REDUCED GRAPHENE OXIDE FOILS FOR ION STRIPPER APPLICATIONS

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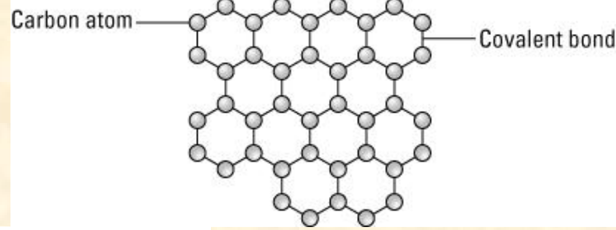
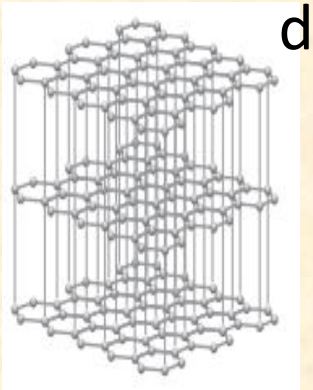
Outline

- Introduction (Graphene based materials)
- Material preparation and characterization
- Objectives : rGO as Ion Strippers
- Preliminar measurements with rGO stripper
- Future developments: Increase and optimize the measurements with rGO strippers in accelerators.

Introduction: Graphene-based materials (C allotropic state)



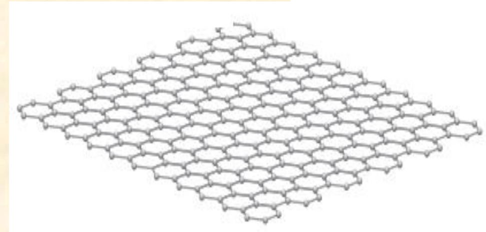
Graphite(Gt)



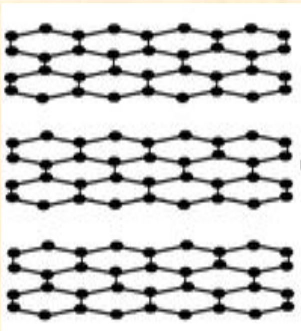
d_p=3.4 Å

Mechanical exfoliation

(the scotch tape technique)



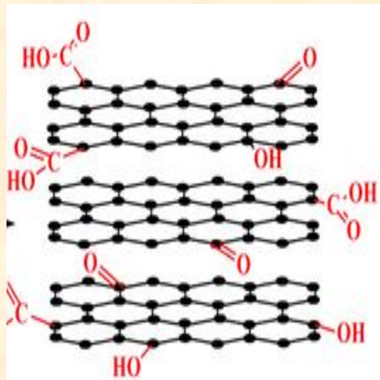
Graphene



Graphite(Gt)

Oxidation
(Hummers method)

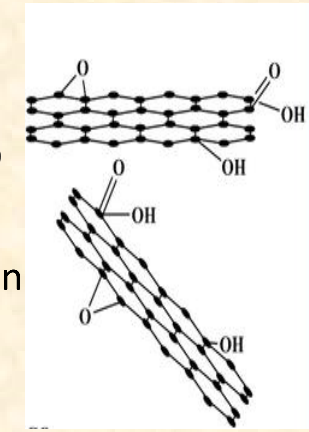
($KMnO_4$, H_2SO_4)



Graphite oxide(GtO)

Exfoliation
(sonication, stirring)

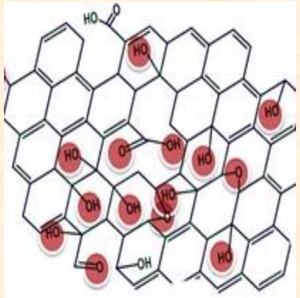
Mechanical exfoliation
(Ultrasonication)



Graphene oxide(GO)

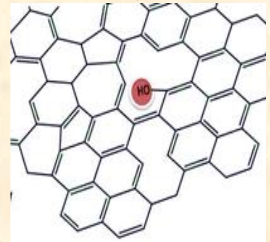
(GO platelets in water)

Graphene oxide(GO)



Reduction
(chemical, thermal, ions, laser,…)

μ–metric platelets



Reduced graphene oxide (rGO)

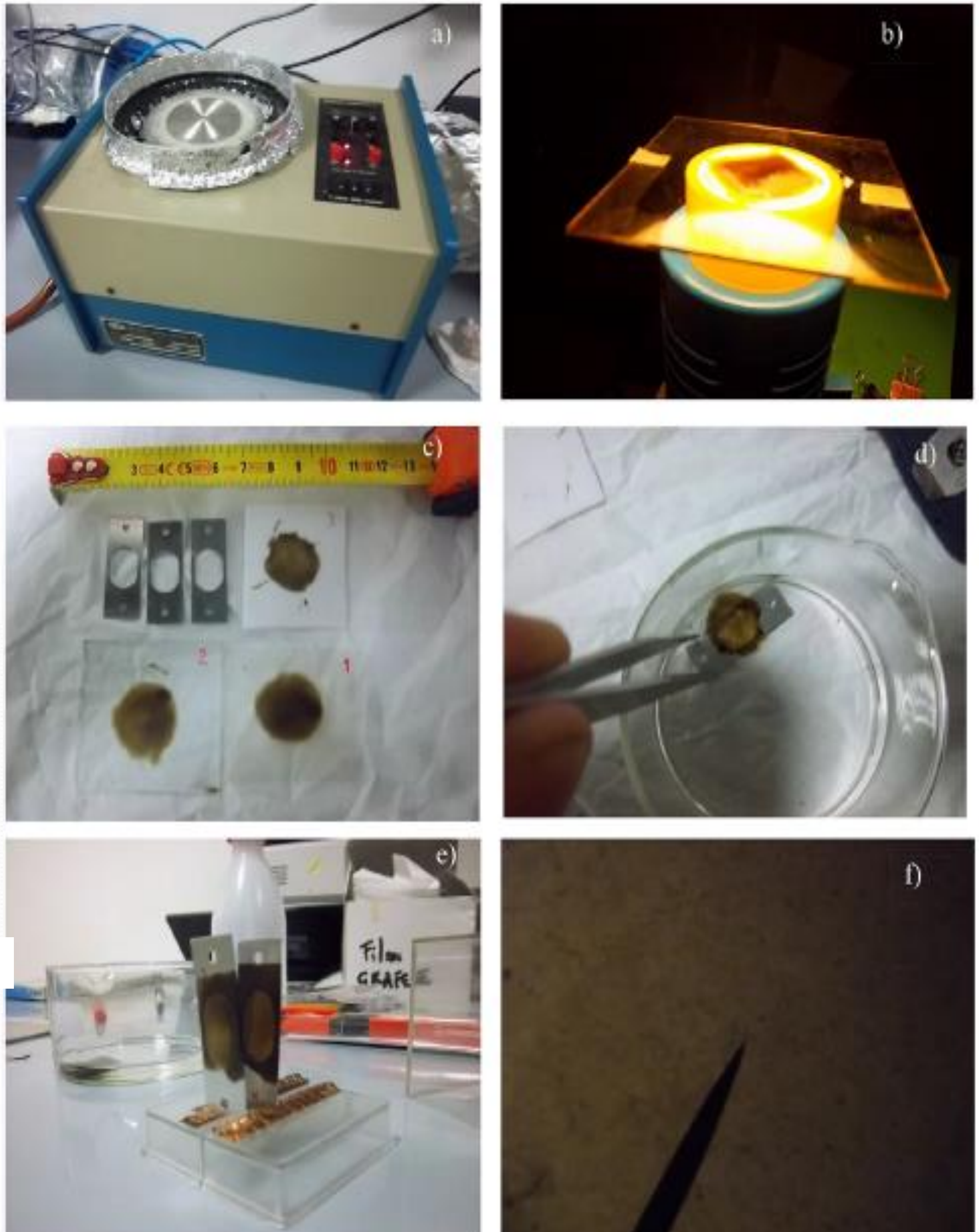
GO preparation as self-supported thin films

(Spin coating
preparation film)

L. Torrisi et Al., *Vacuum 160*, 2019, 1-11

Concentrated GO solution

Diluted GO solution



Φ = 4 cm

Thickness:

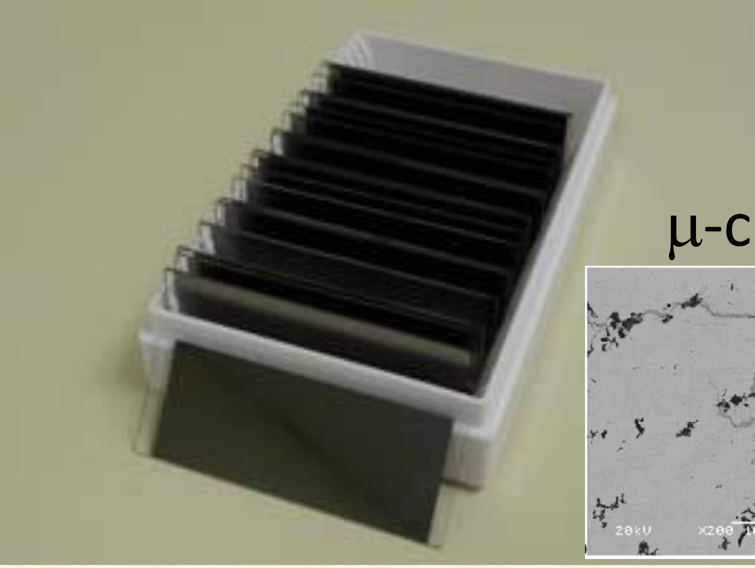
~ 2 µg/cm^2 (10 nm)

~ 20 µg/cm^2 (100 nm)

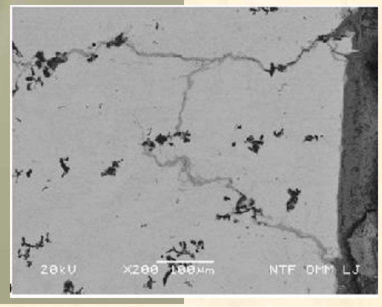
~ 200 µg/cm^2 (1 µm)

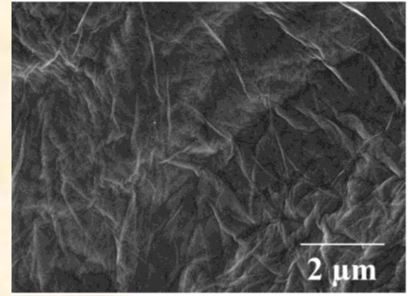
~ 2 mg/cm^2 (10 µm)

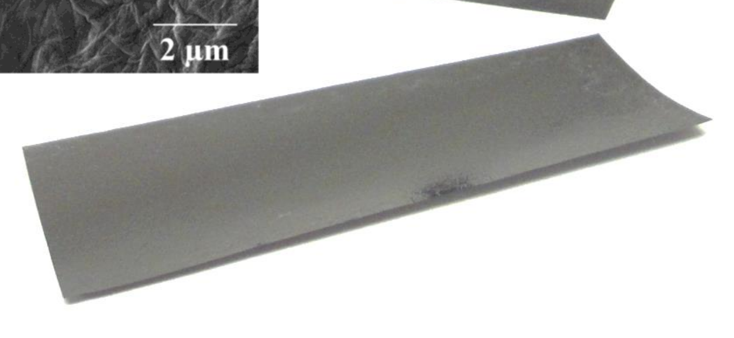
Property	Graphite	Graphene	GO	rGO
In-plane thermal conductivity at RT (W/m·K)	1950-2000	1500-5300	2.9	650
Thermal conductivity along c axis at RT (W/m·K)	0.7-20		0.5	1 (RT) 10 (300°C)
Electrical conductivity (S/cm)	2 $\times 10^5$ ∥ basal plane 3×10^2 ⊥ basal plane	2000	1.2×10^{-5}	1350
Density (g/cm³)	2.09-2.25	0.005	1.5	1.6-1.91
Young's Modulus(GPa)	11.5	1000	207.6	260
Vickers Hardness (kg/mm^2)	7-11			160
Tensile Strength (MPa)	10	130		90
Melting point (°C)	3730	4237	3600	>3800
Specific Surface area (m^2g^{-1})		2630	736	422-500
Carrier mobility ($cm^2V^{-1}s^{-1}$)	$>10^4$	10^3 - 2×10^5	153	0.05-372
Sheet (for graphene) Resistance (W/sq) at RT		400 (<3nm)	10^{12}	14000
Optical transmittance (%)	97.7	94.0	96	85
Refractive index n	2.52-2.67 at 550nm	2.0-3.0 at 550nm	1.957 at 634 nm	1.84-2 at 634 nm



μ-cracks



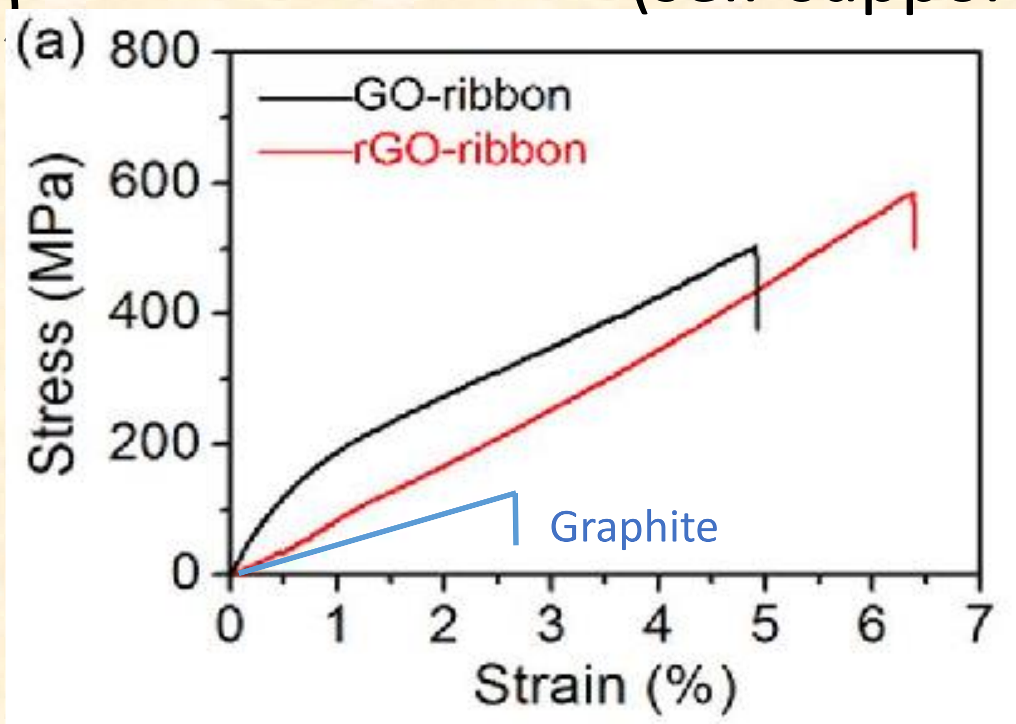




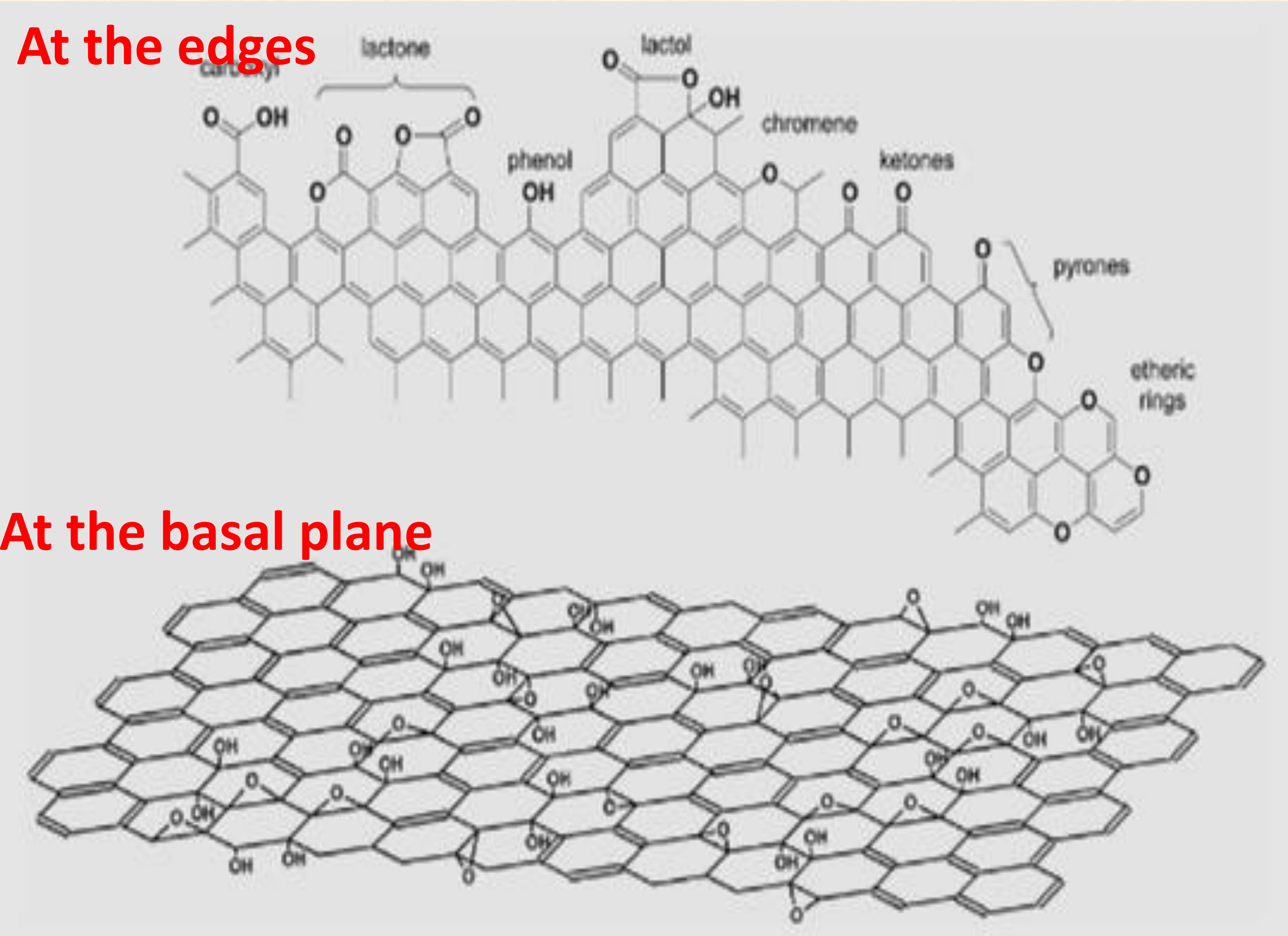
Graphite thin films
(on glass substrate)

Graphene oxide thin films
(self-supported)

Tensile
stress



Graphene Oxide



Functional groups:

- hydroxyl (C-OH)

- epoxy (C-O-C)

- carbonyl (C=O)

- carboxyl (O-C=O)

- Presence of H_2 and H_2O.

