31ST INTERNATIONAL CONFERENCE ON DIAMOND AND CARBON MATERIALS
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Covalent Organic Functionalization of Graphene Nanosheets and Reduced Graphene Oxide via 1,3-Dipolar Cycloaddition of Azomethine Ylide

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Outline

- Why GRAPHENE?

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- 1,3 Dipolar Cycloaddition of GNS and rGO

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- Results (EDX/EELS – XPS – Raman – DFT)

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Outline

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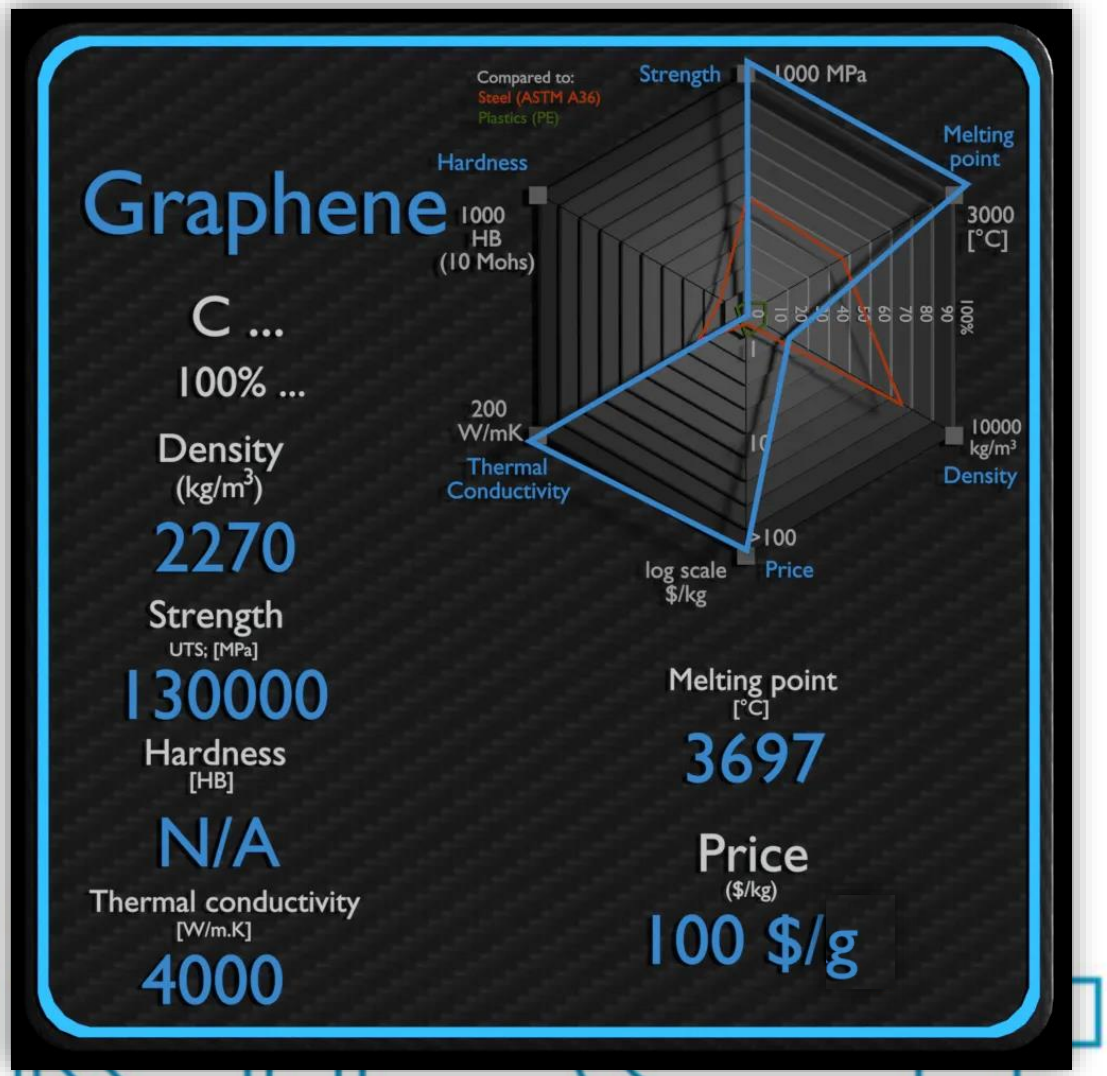
- 1,3 Dipolar Cycloaddition of GNS and rGO
- Results (EDX/EELS – XPS – Raman – DFT)
- Conclusions & Outlooks

