: Graphite Oxide

Graphite Oxide has been reborn after many years again

March 20, 1958 PREPARATION OF GRAPHITIC OXIDE 1339

[CONTRIBUTION FROM THE BAROID DIVISION, NATIONAL LEAD COMPANY[1]]

Preparation of Graphitic Oxide

BY WILLIAM S. HUMMERS, JR., AND RICHARD E. OFFEMAN

RECEIVED SEPTEMBER 25, 1957

The preparation of graphitic oxide by methods described in the literature is time consuming and hazardous. A rapid, relatively safe method has been developed for preparing graphitic oxide from graphite in what is essentially an anhydrous mixture of sulfuric acid, sodium nitrate and potassium permanganate.

- **A positive aspect:** **Efficient and scalable synthesis**
- **A negative aspect:** **Sever degradation of the graphitic structure**

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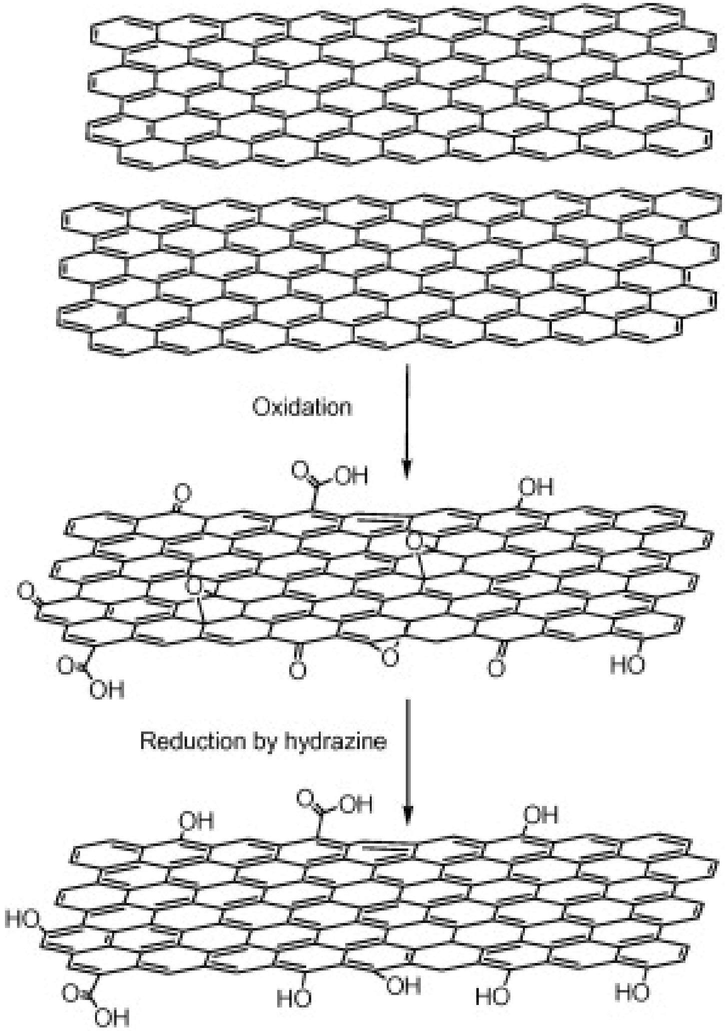
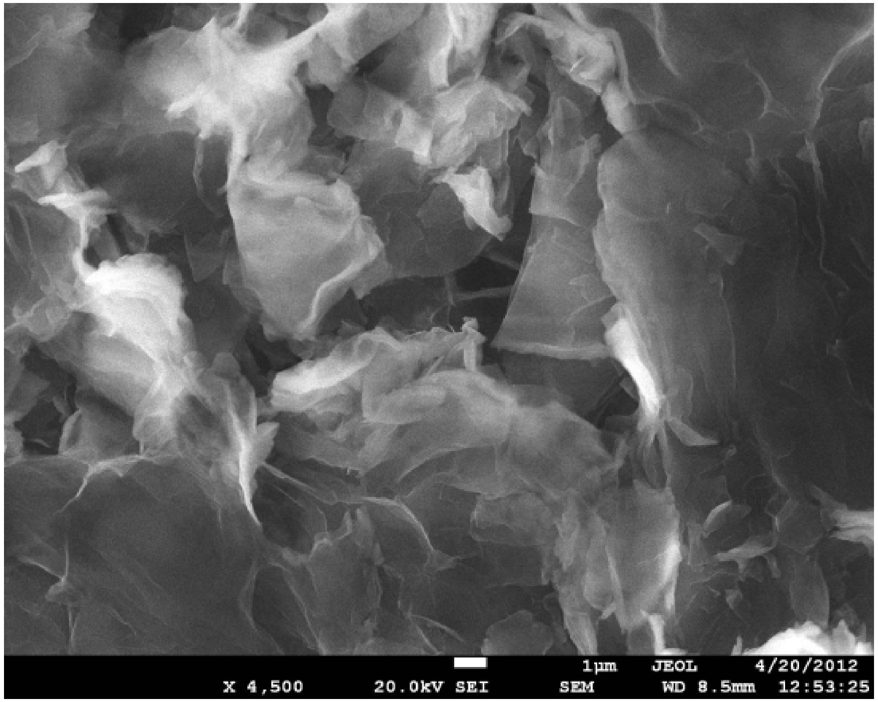
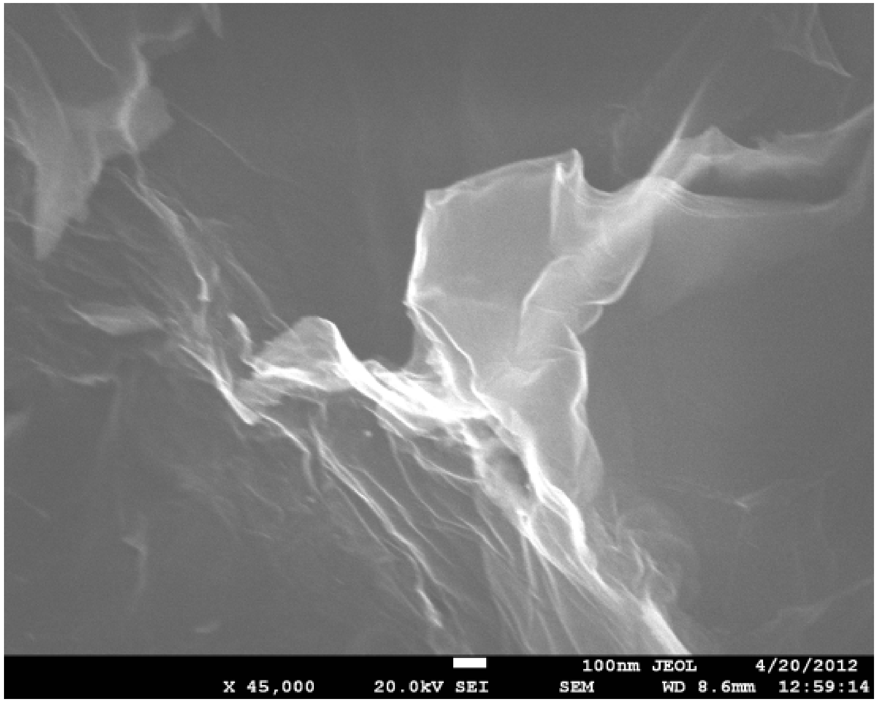
Oxidation of graphite