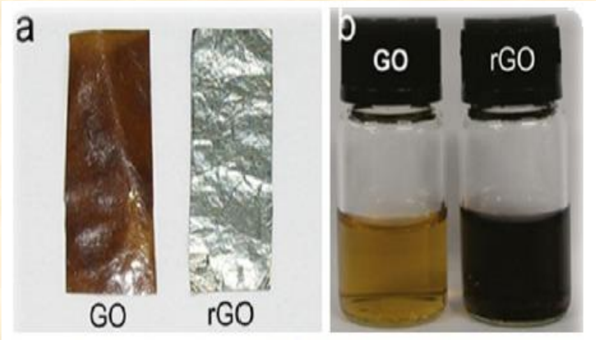
The GO reduction can be obtained by:

1) Thermal processes
(as a function of the temperature in air, nitrogen and vacuum)

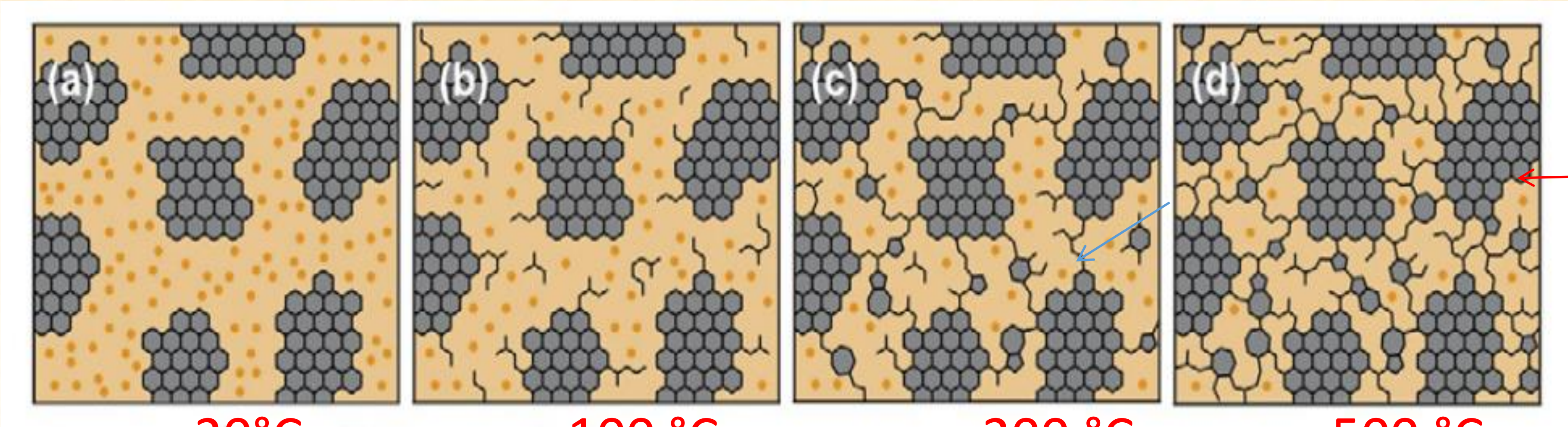
2) Ion beam processes
(in vacuum as a function of the dose: 10^{13}-10^{16} /cm^2)

3) Laser beam processes
(as a function of fluence 1-100 J/cm^2, wavelength, pulse duration. In air, nitrogen, in vacuum,...)

4) Chemical processes (Hydrazine reduction)



Evolution of GO structure with reduction

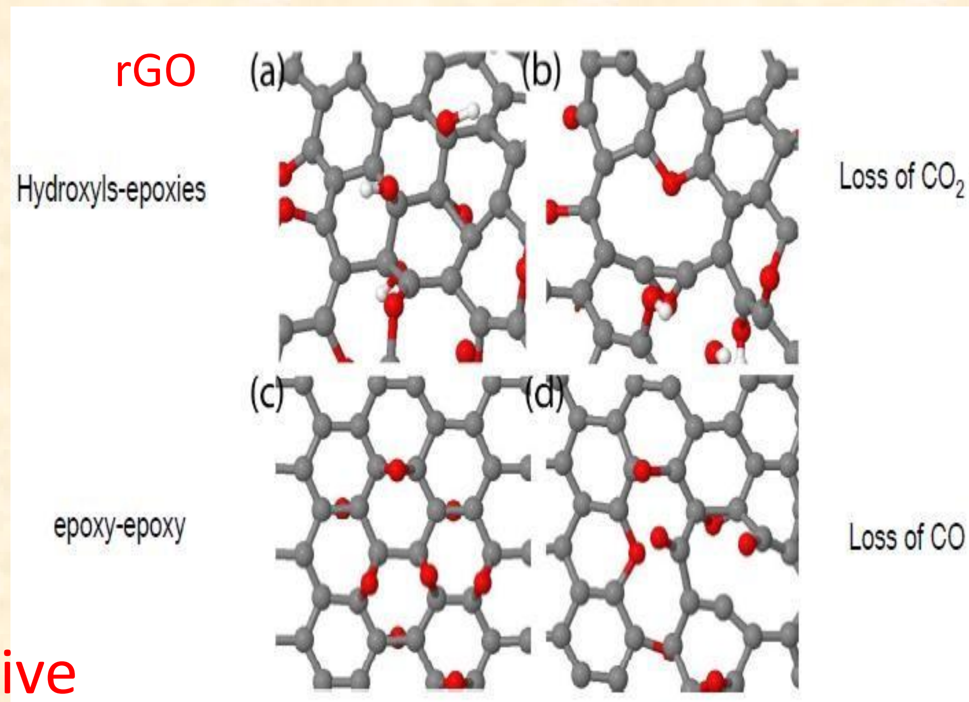


sp^2 domains

20°C 100 °C 200 °C 500 °C

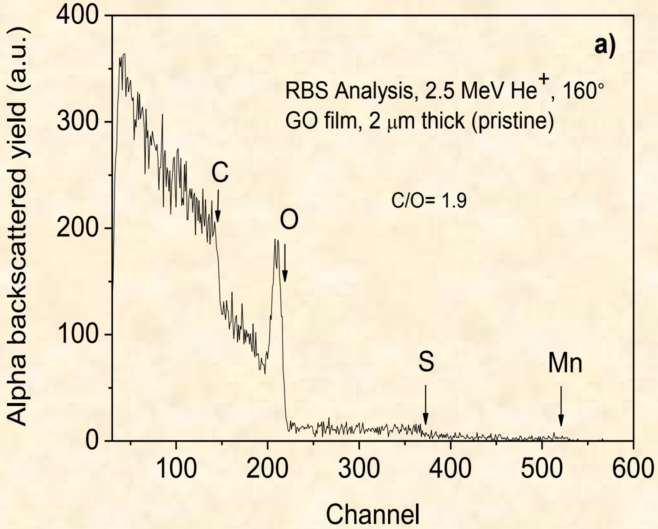
(Temperature, Ion dose, Laser fluence,…)

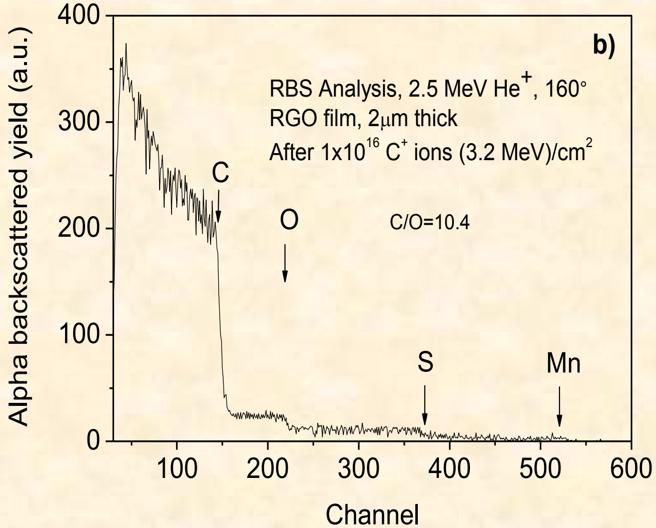
The dark grey areas represent sp^2 carbon clusters and the light brown areas represent sp^3 carbon bonded to oxygen groups (represented by small dots).



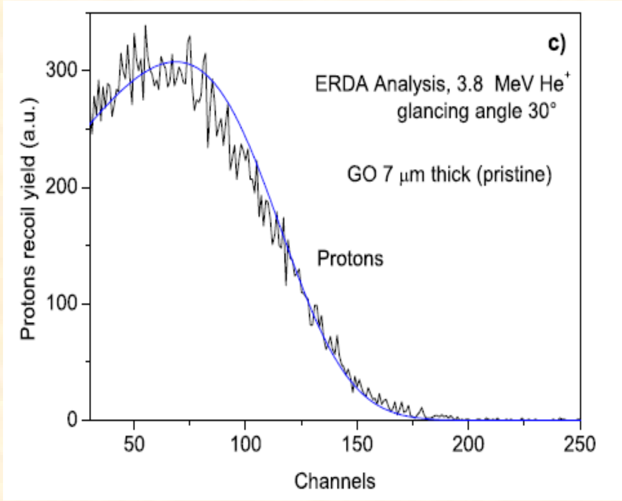
Electrically conductive

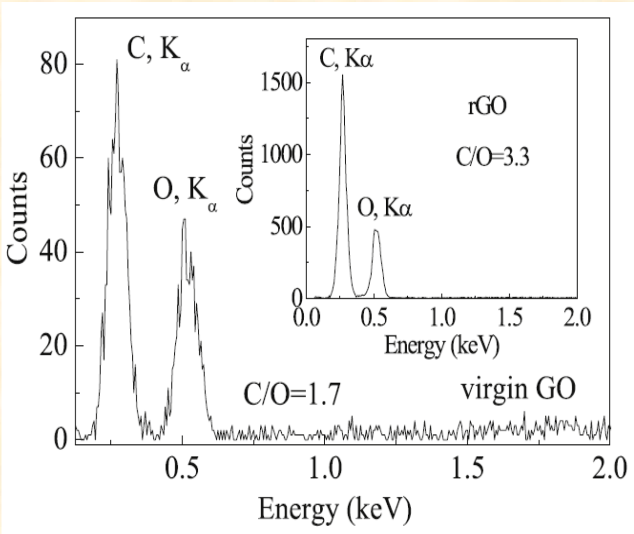
RBS Analysis





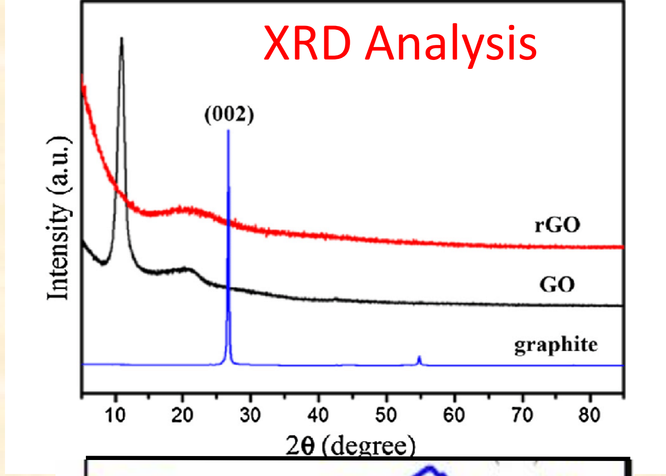
ERDA Analysis

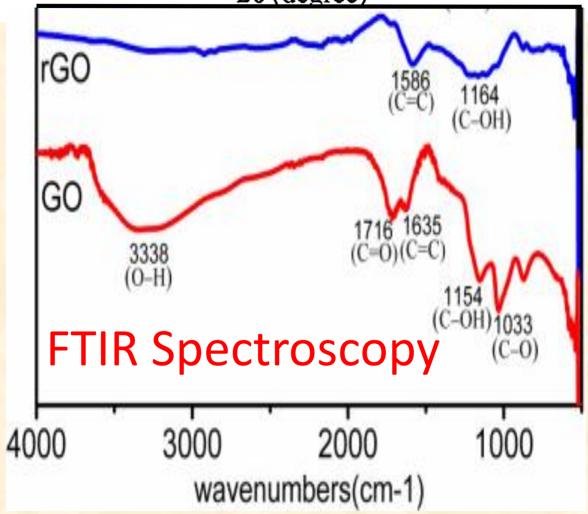




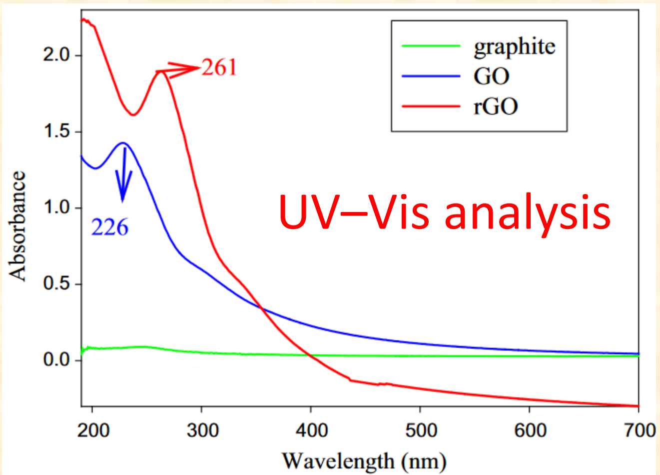
EDX Analysis

XRD Analysis



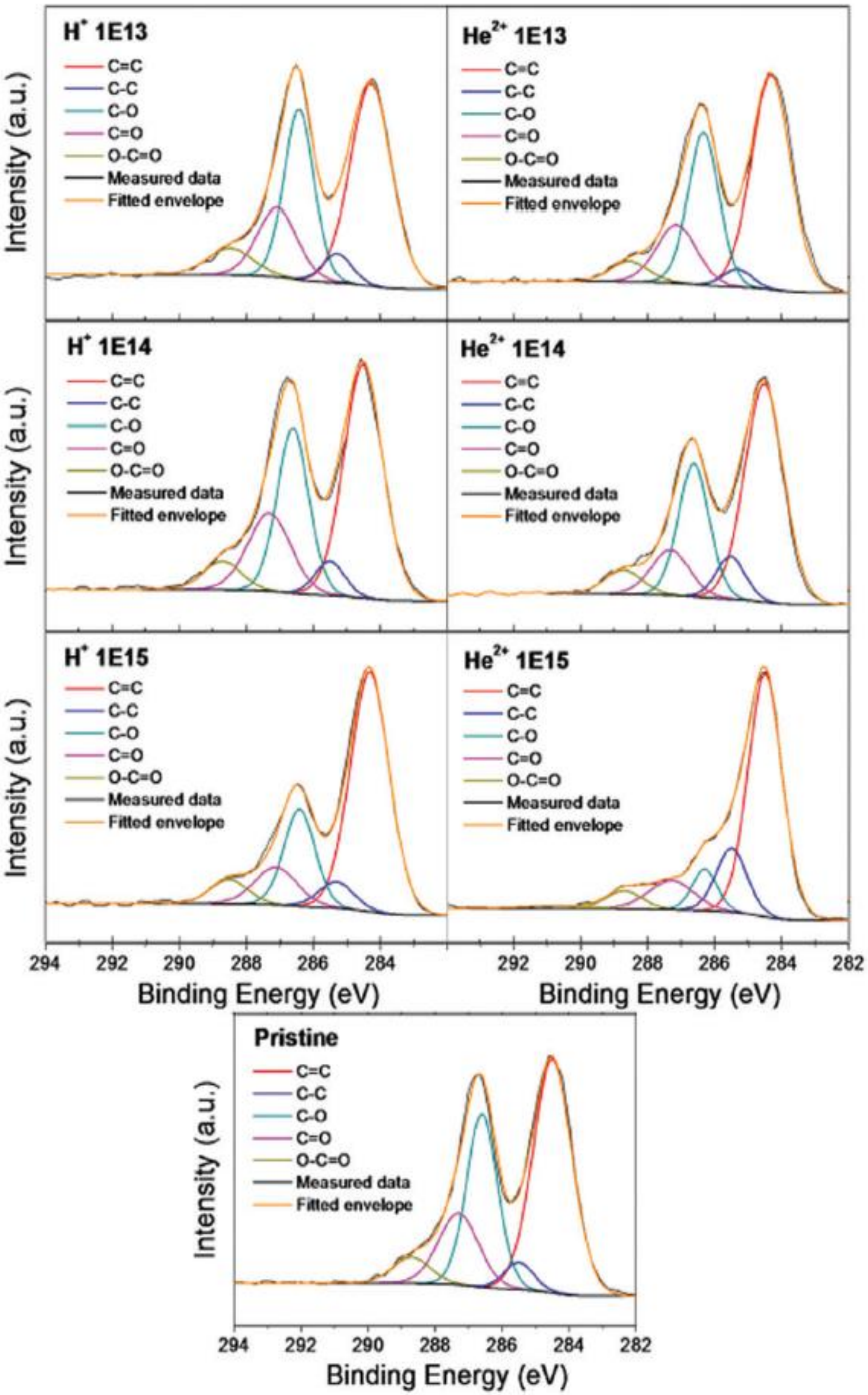


FTIR Spectroscopy



UV–Vis analysis

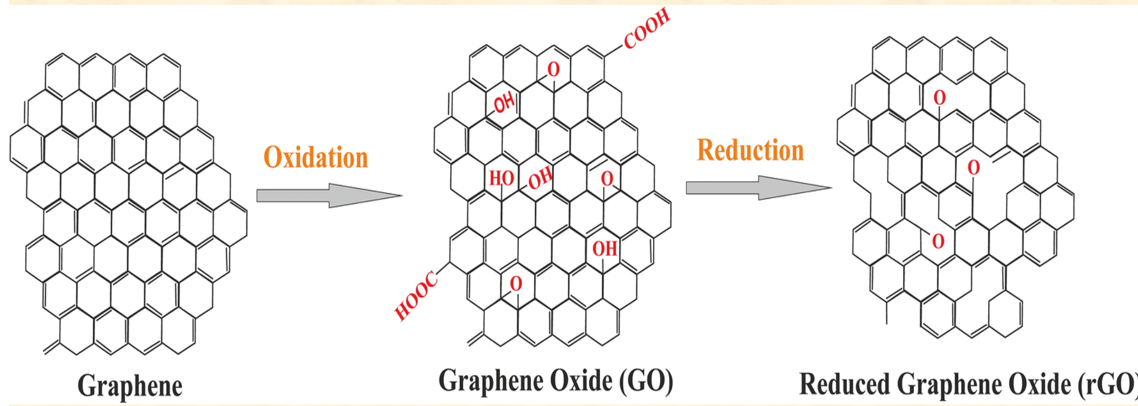
L. Silipigni et al., *Vacuum* 165, 254 (2019)



