Graphene Oxide and reduced Graphene Oxide: focus on electrical conductivity

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Sergio Gallone - Leonardo Finmeccanica S.p.A
Lucrezia Calderaro - Leonardo Finmeccanica S.p.A

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Introduction

Graphene can be used in many industrial application areas, even if the production methods are currently expensive and the relevant outcomes are under study.

A focus on graphene oxide reduction to produce graphene for the advantage of low cost and scalable properties, has been performed.

The reduction by thermal and chemical treatments for both 2mg/ml and 10mg/ml concentrations of GO has been investigated

Characterizations for thickness, morphology and electrical properties of material have been done on the samples obtained.

The result opens the path to the investigation of more efficient thermal reduction techniques in order to get a further increase in rGO electrical conductivity.

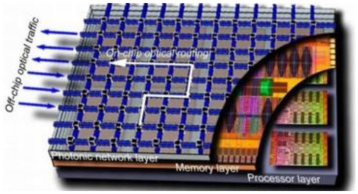
General industrial application areas: examples





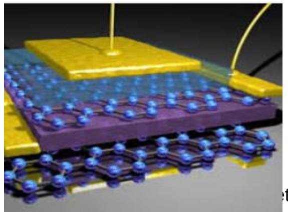
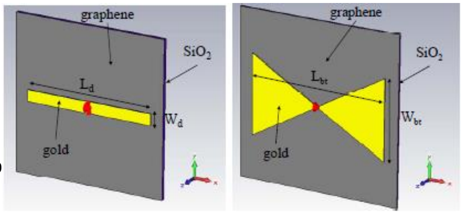
Air and Water Sensors: Anti-Pollution, chemical sensors, Toxic gases

Thermal devices: Radomes Deicing, Disposable buoy sonar



Electronic devices: Photonic devices, GHz and THz Transistors, Novel antennas

Energy Storage: Solar cells, Supercapacitors


Specific industrial application areas: examples

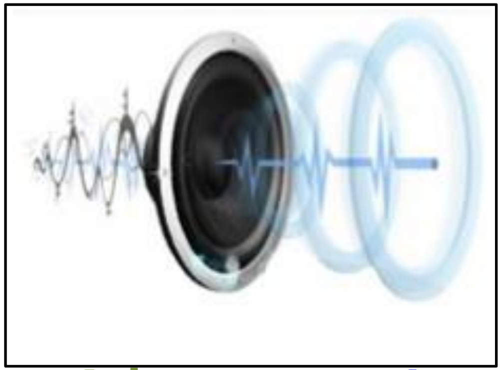
Graphene can be used for the realization of efficient **adsorbents, sensors, supercapacitors** and **local heating** with focus on the environmental protection.

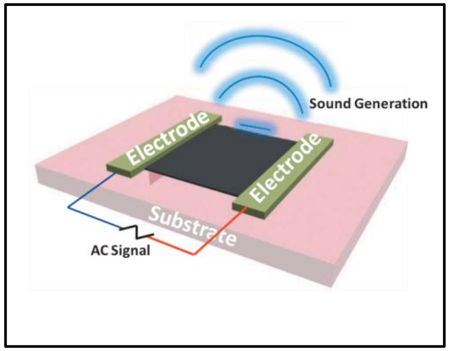
This reduced Graphene Oxide is a promising active material for **molecular sensors**. rGO-TiO2 nanocomposites exhibited much higher photocatalytic activity than TiO2 for degradation of Sarin gas under visible light irradiation. The minimal detection level of the sensor was 5 ppb in 10 s.

Graphene has become the most promising carbon material on the application of **supercapacitors** due to its peculiar properties such as high specific surface area (2630 m^2/g) and theoric very high electrical conductivity (10^7 S/cm)

Specific industrial application areas: examples

Acoustic wave generation in graphene-like materials for aerial and submarine application Fabrication and characterization of speakers without moving parts taking advantage of both graphene-like materials and thermoacoustic effect

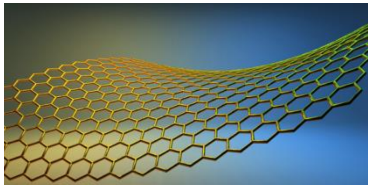




Advantages: **Low weight, reliability, compactness and low-cost**

Drawbacks: **Low Power**

Graphene allows to superseed power limits



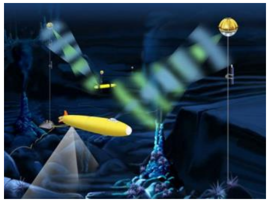
Application Areas

Health care

Defense applications

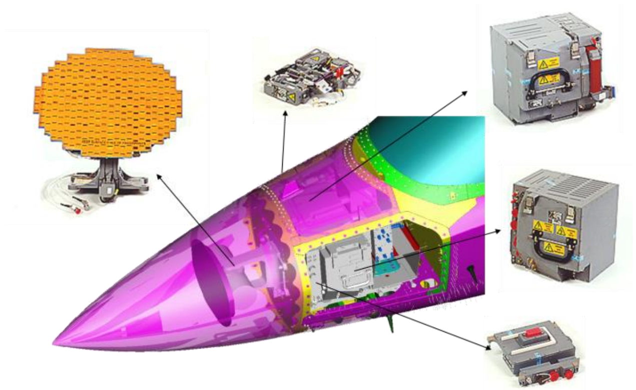
Homeland security and protections

Search and rescue



Specific industrial application areas: examples

A radome is a structural, weatherproof enclosure that protects a radar system or antenna and is constructed of material (fibreglass, PTFE (Polytetrafluoroethylene), etc.) that minimally attenuates the electromagnetic signal transmitted or received by the antenna.