Graphene

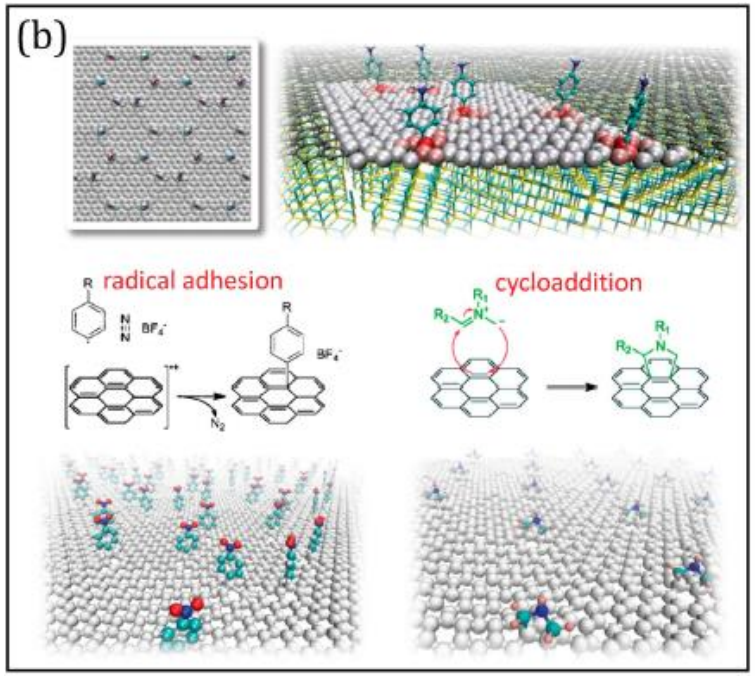
The high specific surface area and the excellent mechanical, electrical, optical and thermal properties of graphene make it an attractive component for high-performance devices.

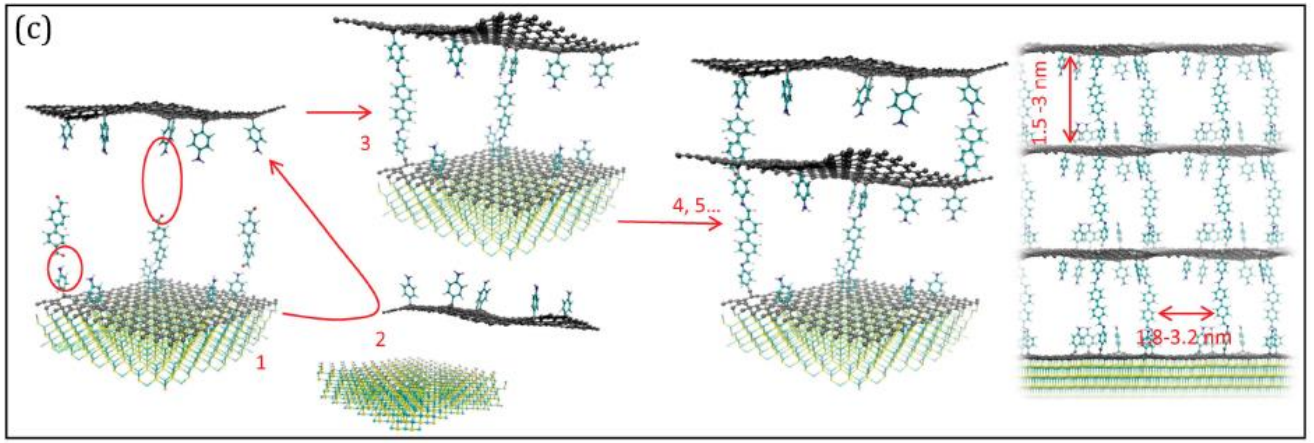


[*Material Properties* (web)]

