Characterization of novel graphene-like materials prepared by new cheap and environmentally friendly synthetic methods

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Sigma-Aldrich standards vs. MUNI products

MUNI products :

1. GRAPHENE OXIDE – TYPE I- C_8O (GO-I)
2. GRAPHENE OXIDE – TYPE II - $C_{16}O$ (GO-II)
3. GO-I REDUCED BY HYDRAZINE - $C_{16}O$ (rGO-I.I)
4. GO-II REDUCED BY HYDRAZINE - $C_{21}O$ (rGO-II.I)
5. GO-I REDUCED BY ASCORBIC ACID - $C_{27}O$ (rGO-I.II)
6. GO-II REDUCED BY ASCORBIC ACID - $C_{21}O$ (rGO-II.II)

On the next slides – Masaryk university products (MUNI) are compared with graphenoids of the same type distributed by Sigma-Aldrich (SA) which were taken as standards for comparison.

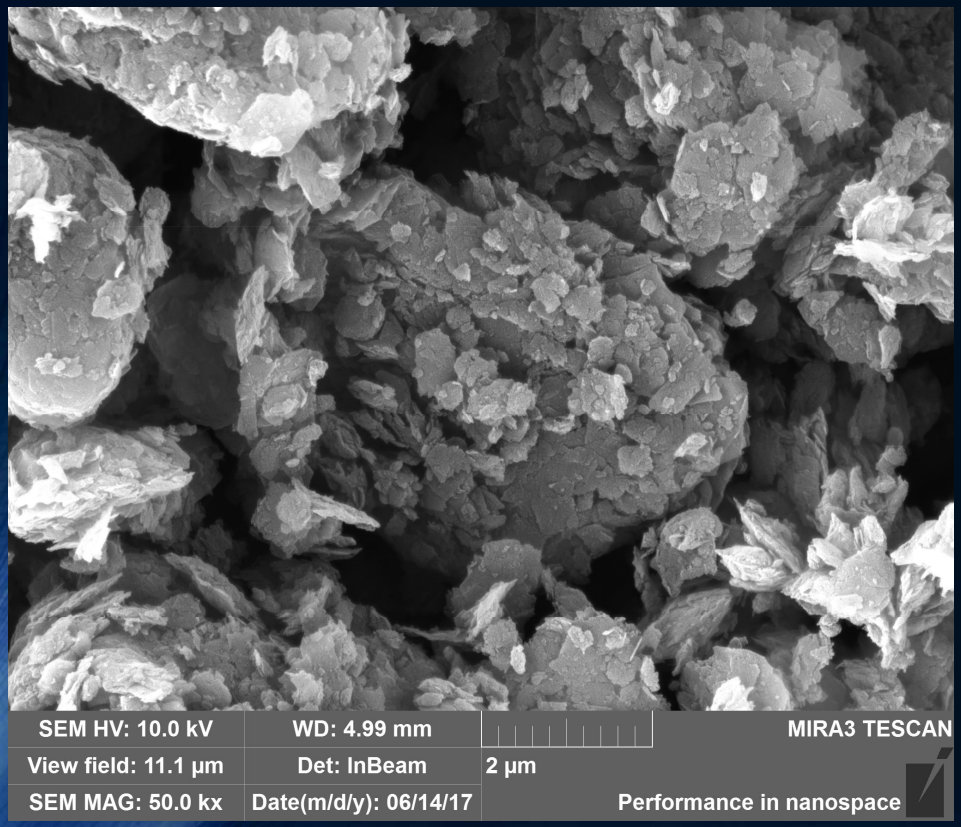
SIGMA-ALDRICH products:

GRAPHENE OXIDE, CAT. NO. 796034-1G - $C_{14}O$ (GO-SA)

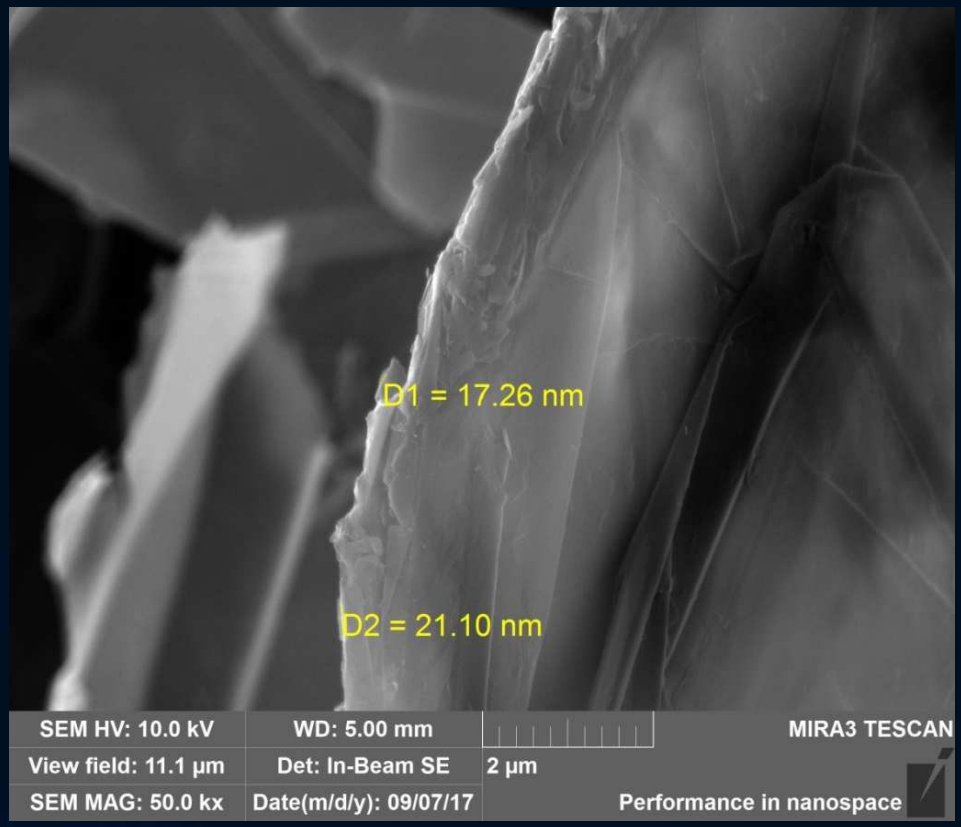
GRAPHENE OXIDE REDUCED BY HYDRAZINE, CAT. NO 805424-500MG - C_8O (rGO-SA)

SEM – *Scanning electron microscopy*

- Thickness and surface of graphitic plates, plate size homogeneity



GO-SA



GO-I

SEM – *Scanning electron microscopy*

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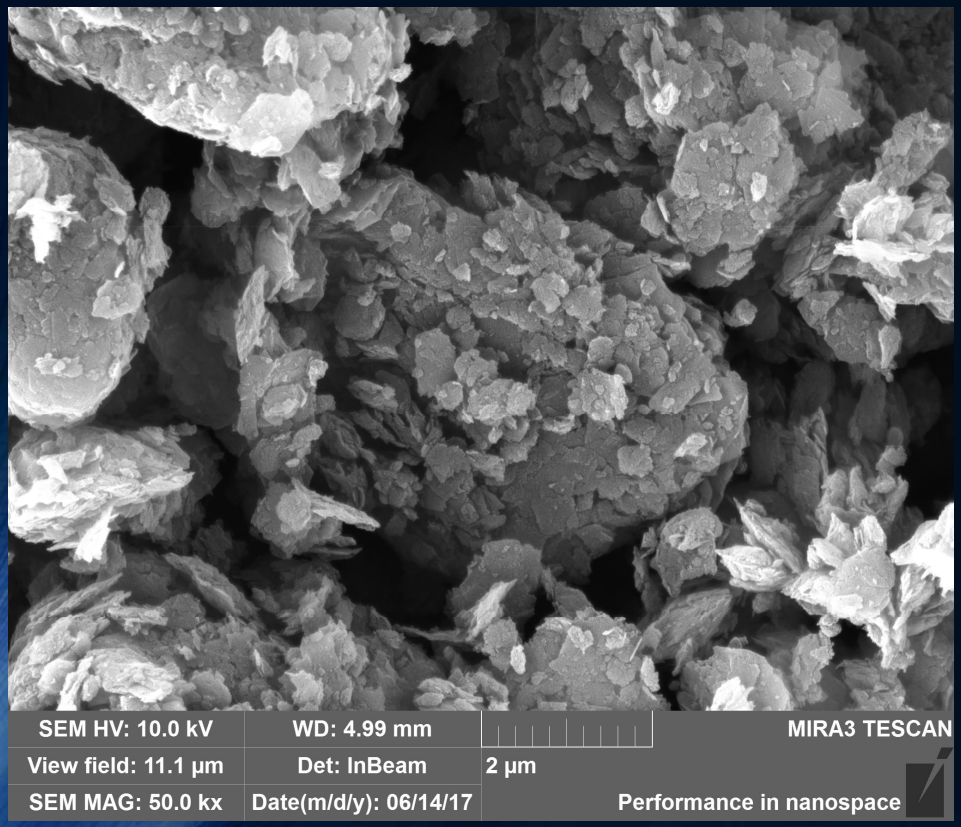

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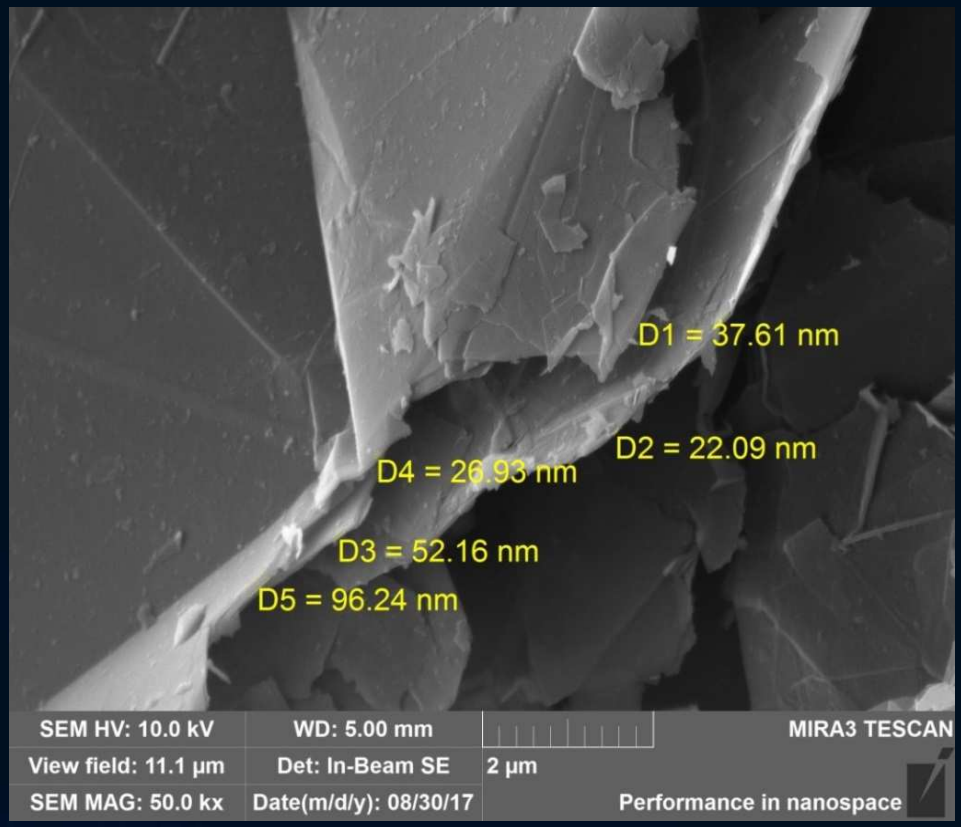