XPS Spectroscopy

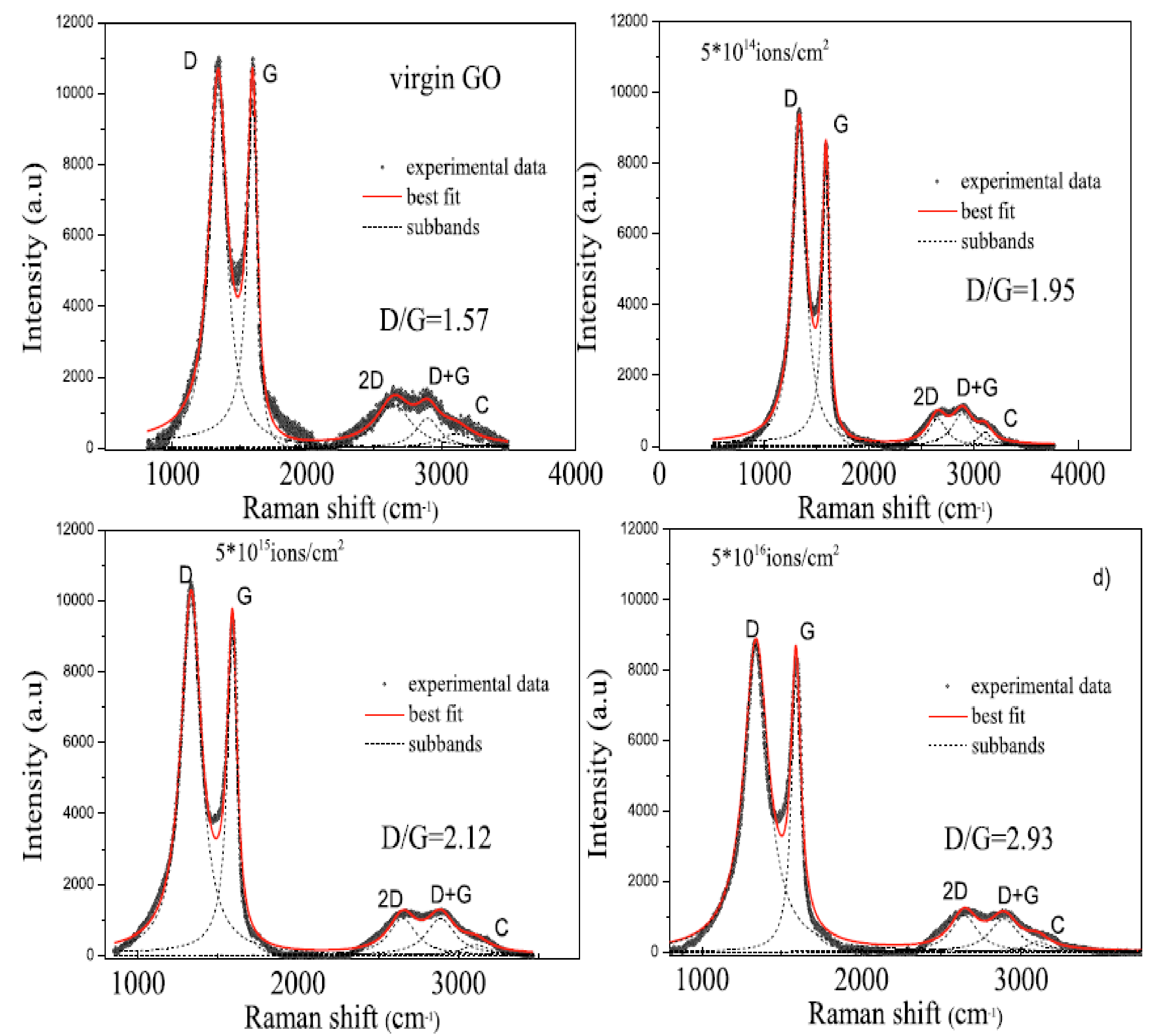
Sample	C 1s (at%)	O 1s (at%)	C/O ratio
Pristine GO foil	71.8	28.2	2.55
2.5 MeV H^+ 1.0×10^{13} cm^{-2}	68.9	31.1	2.15
2.5 MeV H^+ 1.0×10^{14} cm^{-2}	70.3	29.7	2.37
2.5 MeV H^+ 1.0×10^{15} cm^{-2}	75.2	24.8	3.03
5.1 MeV He^{2+} 1.0×10^{13} cm^{-2}	70.7	29.3	2.41
5.1 MeV He^{2+} 1.0×10^{14} cm^{-2}	71.0	29.0	2.45
5.1 MeV He^{2+} 1.0×10^{15} cm^{-2}	78.5	21.5	3.65

C/O α Ion dose and stopping power



L. Torrisi et Al., *Vacuum* 153 (2018) 122-131.
P. Malinski et Al., *NIM B* In press 2019.
M. Cutroneo et Al., *Vacuum* 165 (2019), 134-138.

Raman Spectroscopy



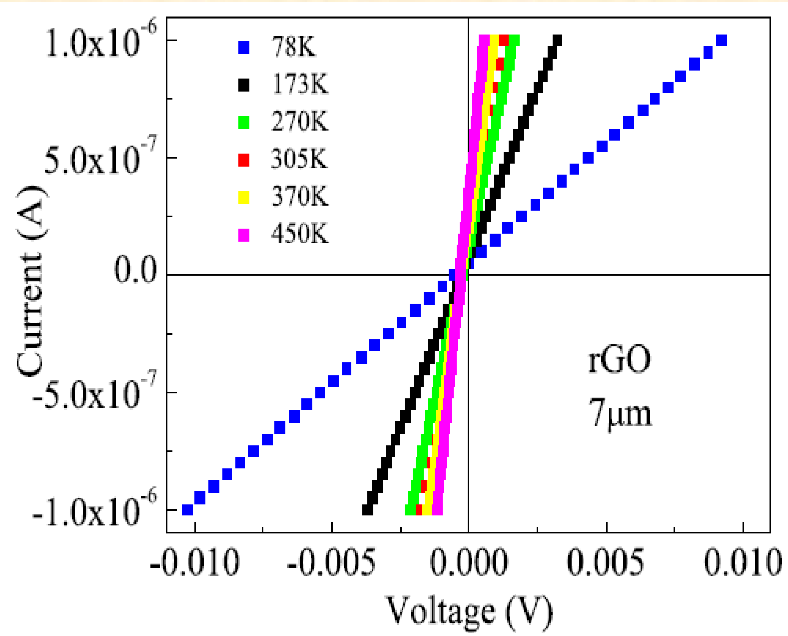
2 MeV He^+ ion beam irradiation

D/G α Ion dose

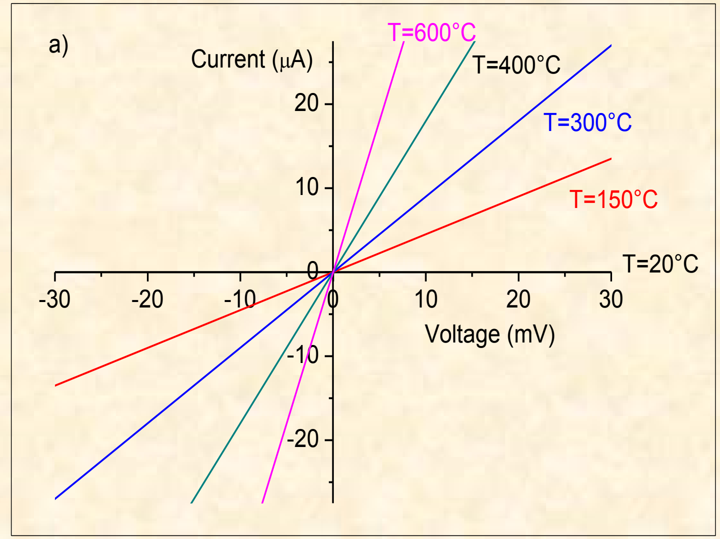
- Reduction of sp^2 domain sizes;
- Increment of the number of sp^2 domains.
- Increment of disorder;

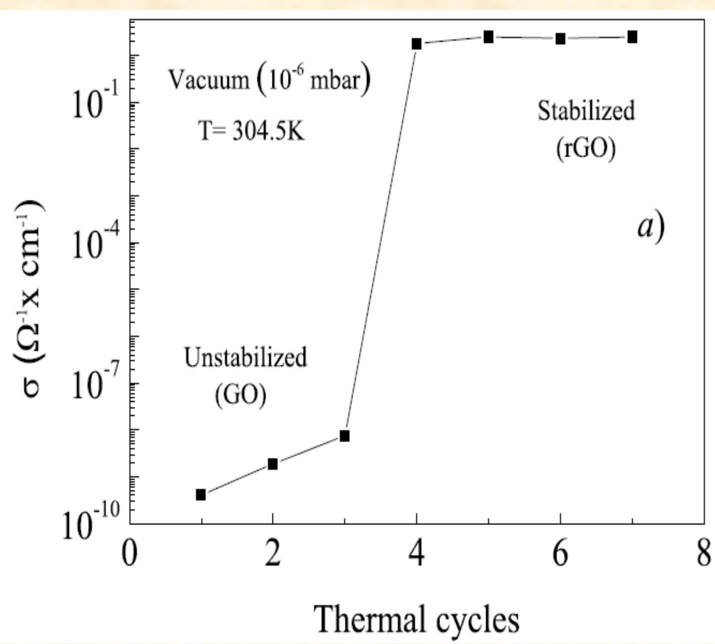
L. Torrisi et Al., *Vacuum* 160 (2019), 1-11.

