Swift heavy-ion irradiation effects in carbon nanostructures

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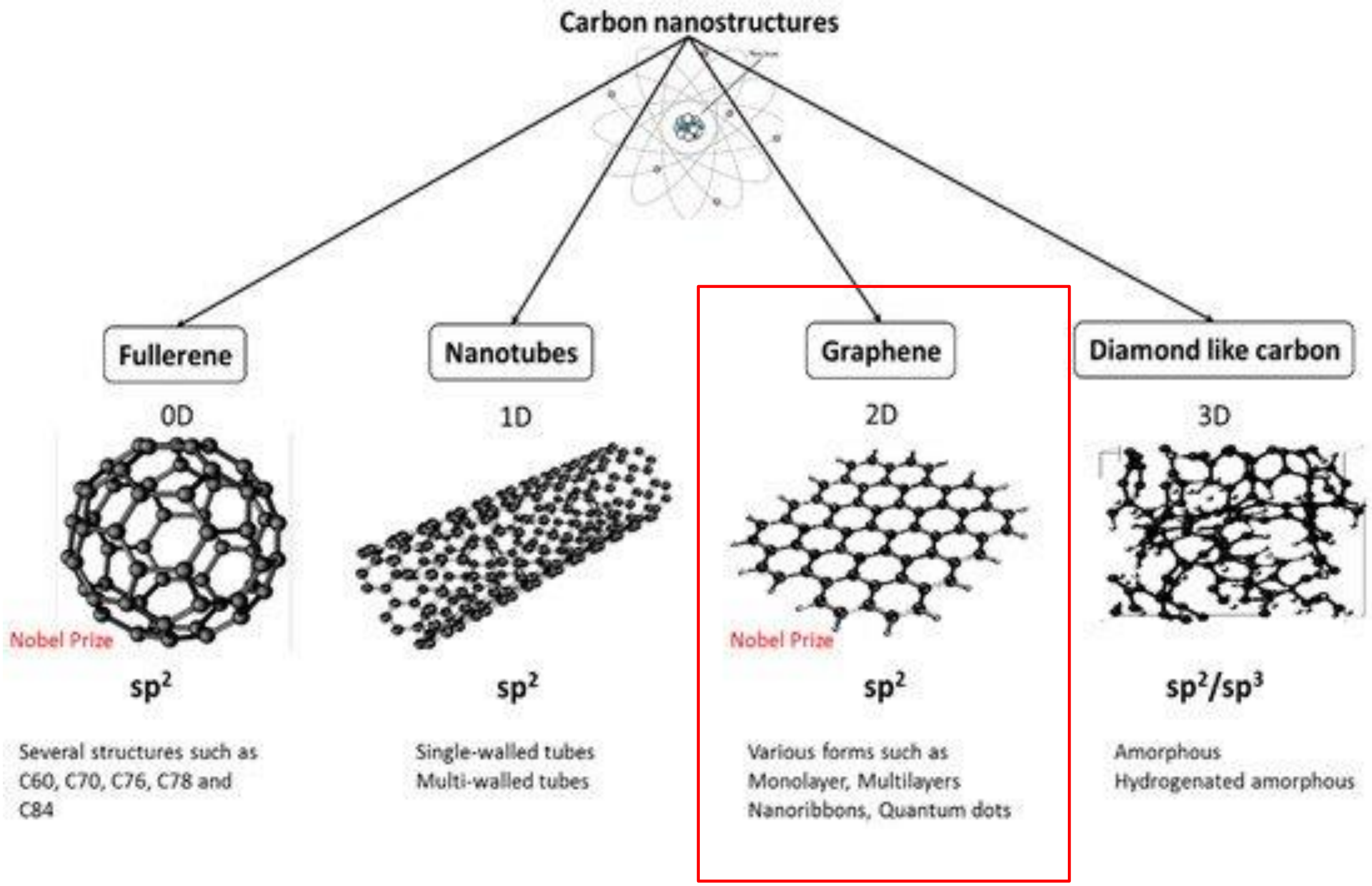
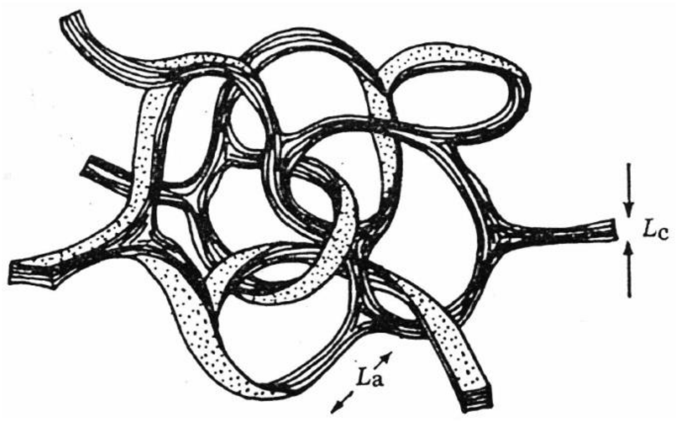
Project has been carried out in Flerov Laboratory of Nuclear Reactions

Carbon nanostructures



https://www.mdpi.com/1996-1944/10/9/1066

Glassy carbon (GC)



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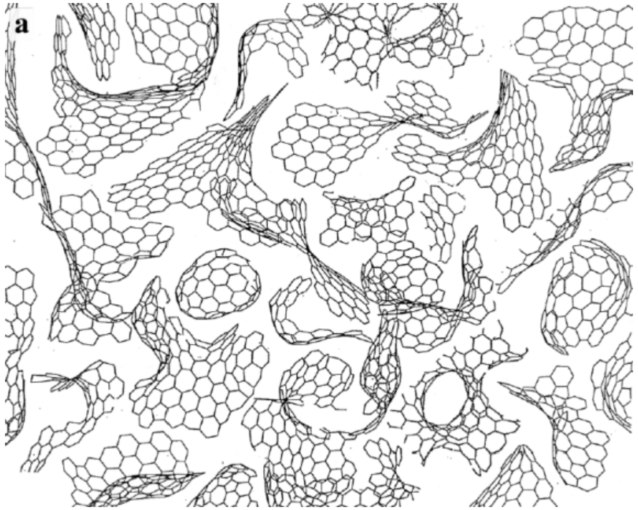

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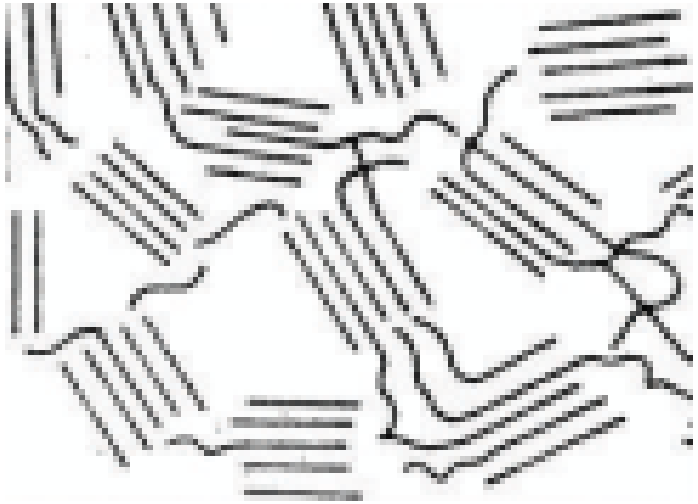