GO-II

SEM – *Scanning electron microscopy*

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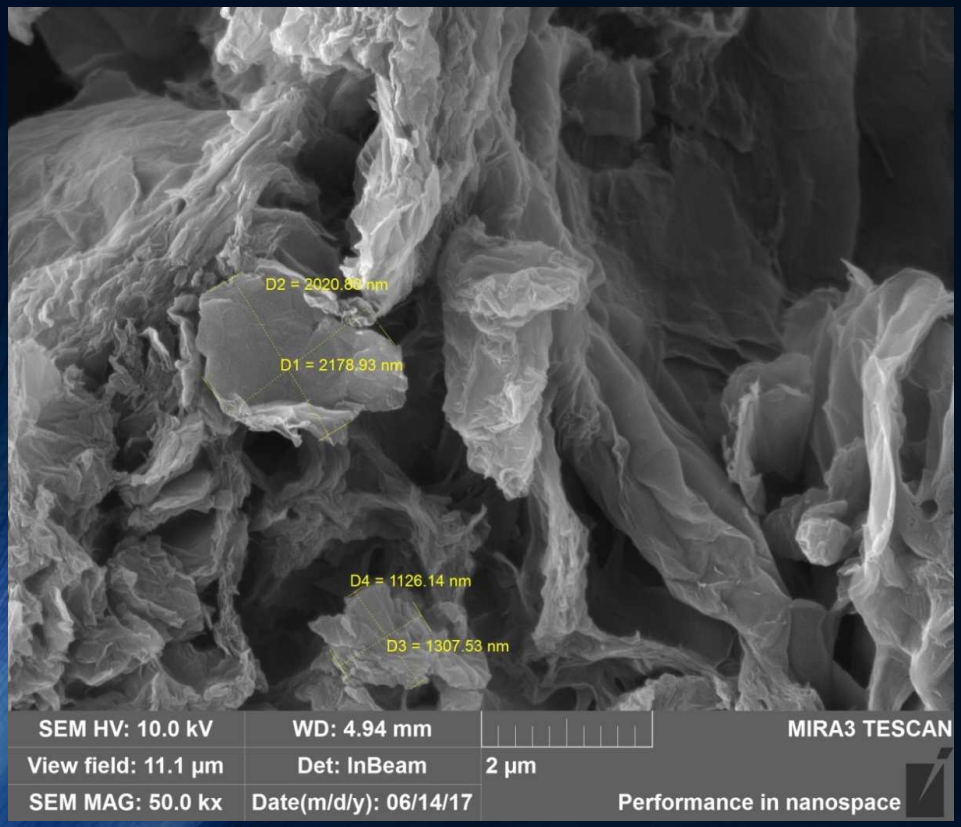
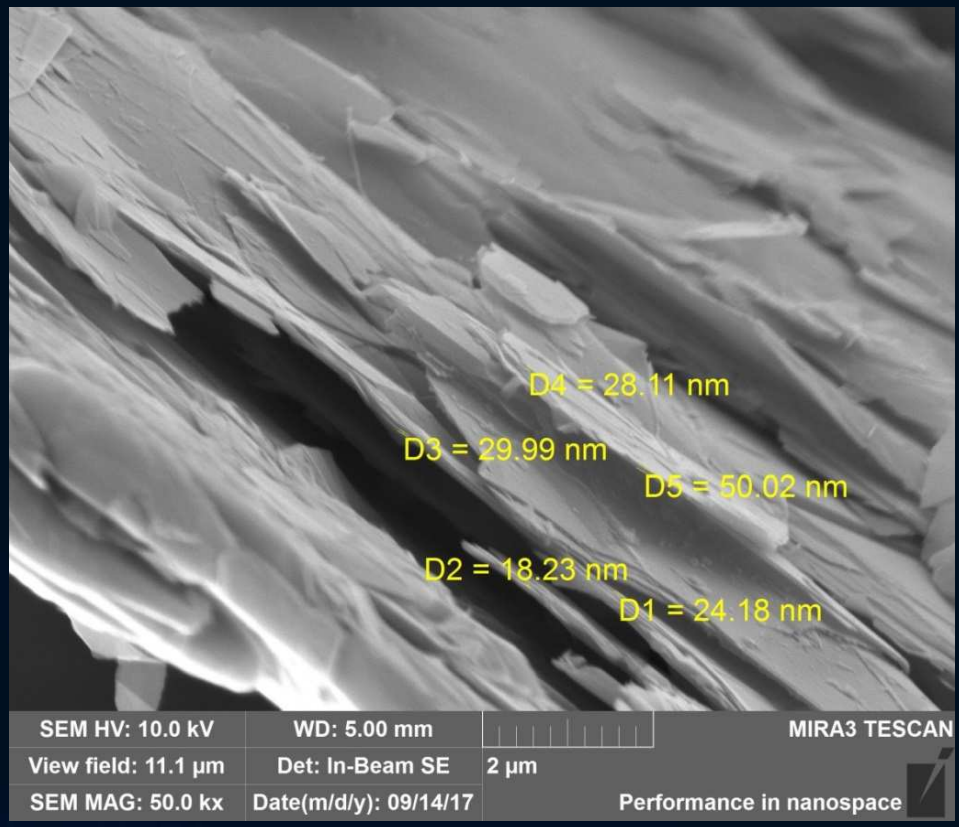


rGO-SA



rGO-I.I

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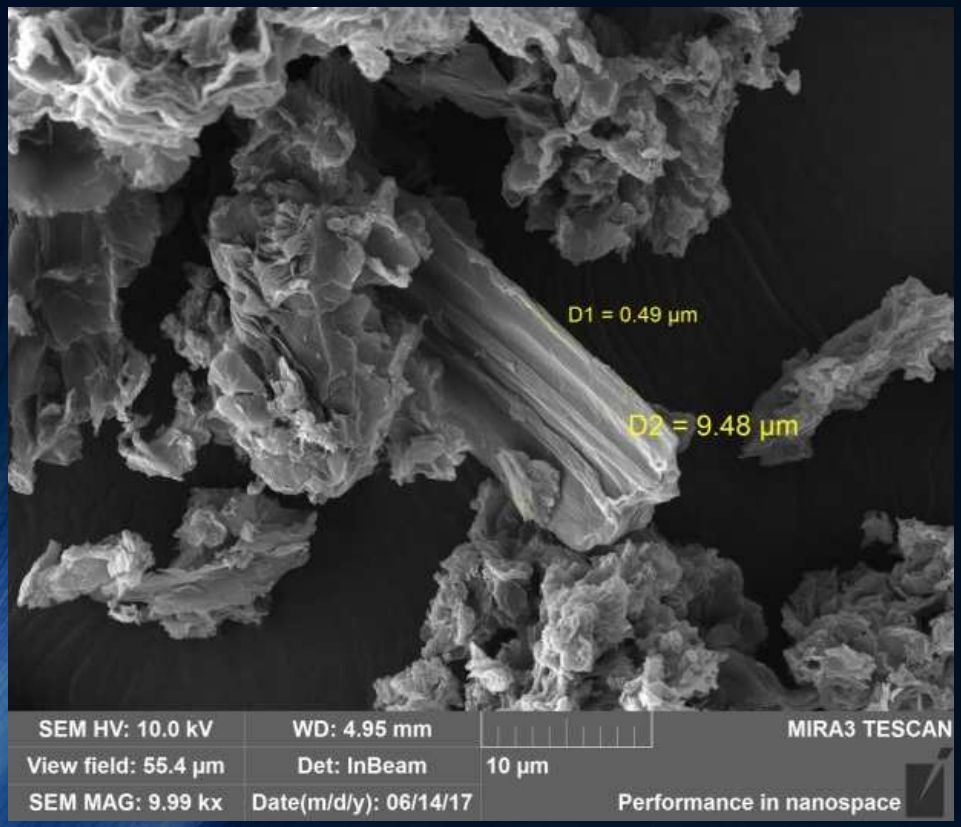
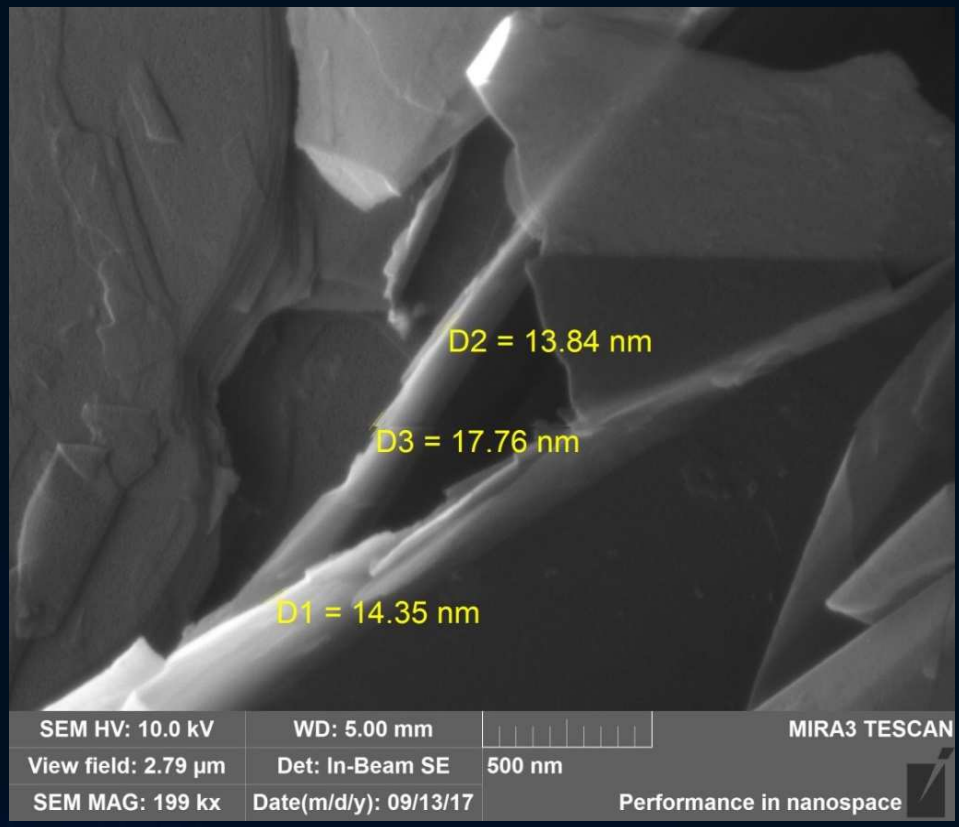


rGO-SA



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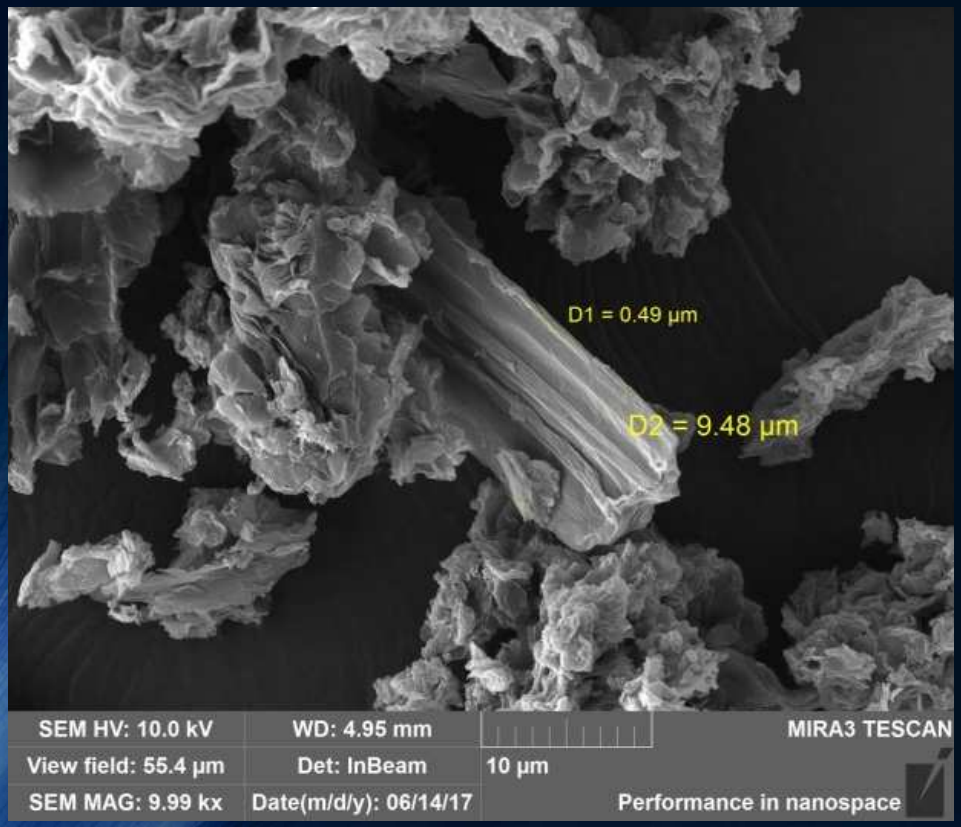
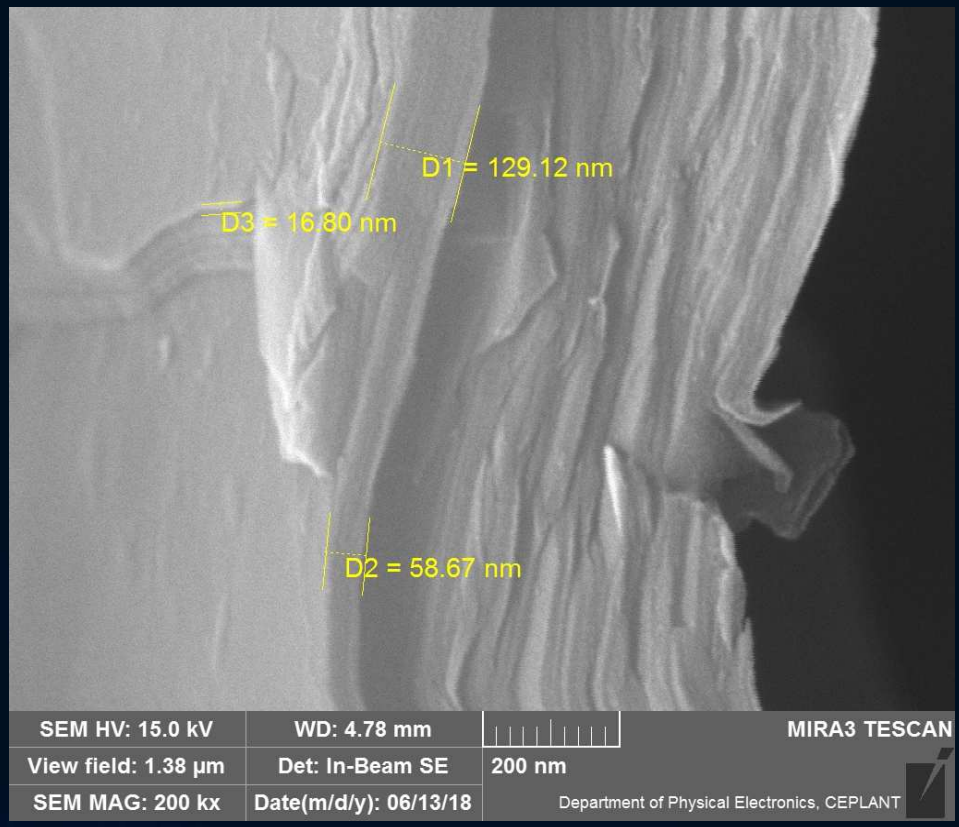