Chemical Functionalization

Covalent functionalization of graphene with organic molecules offers the possibility to finely tune the system's physical and chemical properties





[L. Bellucci and V. Tozzini, *Molecules*, **2020**, 25, 339]

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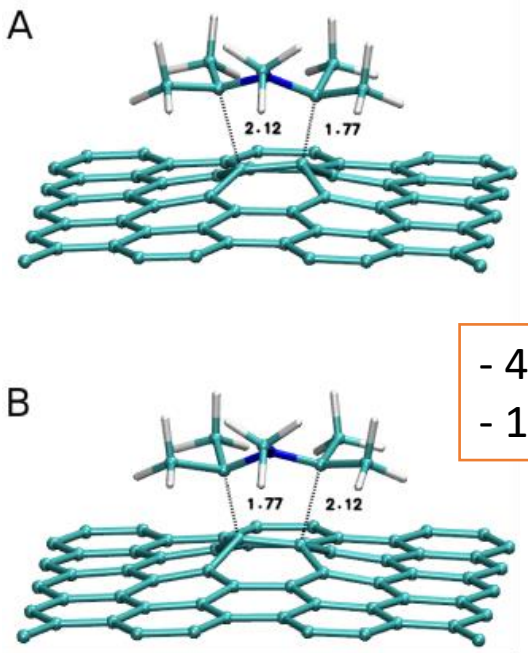
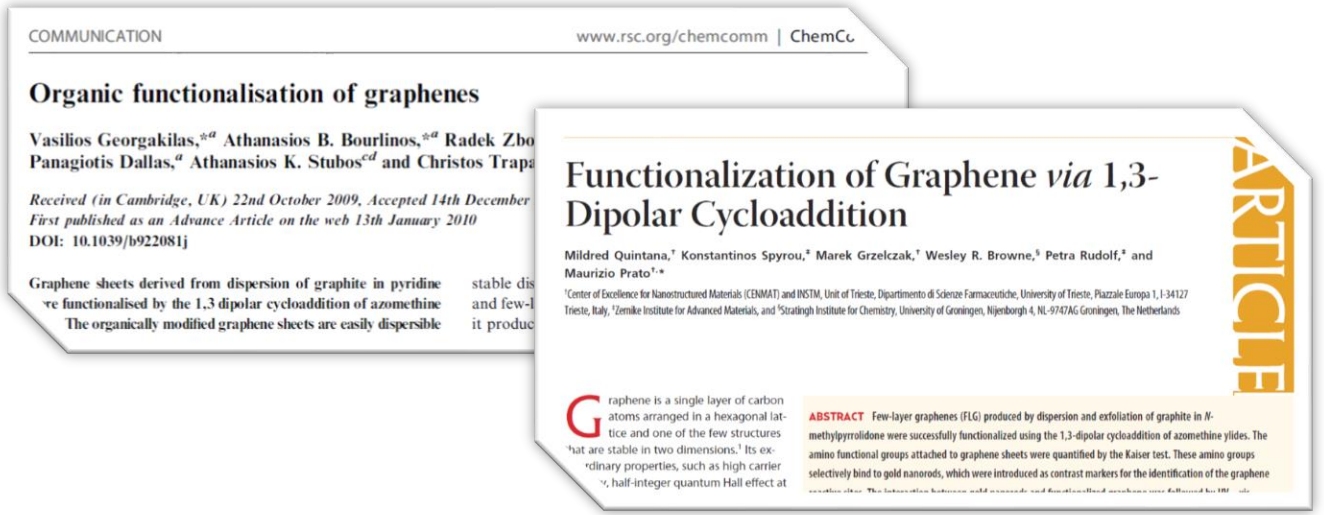
1,3 Dipolar Cycloaddition