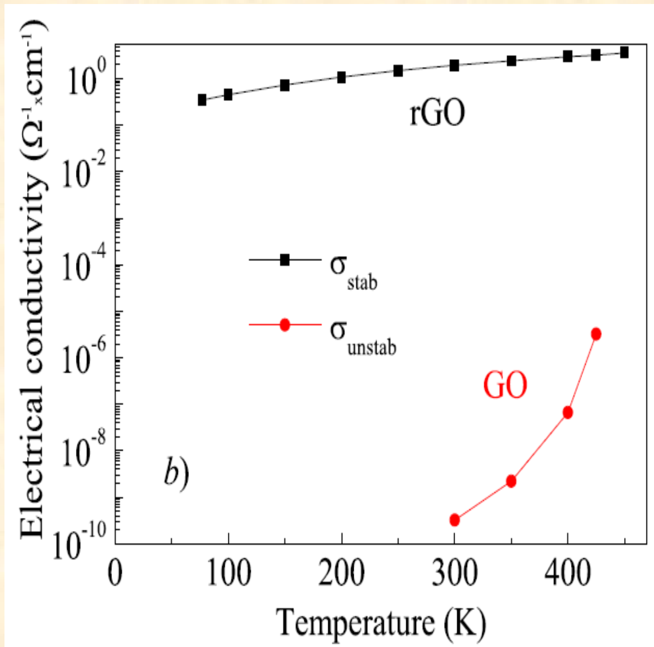
Electrical Characterizations

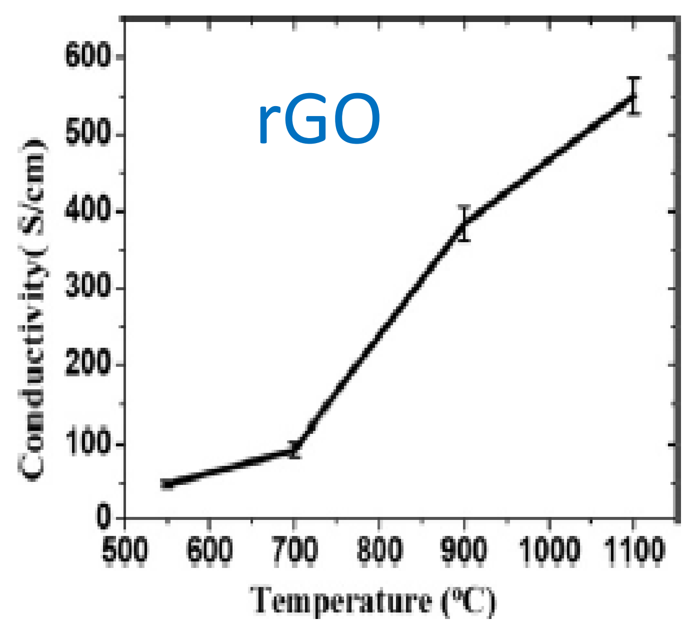


L. Silipigni et Al., *Vacuum* 165, 2019, 254-261.



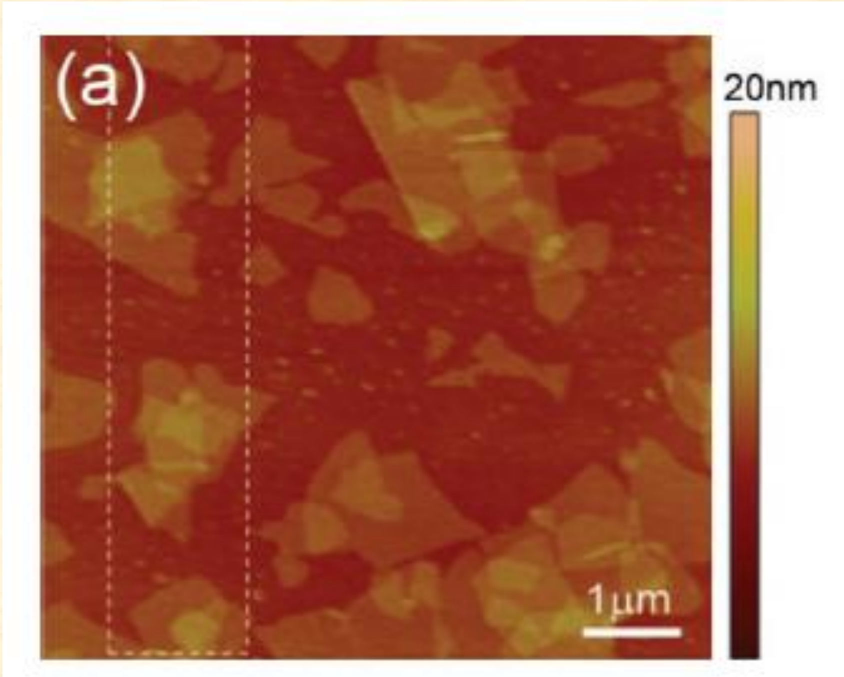


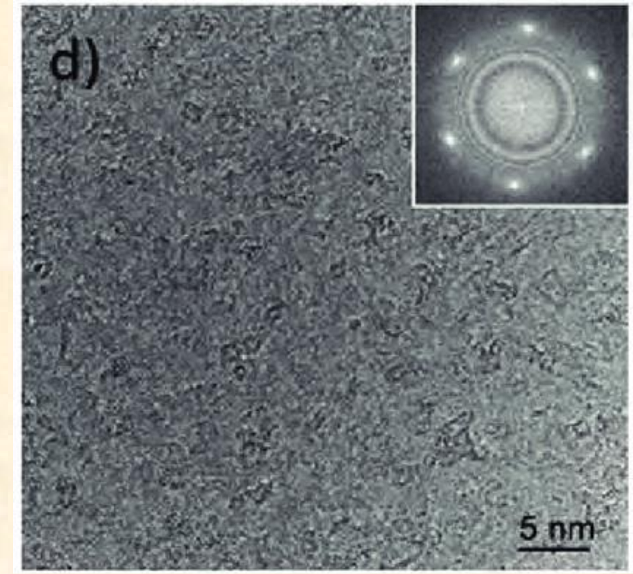




Microscopy investigations

AFM analysis

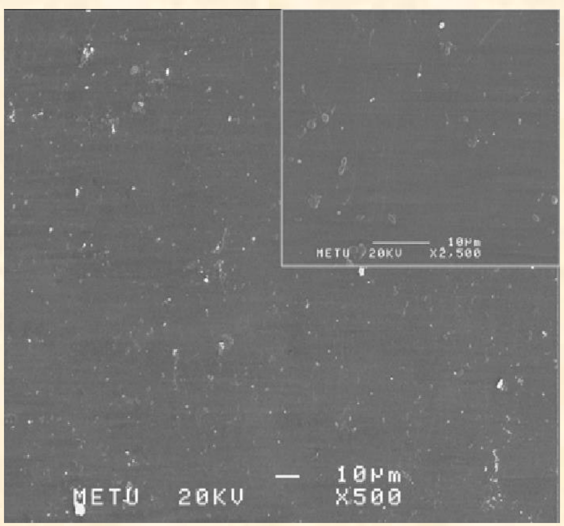




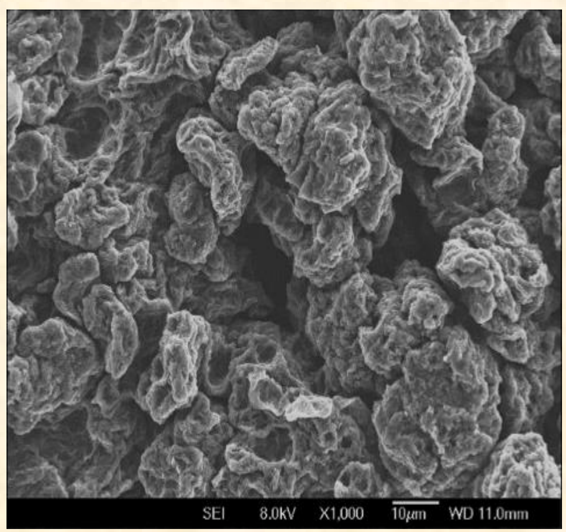
TEM analysis, rGO

SEM analysis

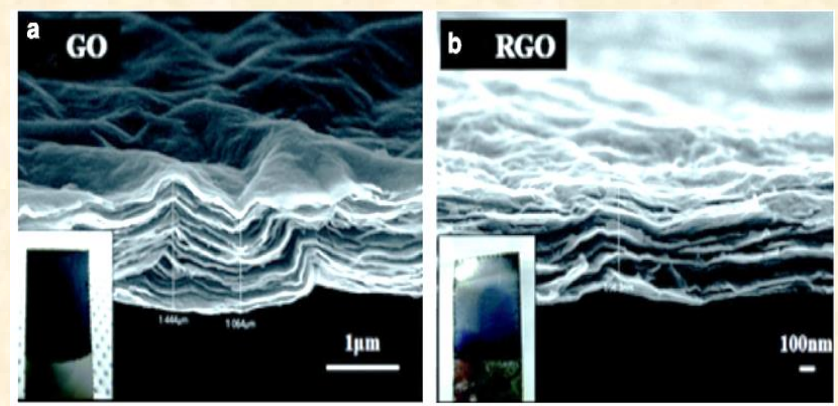
GO



rGO

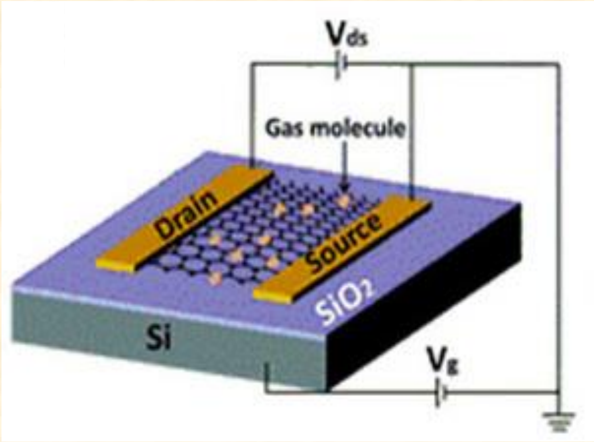


Cross sections

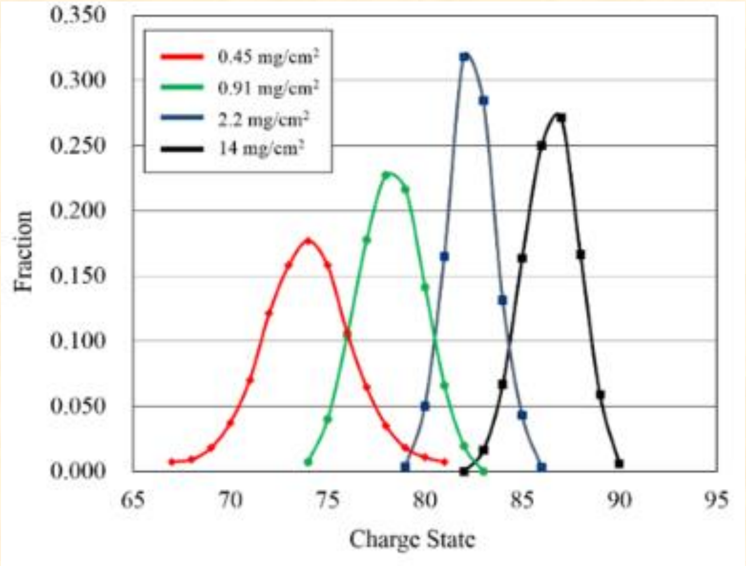


Applications:

- Hydrogen and Deuterium storage material
- Thermal sensor
- Gas sensor
- Biomaterials
- Optical absorber
- Electronic devices (Batteries, resistances, capacitances, supercapacitors, schottky junctions, transistors, semiconductive strips,...)
- Filter membrane
- **Ion Stripper**
- ...



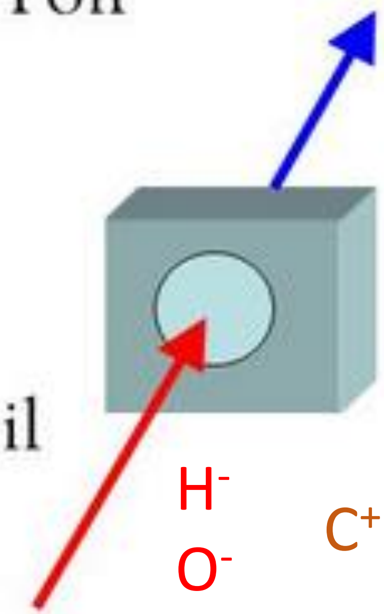
Gas sensor



Charge state distributions vs. foil thickness

The Stripper Foil

- A thin carbon foil is placed in the beam tube at the center of the terminal. As the negatively charged beam strikes the foil (at fairly high energy), electrons are stripped from the ions, leaving them positively charged.



(10-100 μg/cm^2 ≈ 0.05-0.5 μm)

Involved processes inside the stripper foil:

A+B → A+B* Excitation

$e^- + A \rightarrow e^- + A + e^-$ Ionization

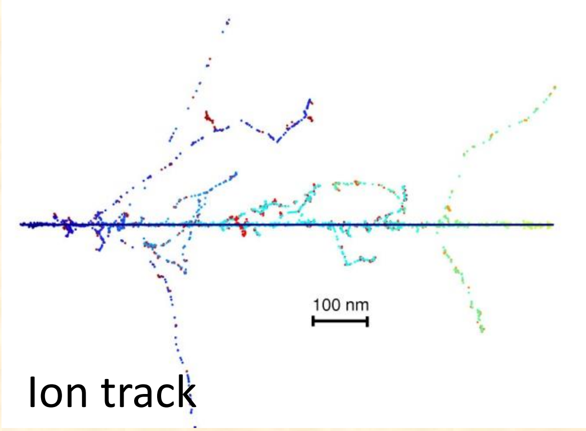
$e^- + A^{i+} \rightarrow A^{(i+1)+} + 2e^-$ Multiple ionization

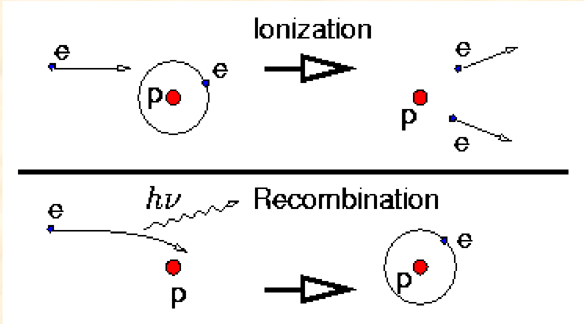
$e^- + A^{i+} \rightarrow A^{(i+k)+} + (k+1)e^-$ Multiple ionization

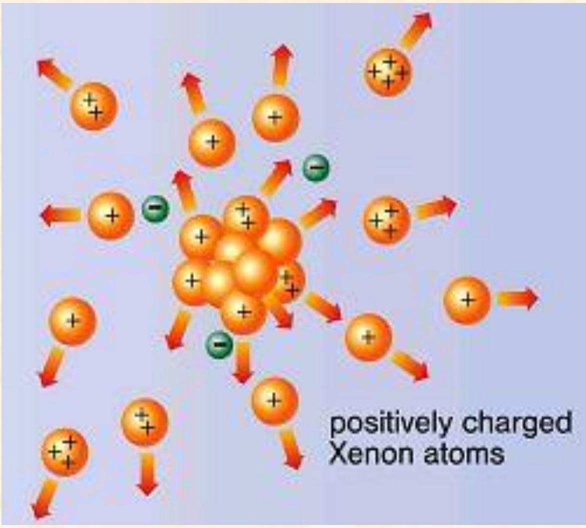
$A^{i+} + B^{k+} \rightarrow A^{j+} + B^{n+} + (j+n-i-k)e^-$ Charge Exchange

$A^+ + e^- \rightarrow A°$ Recombination

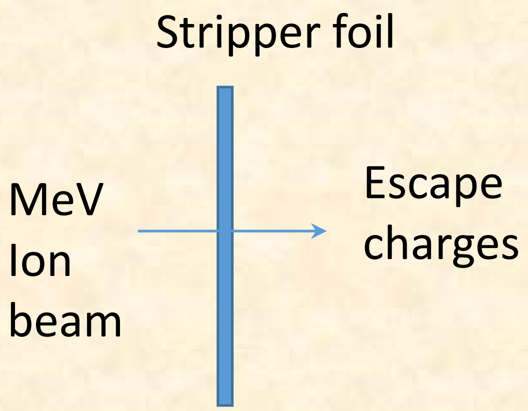
$A^{2+} + e^- \rightarrow A+$ Recombination





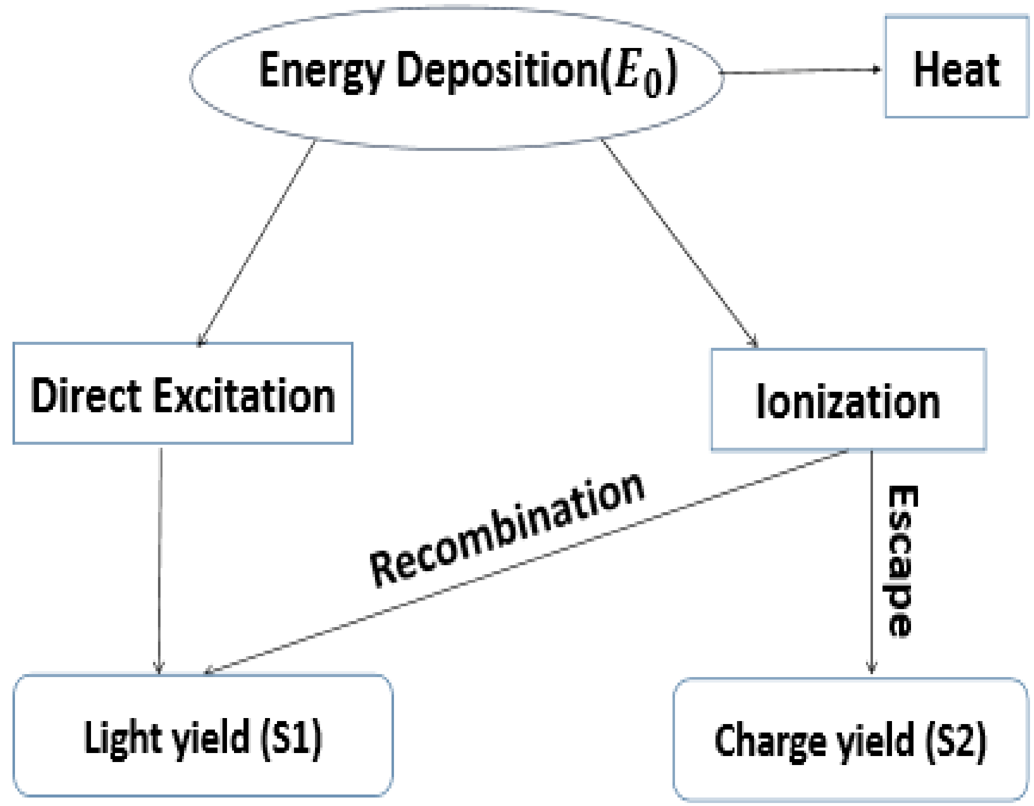


σ cross-section (E, z, Z)



e-e Ionization

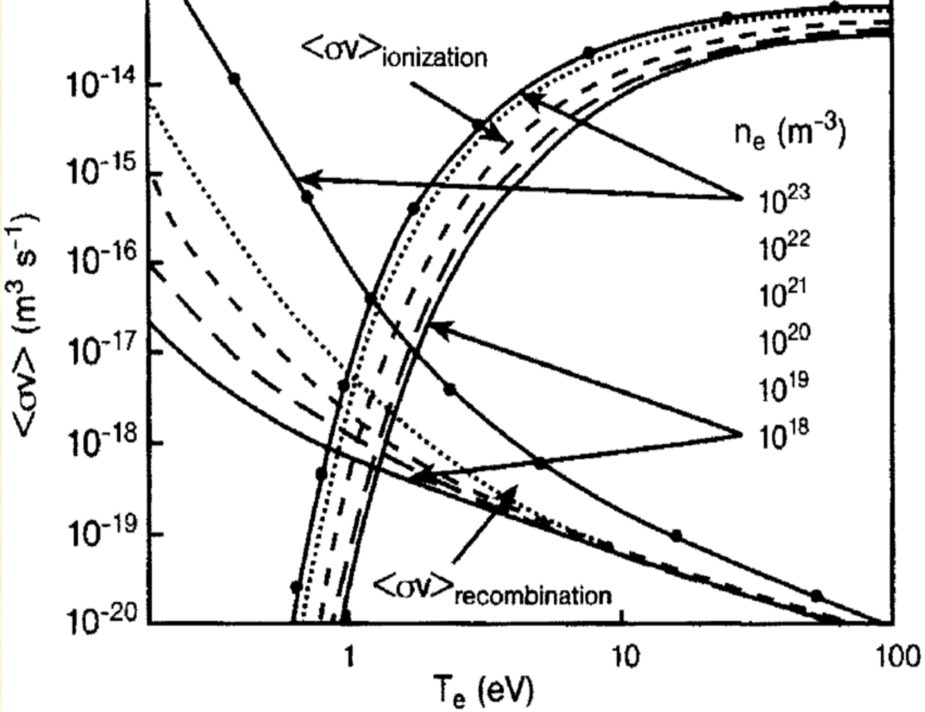
i-e Ionization



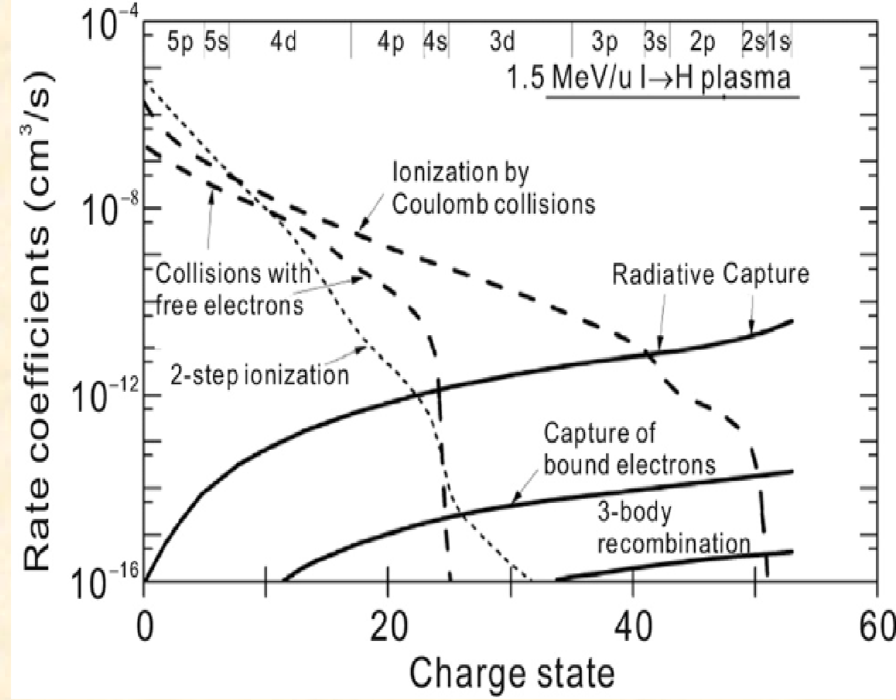
extraction foil

- thin foil, for example carbon, removes the electron(s) with high probability
- new charge state of ion brings it on a new trajectory → separation from circulating beam
- lifetime of foil is critical due to heating, rad.damage; conversion efficiencies, e.g. generation of neutrals, must be considered carefully

i-e Recombination



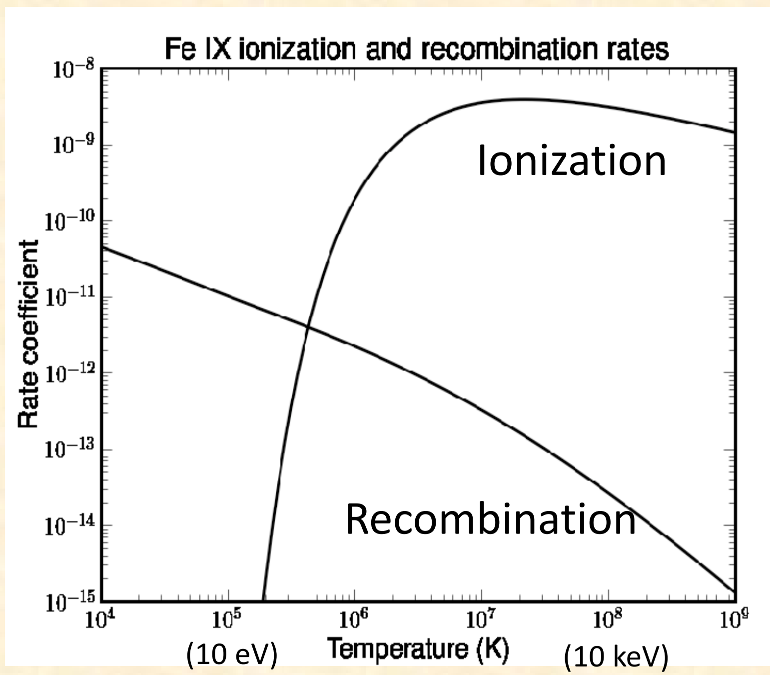
Theory



1) $\sigma_{ionization} \propto E/q$

2) $\sigma_{recombination} \propto q/E$

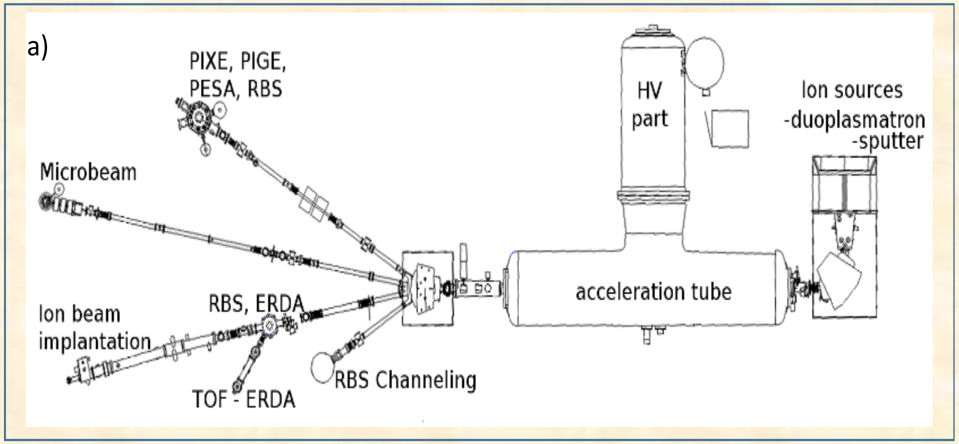
Equilibrium: $\sigma_{ionization} = \sigma_{recombination}$ for each charge state (E, q, Δt, material parameters, …)