rGO-SA



rGO-I.II

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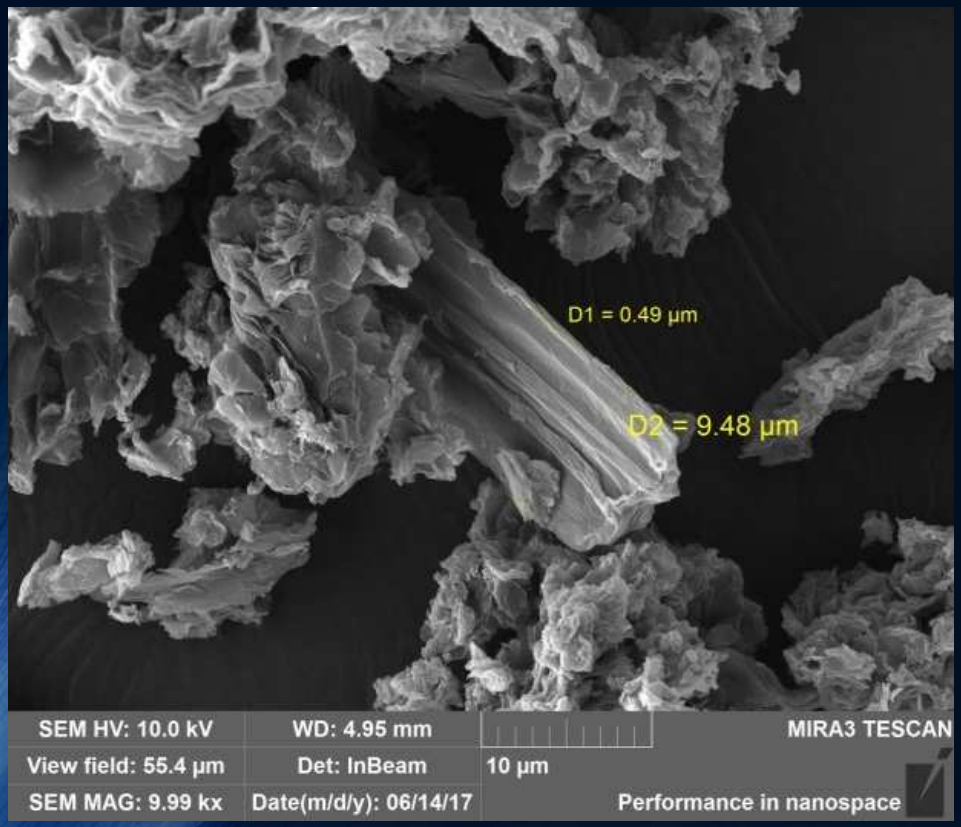
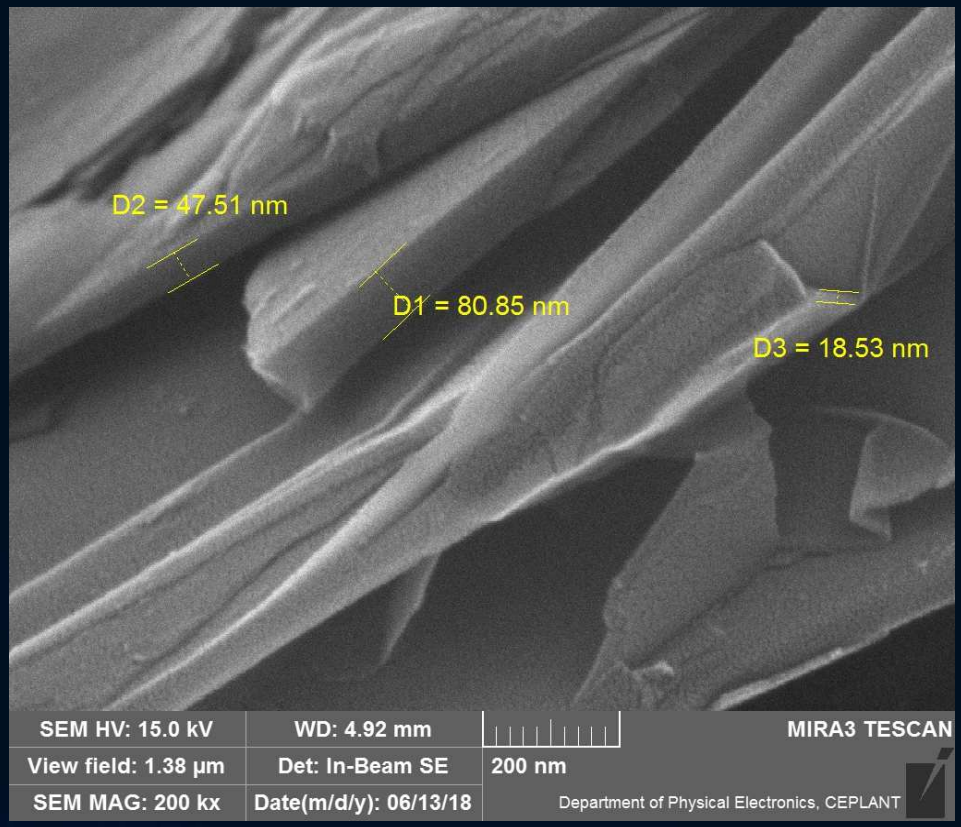


rGO-SA

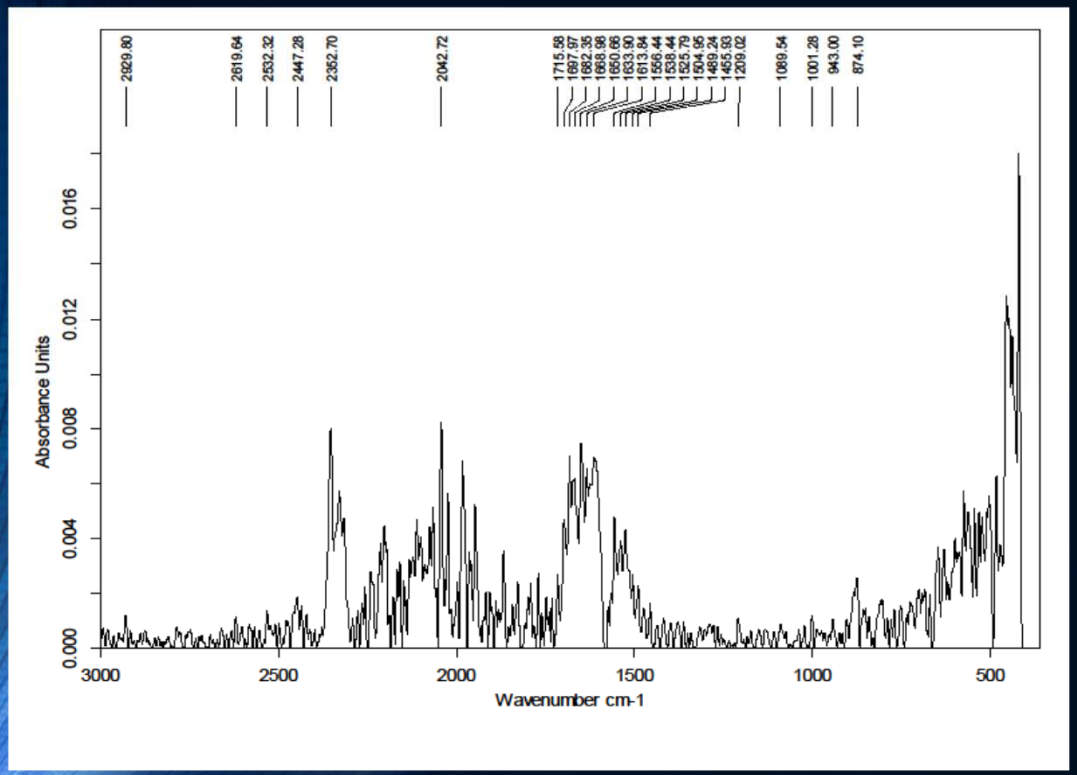


rGO-II.II

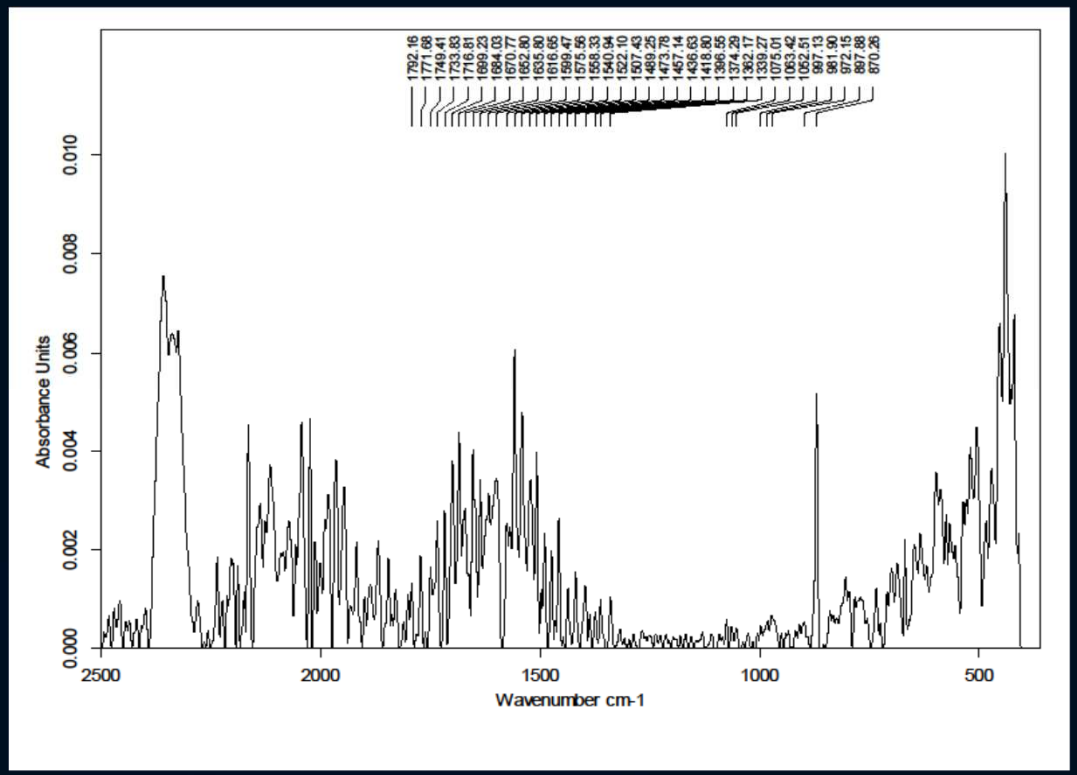
SEM – *scanning electron microscopy*

- **Damage** of graphitic plate core is significantly **lower** in case of all of the MUNI structures – electron delocalization in graphitic planes is preserved thus keeping unique features of graphene/graphite layers
- Graphitic plates of MUNI structures are also **larger in surface** (they can be easily milled in need of smaller particles) but have **similar or lower thickness** compared to SA standards
- 3D nano-structures were not observed in MUNI products and thus bringing **more safety** into graphenoids manipulation
- These advantages can be ascribed to an employment of **gentle oxidation techniques/ procedures**

FTIR spectroscopy - presence of polar functional groups, their abundance and characteristics (C=O, C-O, C(O)-O, C=C, ...)

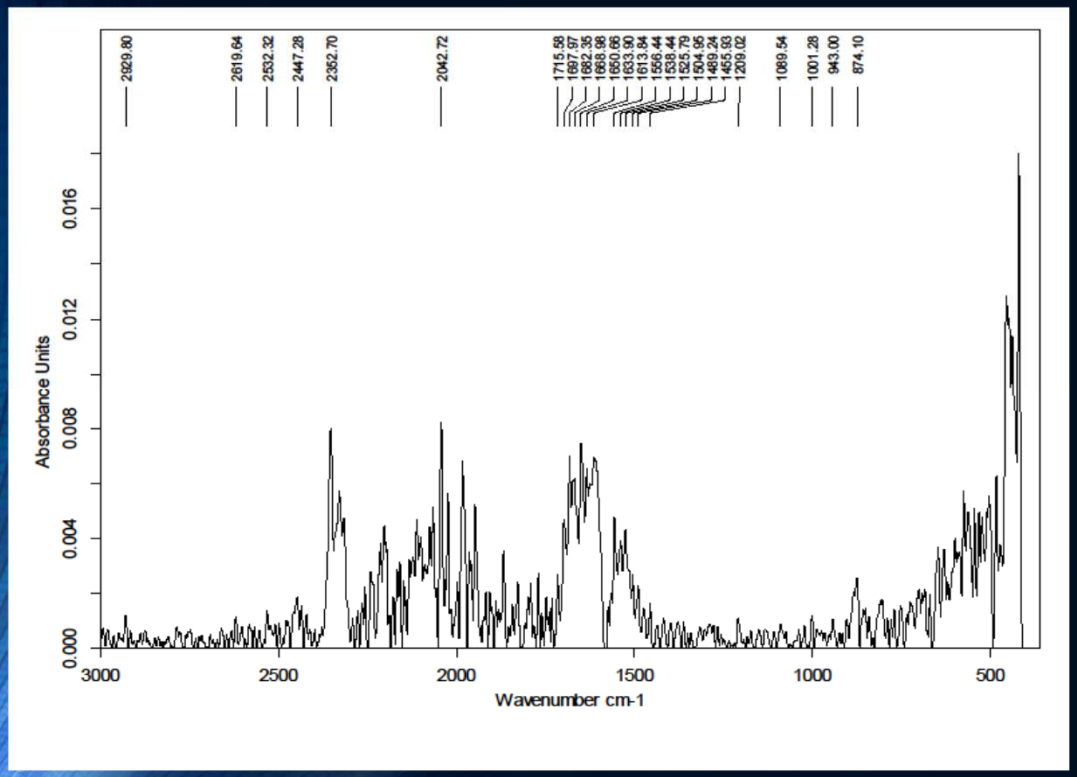


GO-SA



GO-I

FTIR spectroscopy - presence of polar functional groups, their abundance and characteristics (C=O, C-O, C(O)-O, C=C, ...)