1,3-DC of azomethine ylide: selectivity, stability (up to 300 °C), reversibility



- 43 kcal/mol
- 1.87 eV

[*L. Bellucci* @ NEST]



COMMUNICATION www.rsc.org/chemcomm | ChemCo

Organic functionalisation of graphenes

Vasilios Georgakilas,*[a] Athanasios B. Bourlinos,*[a] Radek Zbo
Panagiotis Dallas,[a] Athanasios K. Stubos[cd] and Christos Trapa

Received (in Cambridge, UK) 22nd October 2009, Accepted 14th December
First published as an Advance Article on the web 13th January 2010
DOI: 10.1039/b922081j

Graphene sheets derived from dispersion of graphite in pyridine
re functionalised by the 1,3 dipolar cycloaddition of azomethine
The organically modified graphene sheets are easily dispersible
stable dis
and few-l
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ARTICLE

Functionalization of Graphene *via* 1,3-Dipolar Cycloaddition

Mildred Quintana,[†] Konstantinos Spyrou,[‡] Marek Grzelczak,[†] Wesley R. Browne,[§] Petra Rudolf,[‡] and Maurizio Prato*[†,*]

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raphene is a single layer of carbon atoms arranged in a hexagonal lattice and one of the few structures hat are stable in two dimensions.[1] Its extraordinary properties, such as high carrier , half-integer quantum Hall effect at

ABSTRACT Few-layer graphenes (FLG) produced by dispersion and exfoliation of graphite in *N*-methylpyrrolidone were successfully functionalized using the 1,3-dipolar cycloaddition of azomethine ylides. The amino functional groups attached to graphene sheets were quantified by the Kaiser test. These amino groups selectively bind to gold nanorods, which were introduced as contrast markers for the identification of the graphene

[V. Georgakilas et al., *Chem.Commun.*, **2010**, 46, 1766;
M. Quintana et al., *ACSNano*, **2010**, 4, 6]

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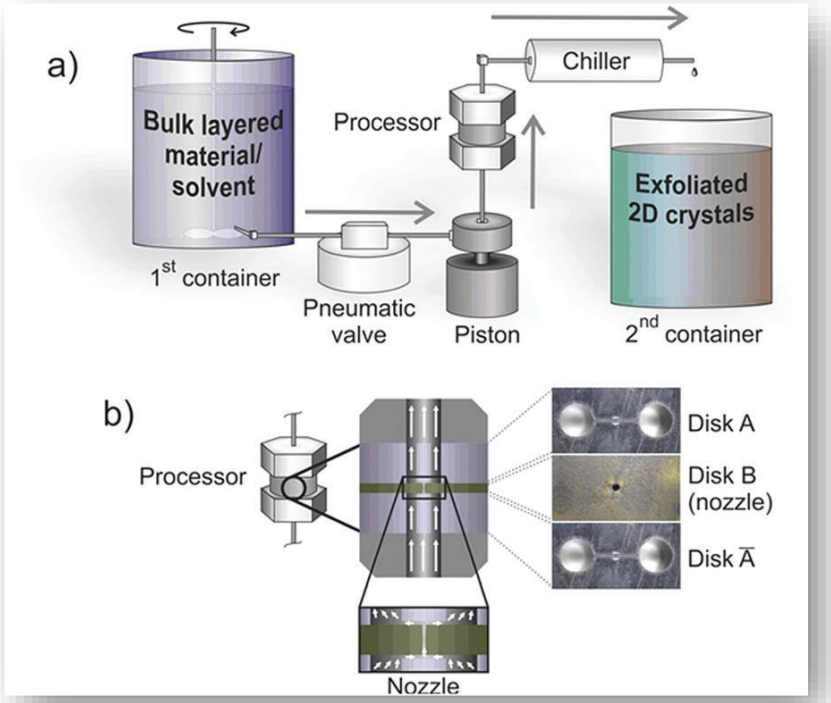
Graphene Nanosheets