Ionization cross sections have a maximum value at the Bohr velocity

C. Deutsch
Matter Radiat. Extremes 1, 277 (2016)

Nuclear Physics Institute, Rez Academy of Science of Czech Republic, CANAM-TANDETRON Laboratory

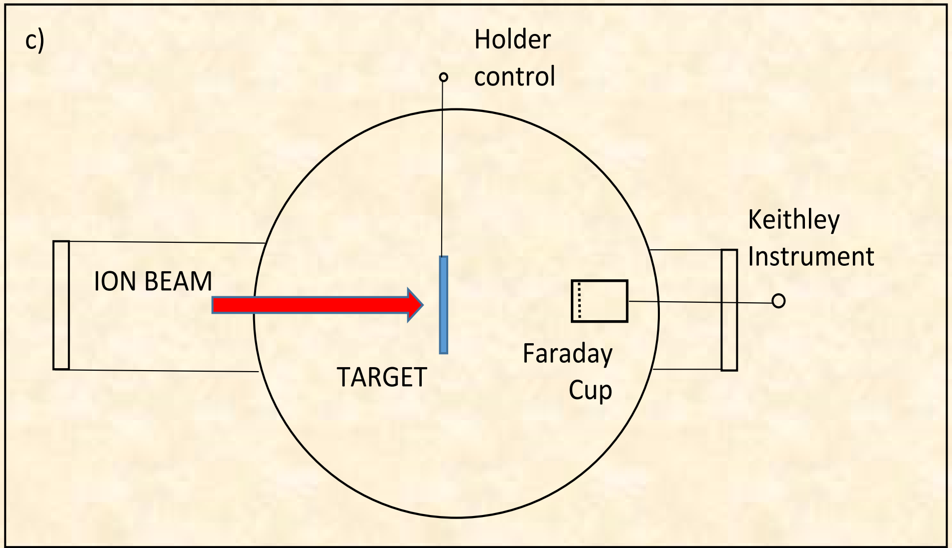


Investigated ions:

He, C, O ion beams
1 - 24 MeV energy

1 - 100 nA currents

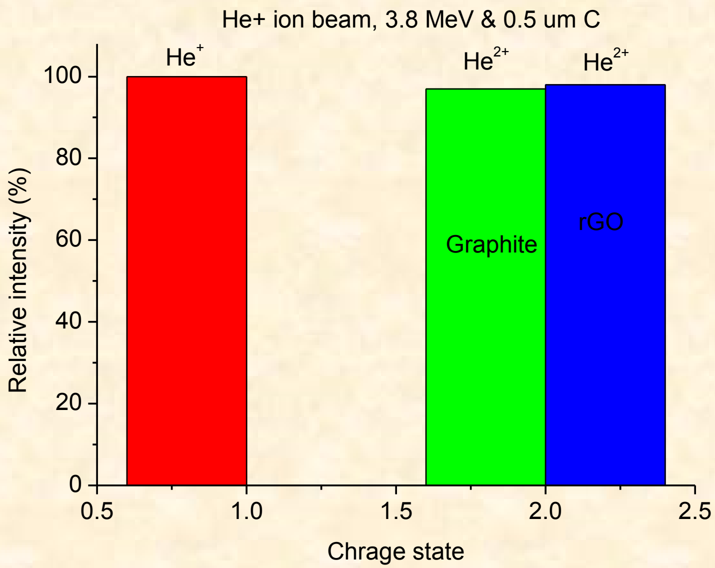
Spot size 1-25 mm^2

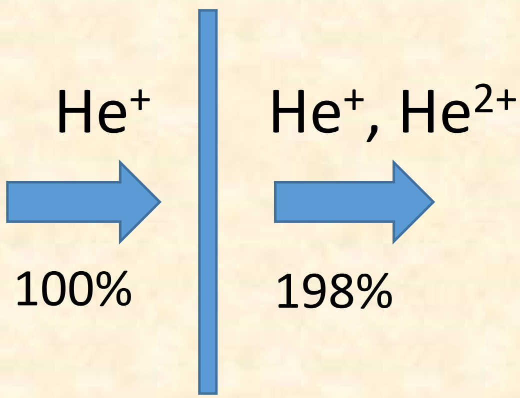


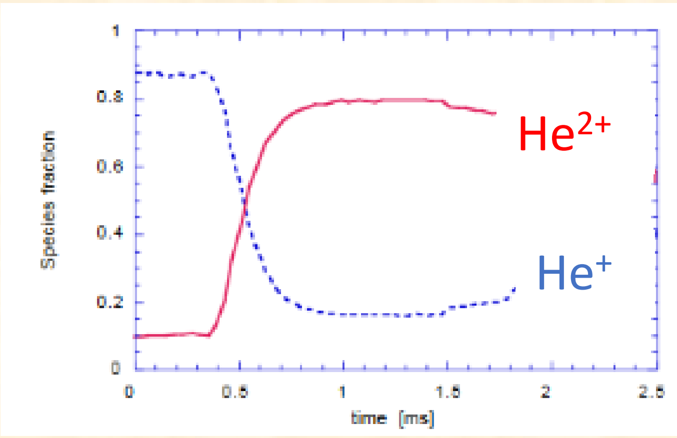
Transmitted current measurements:

$$T = I_t/I_0$$

He$^+$ beam											
	Graphite (ρ = 2.25 g/cm^3), 0.5 µm					RGO (ρ = 1.50 g/cm^3), 0.5 µm, 1.0 µm, 2.0 µm					
Energy (MeV)	Range in Graphite (µm)	Lateral Straggling nm/0.5µm	I_0 (nA)	I_T (nA)	T I_T/I_0	Range in RGO (µm)	Lateral Straggling nm/0.5µm	Δx (µm)	I_0 (nA)	I_T (nA)	T I_T/I_0
1.0	2.70	25	3.5	6.9	1.97	4.05	25	1.0	3.5	6.95	1.98
2.0	5.48	16	3.5	6.9	1.97	8.22	16	1.0	3.5	6.9	1.97
2.9	8.63	13	5.0	9.8	1.96	12.95	13	0.5	5.1	10	1.97
2.9	"	"	5.1	10	1.96	"	"	1.0	5.1	10	1.96
2.9	"	"	5.3	10	1.89	"	"	2.0	5.3	10.1	1.91
3.8	12.41	11	7.4	14.4	1.95	18.62	11	1.0	7.4	14.3	1.93

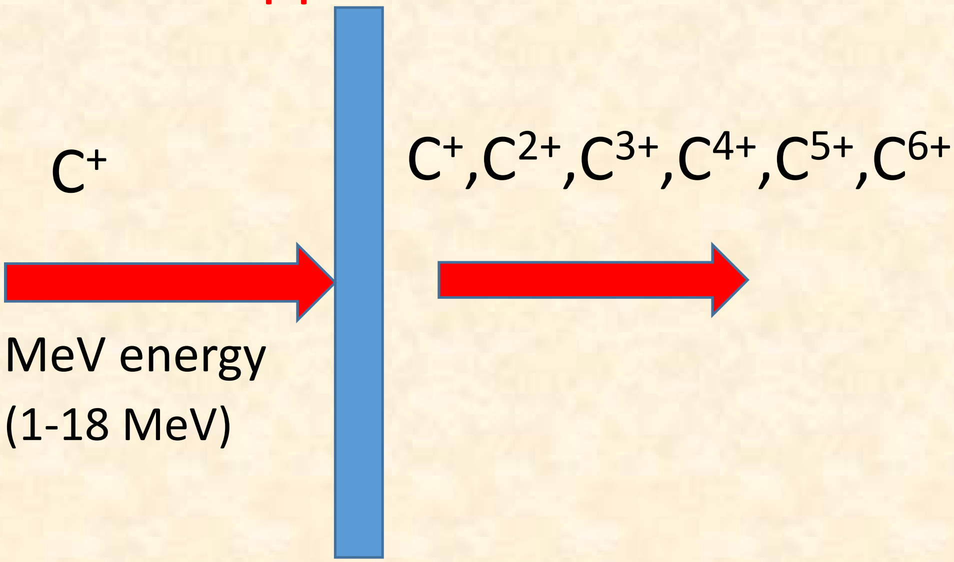




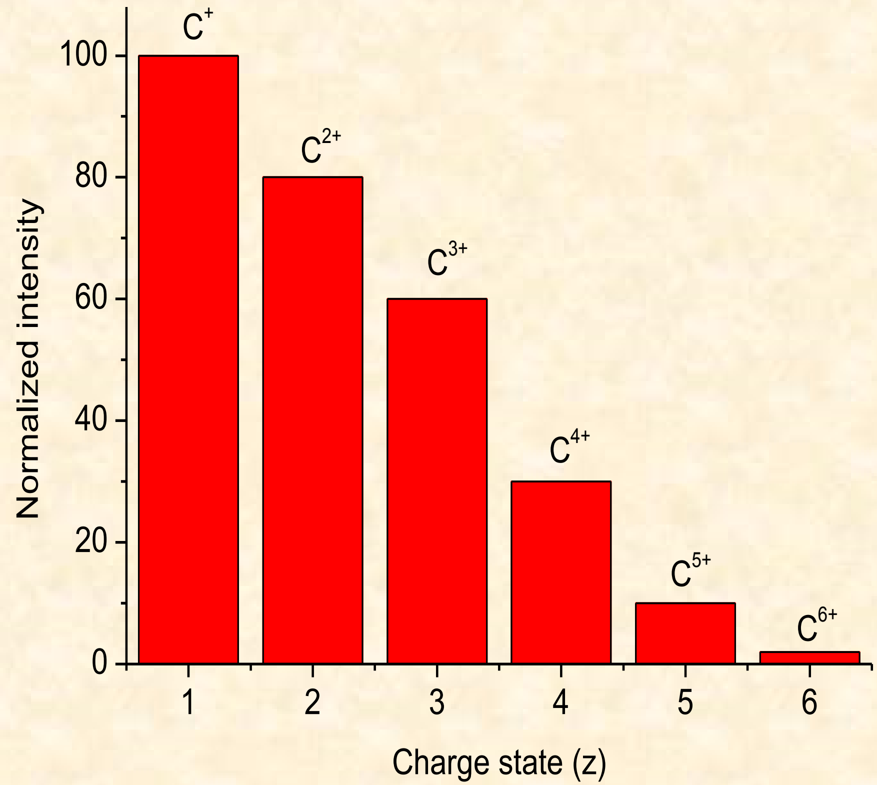


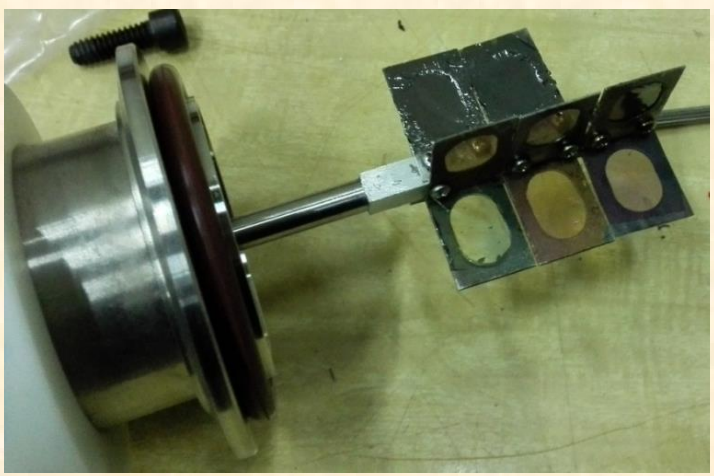
Equilibrium between ionization and recombination effects

rGO Stripper foil



Sub-micrometric foil thicknesses
(10-100 $\mu g/cm^2 \approx$ 0.05-0.5 μm)

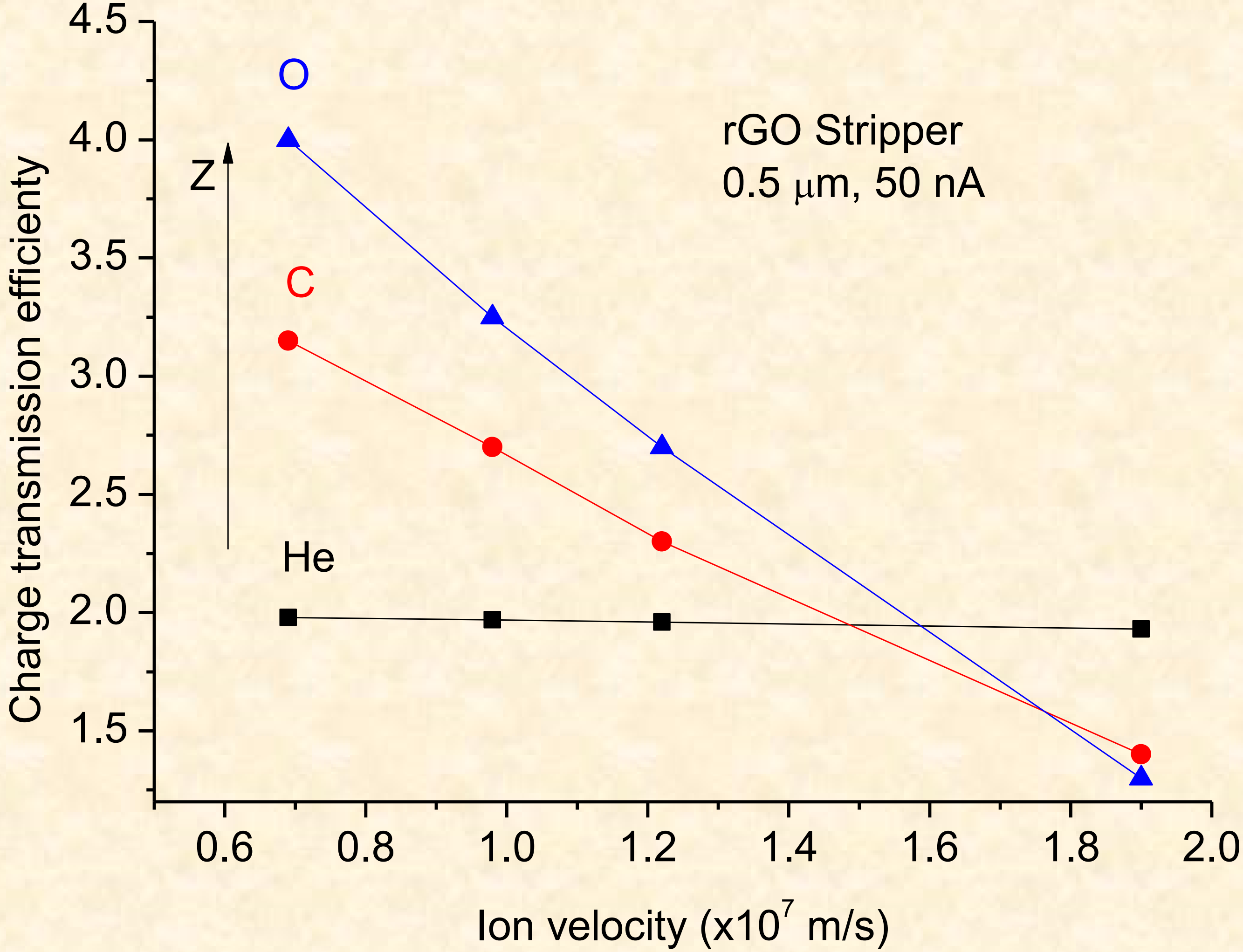




C^{5+} beam											
	Graphite (ρ = 2.25 g/cm³), 0.44 μm					**r GO (ρ = 1.50 g/cm³), 0.5 μm, 1.0 μm**					
Energy (MeV)	Range in Graphite (μm)	Lateral Straggling (nm)	I_0 (nA)	I_T (nA)	T I_T/I_0	Range in RGO (μm)	Lateral Straggling (nm)	Δx (μm)	I_0 (nA)	I_T (nA)	T I_T/I_0
16	11.55	9	2.15	2.18	1.01	17.33	9	0.5	2.09	2.10	1.0
16	"	"				"	"	1.0	2.08	2.10	1.01
C^{4+} beam											
13.3	9.40	7	6.05	7.3	1.21	14.10	10	0.5	6.2	7.53	1.21
13.3	"	"				"	"	1.0	6.2	7.56	1.22
C^{3+} beam											
10	6.98	8.5	7.0	11	1.57	10.48	12	0.5	7.1	11.2	1.58
10	"	"				"	"	1.0	7.2	11.4	1.58
C^{2+} beam											
8	5.63	10	7.38	15.62	2.11	8.44	14	0.5	7.7	16.7	2.16
8	"	"				"	"	1.0	7.4	15.4	2.08
C^{+} beam											
3.2	2.65	19.5	10.45	34.18	3.27	3.98	29	0.5	10.2	32.1	3.15
3.2	"	"				"	"	1.0	9.39	28.2	3.0