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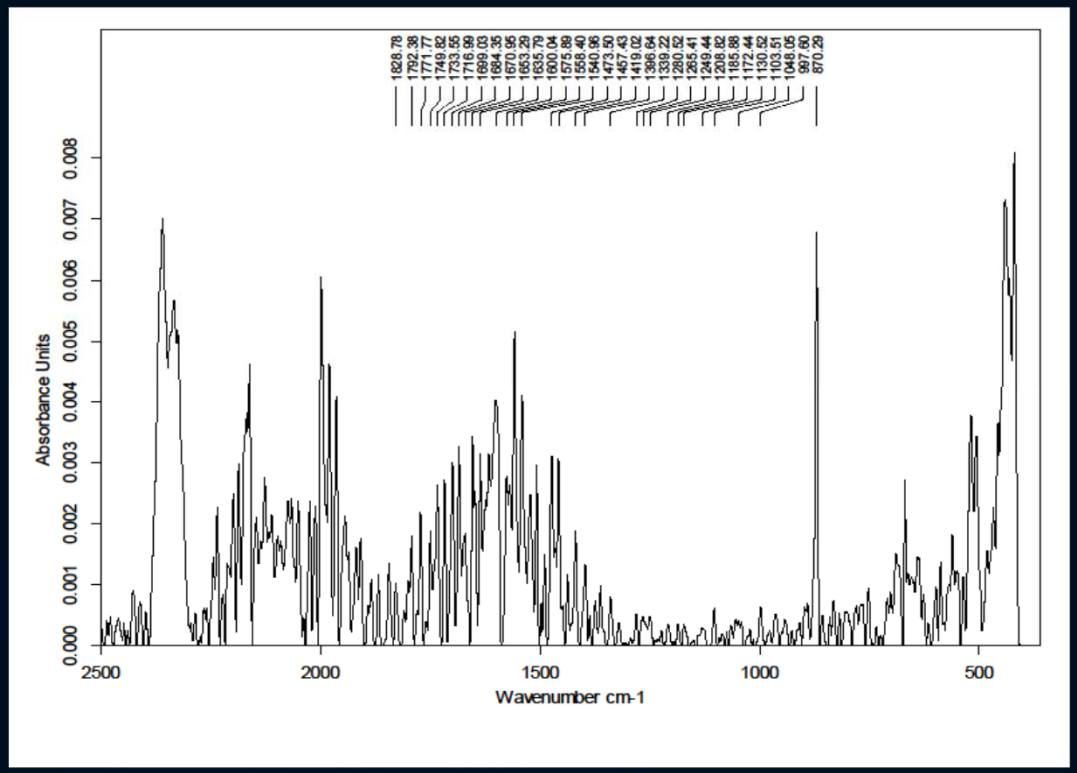

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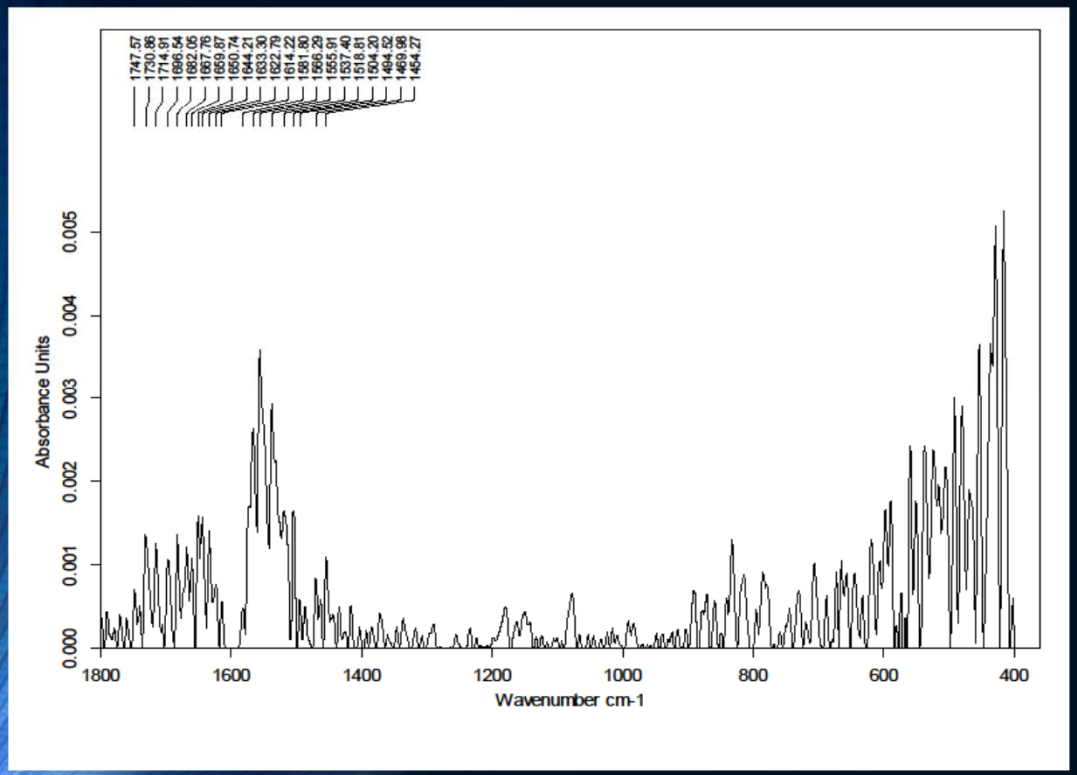
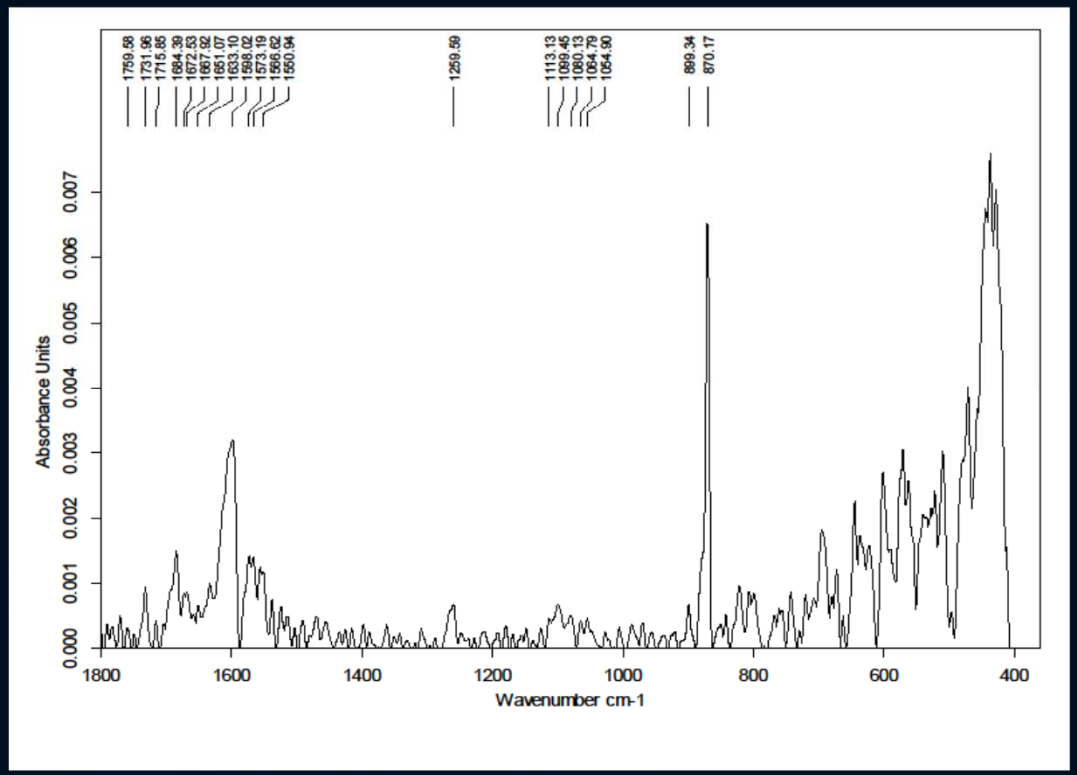


rGO-SA



rGO-I.I

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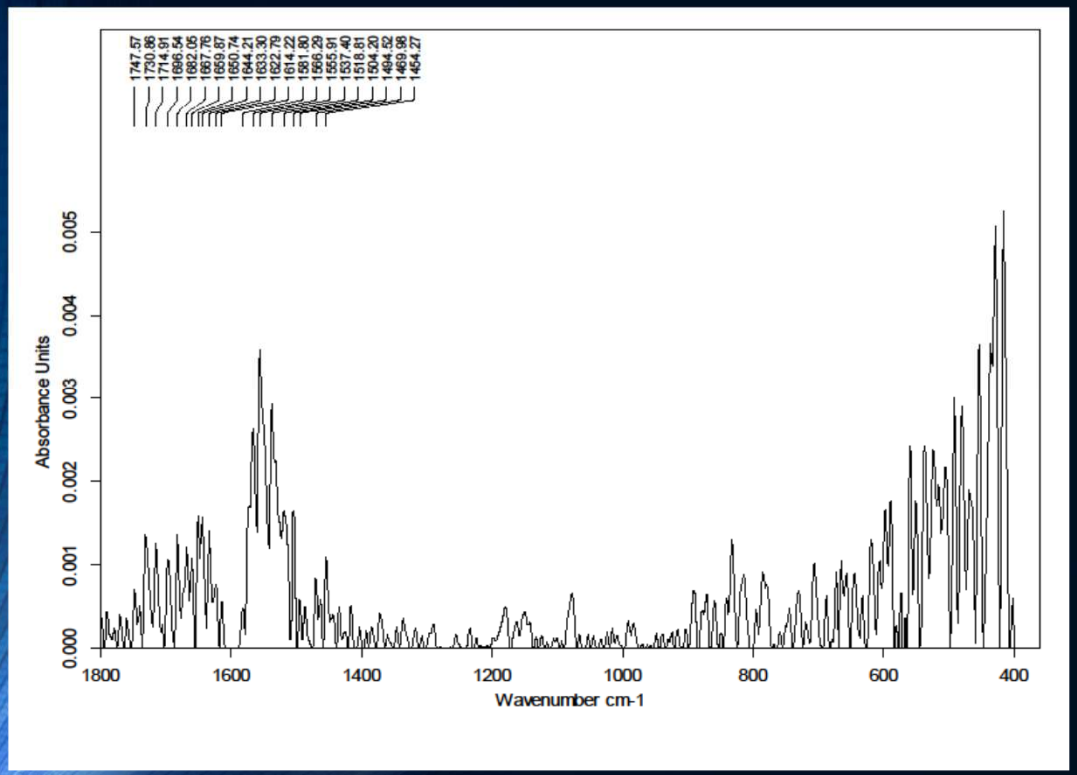
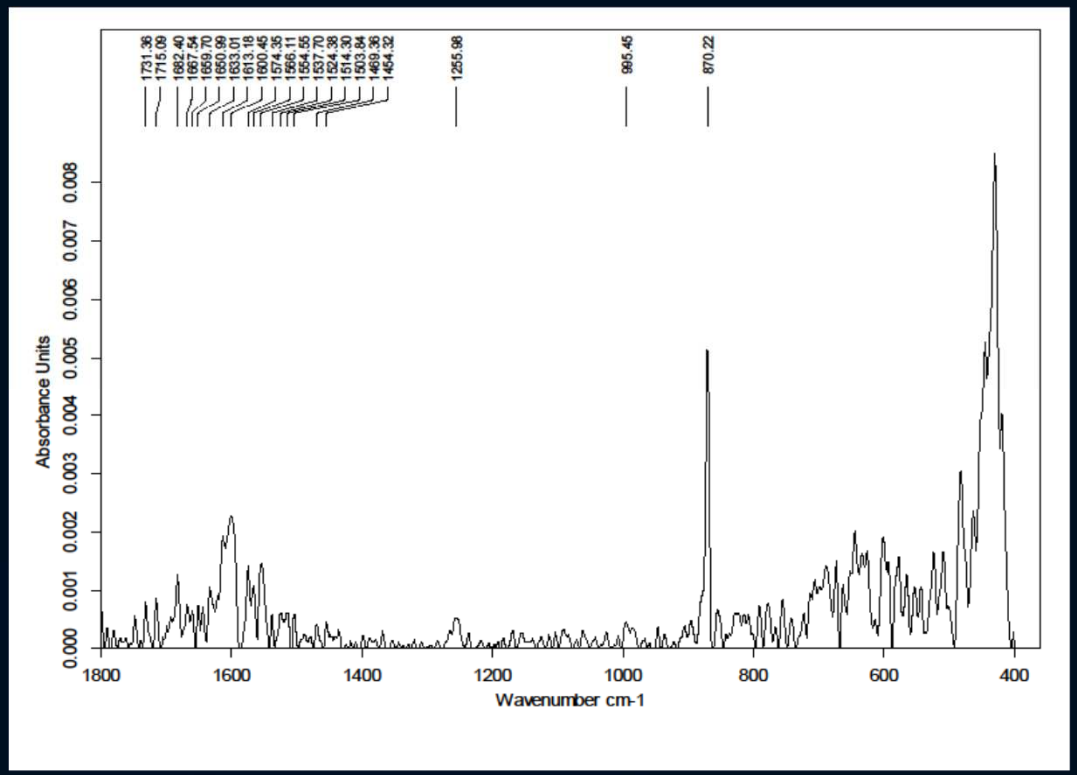