Graphite oxidation:





SEM images of GO prepared by Hummers method

Graphite oxide properties:

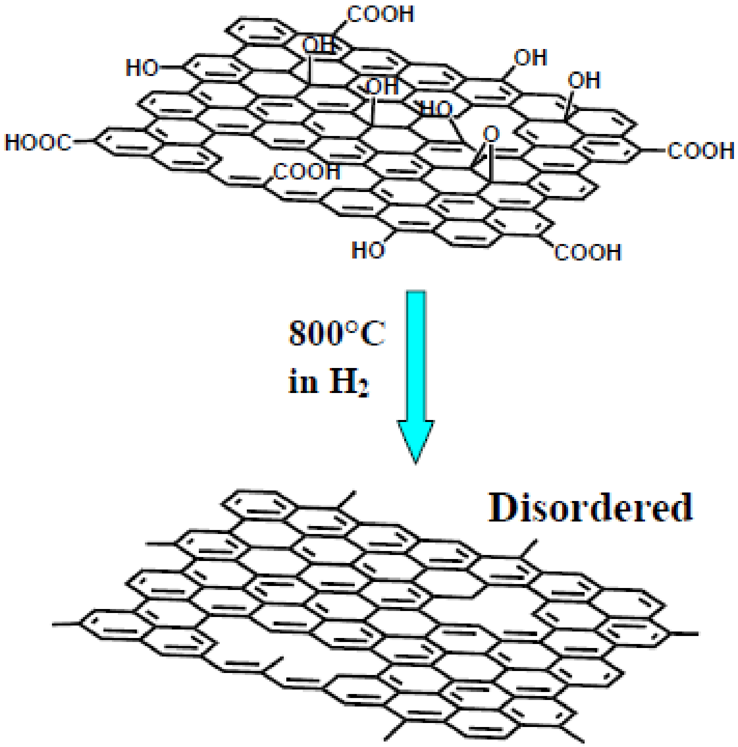
Consequence of the oxidation process:

- High electrical resistivity ☹
- Optical transparency ☺
- High water solubility ☺
- Lower chemical stability ☹
- Structural inhomogeneity ☹

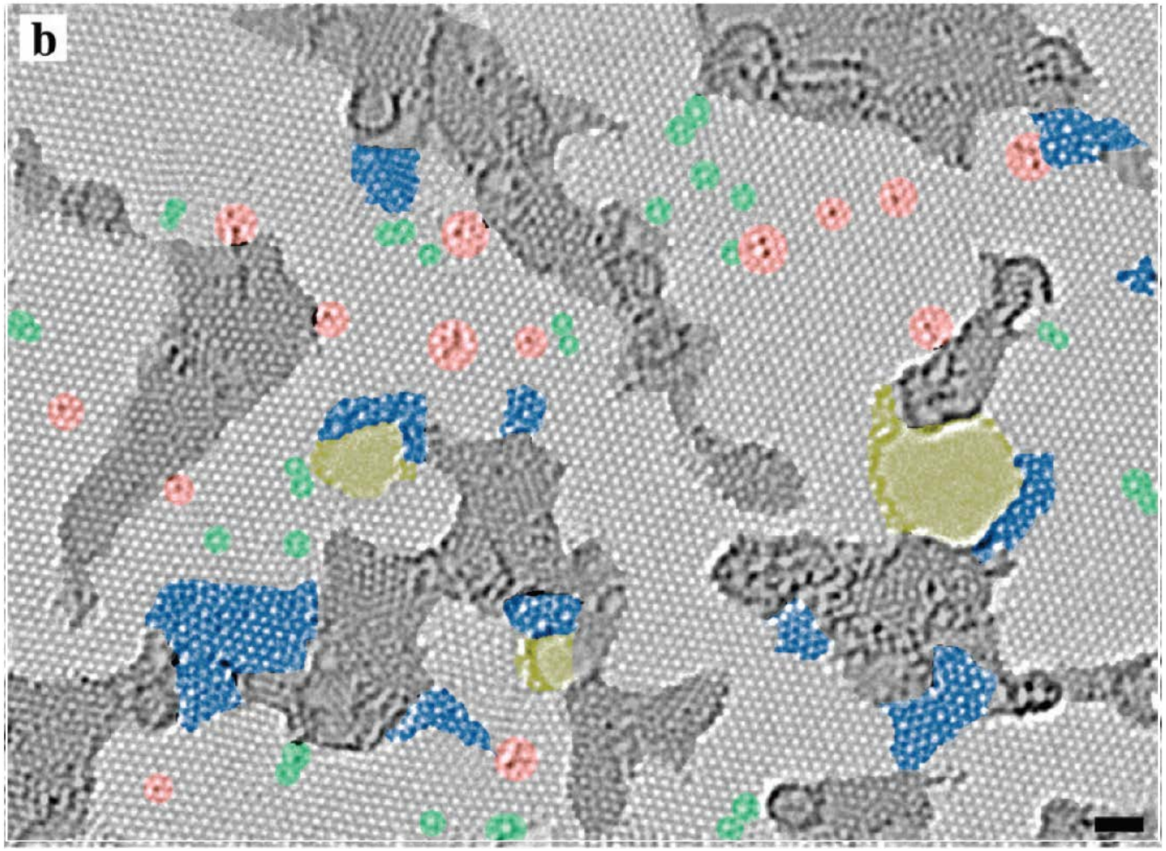
Recovery of the graphene properties through reduction:

- Chemical reduction ☹
- Thermal reduction ☺

Reduction:


COOH
OH
HO
OH
OH
HO
HOOC
O
COOH
COOH
HO
COOH
800°C
in H_2
Disordered

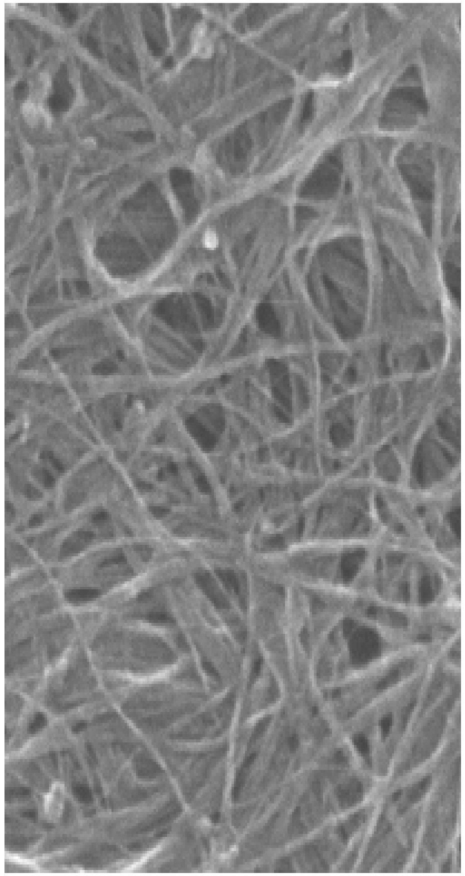
Reduction:



rGO single sheet: damage to the graphene structure after reduction

C. Gomez-Navarro, J. C. Meyer, …. and U. Kaiser, Nano Lett. 10, 1144–1148 (2010)

How will electronic transport change when SWCNT and GO are mixed?



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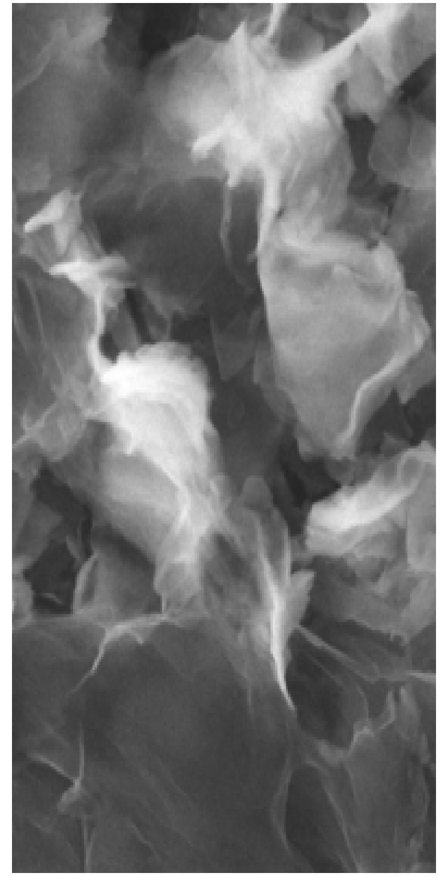
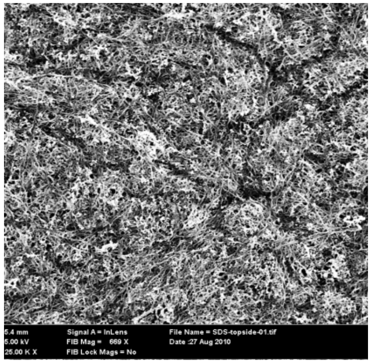


Viera Skákalová, Viliam Vretenár, Ľubomír Kopera, Peter Kotrusz, Clemens Mangler, Marcel Meško, Jannik C. Meyer and Martin Hulman, ***Carbon*** **72, 224 –232 (2014)**

Characteristic features for electronic transport :

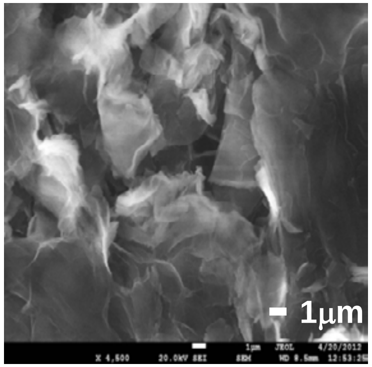


Single Wall Carbon NanoTube papers (SWCNT):

- Ballistic transport, huge current density
- Small contact area between tubes in networks

Graphite oxide (GO):

- Oxide groups localize charge – electrically insulating
- But we can mix GO with SWCNTs (?)



Reduced Graphite Oxide (rGO) :

- Charge delocalization recovered
- But structural disorder persists
- Large contact area between rGO sheets

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Characterization

- **Scanning electron microscopy (SEM)**
- **Elastic modulus**
- **Electronic transport**
- **Raman spectroscopy**

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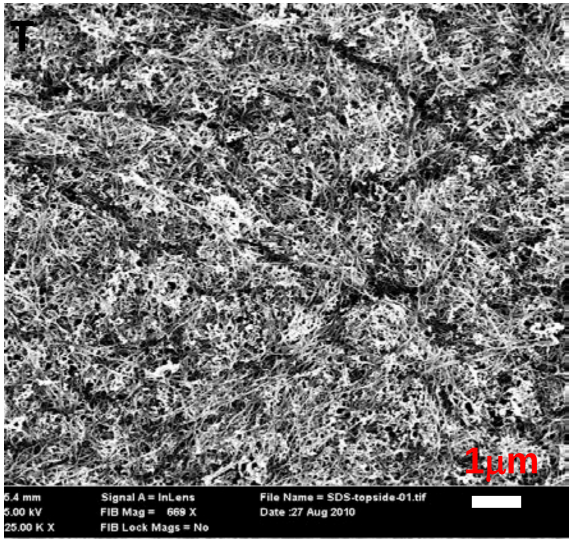
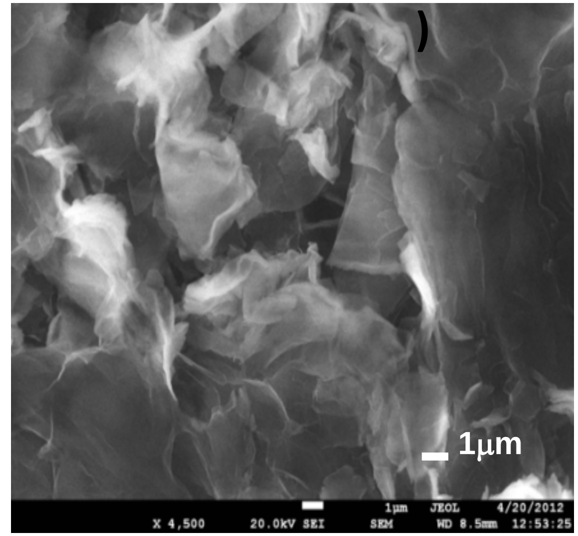
Our samples