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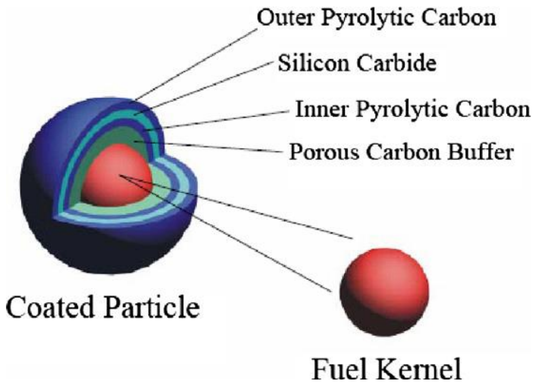
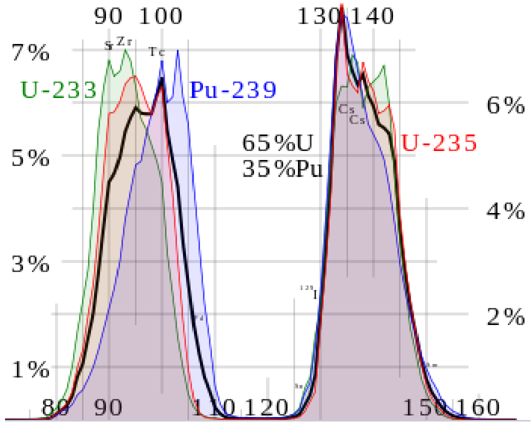
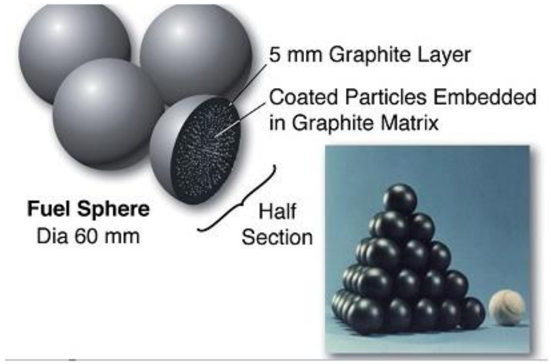
Large sample of glassy carbon

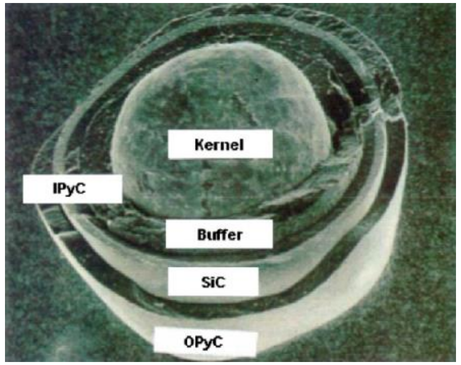
Motivation and practical aspects of GC research: TRISO fuel for next generation nuclear reactors

TRIstructural ISOtropic (TRISO) coated particle fuel:









- Designed to nuclear reactor projects that involve goals of high coolant temperatures or high burnup performance of nuclear fuel.
- Porous C buffer – attenuates recoiling fission products (FPs) and accommodates internal gas buildup and particle dimensional changes
- SiC – acts as main pressure vessel and provides a diffusion barrier to prevent the release of FPs
- PyC layers- protect SiC from chemical attack during particle operation. Additional diffusion barriers for FPs. IPyC protects the fuel kernel during SiC deposition.

Fig. source: Allen. T.. Busby. J.. Meyer. M.. & Petti. D. *Materials today*. (2010) *13*. 14.

Properties and potential applications

Properties

- high thermal and electrical conductivity
- resistance to high temperatures
- chemical and corrosion resistance.
- high hardness and strength
- low density
- extreme resistance to thermal shock

Potential applications

- construction materials for modern molted salt reactors (coatings)
- matrix for disposal/solidification of radioactive waste

GC samples

- Samples synthesized from polyfurfuryl alcohol at four different temperatures: 800, 1000, 1500, and 2000˚C

- Each GC sample were irradiated with the same dose ($6 \bullet 10^{13}$ ions/cm^2) of 167 MeV Xe ions at the IC-100 cyclotron.

- After irradiation cross-sectional specimens were prepared and Raman maps along ion trajectory were recorded using a confocal Raman microscope.