Exfoliated GNS are produced by high-pressure wet-jet milling (BeDimensional)




Materials Horizons

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High-yield production of 2D crystals by wet-jet milling†

Cite this: *Mater. Horiz.*, 2018, 5, 890

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Accepted 6th July 2018

DOI: 10.1039/c8mh00487k

rsc.li/materials-horizons

A. E. Del Rio Castillo, V. Pellegrini, A. Ansaldo, F. Ricciardella, H. Sun, L. Marasco, J. Buha, Z. Dang, L. Gagliani, E. Lago, N. Curreli, S. Gentiluomo, F. Palazon, M. Prato, R. Oropesa-Nuñez, P. S. Toth, E. Mantero, M. Crugliano, A. Gamucci, A. Tomadin, M. Polini and F. Bonaccorso

Efficient and scalable production of two-dimensional (2D) materials is required to overcome technological hurdles towards the creation of a 2D-material-based industry. Here, we present a novel approach developed for the exfoliation of layered crystals, *i.e.*, graphite, hexagonal-boron nitride and transition metal dichalcogenides. The process is based on high-pressure wet-jet-milling (WJM), resulting in a production of 10 g L^{-1} of single- and few-layer 2D crystal dispersion making the scaling-up more affordable. The WJM enables the production of defect-free and high quality dispersions on a large scale, opening the way for their

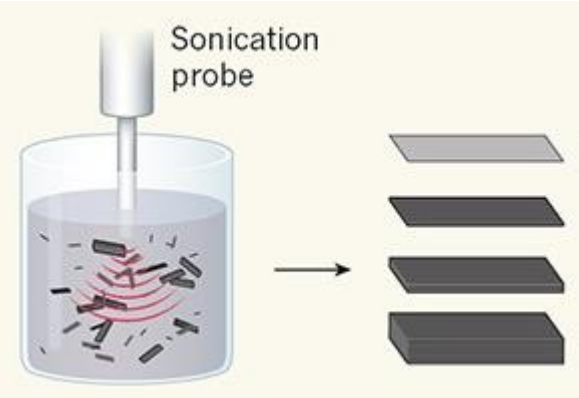
Conceptual insights

A reproducible and large-scale production of high-quality 2D crystals is urgently needed to promote the technological revolution foreseen for this class of nanomaterials. However, there are severe hurdles to be tackled before 2D crystal production methods can fulfil the industrial requirements. In particular, the production time and cost of the 2D crystals have to be minimized without compromising the crystalline-integrity and production yield. Currently, there is no methodology that fulfils the industrial requirements of materials processing for 2D crystals. Here, we present a breakthrough in the exfoliation of bulk layered crystals, based on high-speed

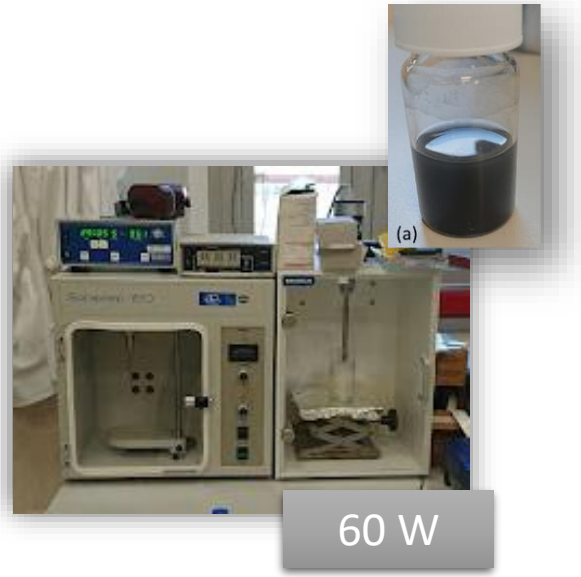
[A. E. Del Rio et al., *Mater. Horiz.*, **2018**, 5, 890]