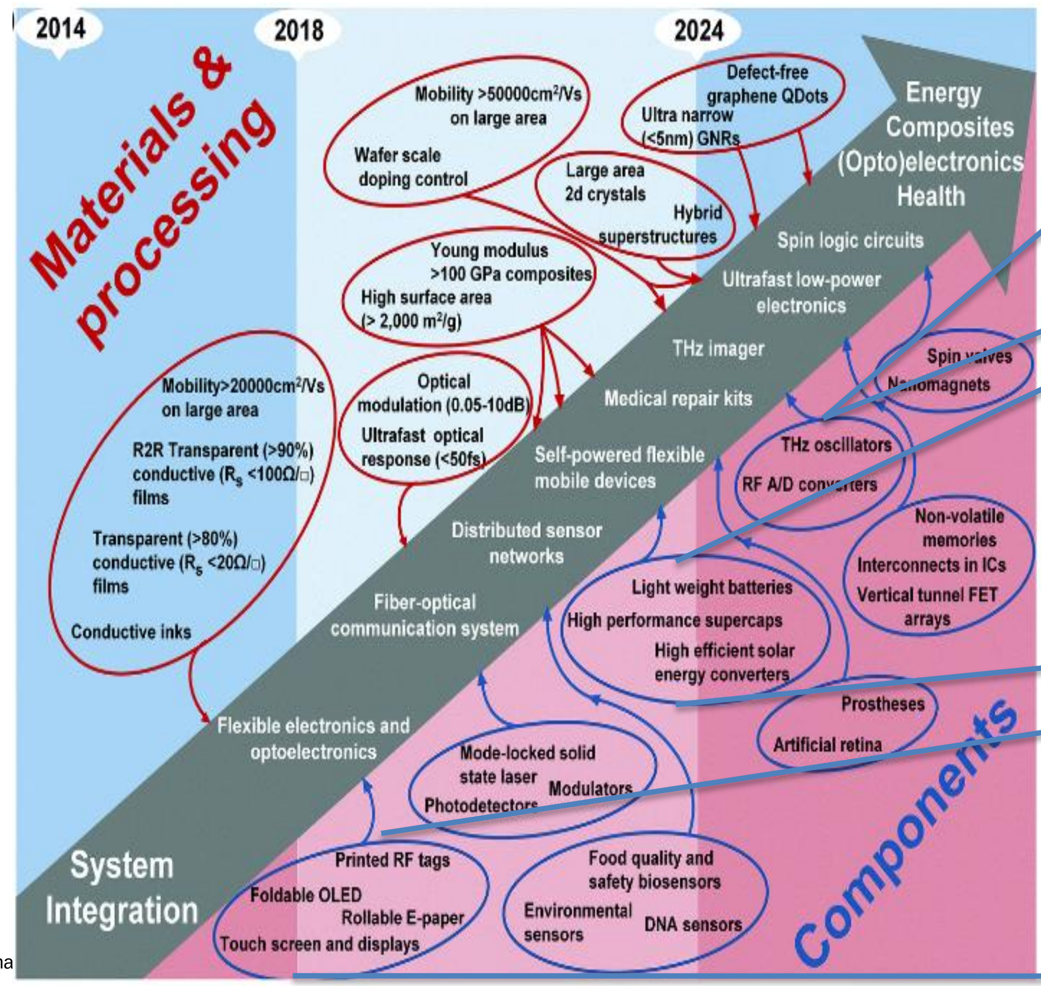
The copper-based de-icing circuit affects the steering angle of the radiated signal and also cause deleterious polarization effects. So this sensitivity is reduced by using multilayer sandwiches containing meander de-icing circuits, but these designs are heavy, costly, and inefficient. So most radome systems are constructed using a metal wire framework with supporting ceramic materials.