Raman spectroscopy Removing spikes and background

```
// Choosing the right points for the fit.
double background_level = (column[0] + column[size - 1]) / 2.0;

points.emplace_back(pair(column[0], 0));
points.emplace_back(pair(column[size - 1], size - 1));

for(int k = 1; k < (size/ 2) && points.size() < points_in_fit; k++)
{
    if(abs(column[k] - background_level) < critical_diff)
    {
        points.emplace_back(pair(column[k], k));
        if(column[k] < background_level) background_level = column[k];
    }
    if(abs(column[size - k - 1] - background_level) < critical_diff)
    {
        points.emplace_back(pair(column[size - k - 1], size - k - 1));
        if(column[k] < background_level) background_level = column[size - k - 1];
    }
    if(abs(column[size / 2 + k] - background_level) < critical_diff)
    {
        points.emplace_back(pair(column[size / 2 + k], size / 2 + k));
        if(column[k] < background_level) background_level = column[size / 2 + k];
    }
    if(abs(column[size / 2 - k] - background_level) < critical_diff)
    {
        points.emplace_back(pair(column[size / 2 - k], size / 2 - k));
        if(column[k] < background_level) background_level = column[size / 2 - k];
    }

}
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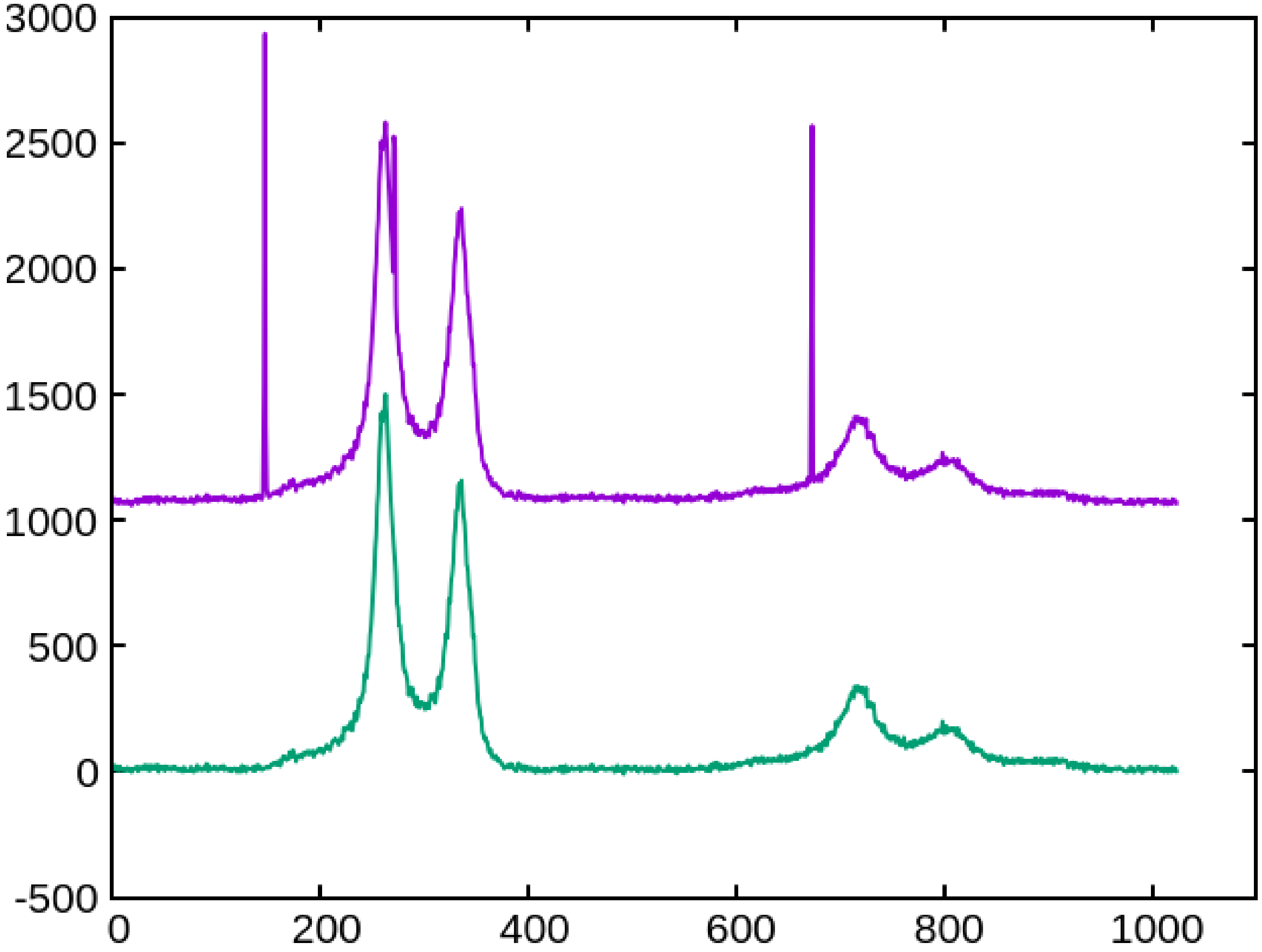
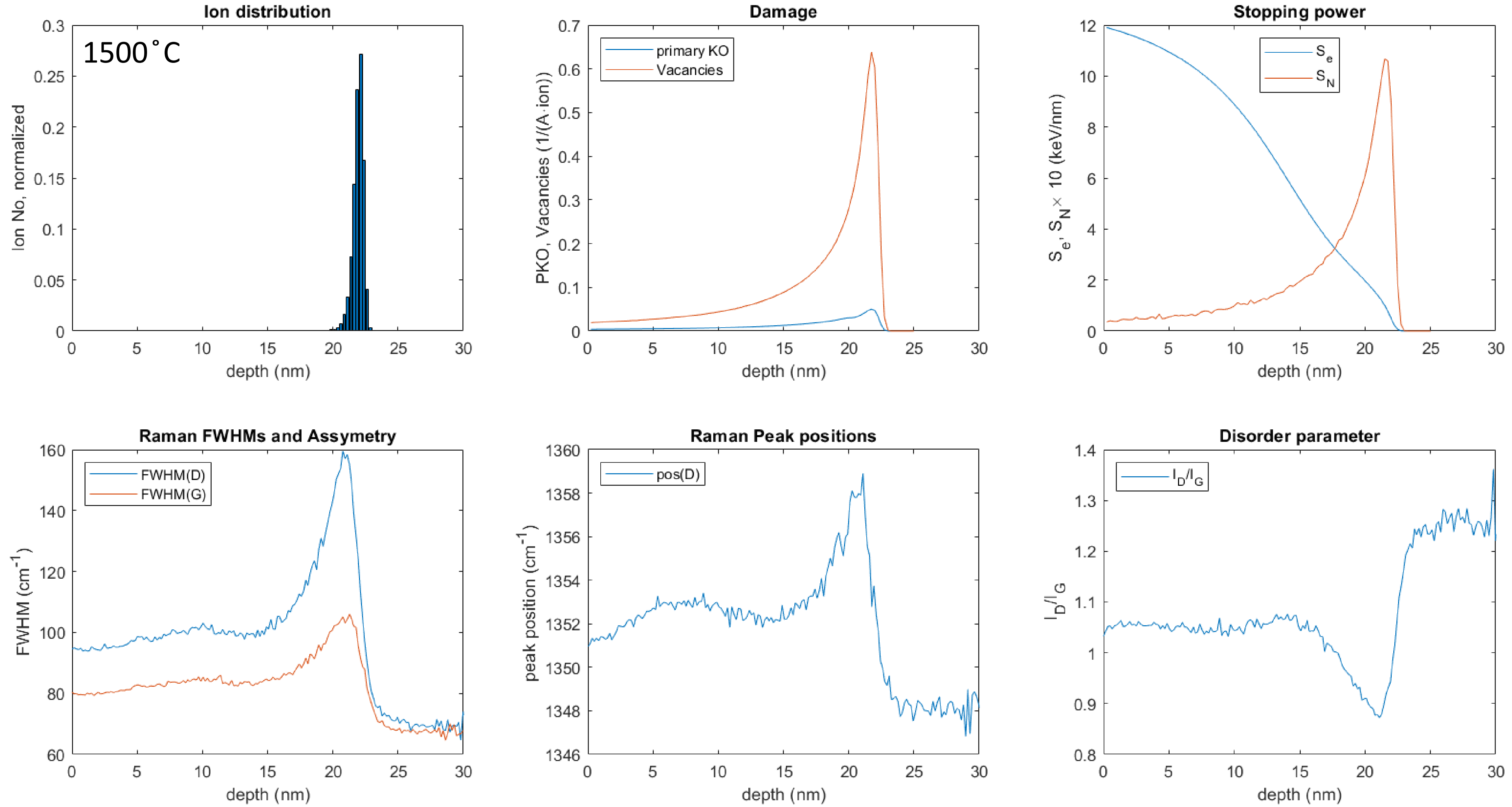
Raman spectroscopy Removing spikes and background

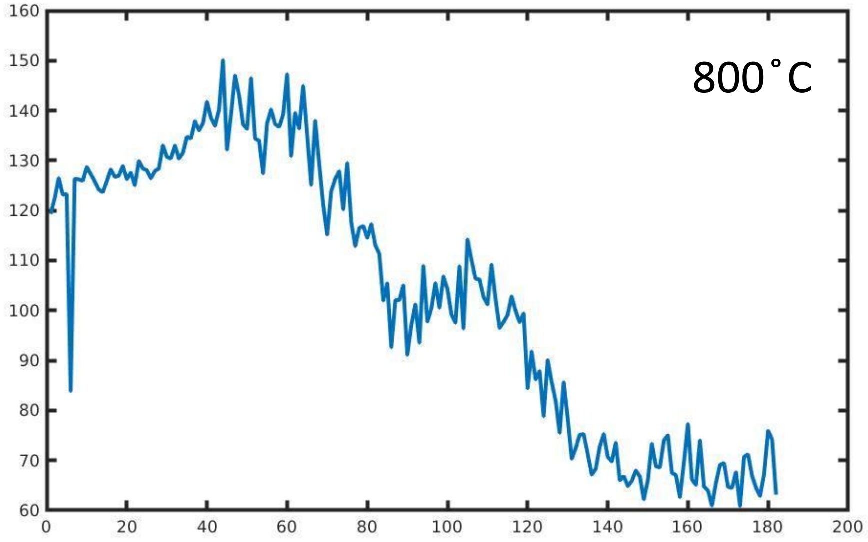


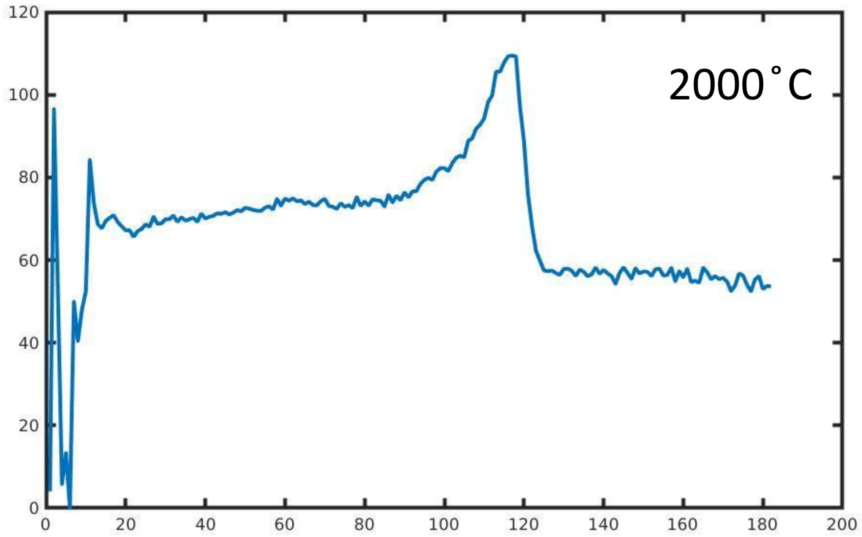
SRIM simulation and experimental depth profile

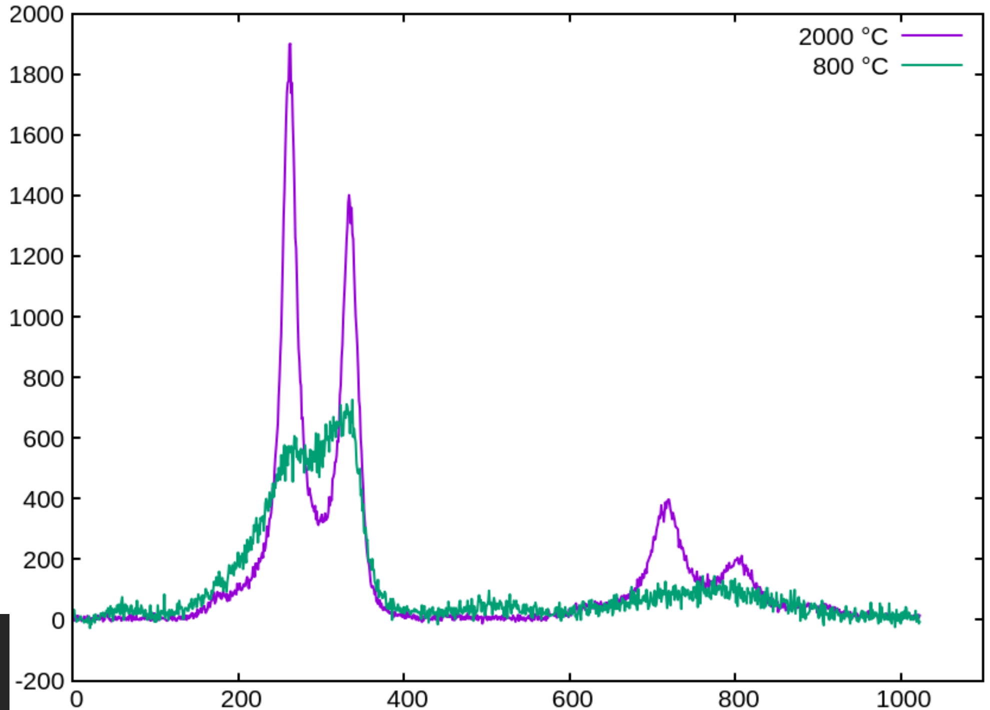


Raman spectroscopy GC

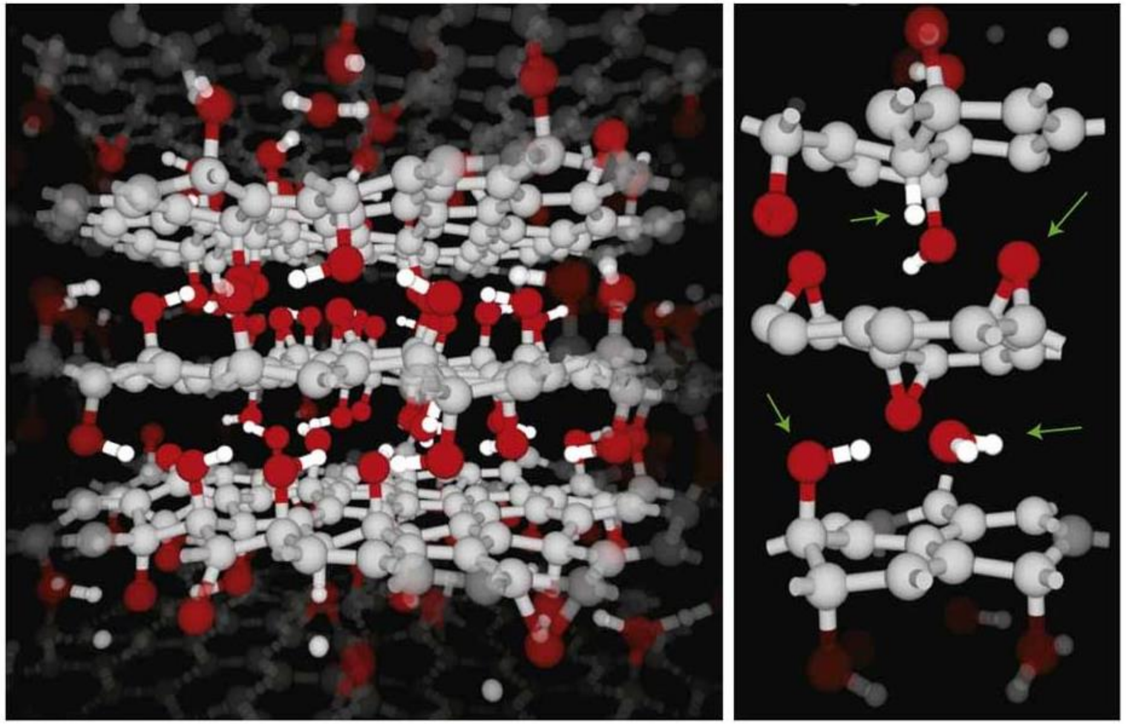
- Good agreement between the experimental and calculated ion ranges and damage profiles
- Samples carbonized at high temperatures are very resistive to irradiation in the electronic stopping regime
- The damage extent (amorphization) increases with decreasing carbonization temperature of the sample
- Existence of the intermediate, less damaged region – low S_e and S_N.
- Damage at the end of ion ranges is due to elastic collisions with target nuclei (high nuclear stopping power)







Graphene Oxide (GO)



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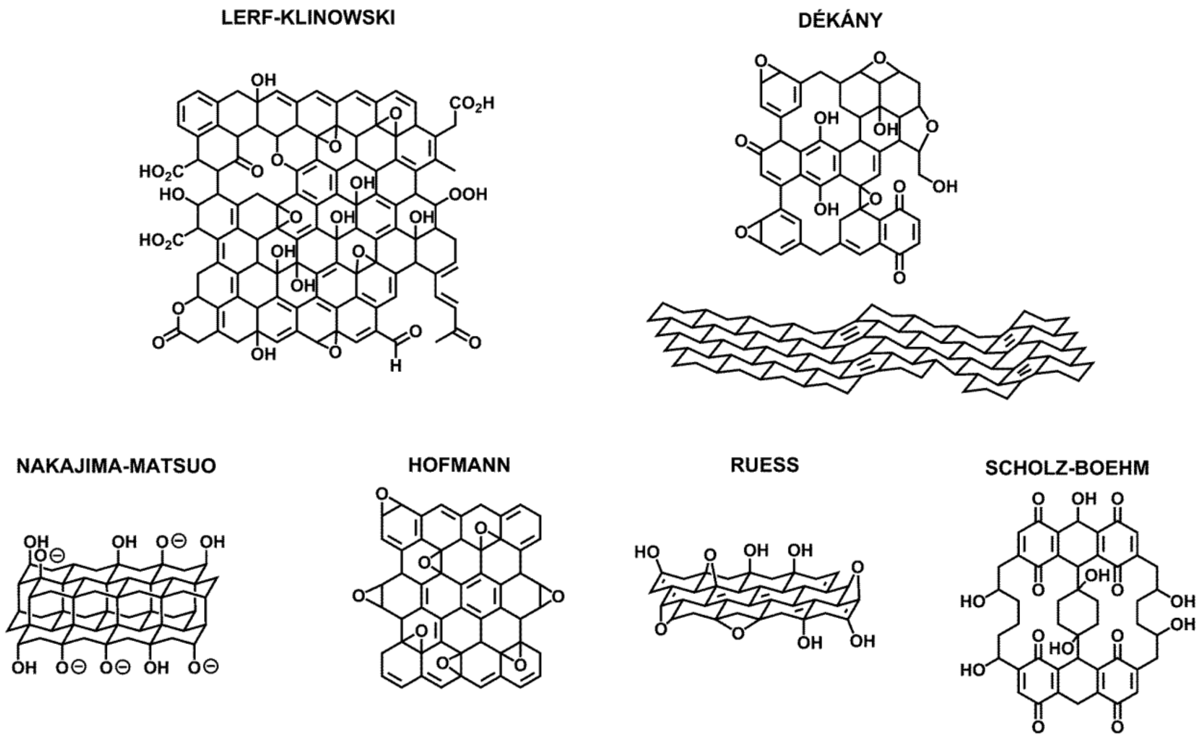