Graphene Nanosheets dispersion

Sonication: exfoliation through growth and collapse of micro-bubbles due to pressure fluctuations in solvents (NMP and DMF)



[P. Bøggild, *Nature* 562, 502, **2018**]



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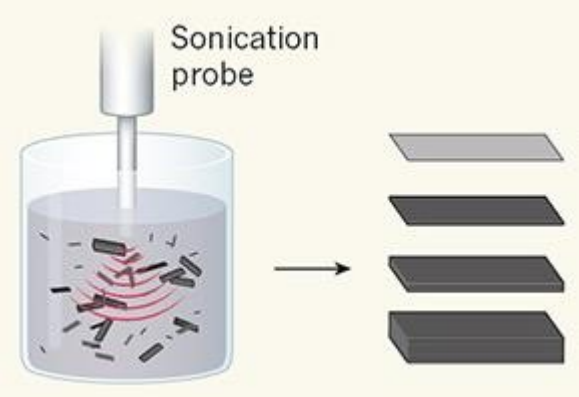
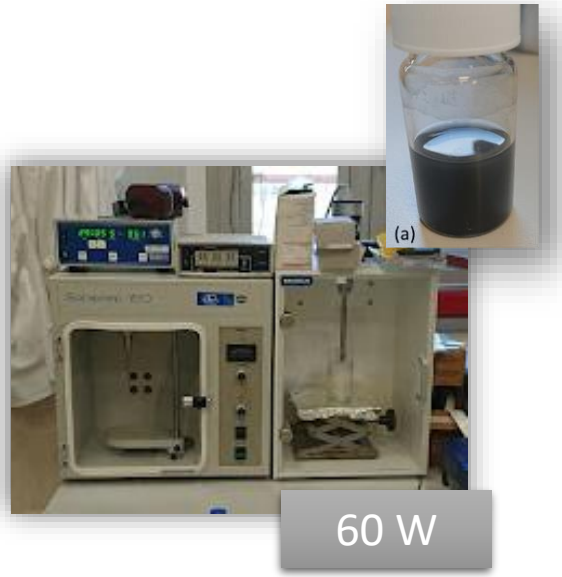
Graphene Nanosheets dispersion

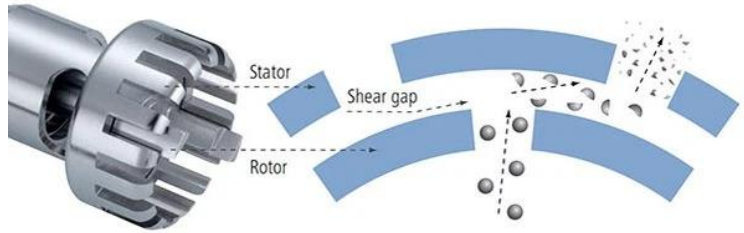
Sonication: exfoliation through growth and collapse of micro-bubbles due to pressure fluctuations in solvents (**NMP** and **DMF**)

Homogenization: exfoliation via shear mixing in suitable stabilizing solvents



[P. Bøggild, *Nature* 562, 502, **2018**]





[*IKA* (Web)]

Dynamic Light Scattering

Average lateral dimension of GNS

Solvent	*Dispersion technique*	*Start*	*After 30 min*	*After 60 min*	*After 120 min*
NMP	*sonication*	(850 ± 100) nm	-	(600 ± 100) nm	(500 ± 100) nm
	homogenization	(850 ± 50) nm	(600 ± 40) nm	(400 ± 20) nm	-
DMF	*sonication*	(950 ± 150) nm	-	(850 ± 150) nm	(800 ± 150) nm
	homogenization	(950 ± 150) nm	(800 ± 50) nm	(600 ± 50) nm	-

[L. Basta et al., *Nanoscale Advances*, **2021**]

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	homogenization	(950 ± 150) nm	(800 ± 50) nm	(600 ± 50) nm	-

BETTER!