Reference

SWCNT

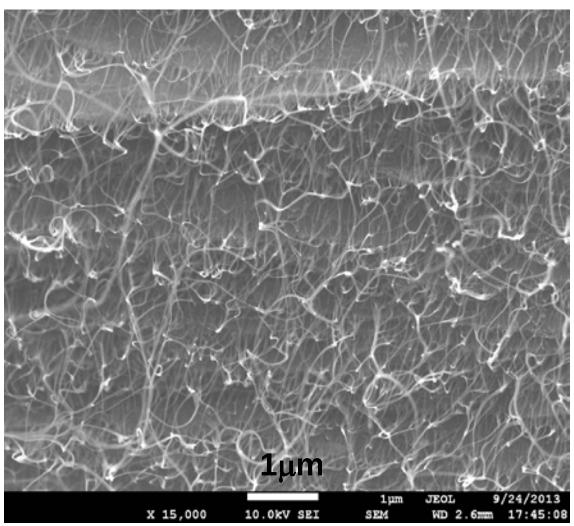


rGO(th)

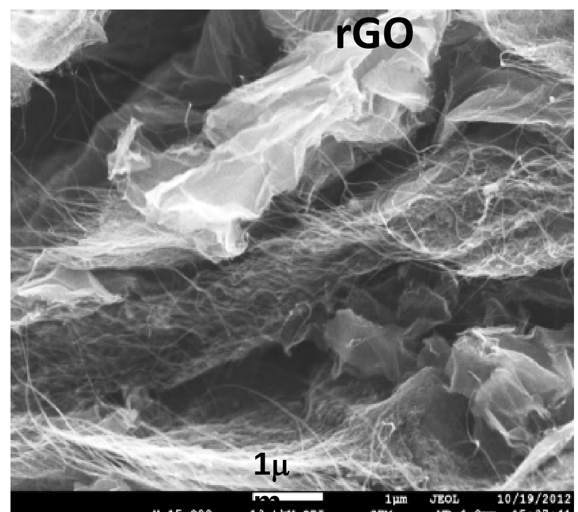


Composites

SWCNT-GO



SWCNT-rGO



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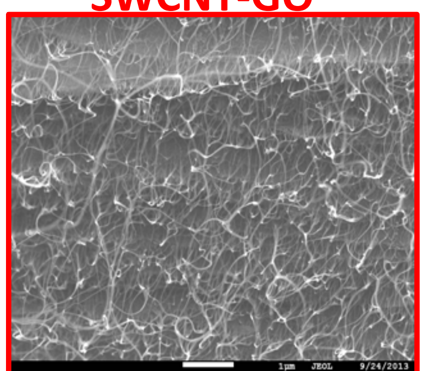
Mechanical properties

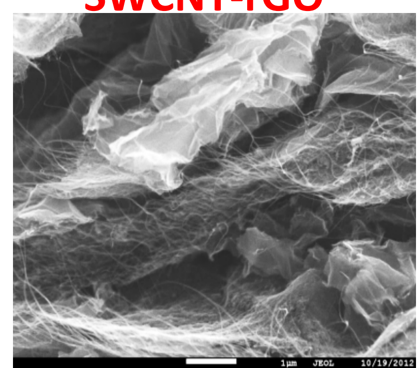
Sample	Volume density (kg/m^3)	Young´s modulus (GPa)
SWCNT	550	4.7
rGO(th)	690	---
SWCNT- GO	820	6.7
SWCNT- rGO	270	0.3

Composites:

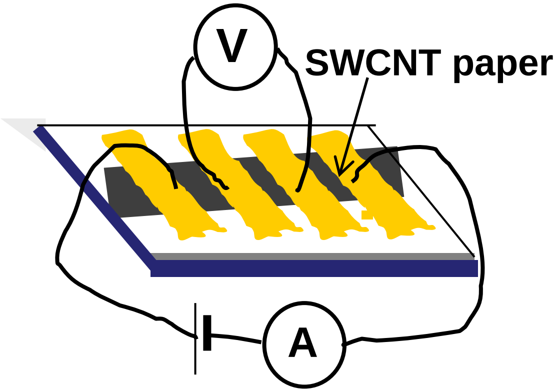
SWCNT-GO

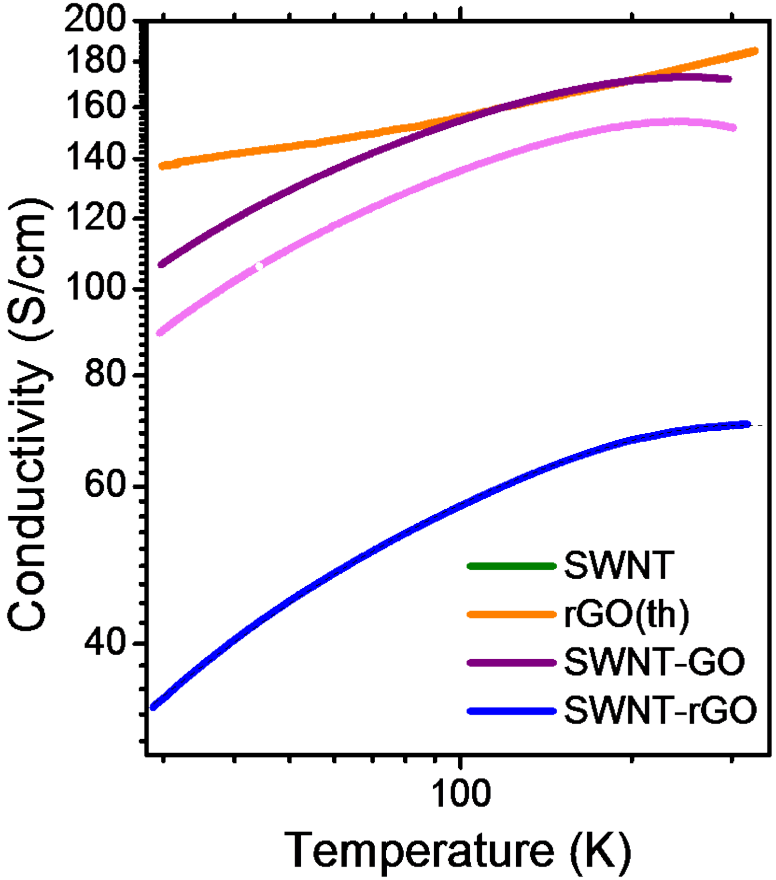


SWCNT-rGO



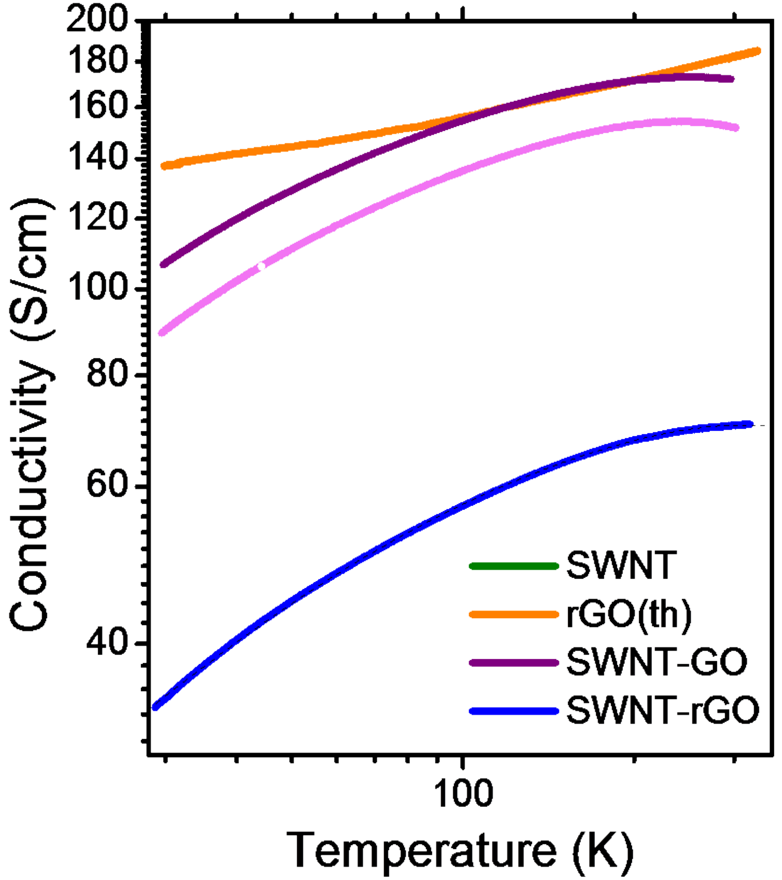
Electronic transport





Observation:

1. SWCNT-GO , SWCNT-rGO – same character of G(T) as in SWCNTs
2. rGO – different shape of G(T) than SWCNT
3. SWCNT-GO : higher conductivity than SWCNT
4. SWCNT-rGO : lower conductivity than SWCNT

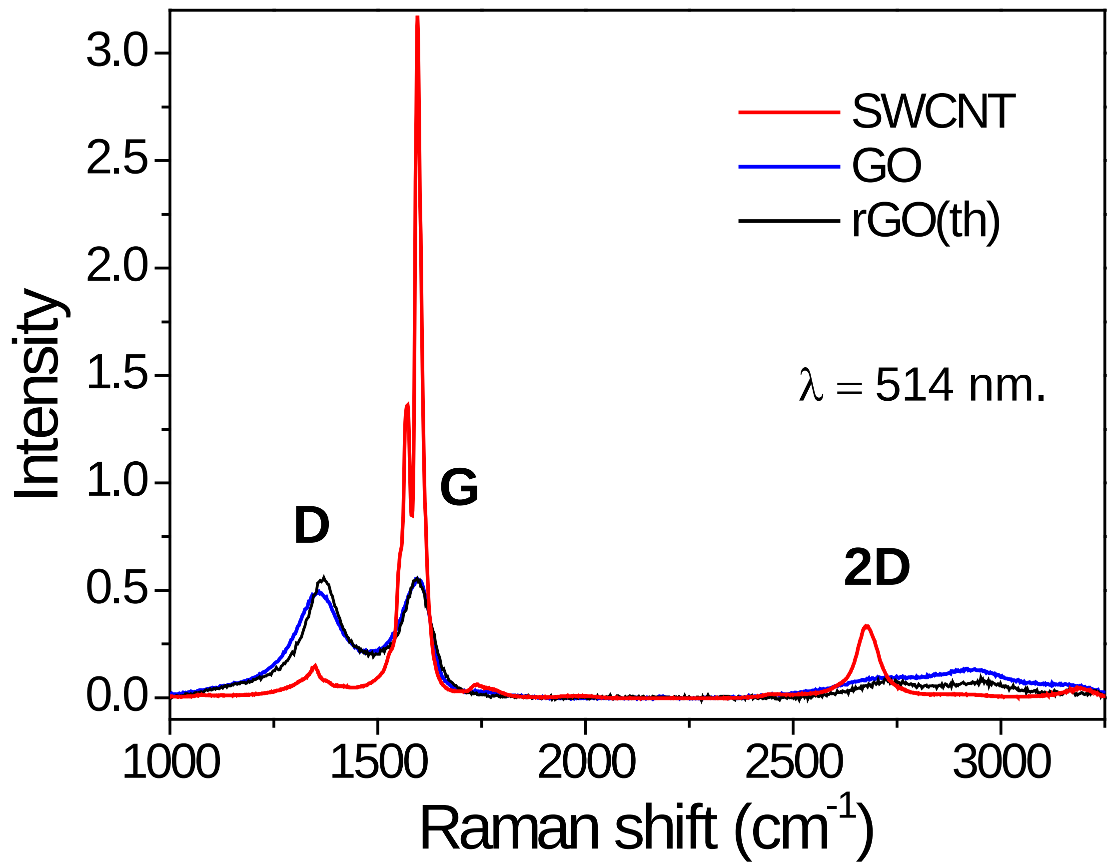


Explanation:

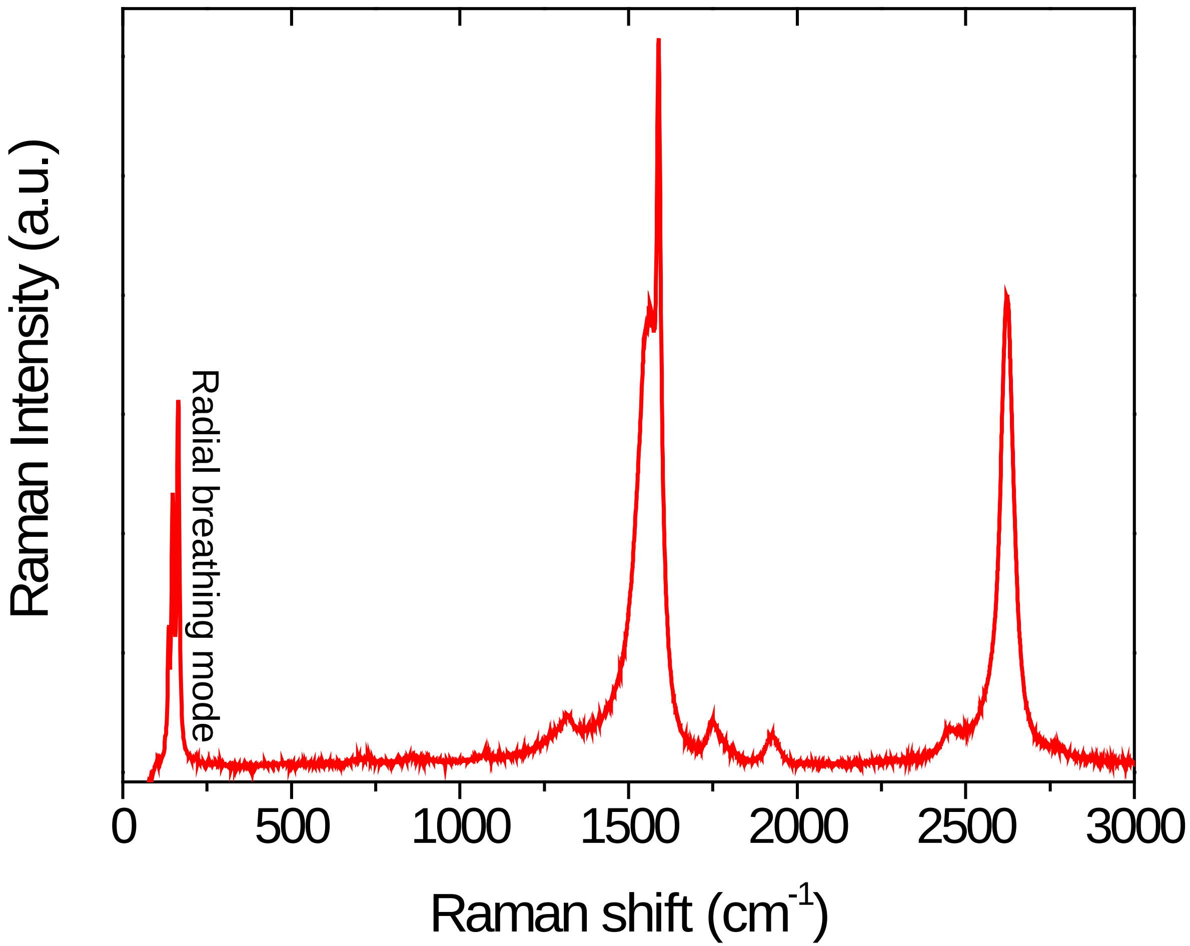
- SWCNTs dominant in the both composites
- GO dopes SWCNT
- rGO does not dope SWCNT

Comparison of Raman spectra

Resonant Raman spectra for **SWCNT, not** for **GO neither rGO**



One more mode for SWCNT : RBM



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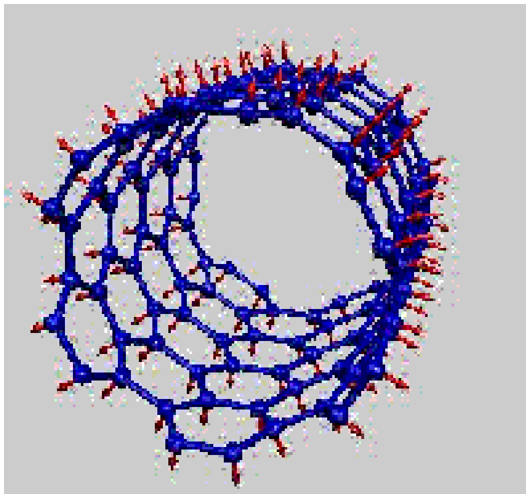
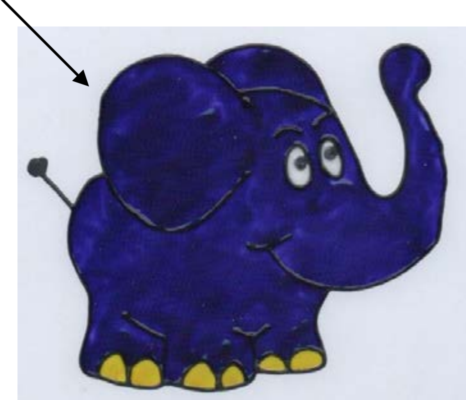
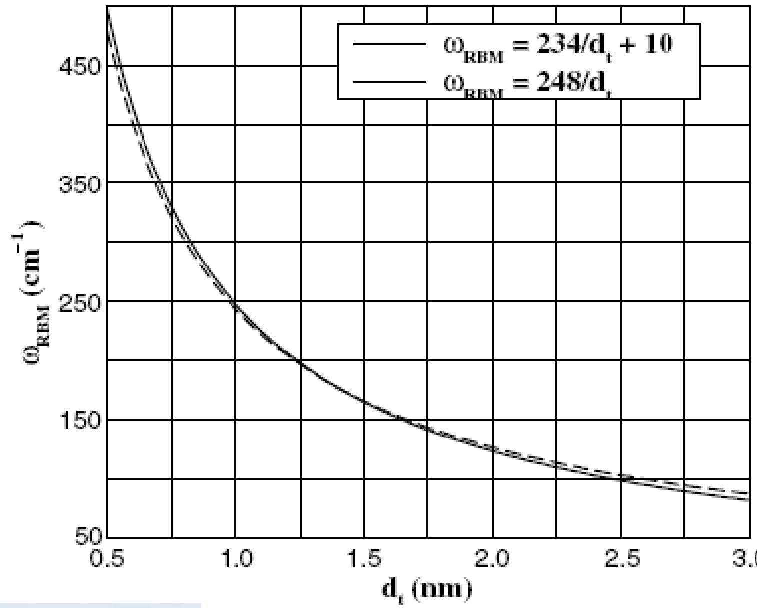
Radial Breathing Mode - RBM