rGO-SA



rGO-II.I

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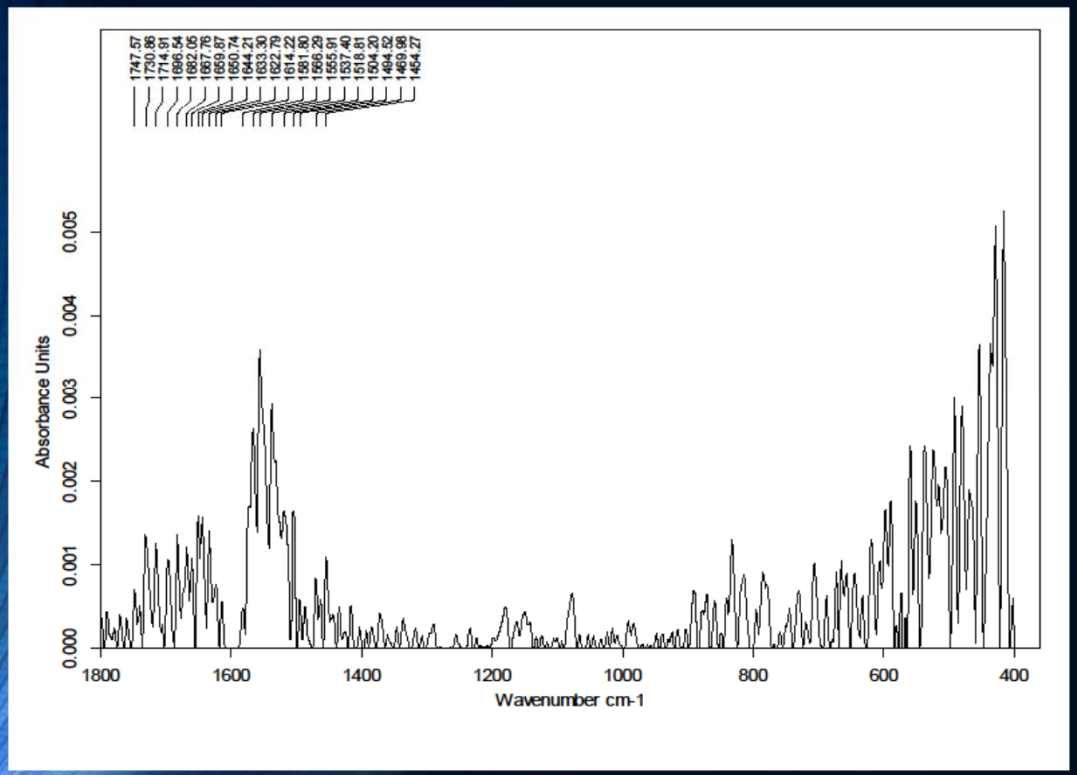
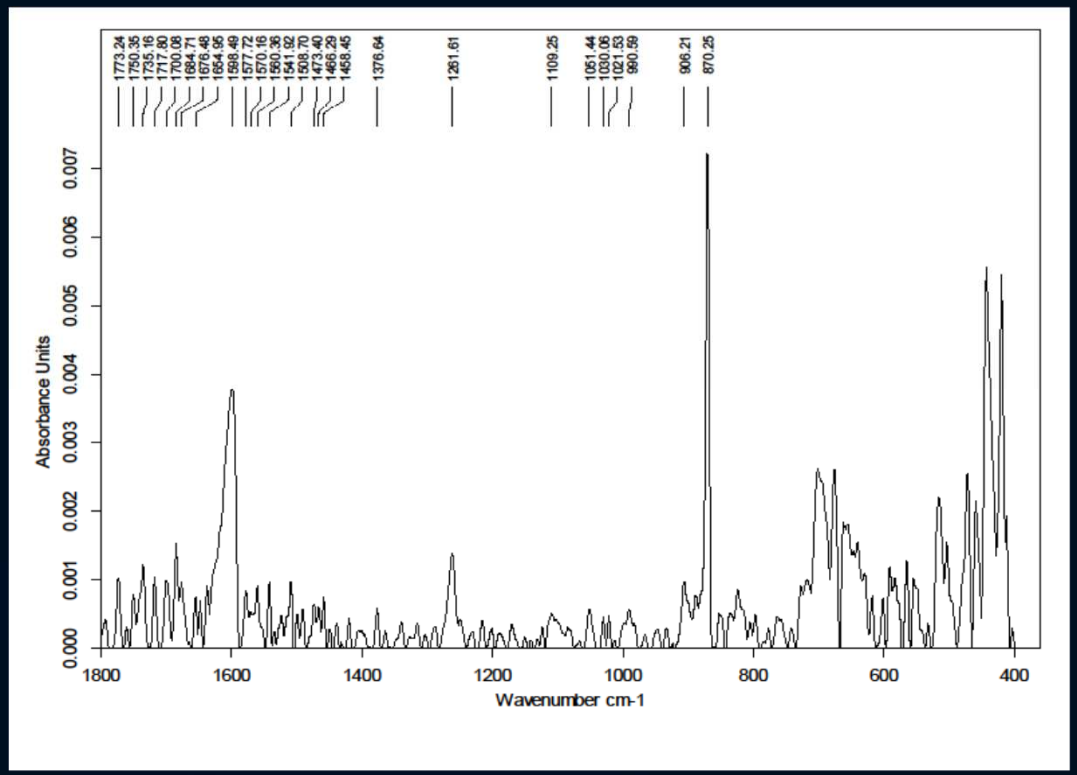


rGO-SA



rGO-I.II

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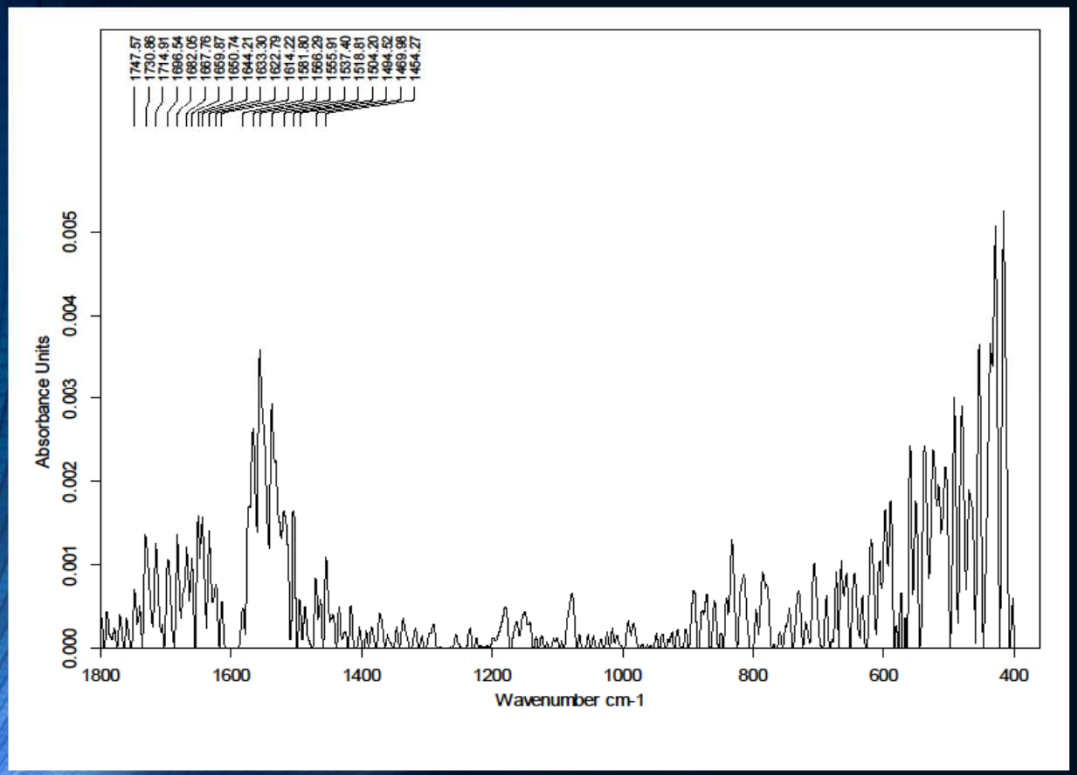
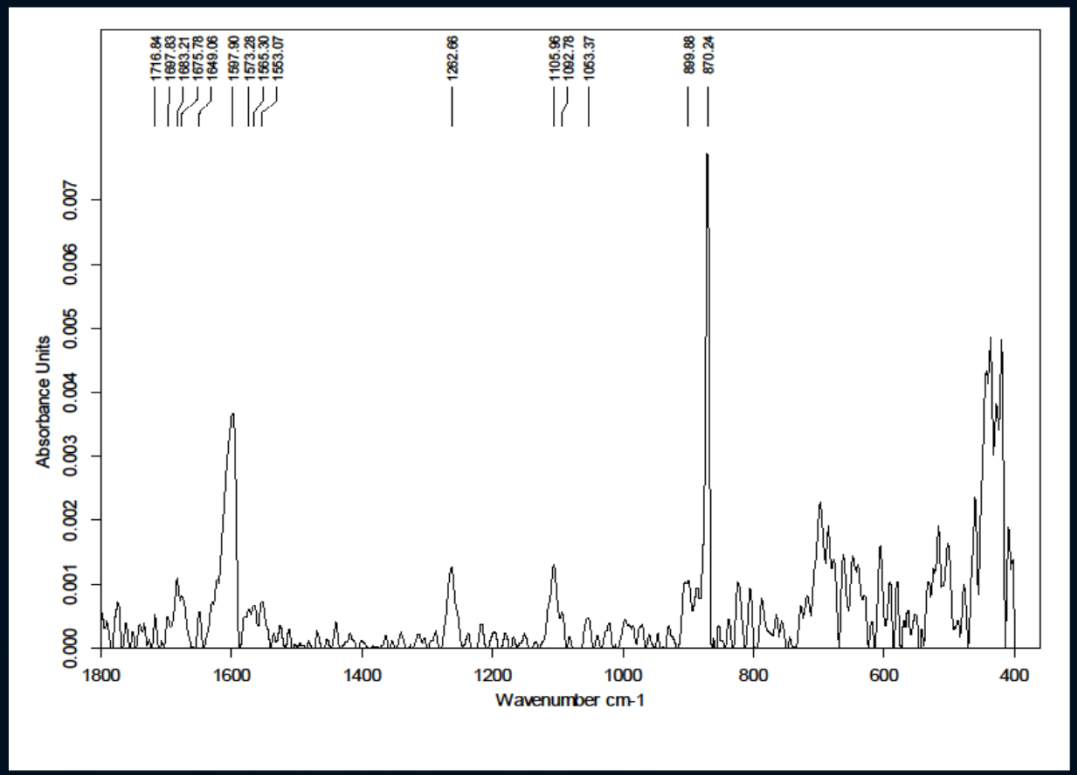