L. Torrisi et Al., submitted to *Rad. Physic and Chemistry,* 2019

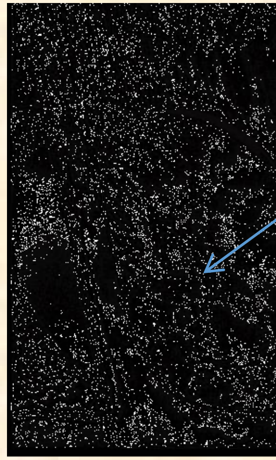
(C-ion velocity comparable to that of He ions $E_C \approx 3\ E_{He}$)



Charge transmission efficienty
4.5
4.0
3.5
3.0
2.5
2.0
1.5
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Ion velocity (x10^7 m/s)
O
C
He
Z
rGO Stripper
0.5 μm, 50 nA

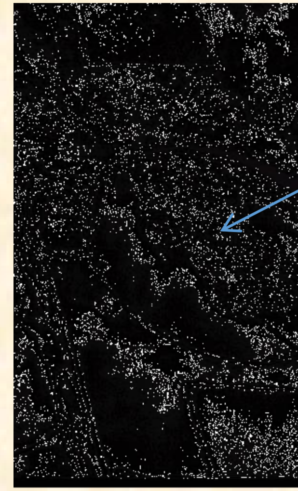
Preparation

Graphite stripper



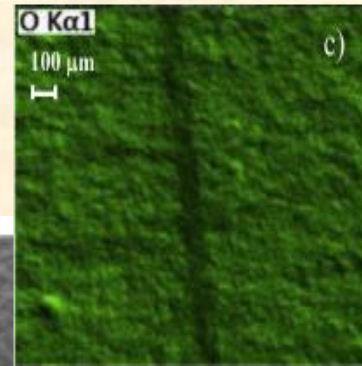
Rupture ($\sim 5 \times 10^{16}$ He/cm^2)

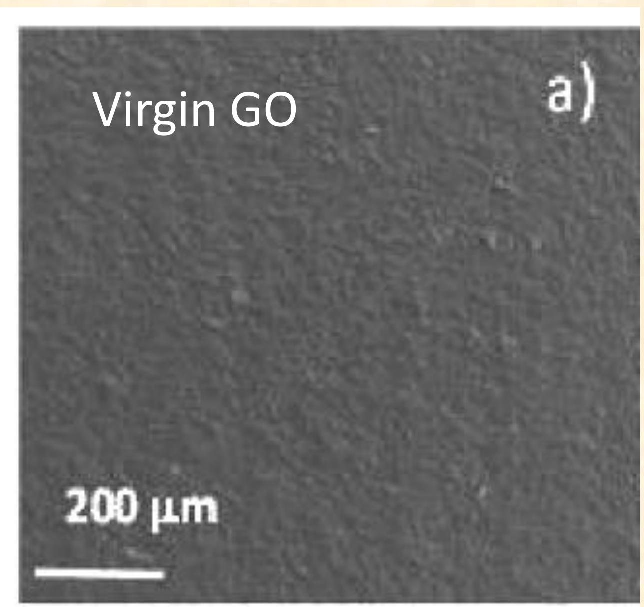
rGO stripper

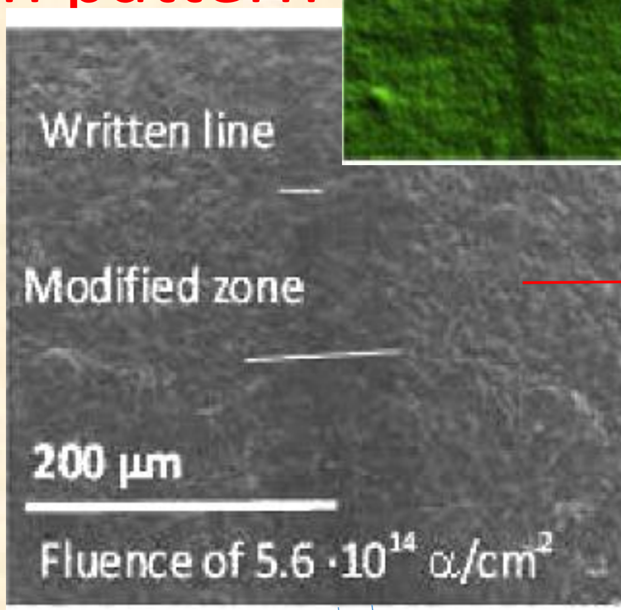


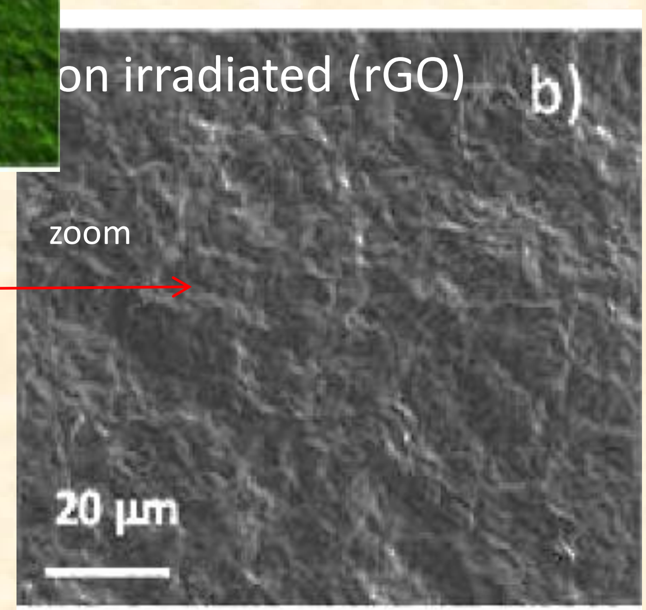
Ion beam rGO

Ion pattern

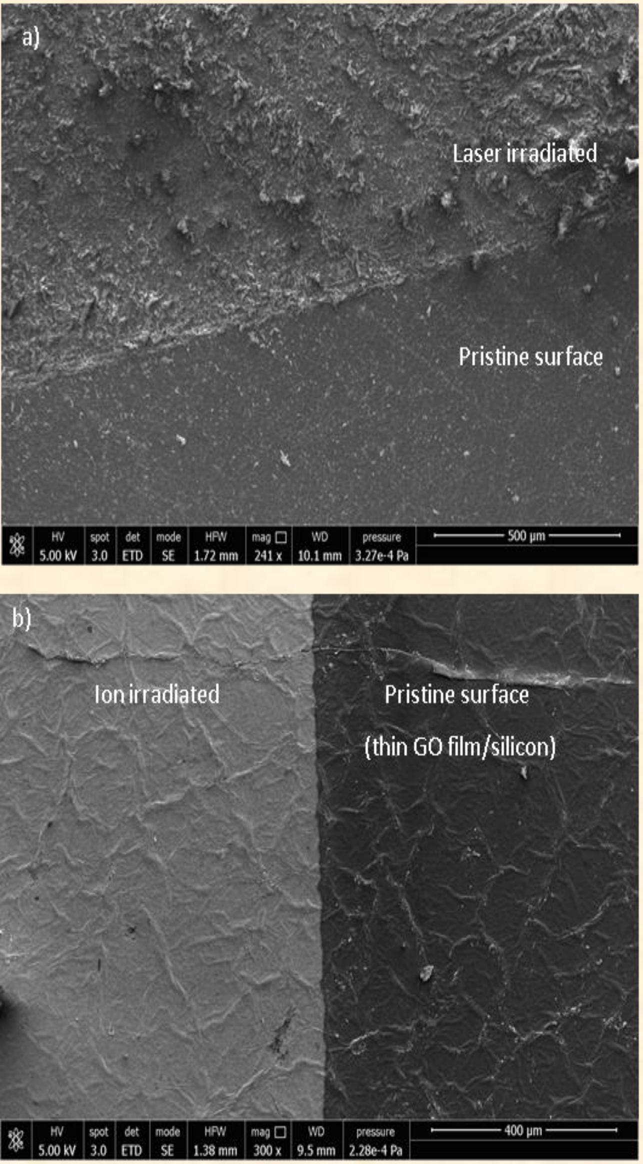








Ion beam line



M. Cutroneo et Al.,
EPJ Web of Conferences 167, 02004 (2018)

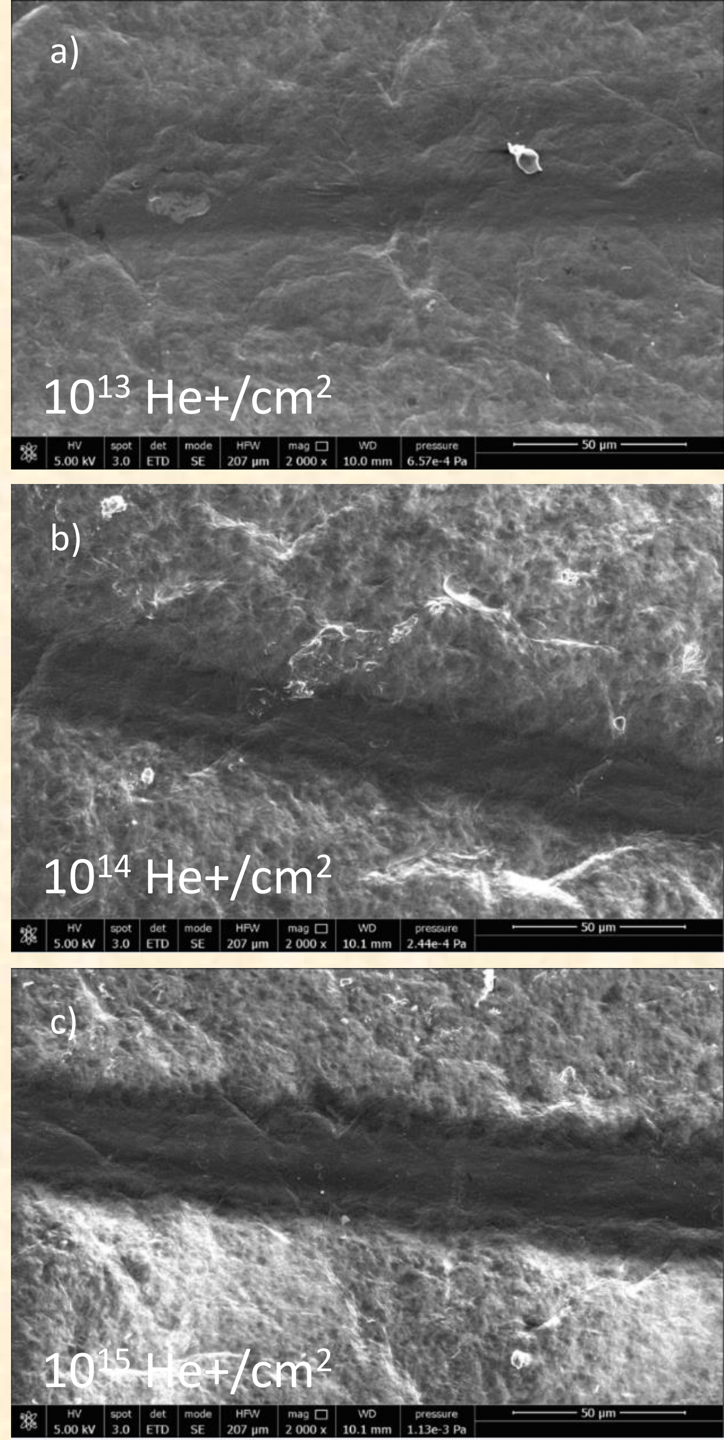
V. Romano et Al.,
EPJ Web of Conferences 167, 04011 (2018)

L. Silipigni et Al.
EPJ Web of Conferences 167, 05011 (2018)

L. Torrisi et Al.,
Rad. Eff. and Def. in solids, 173:1-2, 73-84 (2018)

M. Cutroneo et Al.,
Vacuum 165 (2019) 134–138.

M. Cutroneo et Al.,
Nucl. Instr. and Methods B , in press 2019.



Ion beam reduction with groove production (thinning, increasing density and approaching the sp^2 plains

Main Results

1. Obtained results demonstrated that the stripping effect is similar for Graphite and rGO foils with the same thickness (μg/cm2).

2. Lifetime for rGO is higher than graphite thanks to the better mechanical and thermal properties of rGO

For a good quality of carbon foil is necessary to extract ion beams stable for a long time, thus the lifetime is an important parameter of such films.

Preliminar Observations

- GO foil (0.4 mm) under helium ion bombardment at 100 nA exceeded ~ $5x10^{17}$ He/cm^2 dose without disruption.

- Graphite foil (0.4 mm) at 100 nA was broken at ~ $5x10^{16}$ He/cm^2.

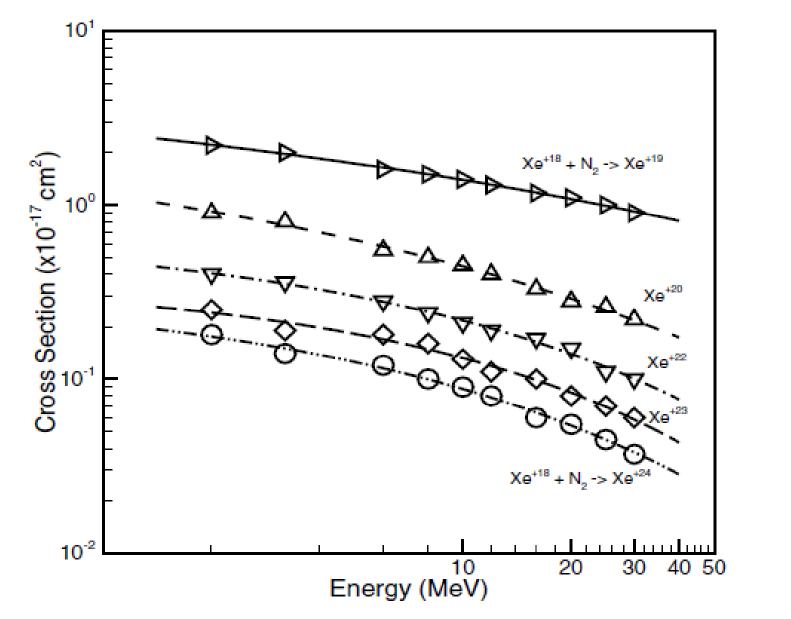
- No micro cracks are observed in GO and rGO with respect to Graphite.

- Graphite foils show micro cracks by thermal gradient effects and mechanical stresses, not observed in rGO foils.

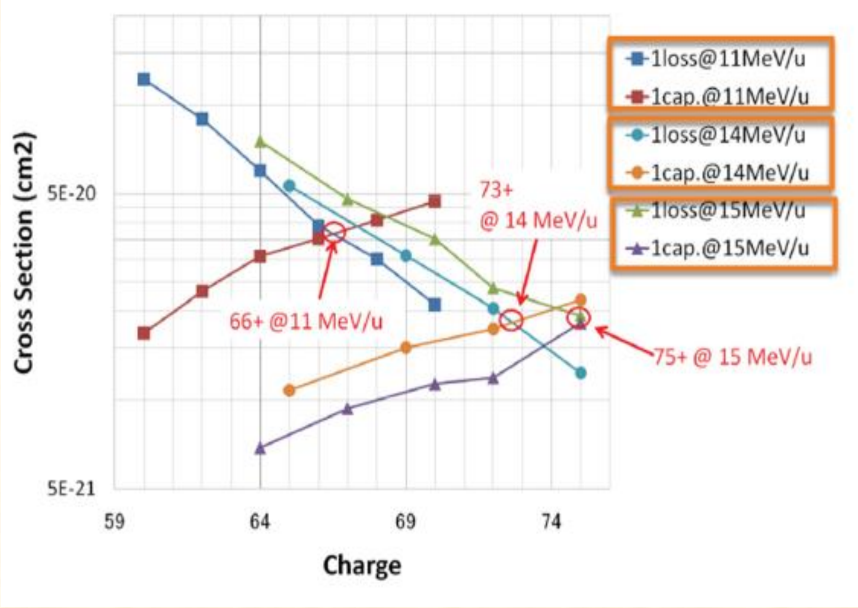
- Important aspects concern the thermal dissipation of the stripper and of its holder.

- The multiple scattering from the foil increases the beam emittance and thus decreases transmission. The foil thickens under bombardment with heavy beams, resulting in a time-varying reduction in beam intensity and an increase in beam loading. The foil lifetimes decrease as the beam mass and intensity increase.