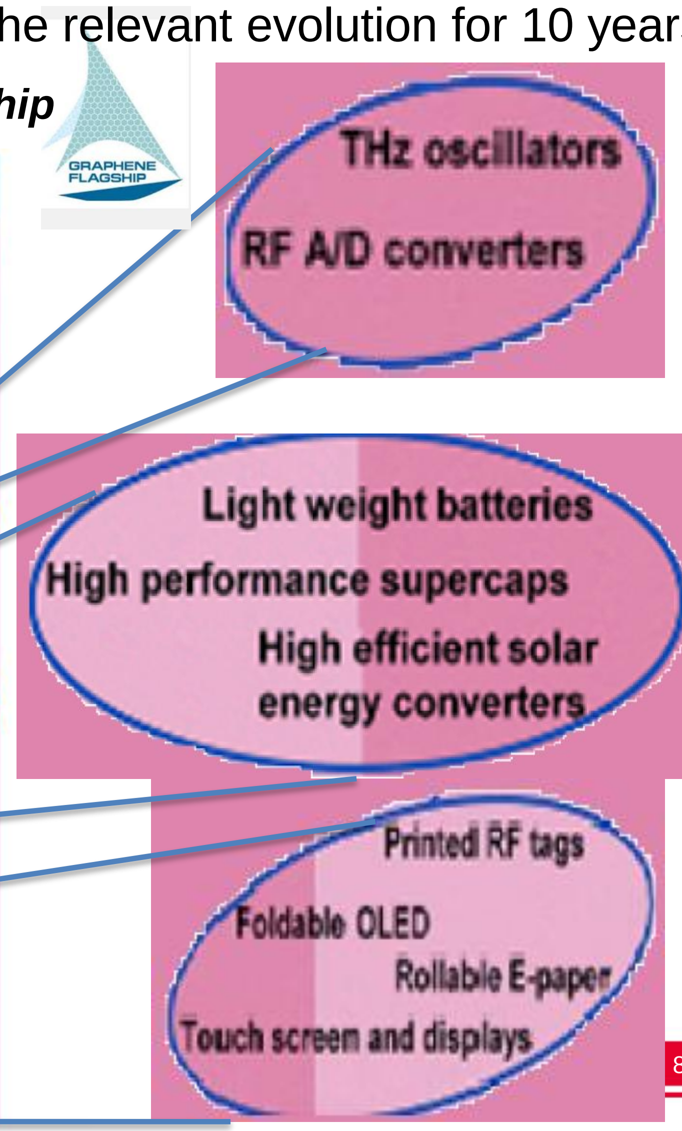
Graphene-like materials used in de-icing circuits for **radar** and **communication device radomes** will gain lightness, heating efficiency and transparent to microwaves

European Flagship Graphene Roadmap

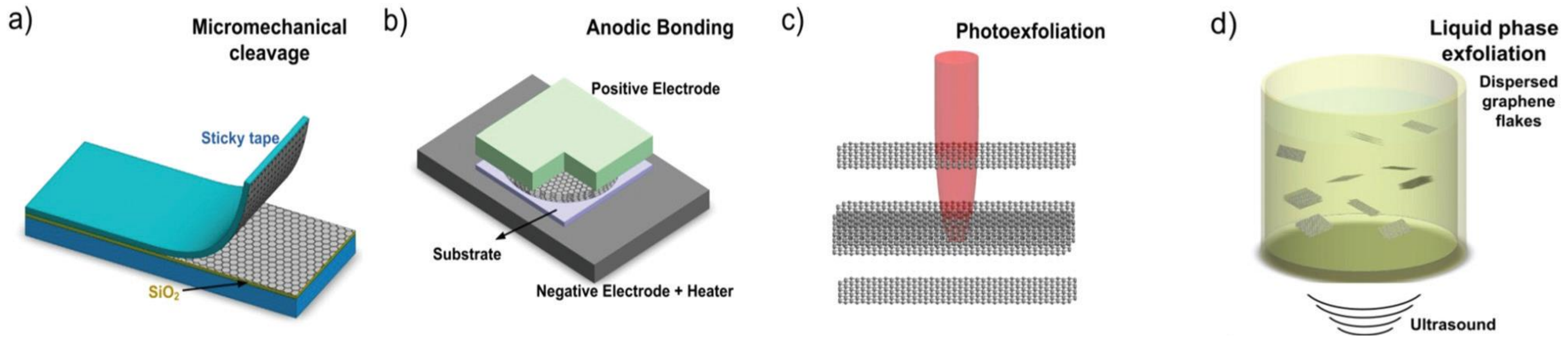
In the Horizon 2020 project the Graphen Flagship area has been established with the aim of analyze all the aspects of the graphene and the relevant evolution for 10 years.