rGO-SA



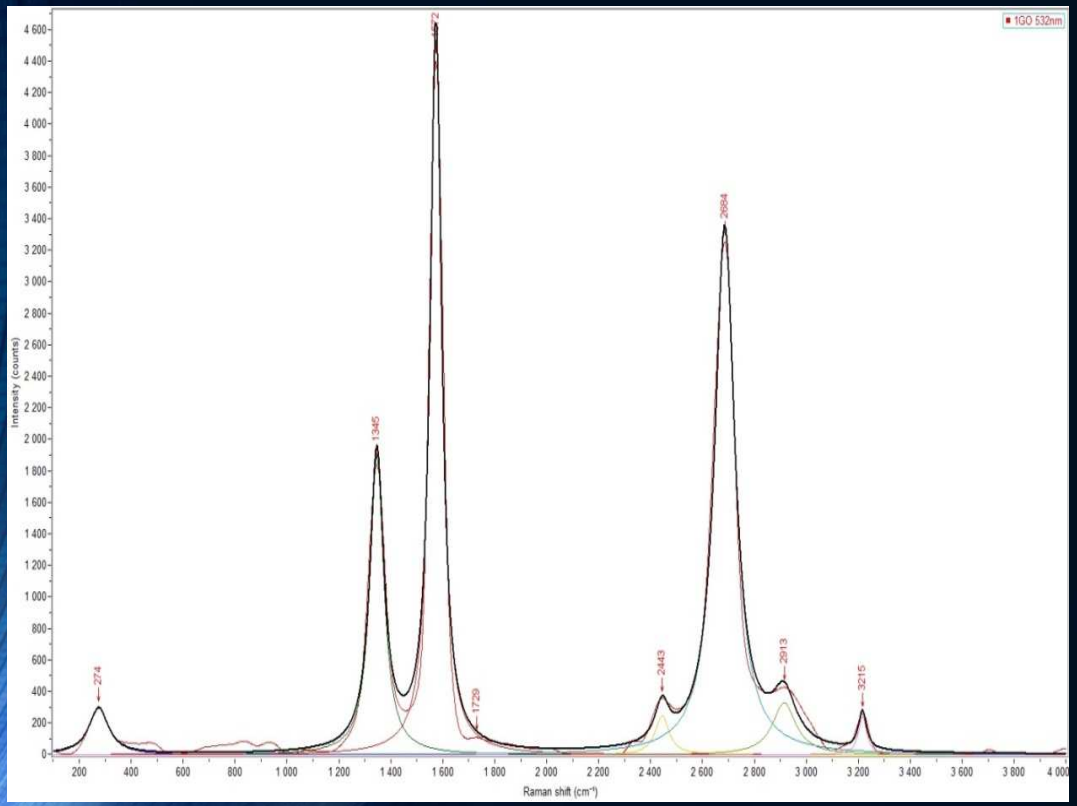
rGO-II.II

FTIR spectroscopy

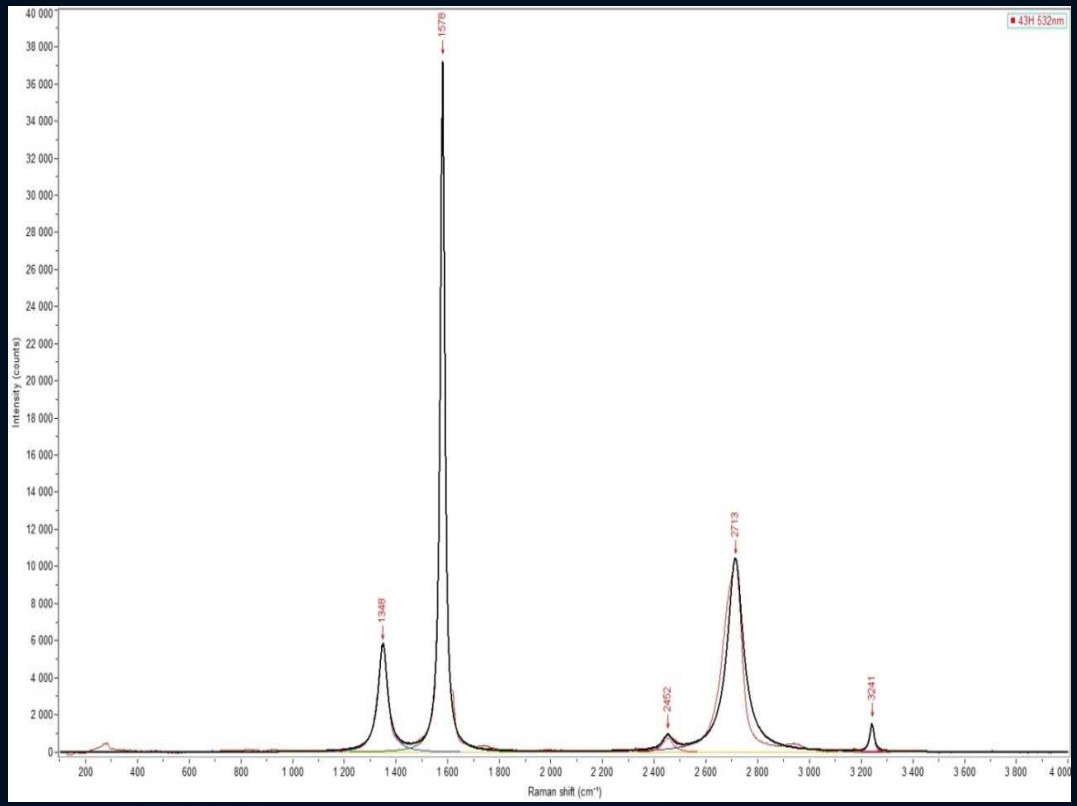
- FTIR spectra of **MUNI** and **SA GO compounds** are very similar, although suffering from low intensities
- Bands of **C=O stretching modes** (carbonyl and/or carboxyl groups) can be clearly seen in the region of ca 1610-1750 cm^{-1} – similar intesity indicates **similar level of oxidation** of all GO structures

- In case of **MUNI rGO structures** FTIR spectra more intense and clear – intense band at cca 1600 cm^{-1} (C=C bond) indicates **low damage of graphitic/graphene plates**
- Presence of **various C~O bonds** is confirmed by the bands at ca 1680 - 1730 cm^{-1} (C=O) and 1260 cm^{-1} and/or 1100 cm^{-1} (C-O)

Raman spectroscopy - presence of nonpolar functional groups, their abundance and characteristics (C=C, C-C, C-H…)



GO-SA



GO-I

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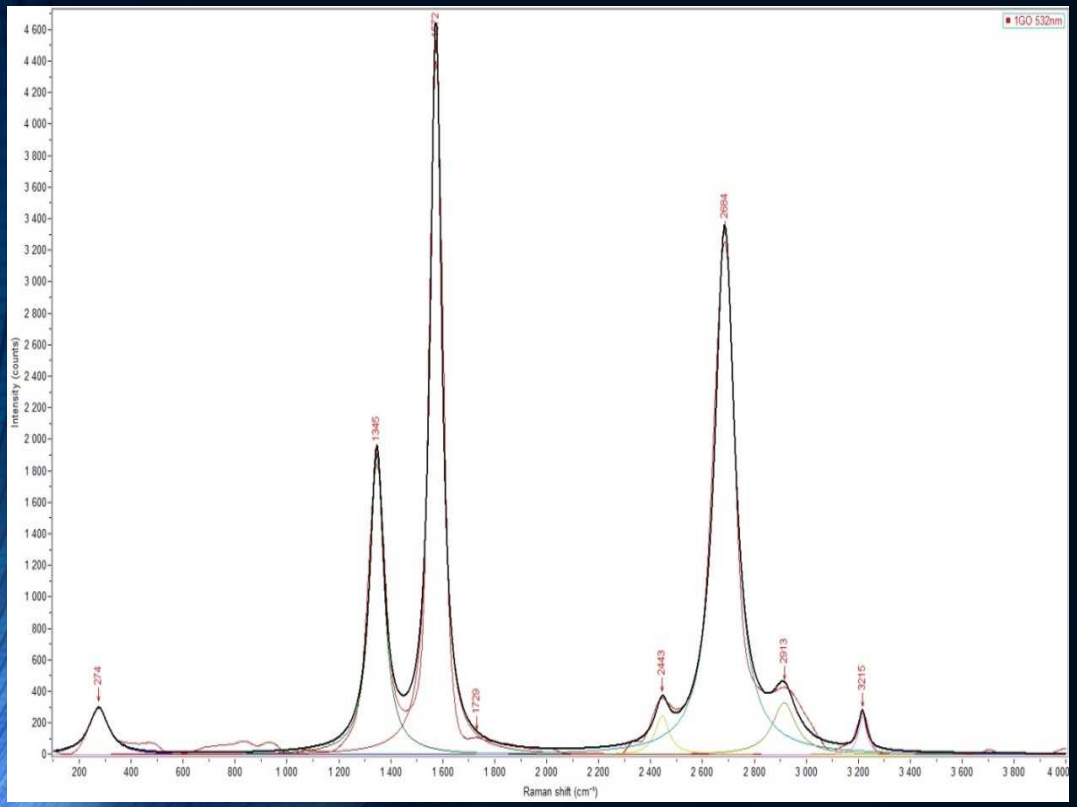
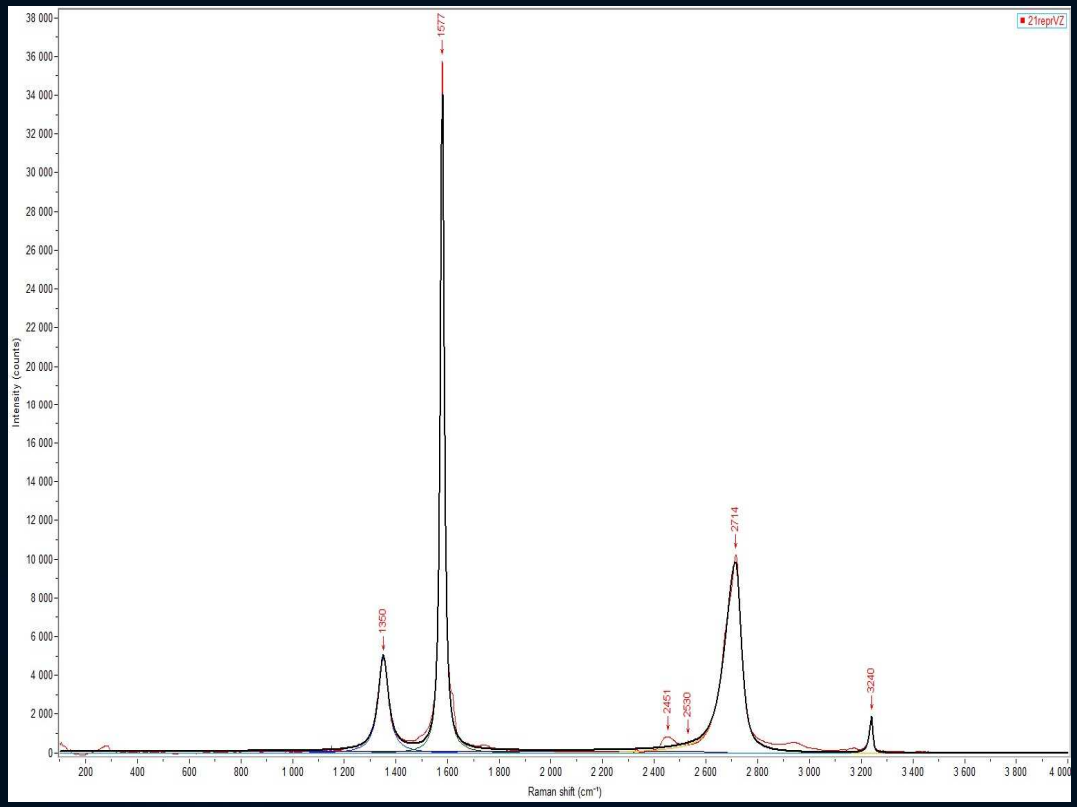


GO-SA



GO-II

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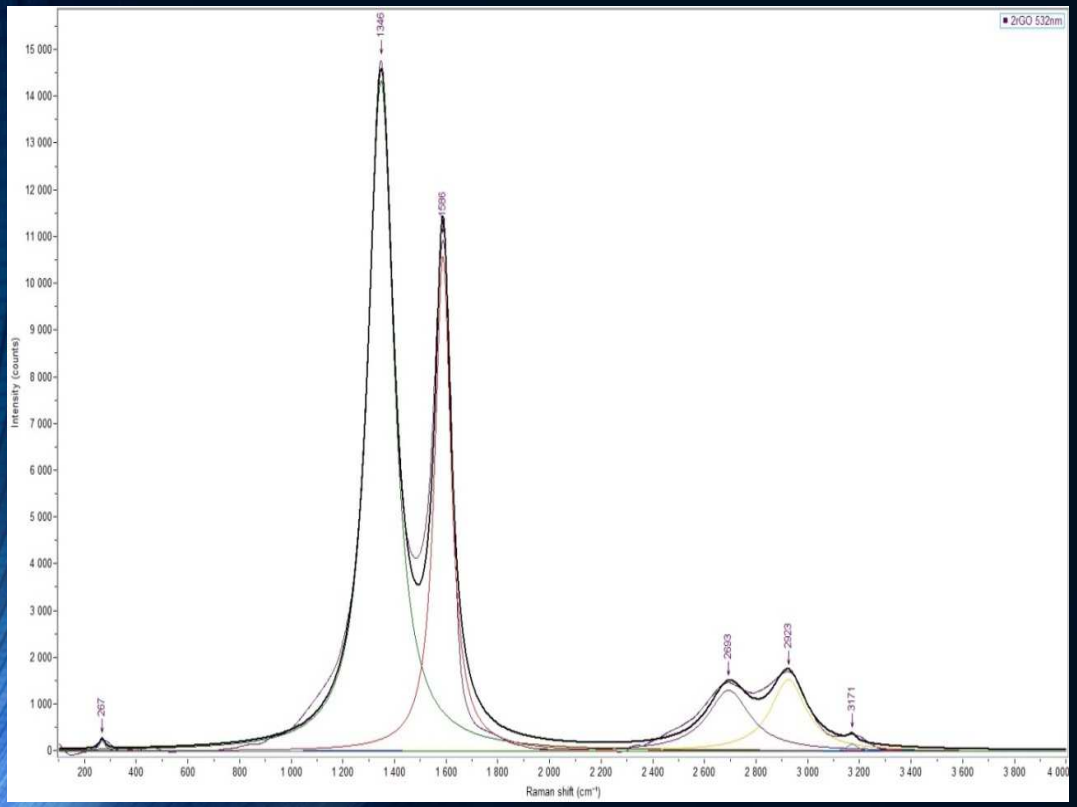
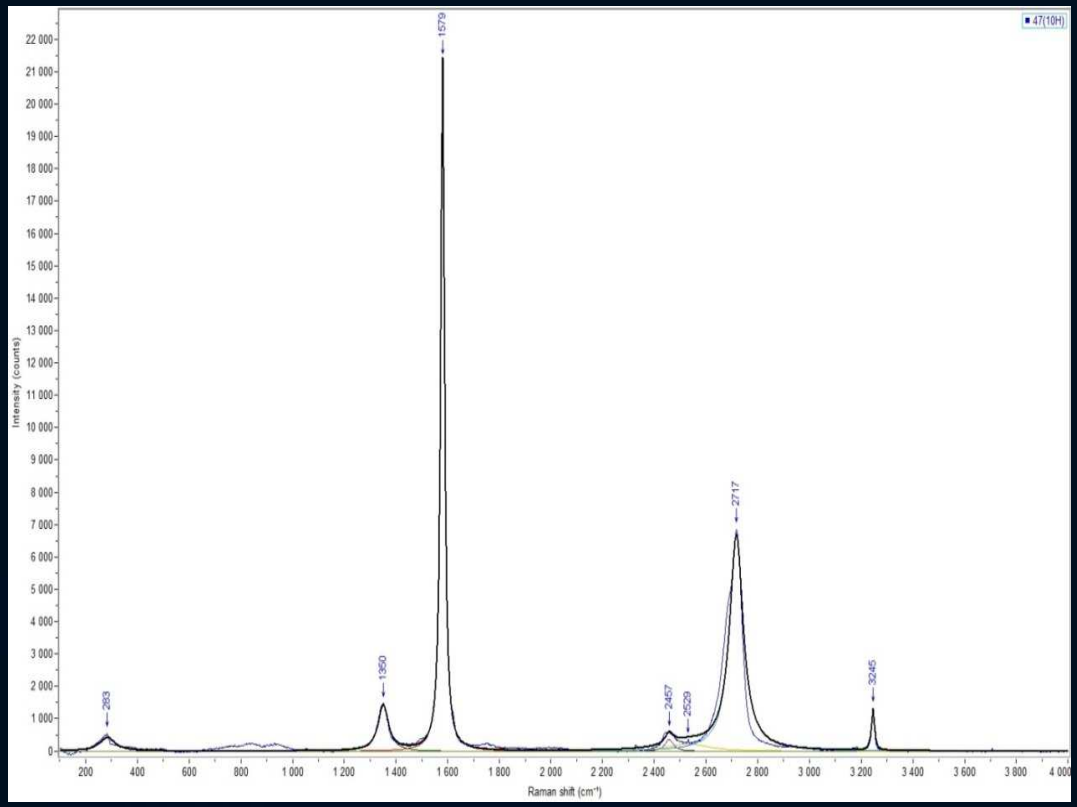