FASTER!

[L. Basta et al., *Nanoscale Advances*, **2021**]

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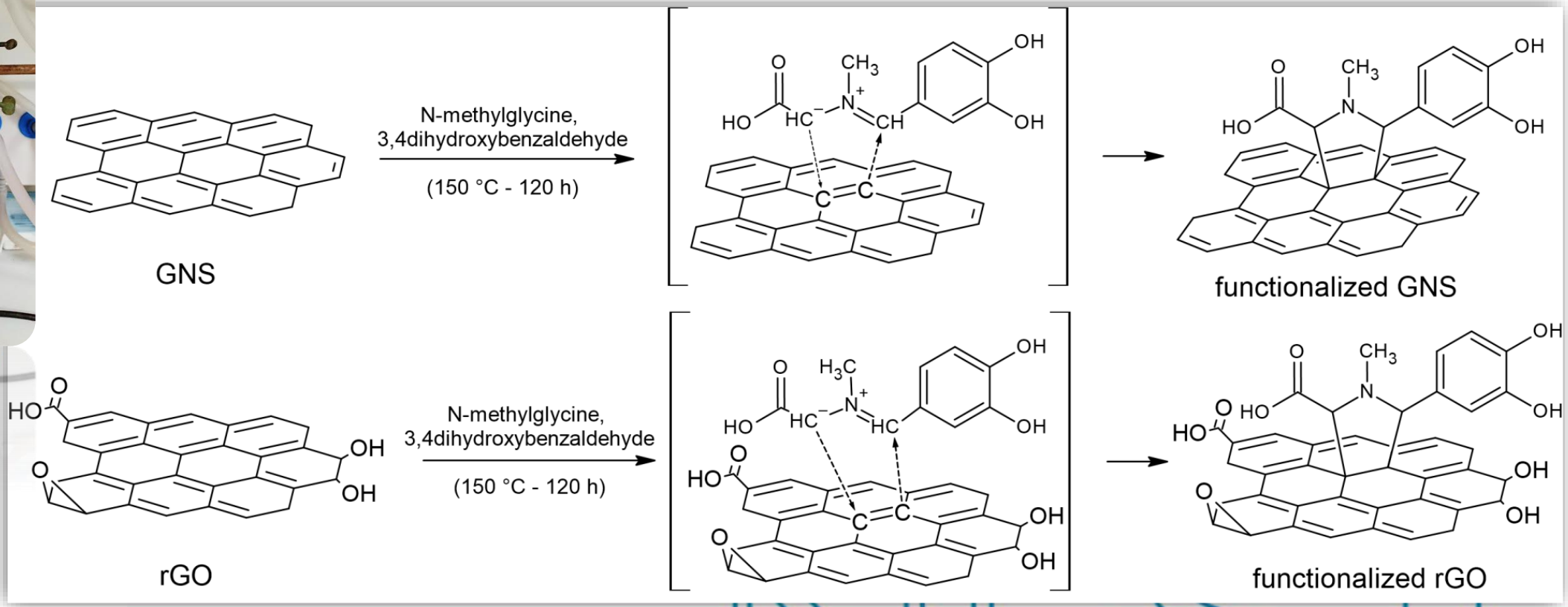
1,3-DC of GNS and rGO