Leonardo Company is member of the Graphene Flagship

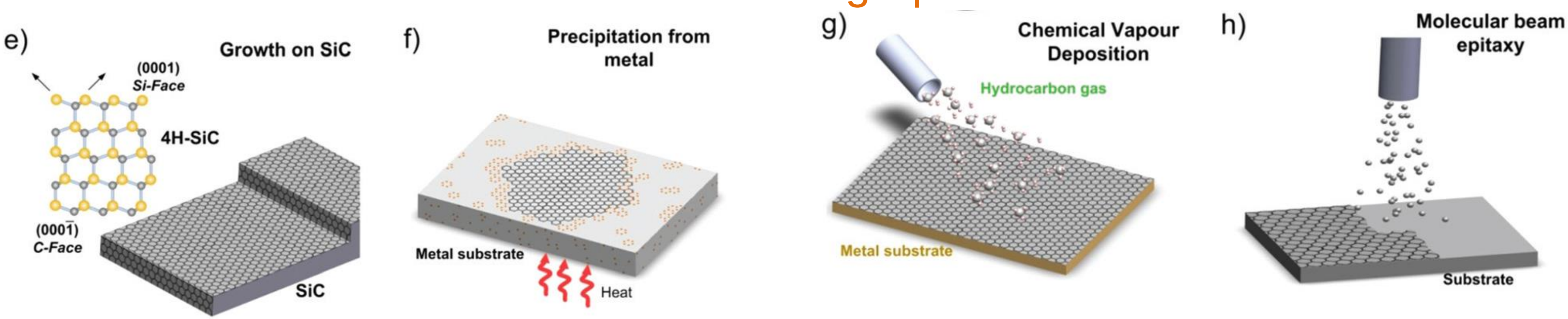




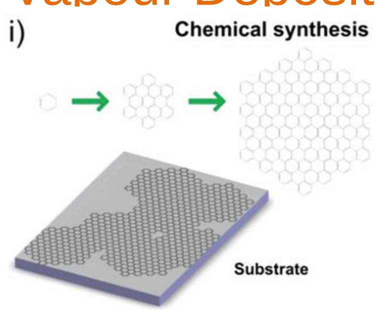
Common methods of Graphene production



Exfoliation of graphite



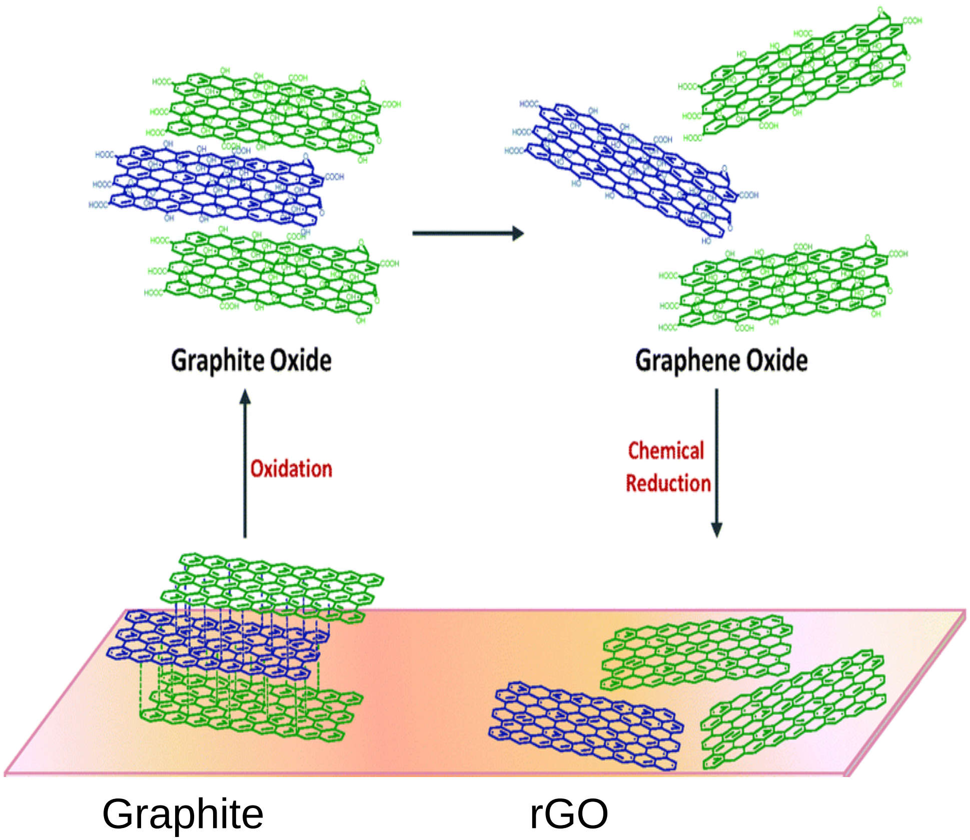
Chemical Vapour Deposition – CVD



Reduction of Graphene Oxide – rGO

rGO Production

Step	Method
GO-water suspension	Ultrasonic Processor
Quartz or Glass cleaning and functionalization	trichloroethylene, acetone, isopropanol, Decon soap and distilled water, Piranha
Quartz or Glass silanization	APTES solution and dry
GO deposition	Spin Coater and dry
GO reduction	Thermal/Chemical reduction
Electrode deposition	Thermal evaporation



rGO Production (cont'd)

- Functionalization of the support
- Preparation of suspension of Graphene/GO
- Deposition of material on support
- Reduction of Graphene Oxide (Thermal and/or chemical reduction)
- Electrodes deposition