rGO-SA



rGO-I.I

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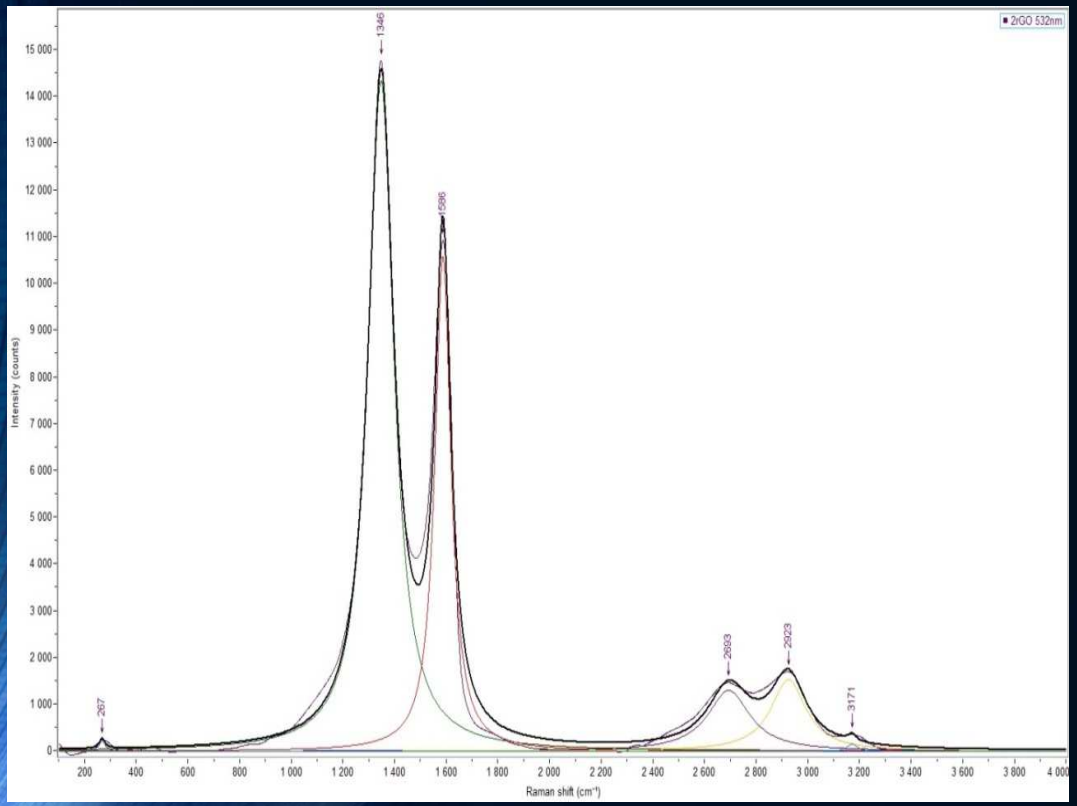
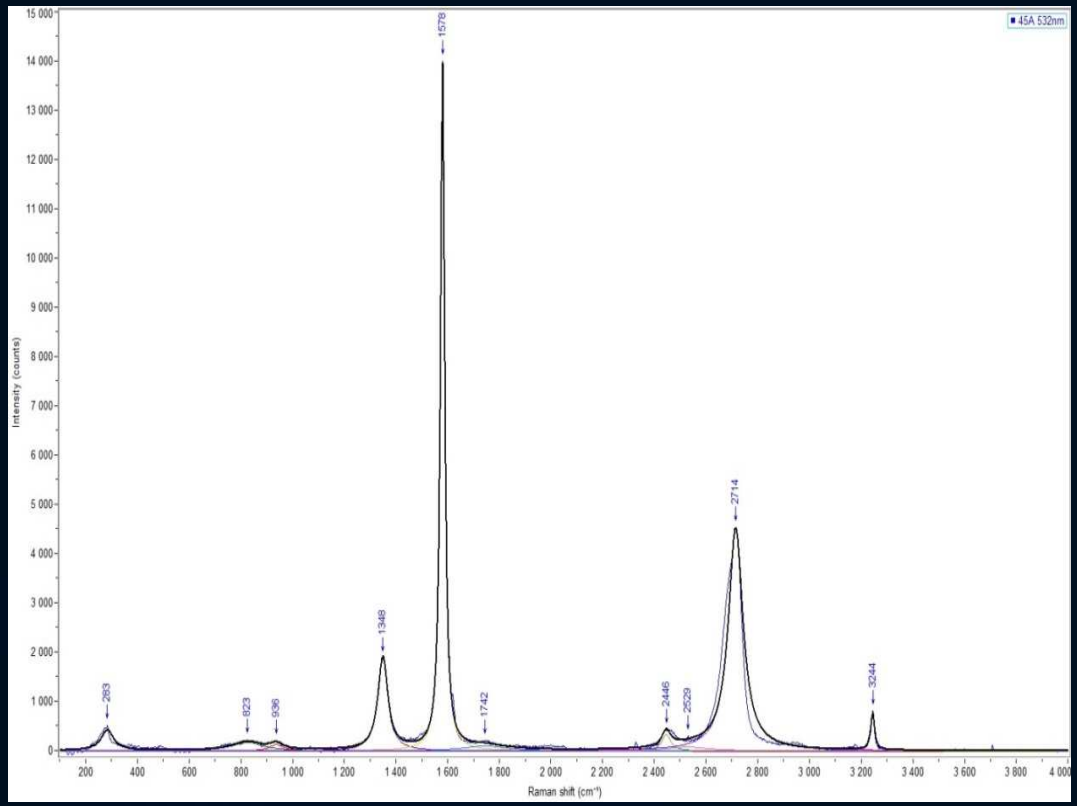


rGO-SA



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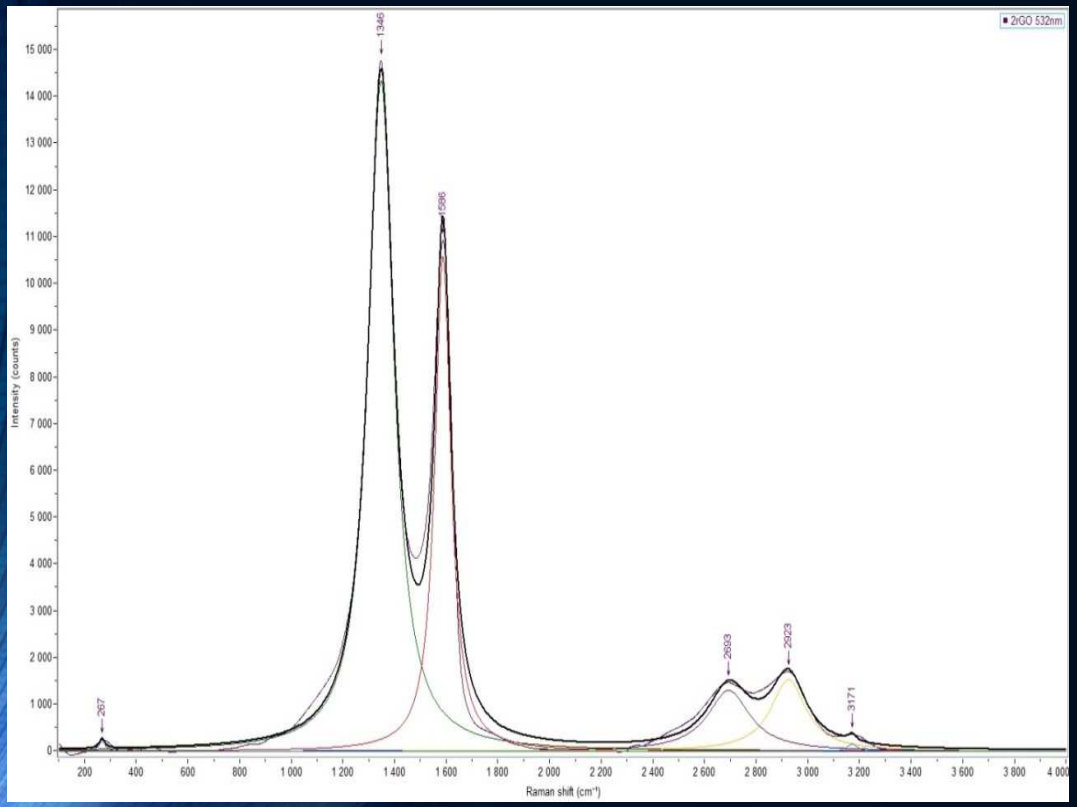

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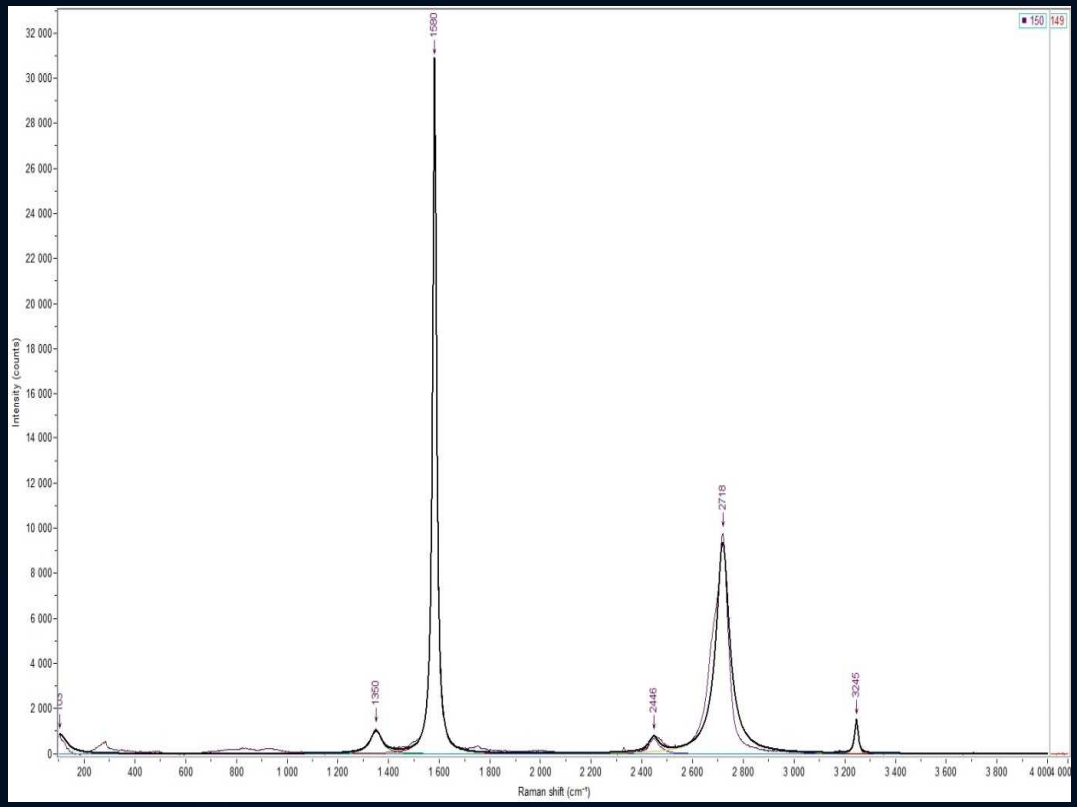

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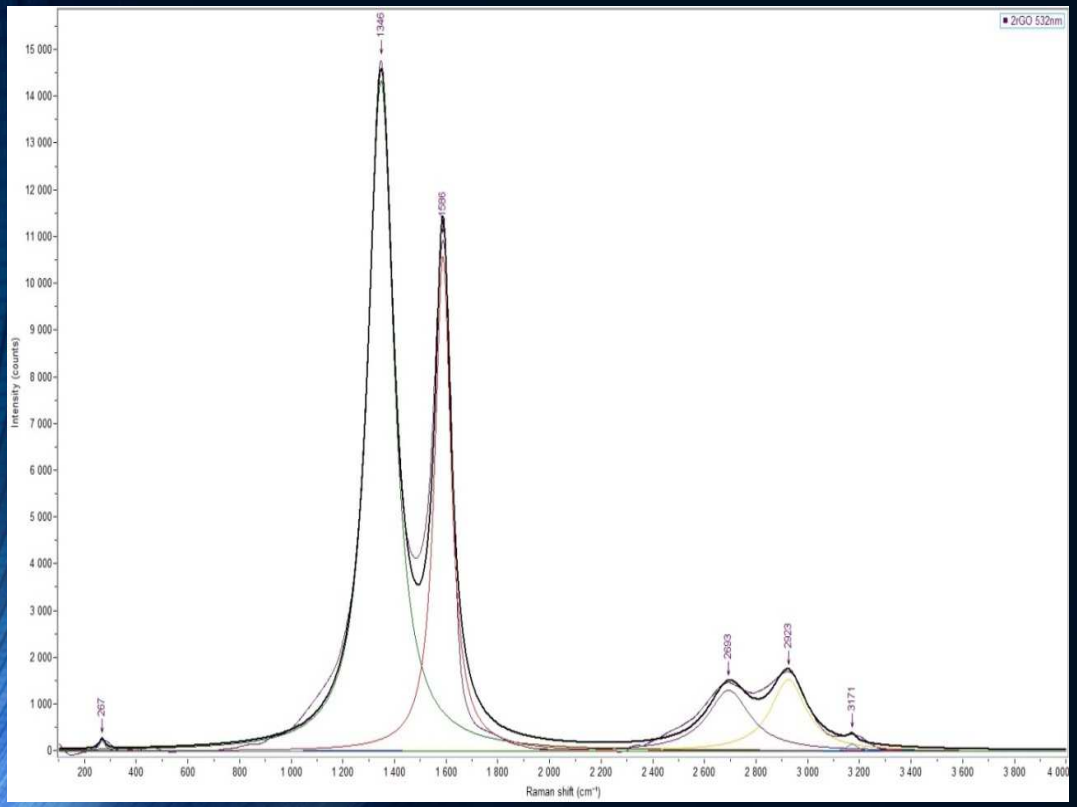