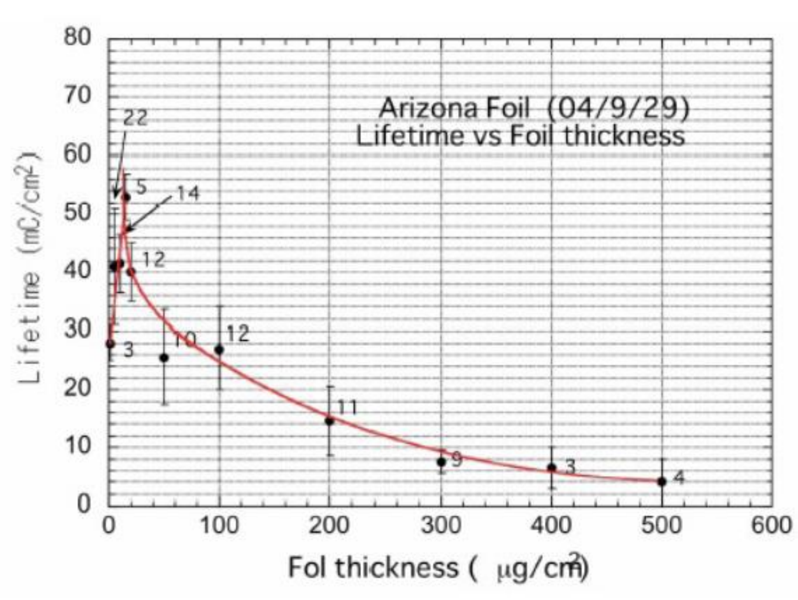
Literature data



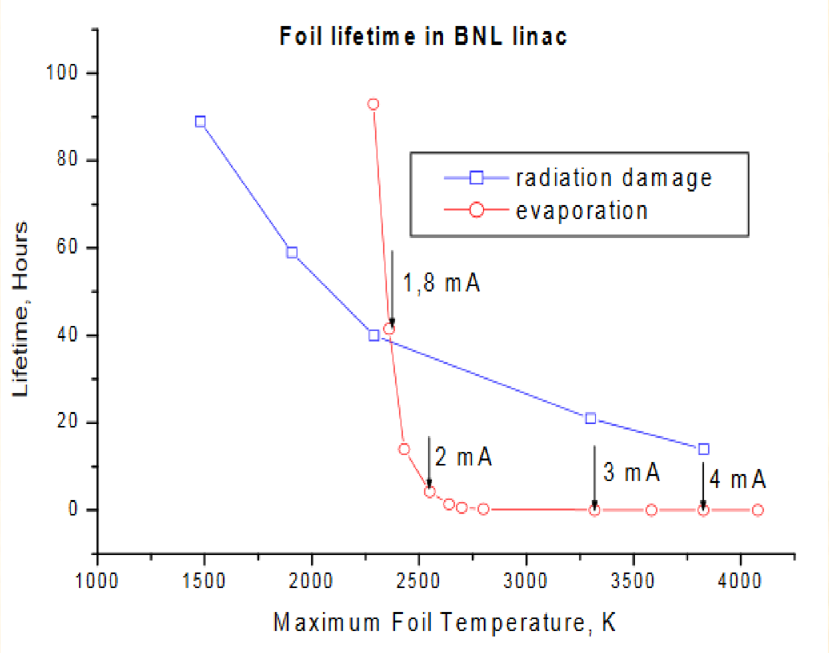
Ionization and recombination cross-sections vs charge



GH Miley et Al., DOI: 10.1109/FUSION.2005.252869 · Source: IEEE Xplore, 2005

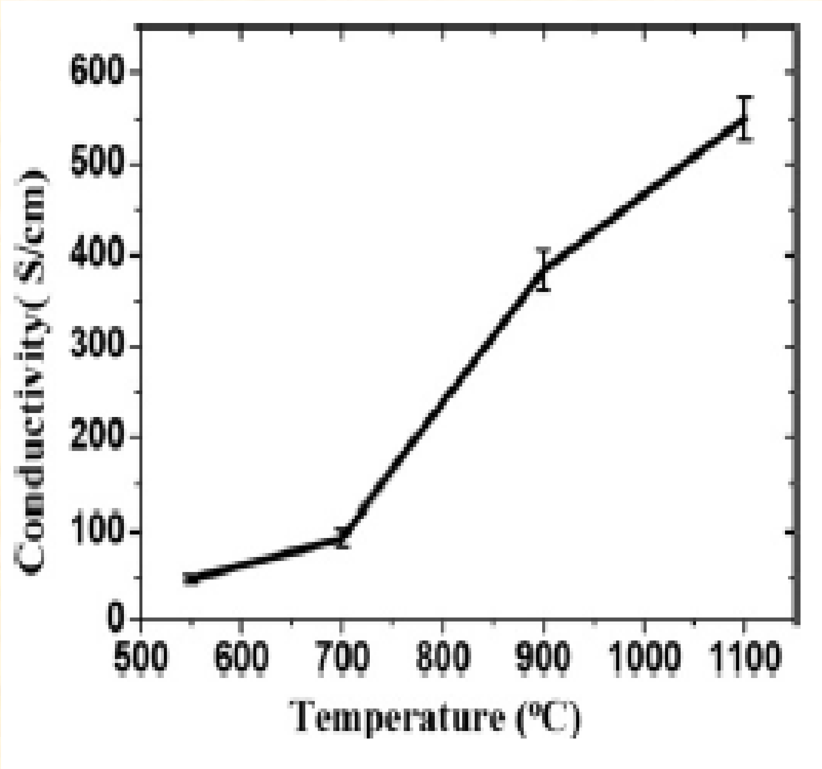


Lifetime versus foil thickness

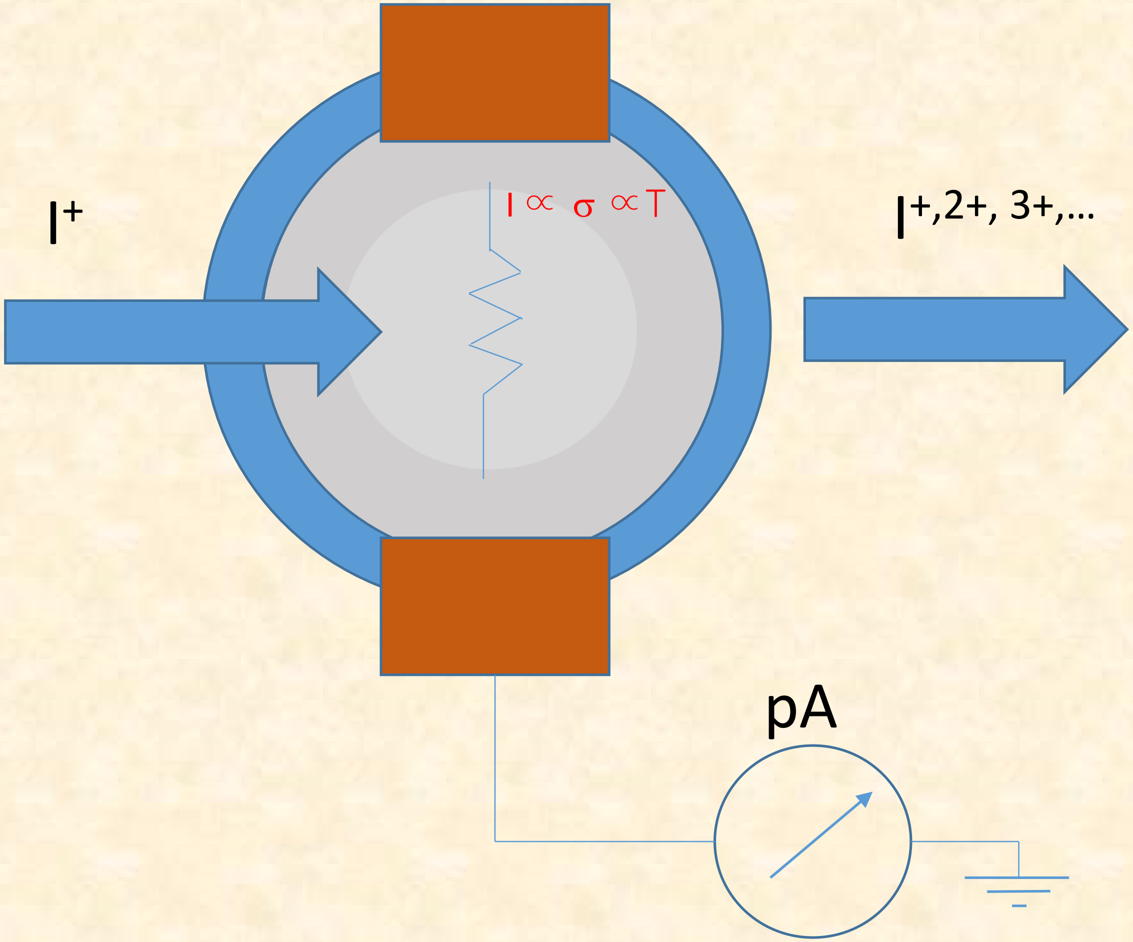


Lifetime versus foil temperature

Future developments: rGO stripper foil sensitive to high temperature



(rGO temperature sensor)



* Feedback signal to stop the ion beam at high stripper temperature

Conclusions

- GO foils have higher mechanical resistance than graphite
- rGO foils have high electrical and thermal conductivity, low density and high mechanical resistance
- GO foils become rGO under ion beam irradiation starting from about 10^{13} ions/cm^2 fluence
- GO foils with sub-micrometric thickness can be used as ion stripper with high efficiency, similarly to Graphite foils
- The stripper lifetime of rGO foils is higher with respect to graphite foils
- Further investigation must be performed using high energy ions (～100 MeV), heavy ions (Z>8) and high ion current (I>100 nA) to evaluate the rGO stripper lifetime response with respect to graphite.

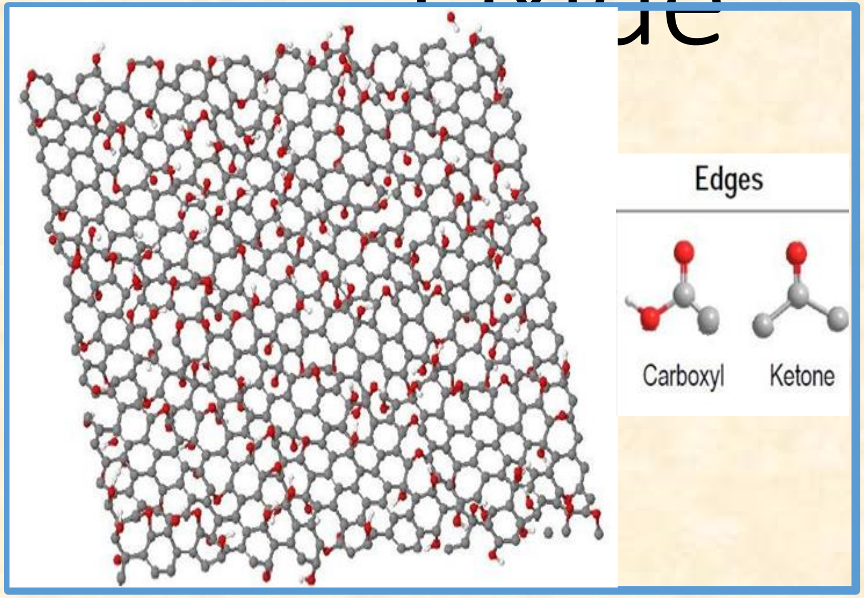
Thank You for the Attention

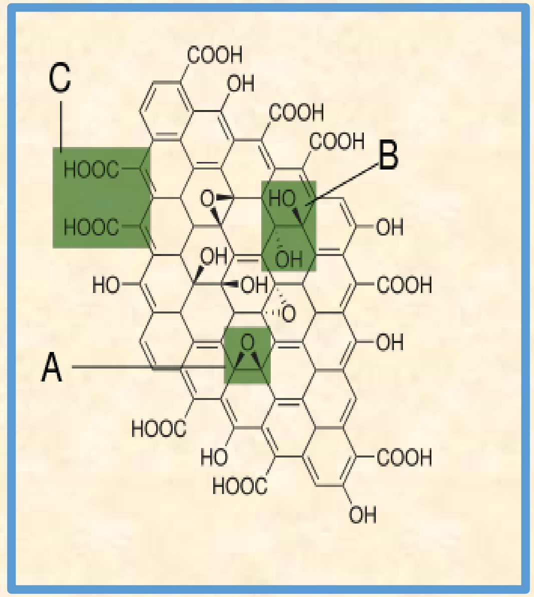
CHERNE 2019

CHERNE 2019 -15th Workshop on European Collaboration in Higher Education on Radiological and Nuclear Engineering and Radiation Protection

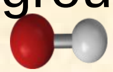
2-5 June 2019
Portopalo di Capo Passero

Graphene Oxide





Functional groups:

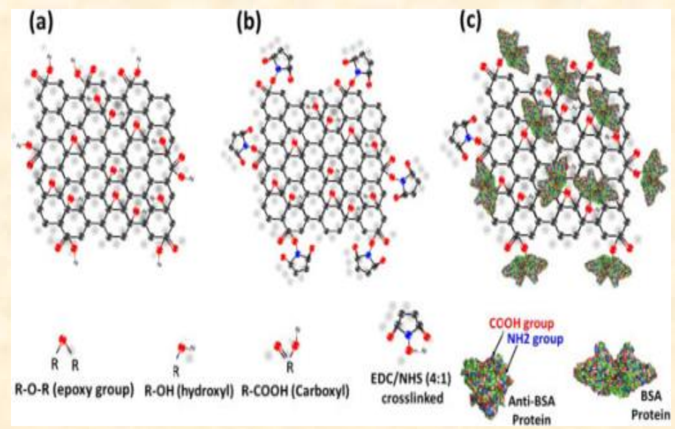


- hydroxyl (C-OH)

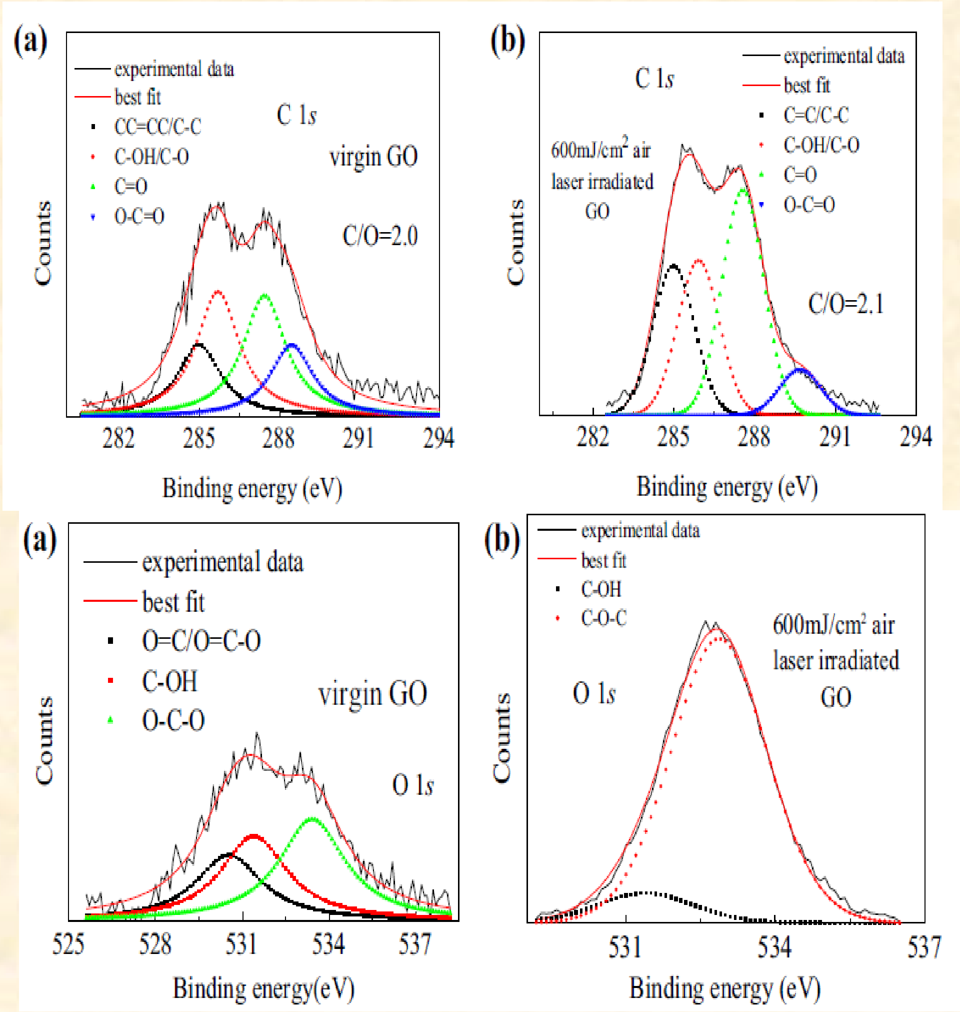
- epoxy (C-O-C)

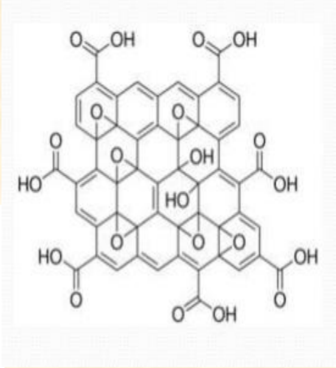
- carbonyl (C=O)

- carboxyl (O-C=O)