Reactive Ion Etching (RIE) sputtering

Dip Coating

Microscope Mask aligner

Chamber vacuum furnace

Spinner

Oxide Graphene solution

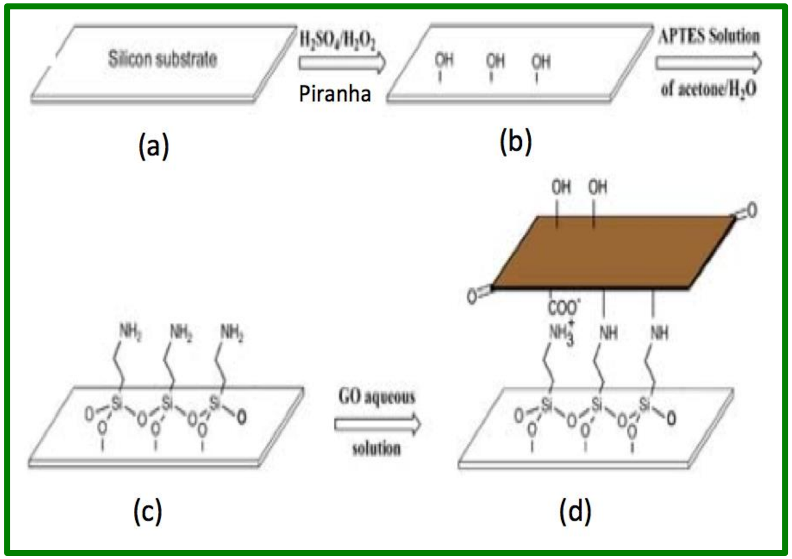
The GO (Cheap Tubes, Inc. (USA)) has been synthesized from natural graphite through the Hummers method. GO has been suspended in distilled water and sonicated using an Ultrasonic Processor (Misonix Incorporated Ultrasonic Processors liquids, U.S.A.) for 4 hours at room temperature so as to produce a yellow-brown colloidal suspension of GO sheets. The solution is then centrifuged at 1400 rpm.

2 concentrations of GO have been taking in account:

- 2 mg / ml
- 10mg / ml.

GO deposition on solid substrates

The GO can be deposited on a solid substrate (quartz or silicon) by spin-coating technique after performing a functionalization of the surface by a chemical process based on Piranha and APTES

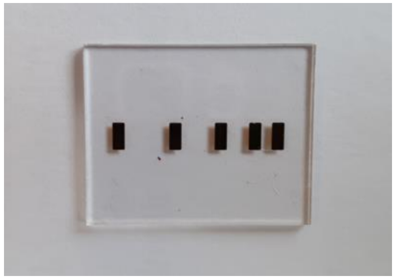


Reduction of GO and electrode deposition

Reduction of GO by means of several methodologies:

- Chemical reduction (hydrazine, sodium borohydride, etc.)
- Plasma etching
- Thermal reduction
- A combination of the techniques listed above

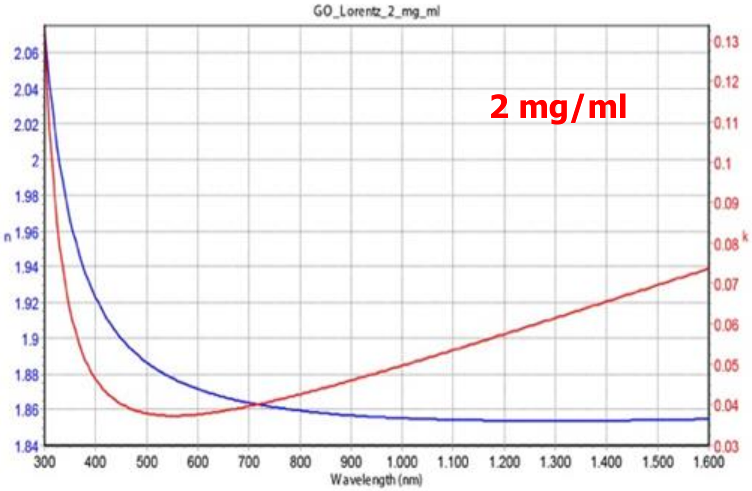
The thermal reduction has been performed via thermal evaporators, programmed at different temperatures with different gradients (300-800 deg). Vacuum pump or nitrogen flow were used to remove the Oxygen produced by the reduction.

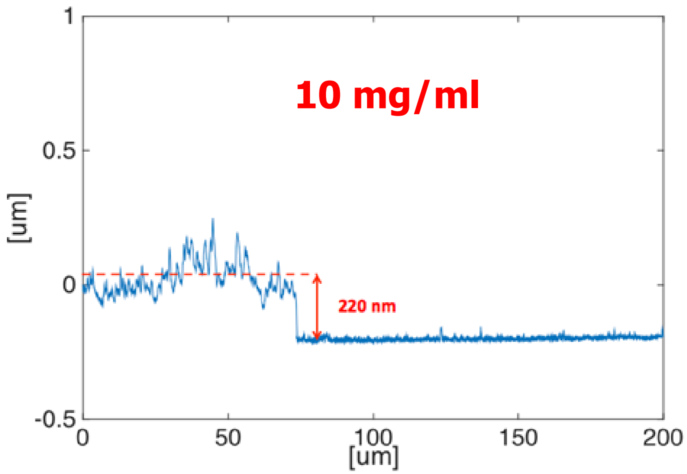


A thermal evaporator was used to deposit the electrodes made of 5 nm of chromium (Cr) and 100 nm of Gold (Au) and a pressure of 3 x 10^{-6} mbar. A thin Cr film were used to promote adhesion between Au electrode and GO. Iron shadow mask were used for metal patterning.