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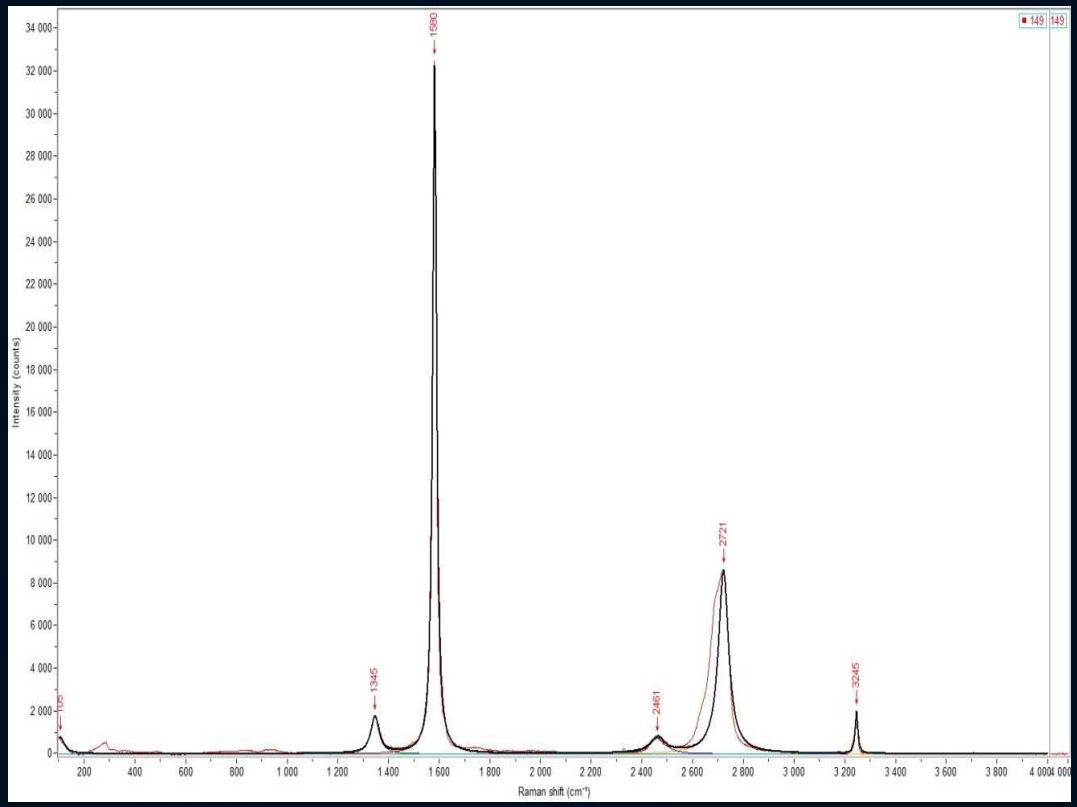


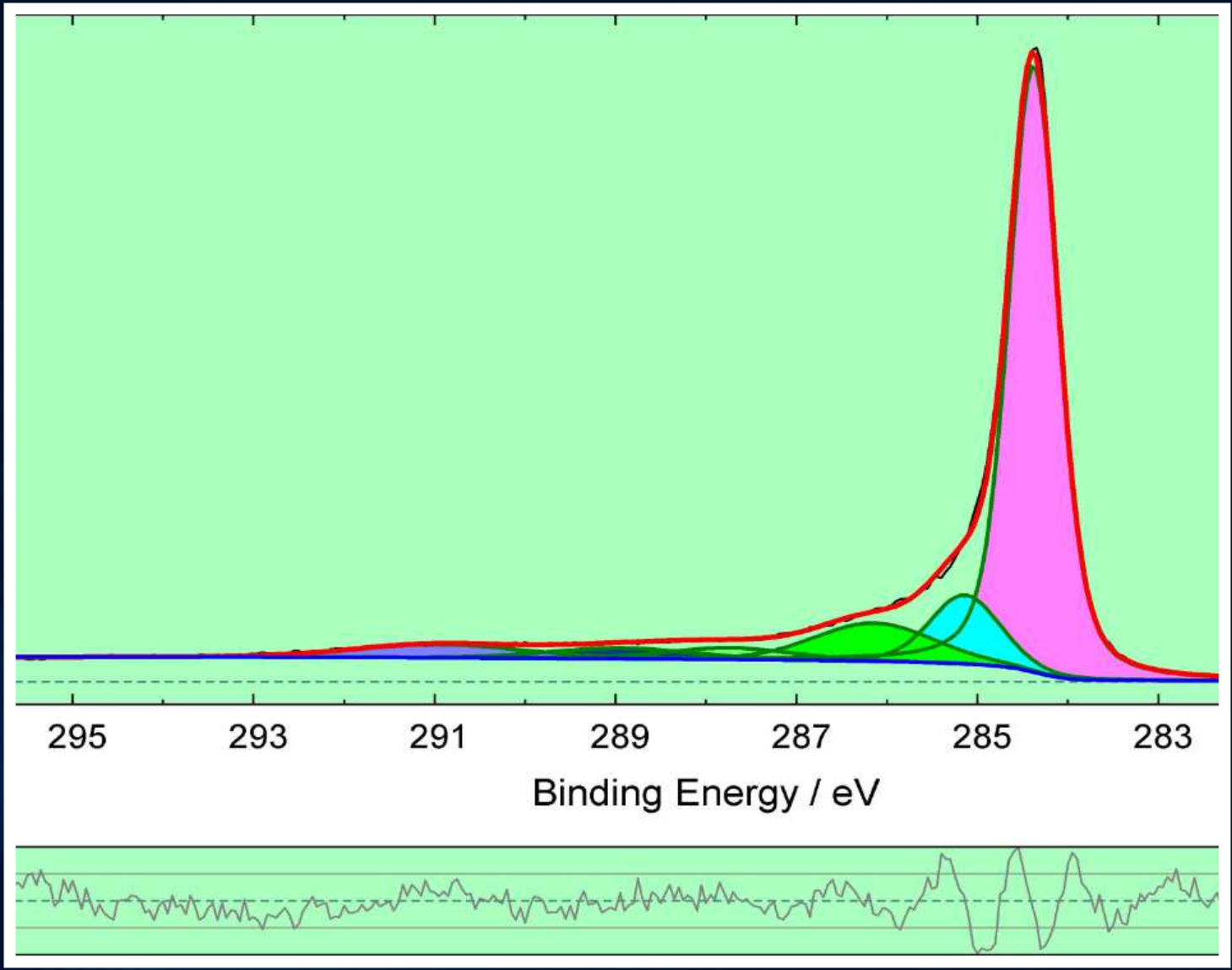
rGO-II.II

Raman spectroscopy

- Results confirm the observations from SEM – significantly **lower damage of graphitic plate core in MUNI structures** – as D-peak related to graphitic/graphene plane disorder (cca 1350 cm^{-1}) has much lower intensity in case of all of the **MUNI structures** (especially in case of GO-II)
- In case of **SA rGO** products it is evident that **reduction brings more disorder** (damage) into graphitic/graphene planes – D-peak (cca 1350 cm^{-1}) is even more intense than G-peak (cca 1580 cm^{-1})
- Reduction of **MUNI GO materials** is on the contrary performed in a gentle way to avoid further damage of graphitic/graphene plates – **MUNI rGO materials** are thus **closer to graphene** structure as in addition intense 2D-peak at cca 2710 cm^{-1} is missing/split in case of SA rGO structures

XPS
X-ray photoelectron spectroscopy

- Peak position in spectrum reflects the nature of a specific functional group in the molecule
- Peak width is influenced by different chemical bonding around the specific functional group
- Peak intensity depends on a number of functional groups of a specific type (C=O, C(=O)O, C-O, …)
- Particular peak area ratio corresponds to relative abundance (%) of respective functional groups



XPS – particular peak area ratio corresponds to relative abundance (%) of respective functional groups

Sample	C=C (rel. %)	C-C (rel. %)	C-O (rel. %)	C=O (rel. %)	(C(O)-O) (rel. %)	C≈O (rel. %) (sum, oxygen functional groups)
GO-SA	69.88	18.52	8.69	1.24	1.67	**11.60**
rGO-SA	61.74	21.16	12.19	2.93	1.99	**17.11**
GO-I	61.96	23.66	6.69	2.62	2.69	**12.00**
GO-II	63.72	24.10	5.38	1.76	4.71	**11.85**
rGO-I.I	62.50	26.92	6.02	2.55	1.99	**10.56**
rGO-II.I	60.96	29.24	5.44	2.04	2.32	**9.80**
rGO-I.II	61.29	28.88	5.84	2.33	2.00	**10.17**
rGO-II.II	63.23	25.08	7.12	2.30	2.28	**11.70**

XPS

- Despite the fact that **MUNI GO structures** have significantly less damaged graphitic/graphene plates caused by oxidation, they show **identical oxygen content** - 12.00 % (GO-I) and 11.85 % (GO-II) vs. 11.60 % (GO-SA)
- Employment of two different oxidation agents resulted in different distribution of oxygen containing groups in **MUNI GO products**:

  GO-I - high abundance of C-O and C=O groups

  GO-II - lower abundance of C-O and C=O groups, higher content of –COOH groups

  - variability in oxygen containing groups can be utilized in **practical applications** or **graphenoid structure modification**

- Although rGOs should contain lower oxygen content, all of the compounds including standard rGO-SA show increase in oxygen content
- **MUNI rGO products** have **lower oxygen content** (9.1 - 11.7 %) compared to rGO-SA (17.11 %)

RA - XRD - XPS - TGA

- comparison of analytical results of graphenoid structures

Graphenoid	RA (cm^{-1})	TGA (°C) Decomp. begin. (int.) / inflexion	XPS C1s - oxygen functional groups (rel. %), (rel. ratio)				XRD (2Θ, °)
			C-O	C=O	(C(O)-O)	sum	
GO-SA	1345 (s) 1572 (vs) 2684 (vs)	355 / 580	8.69 (5.20)	1.24 (0.74)	1.67 (1)	**11.60**	26.51 (s) 42.58, 44.25 54.52 77.59
GO-I	1350 (vw) 1577 (vs) 2714 (m)	550 / 725	6.69 (2.49)	2.62 (0.97)	2.69 (1)	**12.00**	26.46 (s) 42.33, 43.33, 44.38 54.50 77.43
GO-II	1348 (w) 1580 (vs) 2718 (m)	630 / 745	5.38 (1.14)	1.76 (0.37)	4.71 (1)	**11.85**	26.41 (s) 43.27, 43.41, 44.35 54.46 77.23

RA - XRD - XPS - TGA

- comparison of analytical results of graphenoid structures

Graphenoid	RA (cm^{-1})	TGA (°C) Decomp. begin.(int.) / inflexion	XPS C1s - oxygen functional groups (rel. %), (rel. ratio)				XRD (2Θ, °)
			C-O	C=O	(C(O)-O)	sum	
rGO-SA	1346 (vs) 1586 (s) 2693 (w)	510 / 600	12.19 (6.13)	2.93 (1.47)	1.99 (1)	**17.11**	21.31 (s) 23.43 (s) 26.47 (s) 42.86 78.08
rGO-I.I	1343 (w) 1568 (vs) 2705 (m)	560 / 740	6.02 (3.03)	2.55 (1.28)	1.99 (1)	**10.56**	26.46 (s) 44.38, 54.55 77.25
rGO-II.I	1346 (w) 1575 (vs) 2711 (m)	580 / 680	5.44 (2.35)	2.04 (0.88)	2.32 (1)	**9.80**	26.42 (s) 44.31, 54.52 77.31
rGO-I.II	1350 (w) 1580 (vs) 2718 (m)	600 / 770	5.84 (2.92)	2.33 (1.17)	2.00 (1)	**10.17**	26,43 (s) 44,32, 54,50 77,35
rGO-II.II	1345 (w) 1580 (vs) 2721 (m)	550 / 730	7.12 (3.12)	2.30 (1.01)	2.28 (1)	**11.70**	26,40 (s) 44,41, 54,49 77.37

TGA - XRD

TGA

- Owing to lower damage of graphitic/graphene plates in **MUNI products**, they show significantly **higher thermal stability** than respective SA standards, especially in case of **GO structures** (550 °C for GO-I, 630 °C for GO-II vs. 355 °C for GO-SA)

XRD

- XRD paterns are the same for all of the **GO structures** (MUNI and SA)
- In case of rGO-SA, XRD analysis confirms further damage which is reflected in **changes in interplanar distances** (a few peaks are observed)
- **MUNI products** still keep XRD patterns of starting GO structures indicating **no further damage** during reduction process

new MUNI products
vs.
commercial standard

Structure characteristics of MUNI graphenoids:

- MUNI graphitic/graphene plates are larger in surface than SA plates, but have similar thickness (the same or lower). Moreover thickness can be further adjusted.
- MUNI graphitic/graphene plates damage, esp. in a middle segment, is lower than in case of SA plates as a consequence of delicate technologies usage
- Aromaticity, and related features, is thus higher in MUNI structures.
- Moreover SA products contain high amount of intercalated low-molecular condensed aromatic compounds (as confirmed by MS-LDI, MALDI)
- Oxidation state of MUNI GO compounds is the same but more selective concerning functional group types, it can be controlled by the employment of different oxidation agents

new MUNI products
vs.
commercial standard

- Variations on oxygen containing groups can be utilized in practical applications and in further structure modification
- MUNI rGO compounds have lower oxygen content than SA standard, thus bringing rGO structures closer to idealized graphene
- No further damage of plates occurs during reduction process of MUNI GOs
- MUNI graphenoid structures are thermally more stable than SA compounds, especially in case of GO structures
- Technologies and chemicals used can be marked as environmentally sustainable
- The above-mentioned positives of the new MUNI graphenoids provide an opportunity for their further research, development and utilization in various applications