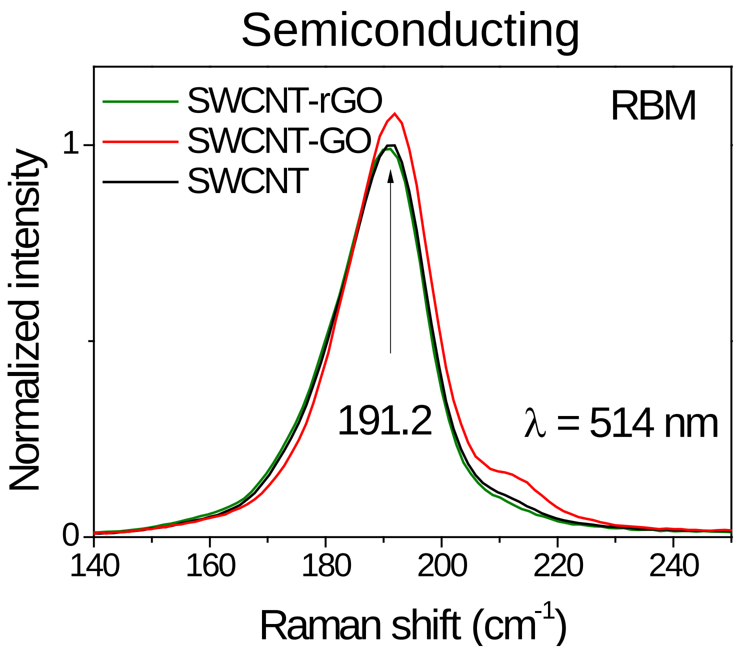


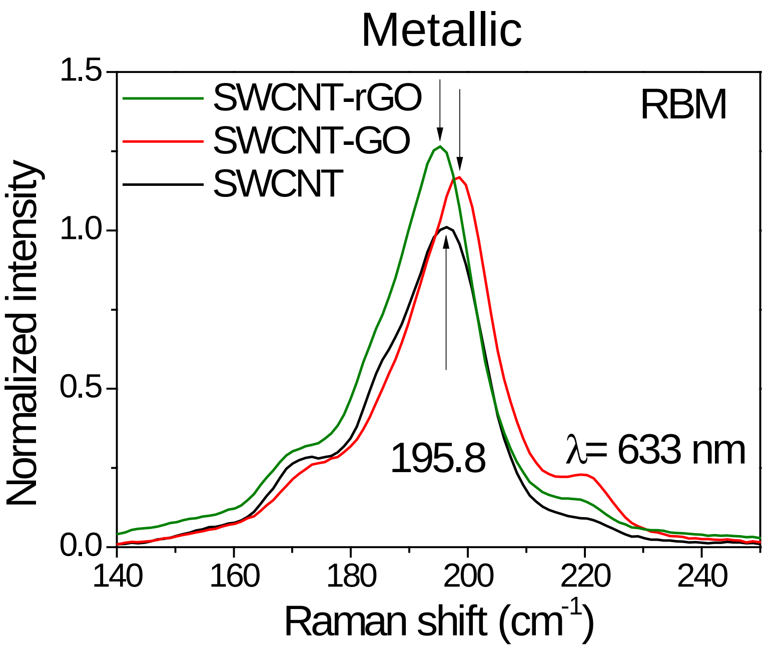
Different diameter of SWCNT – different "breathing" frequency:

Possibility to identify and distinguish semiconducting from metallic tubes!