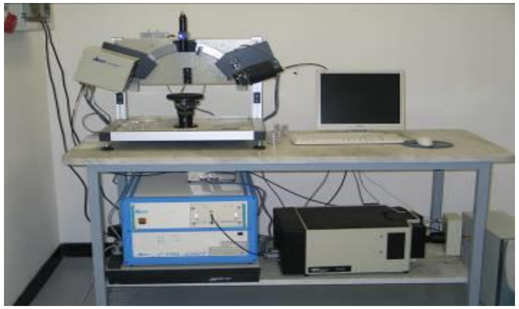
Characterization : Ellipsometry and Profilometry

By ellipsometry and profilometric technique it is possible to measure the thickness of material





The ellipsometry technique, also, provides the optical properties of the material.

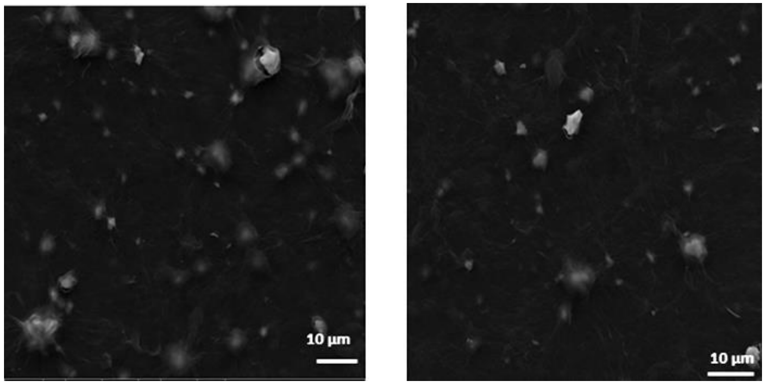


- GO 2mg / ml thickness measured via ellipsometry is 3.5 nm.
- A Concentration of higher GO (10 mg / ml), the material is superficially very wrinkled and the ellipsometry technique can not be used anymore.For GO 10mg / ml the thickness measured via profilometry is 220 nm.

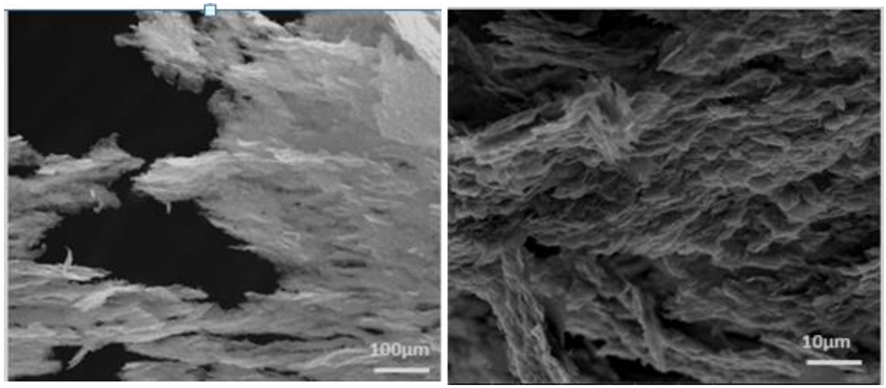
Characterization - Morphological

Scanning Electron Microscopy (SEM)