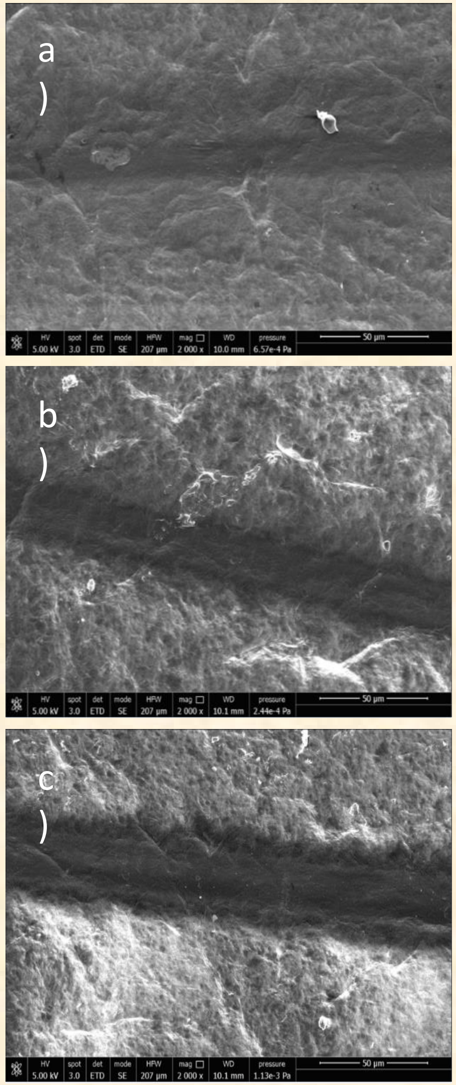
XPS Analysis

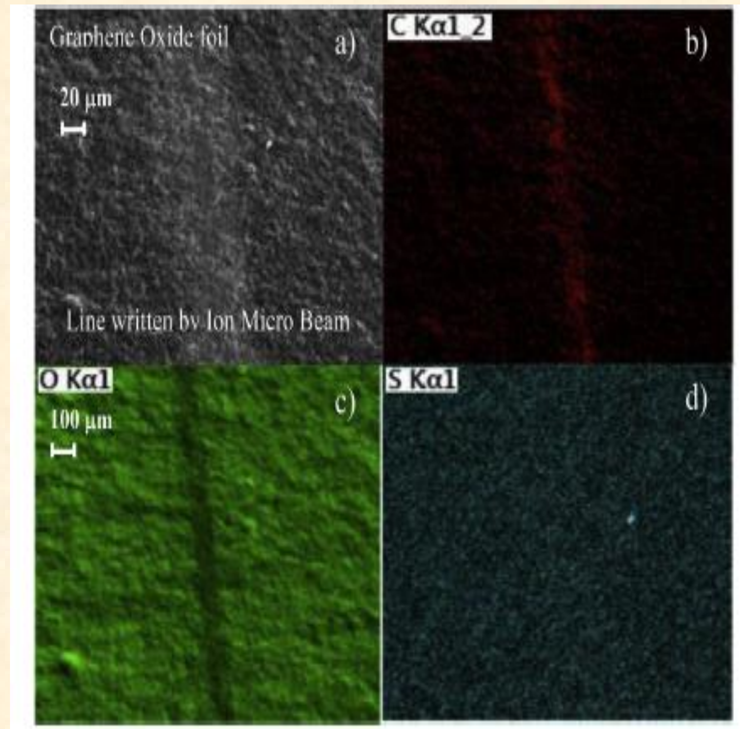




L. Torrisi et Al., *Vacuum* 153 (2018) 122-131.

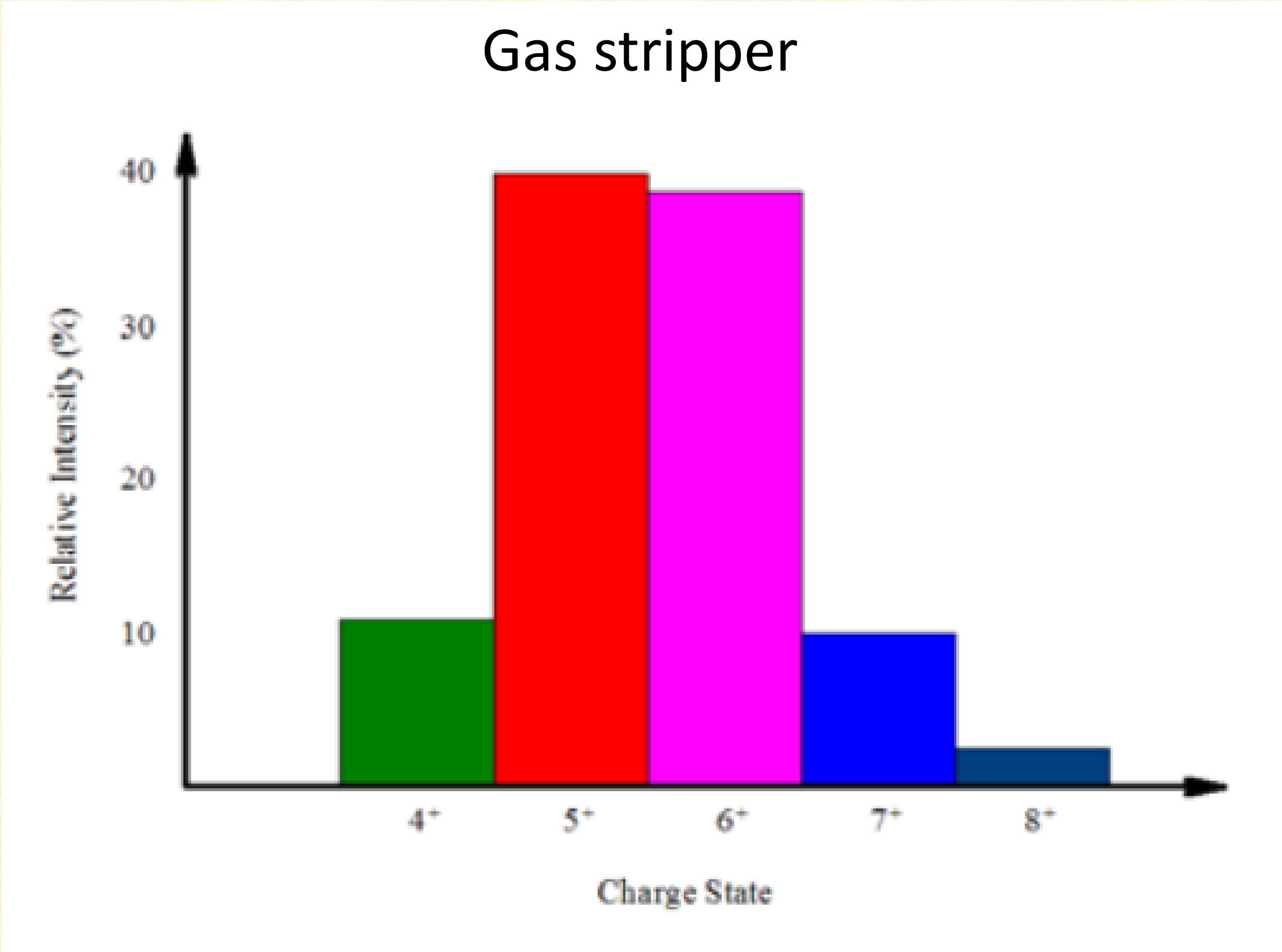
Ion beam reduction and Patternig in insulator GO





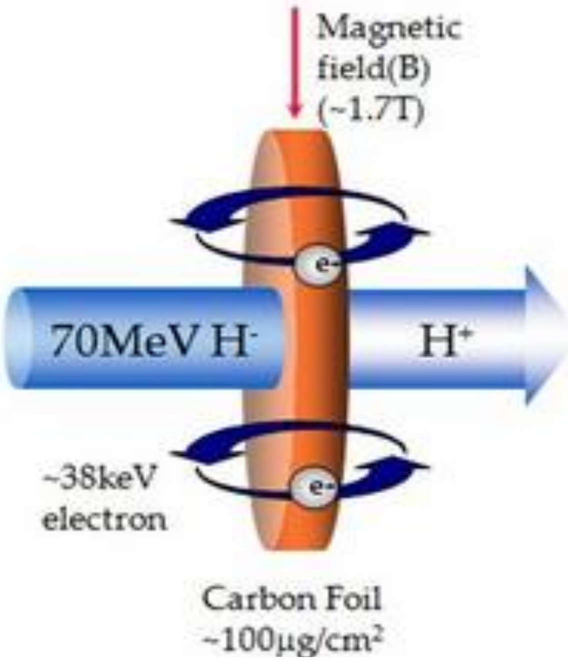
The charge state distribution for $(16O)^{-1}$ ions with 3.0 MV at the HV Terminal was:

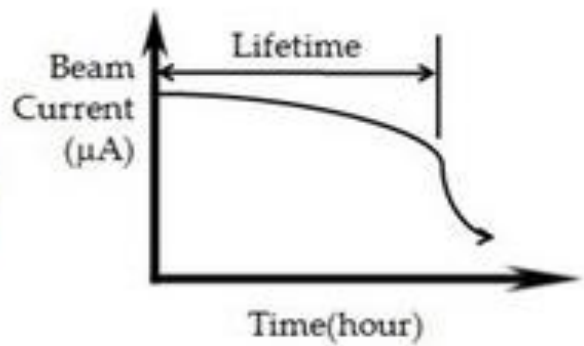
$O^{+} = 0.5\%$
$O^{2+} = 0.8\%$
$O^{3+} = 1\%$
$O^{4+} = 10\%$
$O^{5+} = 41\%$
$O^{6+} = 36\%$
$O^{7+} = 10\%$
$O^{8+} = 1\%$

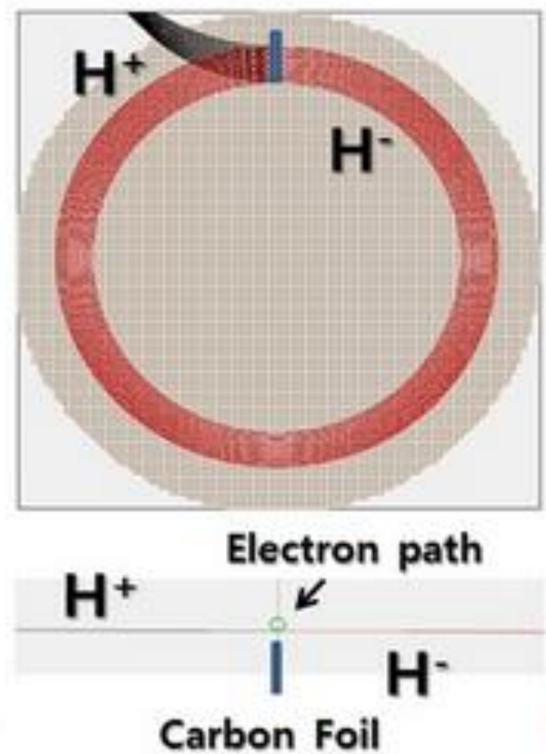


Principle of Stripper

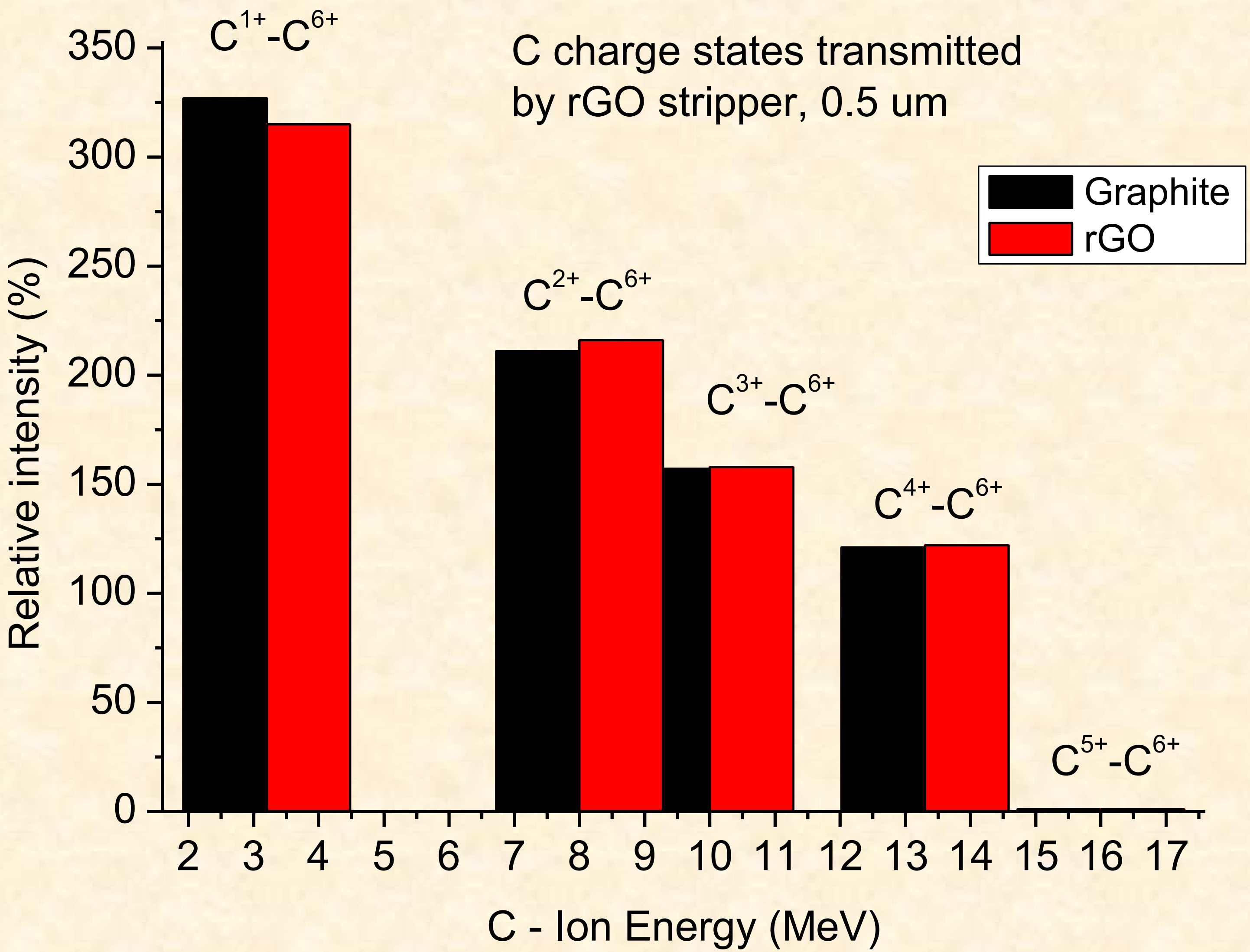
- Carbon foils to extract positive protons by stripping two electrons from accelerated negative protons.
- Therefore a good quality of carbon foil is necessary to extract proton beam stable for a long time.
- The lifetime of stripping foils is limited by several factors- extracting currents, the foil thickness, the repetition rate







Ref : Submitted, J.H.Kim et al., JKPS (2012)



C charge states transmitted
by rGO stripper, 0.5 um
Graphite
rGO
C1+-C6+
C2+-C6+
C3+-C6+
C4+-C6+
C5+-C6+
Relative intensity (%)
0
50
100
150
200
250
300
350
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
C - Ion Energy (MeV)

Ionization potentials of the projectile atoms C atoms

C - ATOMS

At. Num.	Sp. Name.	Ion Charge	El. name	Isoel. Seq.	Ground Shells	Ground Level	Ionized Level	Ionization Energy (eV)	Uncertainty (eV)	References
6	C I	0	Carbon	C	$1s^22s^22p^2$	$^3P_0$	$2s^22p\ ^2P°_{1/2}$	11.2602880	0.0000011	L20057
6	C II	+1	Carbon	B	$1s^22s^22p$	$^2P°_{1/2}$	$2s^2\ ^1S_0$	24.383154	0.000016	c190
6	C III	+2	Carbon	Be	$1s^22s^2$	$^1S_0$	$2s\ ^2S_{1/2}$	47.88778	0.00025	L876c191
6	C IV	+3	Carbon	Li	$1s^22s$	$^2S_{1/2}$	$1s^2\ ^1S_0$	64.49352	0.00019	L11667
6	C V	+4	Carbon	He	$1s^2$	$^1S_0$	$1s\ ^2S_{1/2}$	[392.090515]	0.000025	L10054
6	C VI	+5	Carbon	H	$1s$	$^2S_{1/2}$		(489.993194)	0.000007	L7188

O - ATOMS

At. Num.	Sp. Name.	Ion Charge	El. name	Isoel. Seq.	Ground Shells	Ground Level	Ionized Level	Ionization Energy (eV)	Uncertainty (eV)	References
8	O I	0	Oxygen	O	$1s^22s^22p^4$	$^3P_2$	$2p^3\ ^4S°_{3/2}$	13.618055	0.000007	L74,L3760
8	O II	+1	Oxygen	N	$1s^22s^22p^3$	$^4S°_{3/2}$	$2p^2\ ^3P_0$	35.12112	0.00006	L11267,L10621
8	O III	+2	Oxygen	C	$1s^22s^22p^2$	$^3P_0$	$2p\ ^2P°_{1/2}$	[54.93554]	0.00012	L11770
8	O IV	+3	Oxygen	B	$1s^22s^22p$	$^2P°_{1/2}$	$2s^2\ ^1S_0$	77.41350	0.00025	L648
8	O V	+4	Oxygen	Be	$1s^22s^2$	$^1S_0$	$2s\ ^2S_{1/2}$	113.8990	0.0005	L7288
8	O VI	+5	Oxygen	Li	$1s^22s$	$^2S_{1/2}$	$1s^2\ ^1S_0$	[138.1189]	0.0021	L4713
8	O VII	+6	Oxygen	He	$1s^2$	$^1S_0$	$1s\ ^2S_{1/2}$	[739.32682]	0.00006	L10054
8	O VIII	+7	Oxygen	H	$1s$	$^2S_{1/2}$		(871.40988)	0.00003	L7188

Graphene-based materials: Properties (rGO)

- **Electrical**
  - Semiconductor with both holes and electrons as charge carriers
  - Very high electrical conductivity (depending on the quality of graphene oxide)

- **Mechanical**
  - Young's modulus ~ 260 GPa

- **Optical**
  - Transmittance ~ 85% (IR); ~ 5% (Visible);

- **Thermal**
  - Conductivity Above 600 W/(m K) (in plane)

- **High Specific Surface Area**
  - Theoretically ~ 500 $m^2.g^{-1}$

- **Low density**

  GO: ~ 1.8 g/cm^3

Metallic color