Raman spectra analysis: RBM

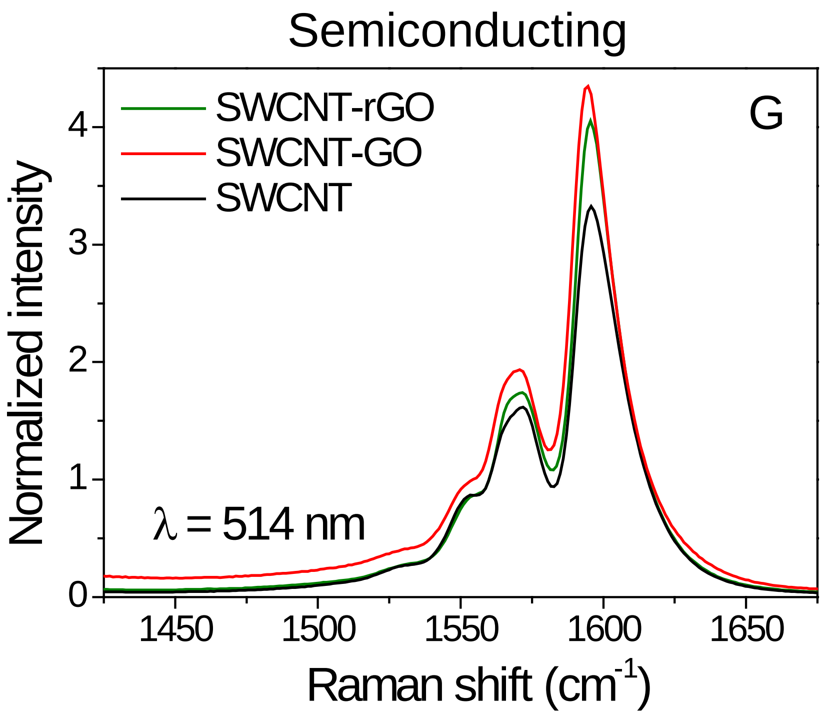
Two wavelengths: 514 nm, 633 nm

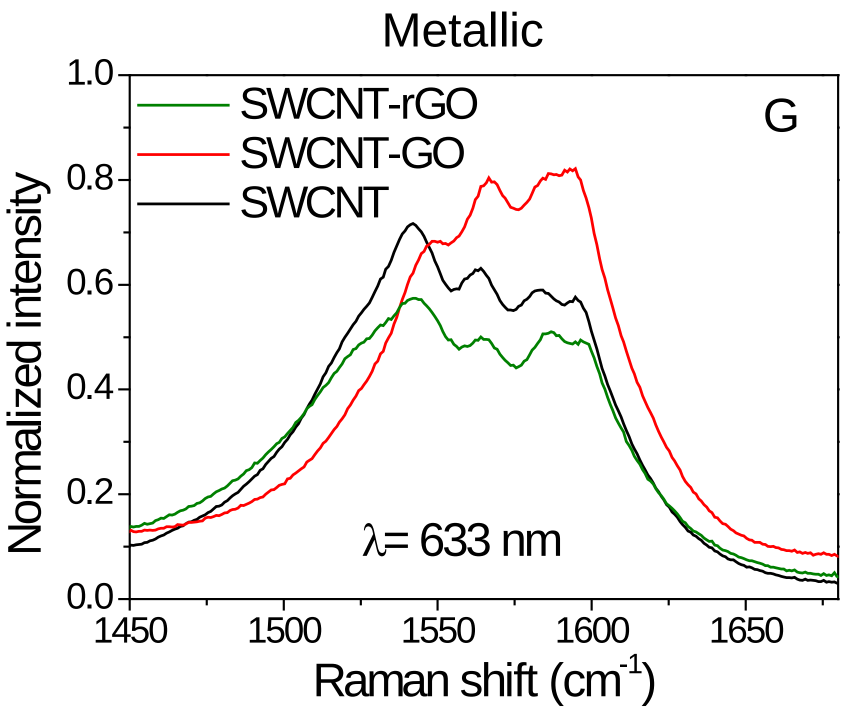




Wavelength (nm)	RBM $_{Exper.}$ (cm^{-1})	RBM $_{Theor.}$ (cm^{-1})	m	n	D (nm)	Character
633 (1.93eV)	195.8	195.9	13	4	1.21	metallic
514 (2.41eV)	191.2	191.71	11	7	1.23	semiconducting

Raman spectra analysis: G-mode





No doping

Doping in SWCNT-GO

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Fluctuation- Assisted Tunneling (FAT):

$$\boldsymbol{R(T)} = A\exp\left(-\frac{T_m}{T}\right) + B\exp\left(\frac{T_b}{T_s + T}\right)$$

Phonon scattering
$\boldsymbol{k_B T_m}$

(Pietronero, 1983)

FAT through barriers
$\boldsymbol{k_B T_b}$

(Sheng, 1980)

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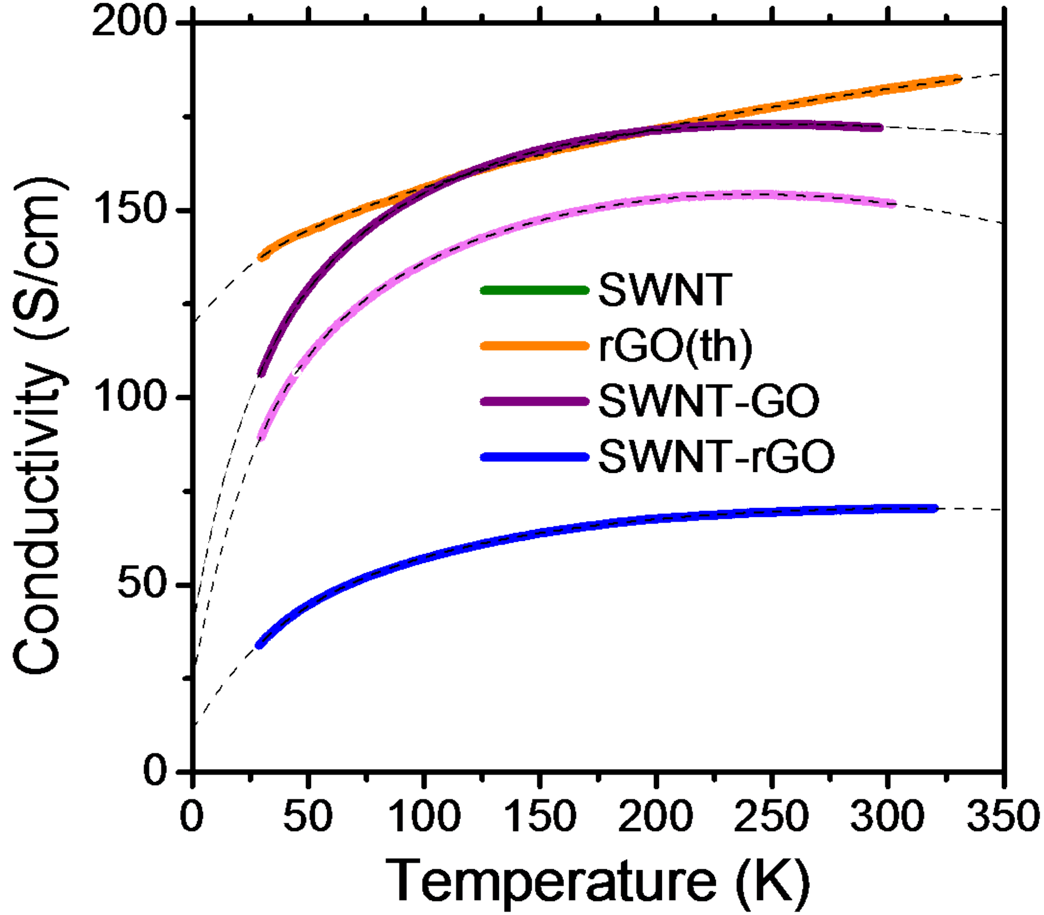
Fitting measured *G*(*T*) by FAT

- In SWCNT networks: high intrinsic conductivity of SWCNT versus poor coupling between nanotubes.
- In rGO networks: good coupling between the sheets versus poor intrinsic conductivity within the sheet.



Summary

1. **Strong electrostatic interactions** between **GO** and **SWCNT**

2. **Weak interactions** between **rGO** and **SWCNT**

3. **SWCNT-GO** composite: **high conductivity, high Young´s modulus**

4. **SWCNT-rGO** composite: **low** conductivity, **low** Young´s modulus

Acknowledgement