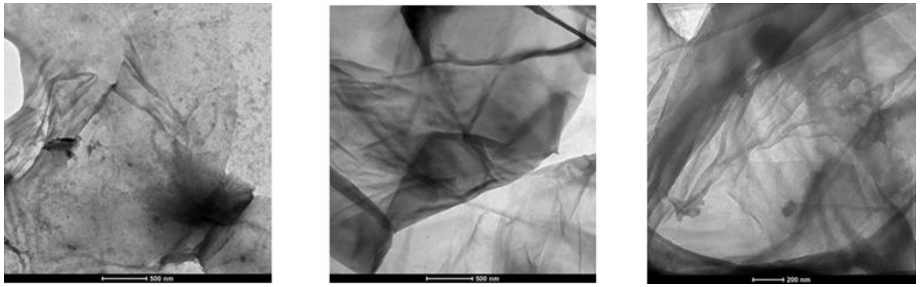
GO

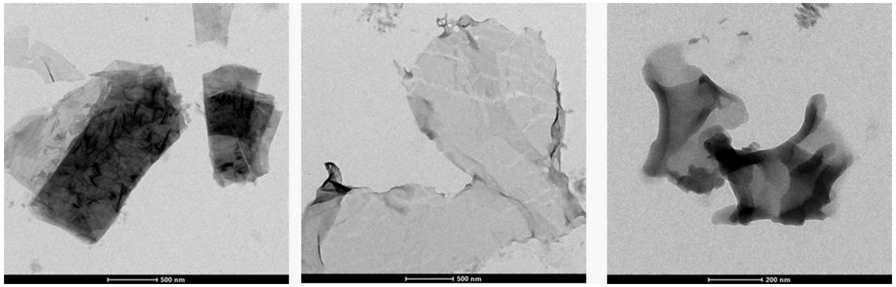


rGO thermal reducted



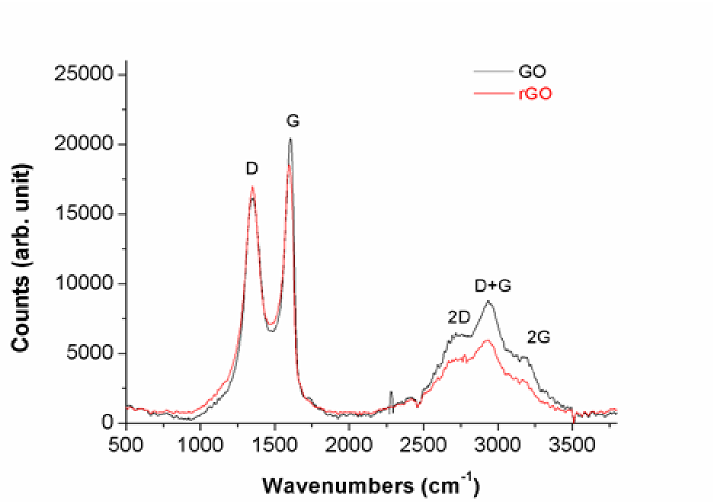
Trasmission Electron Microscopy (TEM)