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Motivation and practical aspects of GO research

Localized reduction of GO is of particular interest from a nanoelectronics point of view - the potential to precisely engineer conductive and insulating regions.
To date GO nanopatterning has been archived by:

- laser beams
- focused ion beams
- electron beams
- scanning probe microscopy techniques
- (e.g. based on heated-tip. electrochemical. and catalytic lithography)

Swift heavy ions -> highly localized structural modification. i.e.. ‘tracks’.
We intended to employ this unique feature of SHI irradiation to create nanometer-sized deoxygenated regions in GO films:

- rGO spots as QDs
- rGO spots with damaged cores as coupled
- QD-antidot system

Properties

- inexpensive material, obtained by oxidation of graphite
- graphene sheets with covalently bonded oxygen-bearing groups
- epoxy and hydroxyl groups at the basal plane
- carbonyl, carboxylic acid, and lactol groups at the edges
- typical composition of fully oxidized graphene $C_6H_2O_3$. C:O 2:1
- no longer flat (sp^2 -> sp^3)
- higher interlayer distance ~ 9-10 Å
- easy exfoliation
- can be easily dispersed in water and polar solvents
- dielectric (band gap ~ 3.5 eV)
- can be easily reduced. sp^3-> sp^2

GO samples

Samples were synthesized from expandable graphite by the Hummers method (oxidation with conc. sulphuric acid, potassium permanganate, and sodium nitrate), then extensively washed to remove inorganic contaminants and centrifuged to separate residual graphite particles.

GO thin films prepared by drop-casting the GO suspension onto freshly cleaned HF-etched Si wafers.

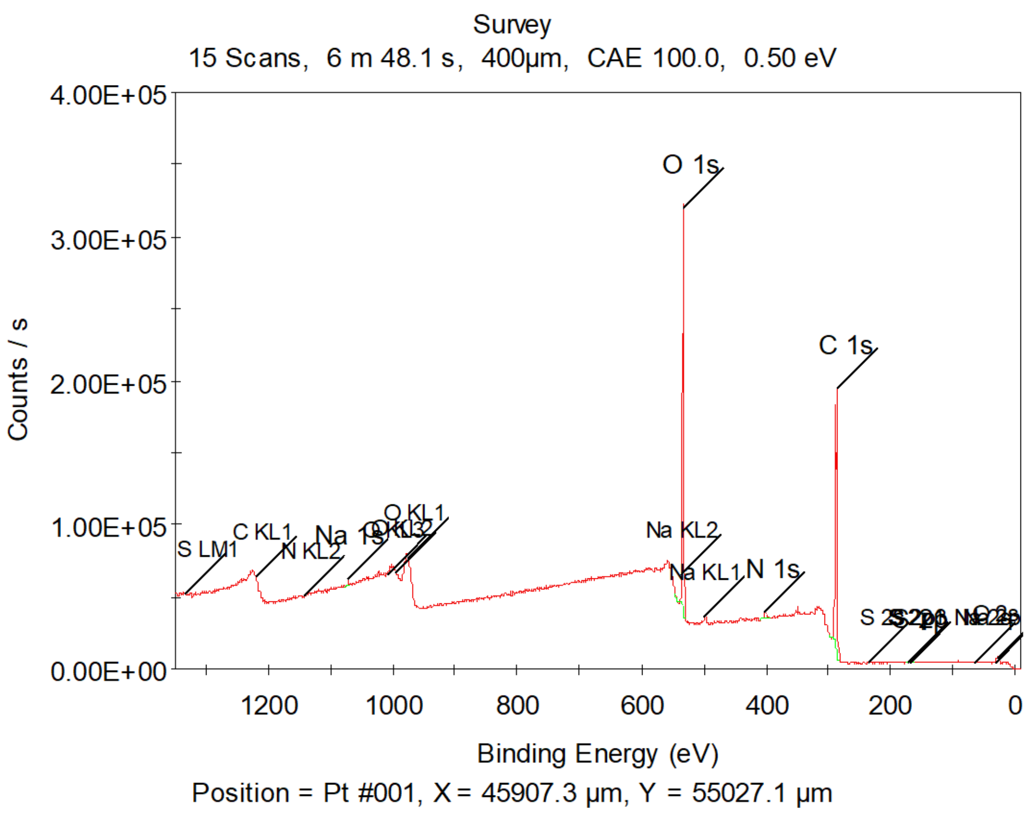
The films were irradiated with 61 MeV V ions at the IC-100 cyclotron. The ion fluences were $2 \bullet 10^{11}$, $6 \bullet 10^{11}$, $6 \bullet 10^{12}$, and $2 \bullet 10^{13}$ ions/cm^2

Raman spectra and AFM images were recorded for virgin and irradiated GO films.

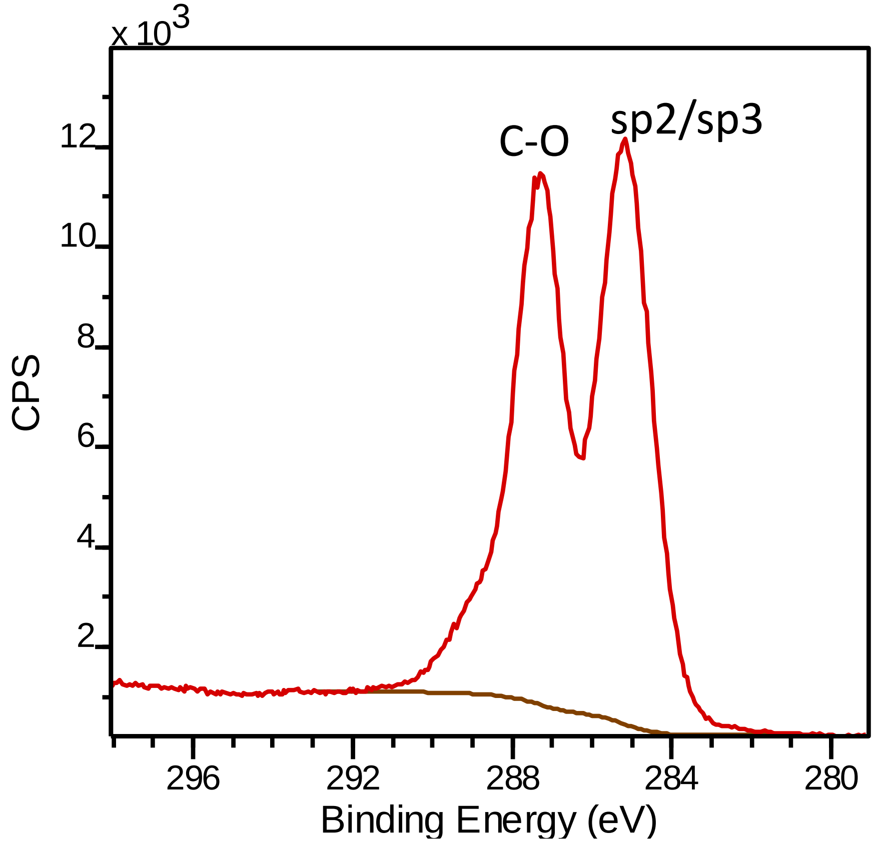
Elemental composition of GO films (XPS)

- X-ray photoelectron spectroscopy (XPS)
- The oxidation degree of the prepared films lower (C/O ratio of 2.5) than that of fully oxidized GO (C/O = 2)
- Trace level of inorganic contaminants mainly: Na, S, and Ca