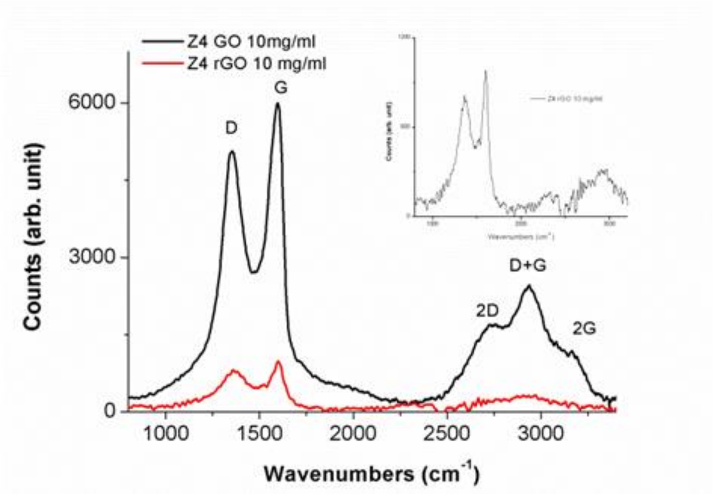




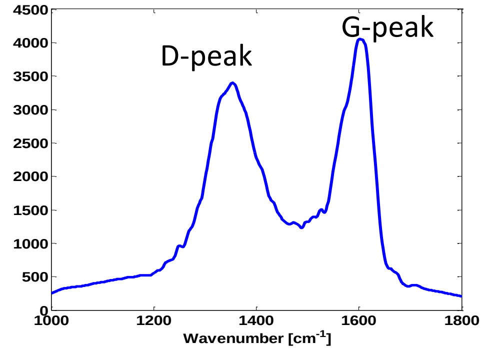
Characterization - Raman

Raman Spectra of rGO 2mg/ml





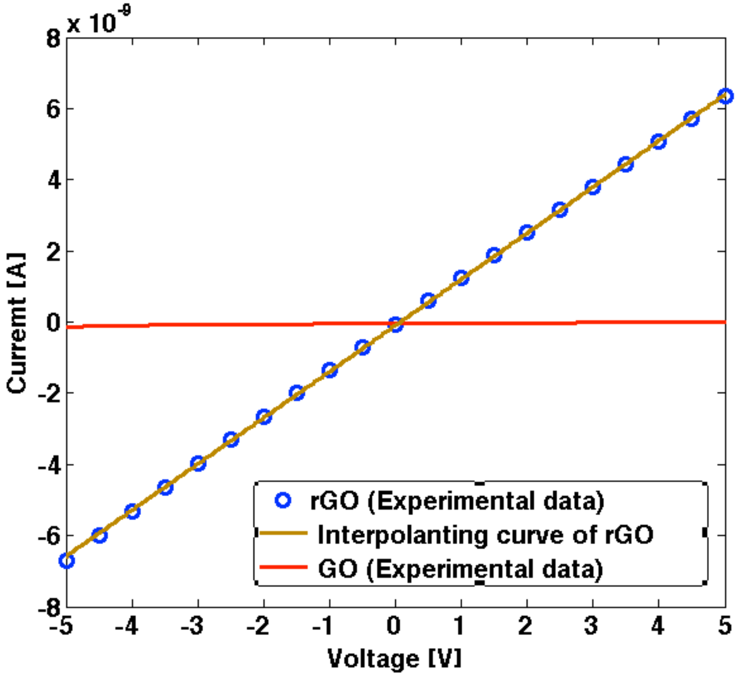
Raman Spectra of rGO 10mg/ml



Raman Spectra of Graphene

Electrical Characterization - metodology

- Measurements of resistivity by mean of Electrode Deposition
- Four-point measurement method enabling electrical conductivity measurements of nanoscale materials

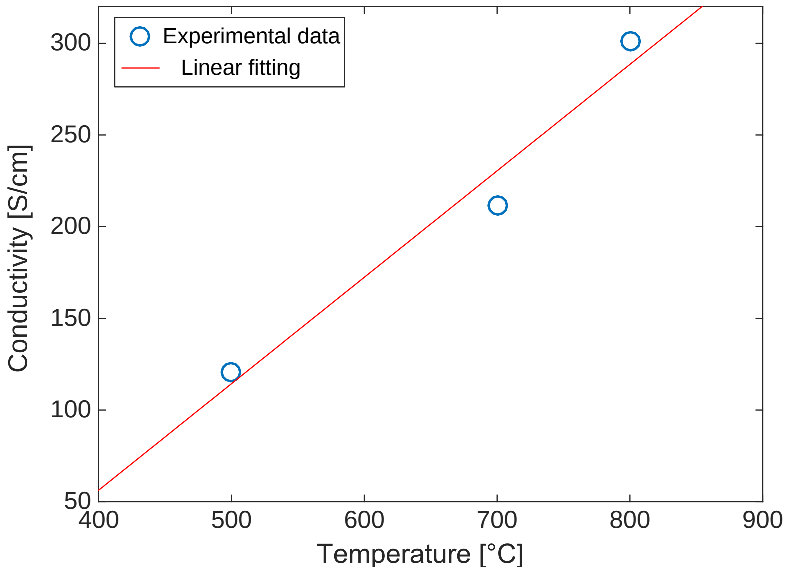


Electrical Characterization Results

Electrical characterization Results of the material (GO 2 mg / ml) did not show relevant values and the conductivity values out came much lower than the expected values.

Electrical characterization of the material (GO 10 mg / ml) before and after the thermal reduction are the followings:

Type of reduction	***Sheet Resistance [Ω/sq]***	***Resistivity [Ωm]***	***Conductivity [S/cm]***
No reduction	30 x 106	6.62	0.00151
300°C in nitrogen flow	23.5 x 103	5.1 x 10-3	1.93
500°C in nitrogen flow	376	8.2 x 10-5	120.7
700°C in nitrogen flow	215	4.7 x 10-5	211.4
800°C in nitrogen flow	151	3,3 x 10-5	301.2



Consideration of the obtained results

- The GO was deposited on common solid substrates (Silicon and Quartz) by spin-coating.

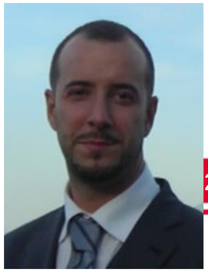
- Measurements of thickness of the material (ellipsometry and profilometry) and morphological characterization (TEM, SEM) and spectroscopy (Raman) have provided exaustive information of the obtained material

- It is possible to vary the conductivity of the GO 10 mg / ml controlling the parameters of the thermal reduction.

- Poor results have been obtained on the GO 2 mg / ml, due to the non uniform distribution of the Graphene on the substrate (electronic microscope analysis revealed the presence of holes in the Graphene surface).

- Therefore the profilometry has shown that GO material 10 mg / ml is characterized by a high surface roughness and its uniformity needs to be improved.

Team



Leonardo Company:

- Electronics, Defence and Security Systems Sector

Ing. Sergio Gallone - Master degree in Electronic Engineering at University of Rome “La Sapienza"

Ing. Lucrezia Calderaro - Master degree in Telecomunication Engineering at University of Naples "Federico II“

CNR (National Council of Research):

- IPCB (Institute for Polymers, Composite and Biomaterials)

Dr. Lucia Sansone - Master degree in Industrial Chemistry at University of Naples “Federico II”

Ing. Michele Giordano - Master degree in Electronic Engineering at University of Naples "Federico II"

- IMM (Institute for Microelectronic and Microsystem)

Ing. Maurizio Casalino – Master degree in Electronic Engineering at University of Naples "Federico II"

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Lista Acronimi

Acronym	Definition
CVD	Chemical Vapour Deposition
GO	Graphene Oxide
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
TEM	Trasmission Electron Microscopy
THz	Tera Hertz

THANK **YOU** FOR YOUR ATTENTION