- C1s core level spectrum – dominant component due to epoxide and hydroxyl groups (oxygen single bonded to carbon)

Elemental composition of GO films (XPS)



Survey spectrum of GO film



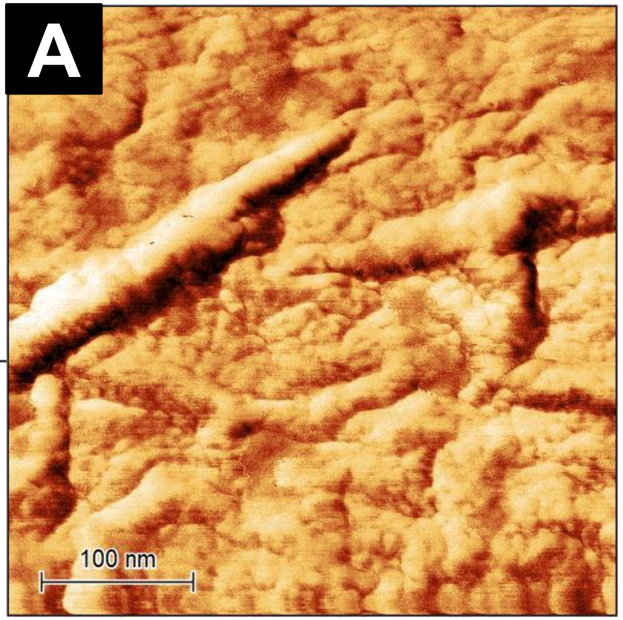
C1s core level spectrum

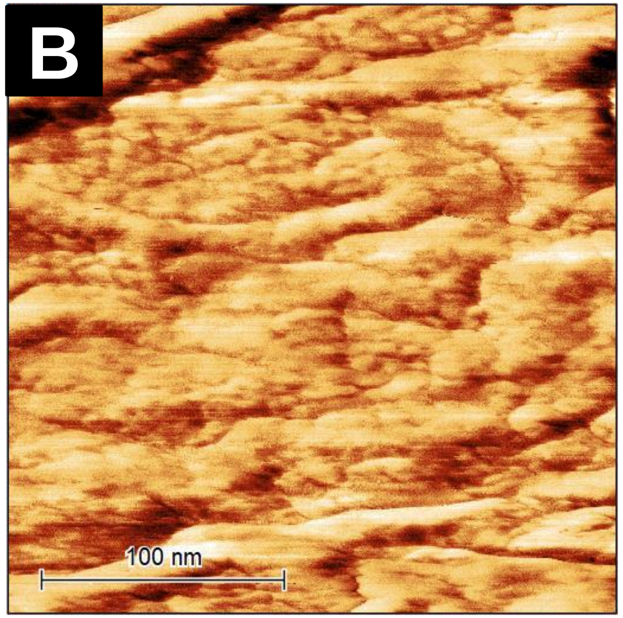
Surface morphology of GO (AFM)

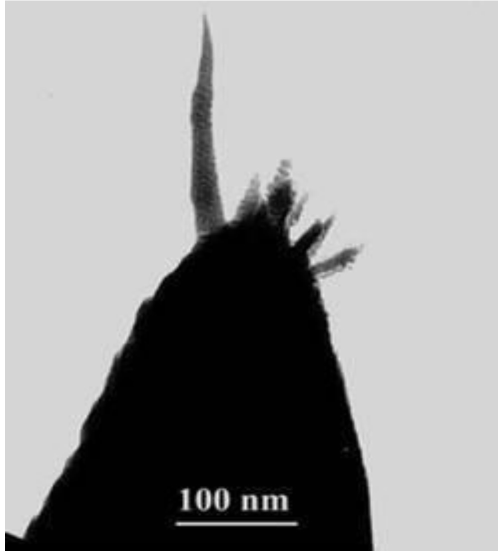
Atomic force microscopy (AFM)

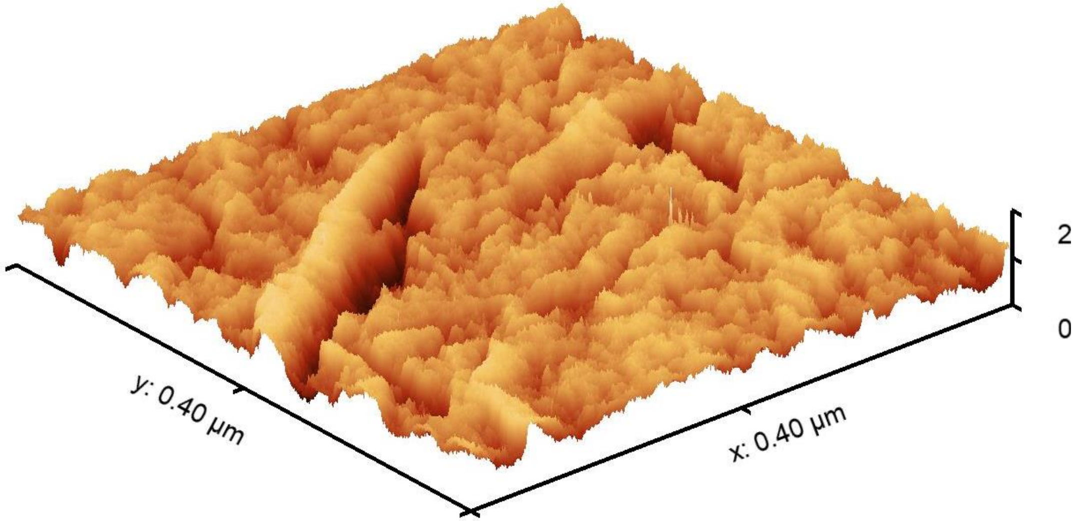
Imaging mode: tapping mode with a NSG01_DLC tip (diamond like carbon nanostructure, tip radius ~ 2 nm)

Image size: 250 ×250 and 400 × 400 nm^2

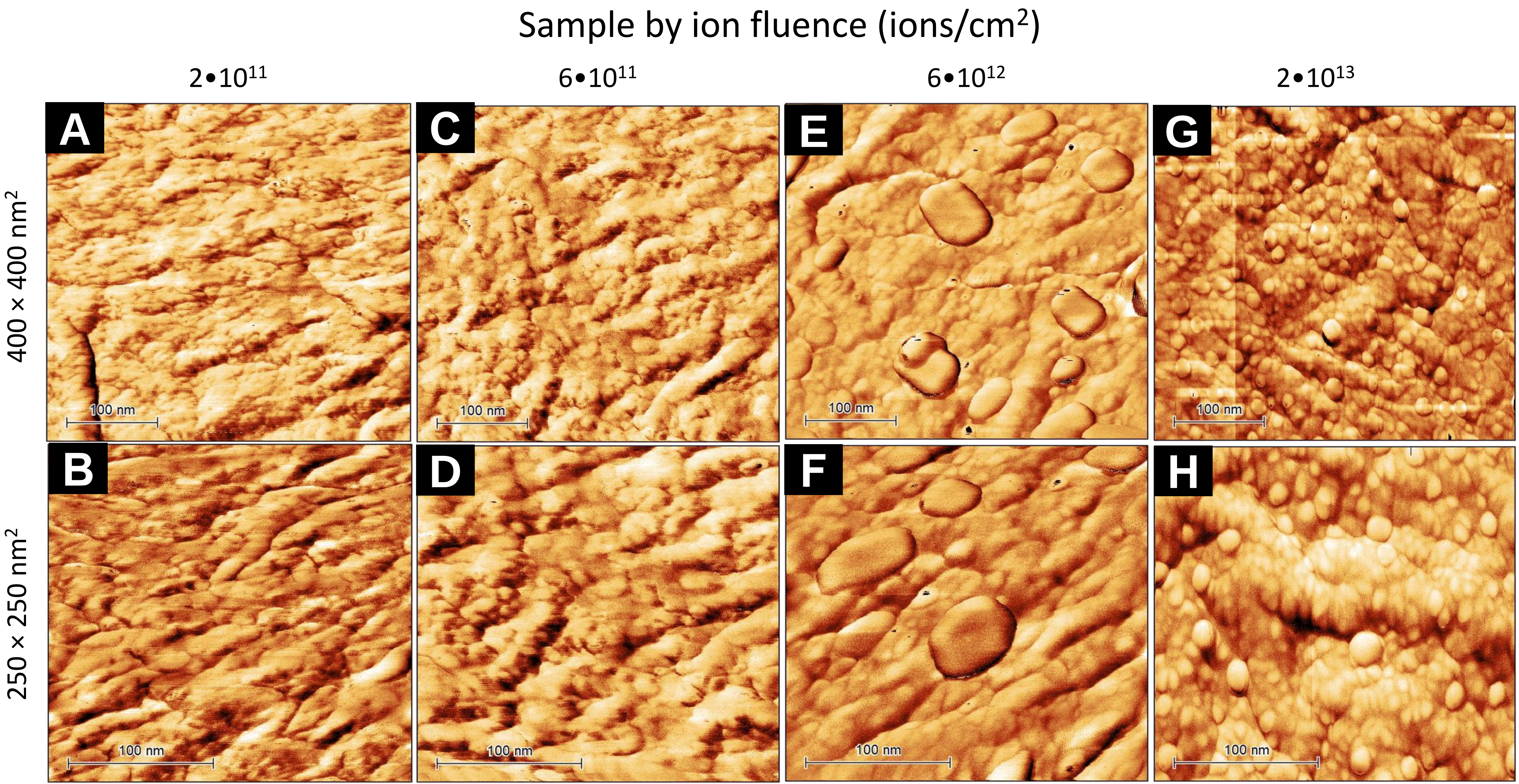




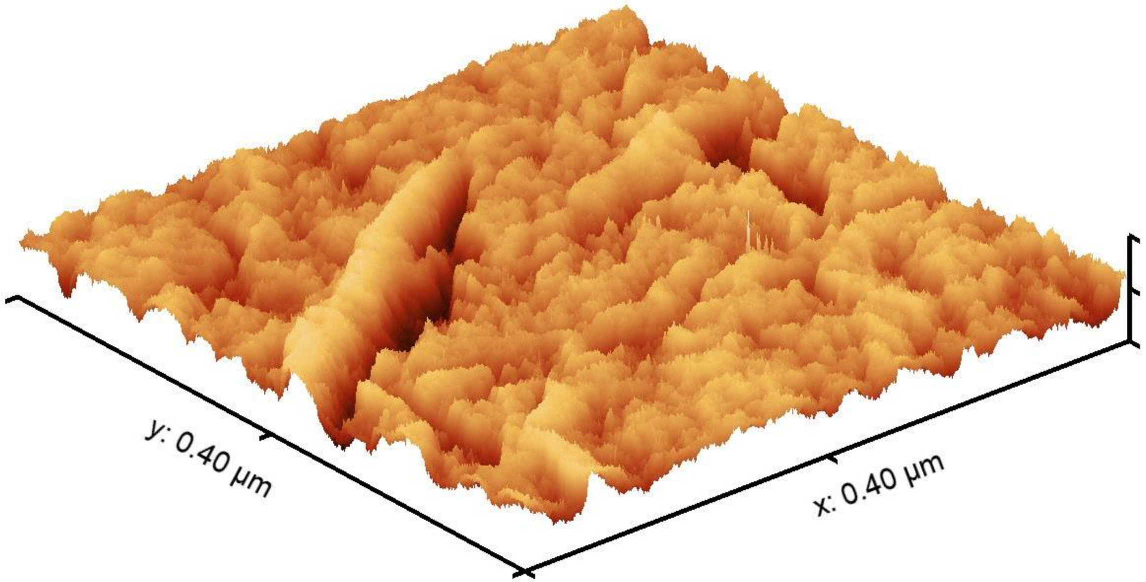


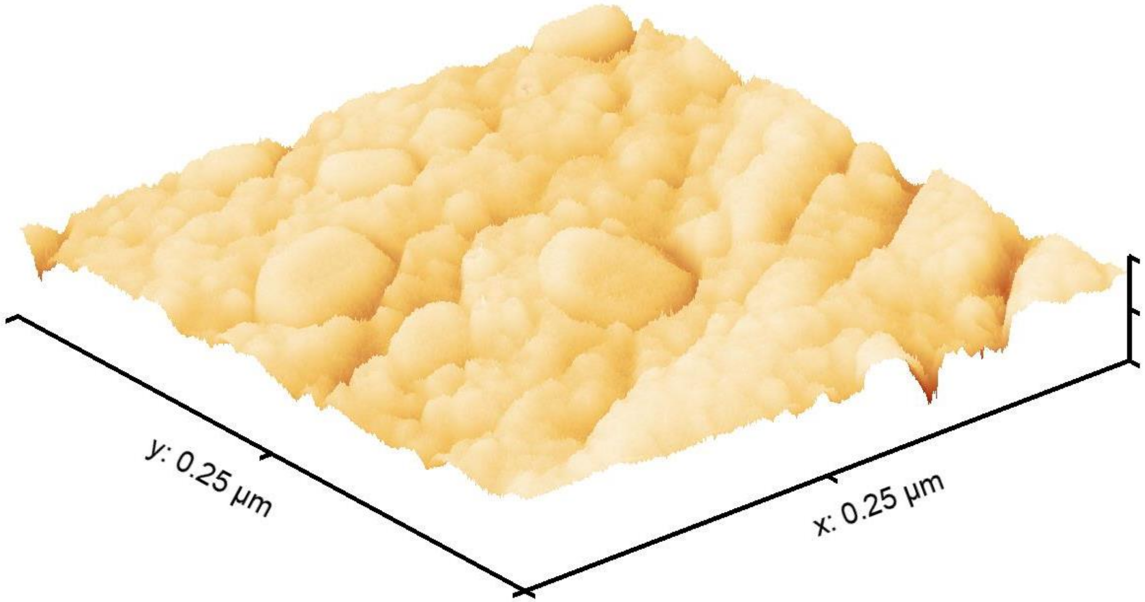


Surface morphology of GO (AFM)



Surface morphology of GO (AFM)

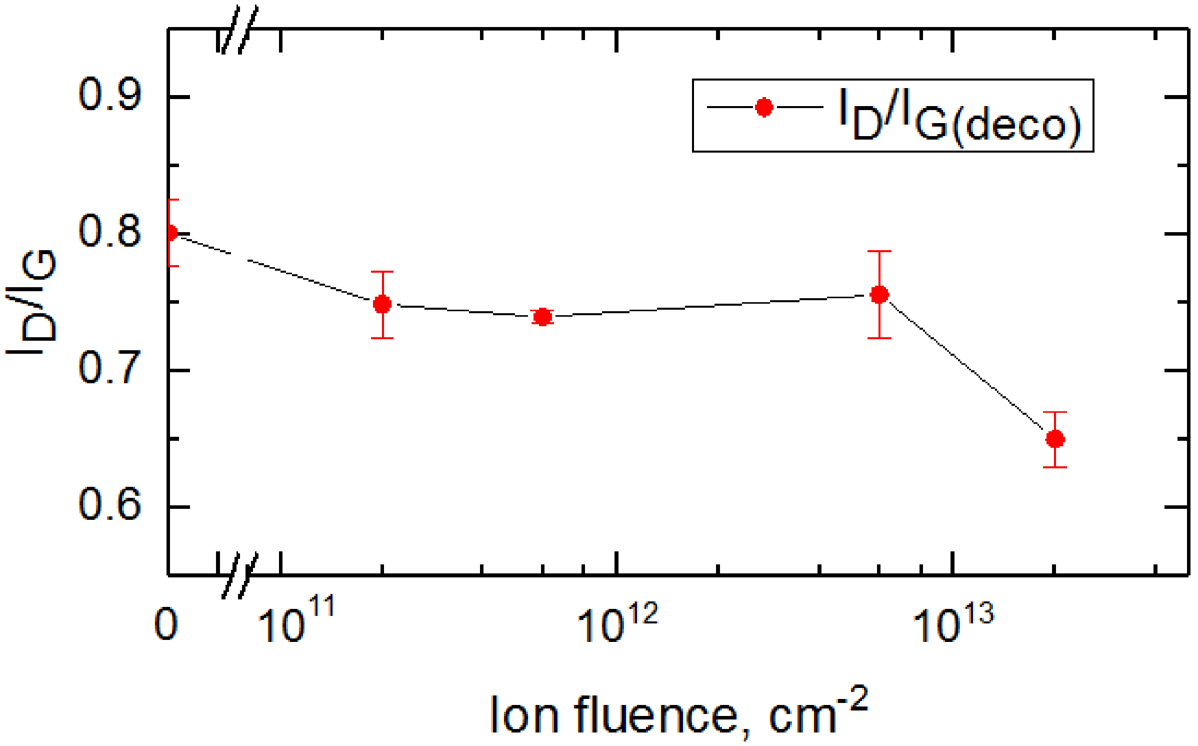


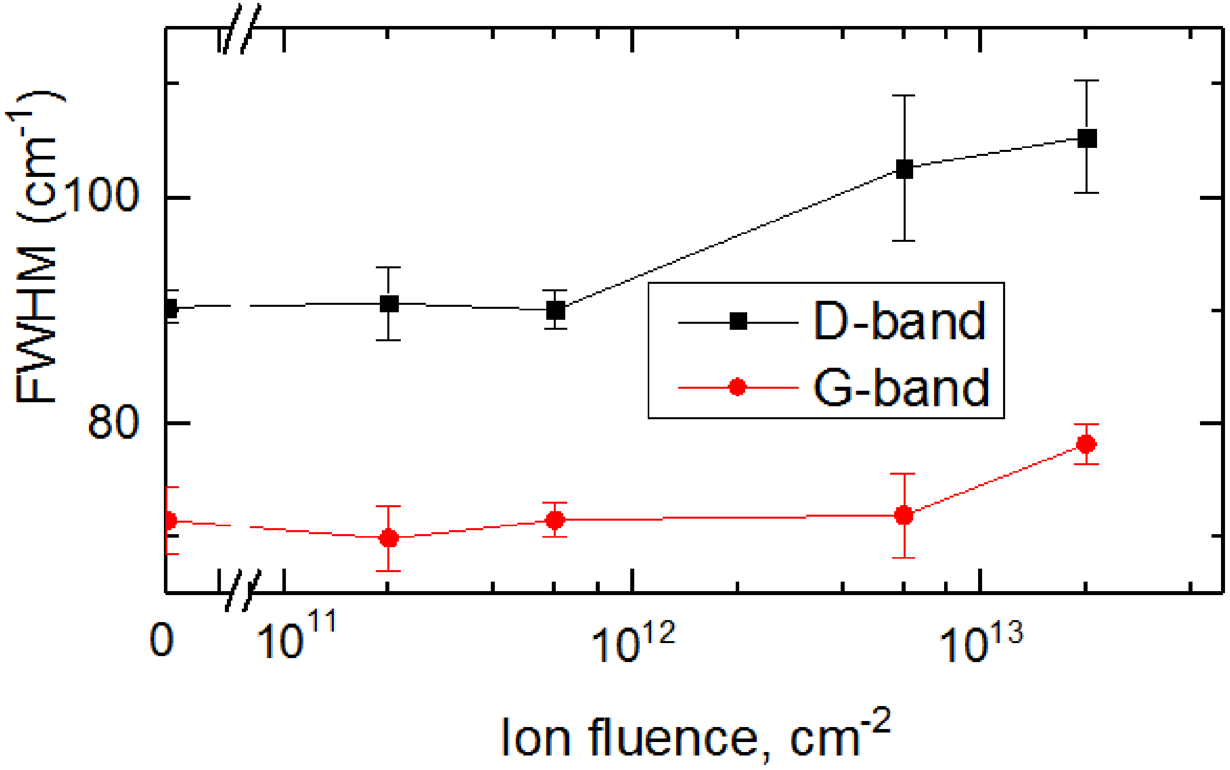


Surface morphology of GO (AFM) Average grain size

Sample by ion fluence (ions/cm^2)	Average grain size (nm)
Non irradiated	34.53
$2x10^{11}$	30.46
$6x10^{11}$	25.76
$6x10^{12}$	51.13
$2x10^{13}$	21.21

Raman experimental mesurements





Changes in disorder parameter and peak width for films irradiated with different doses of vanadium ions

Heavy-ion irradiation: ion ranges and energy losses simulation in SRIM

Ion	E (MeV)	S_e (keV/layer)	S_N (eV/layer)
Xe	167	5.76	26.6
Kr	167	3.80	12.0
V	**61**	**2.53**	**2.7**
Ar	46	1.88	4.7

Studied ions. their energies and corresponding stopping power values calculated per single layer of graphene sheet (SRIM-2013 code).
S_e threshold for damage creation : graphite 2.41 keV/layer
For suspended (free-standing) graphene 1.22-1.48 keV/layer

Conclusions

GC

- Good agreement between the experimental and calculated ion ranges and damage profiles
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GO

Significant surface morphology change upon ion-bombardment:

- unirradiated sample - wrinkled GO sheets, samples
- irradiated with low doses - roughness increases, possible formation of nanosized protrusions,
- samples irradiated with high doses – sheet structure is lost, formation of round-shaped nanoobjects

Small broadering of Raman specral features even at high doses (possible structural ordering at low doses?). Electronic stropping power is low and close to theshold value for defect creation in graphite.