GNS in NMP/DMF, rGO in DFM: 0.2 mg/mL

150 °C – 120 h

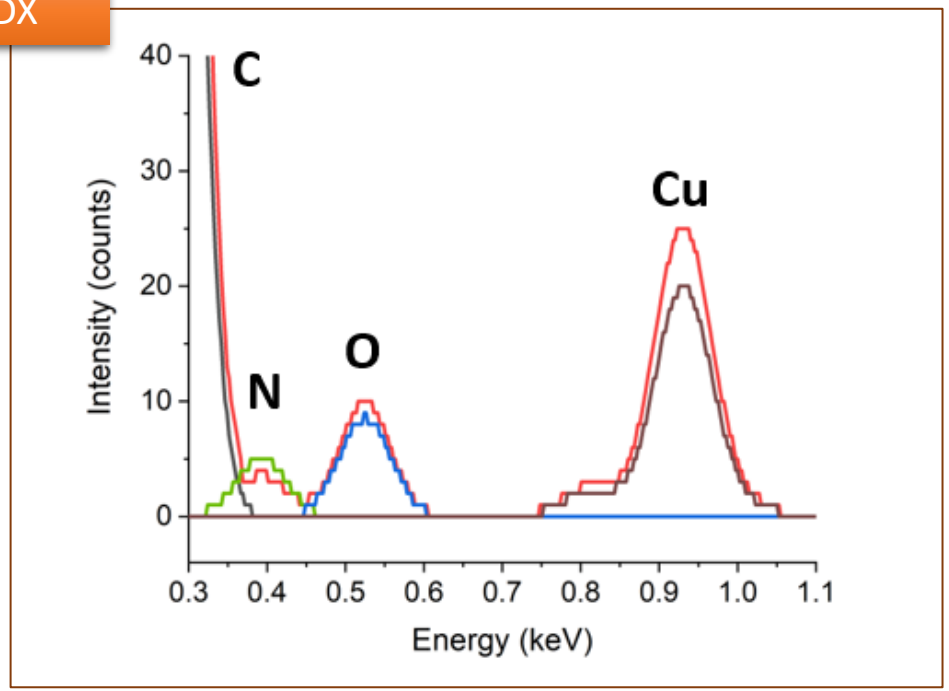
(under N_2 flux)



EDX – EELS

(functionalized GNS and rGO)

EDX



[L. Basta et al., *Nanoscale Advances*, **2021**]

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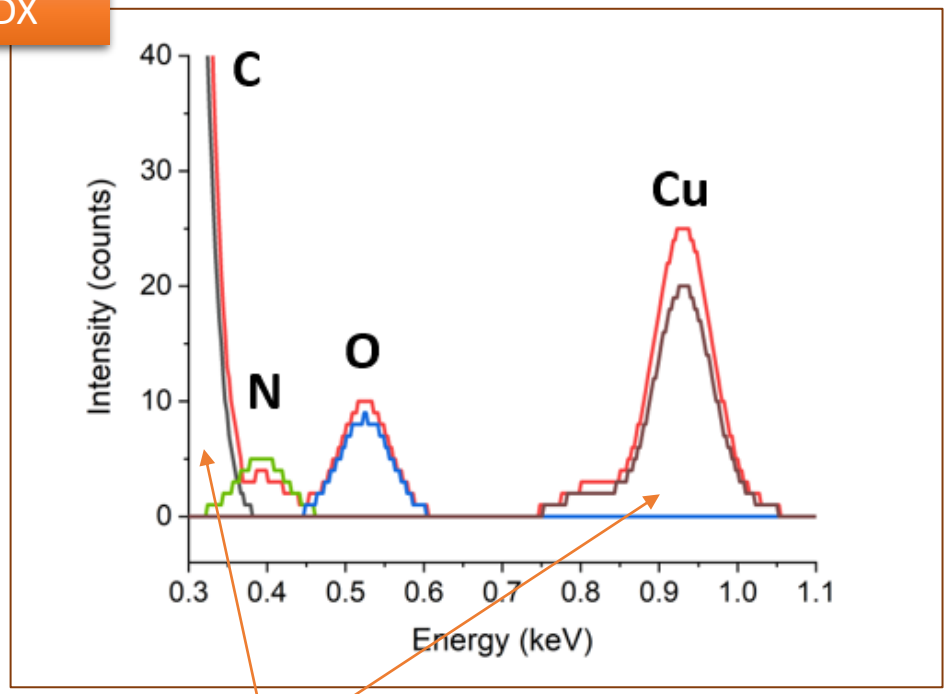
EDX



Carbon film-supported copper grids

[L. Basta et al., *Nanoscale Advances*, **2021**]

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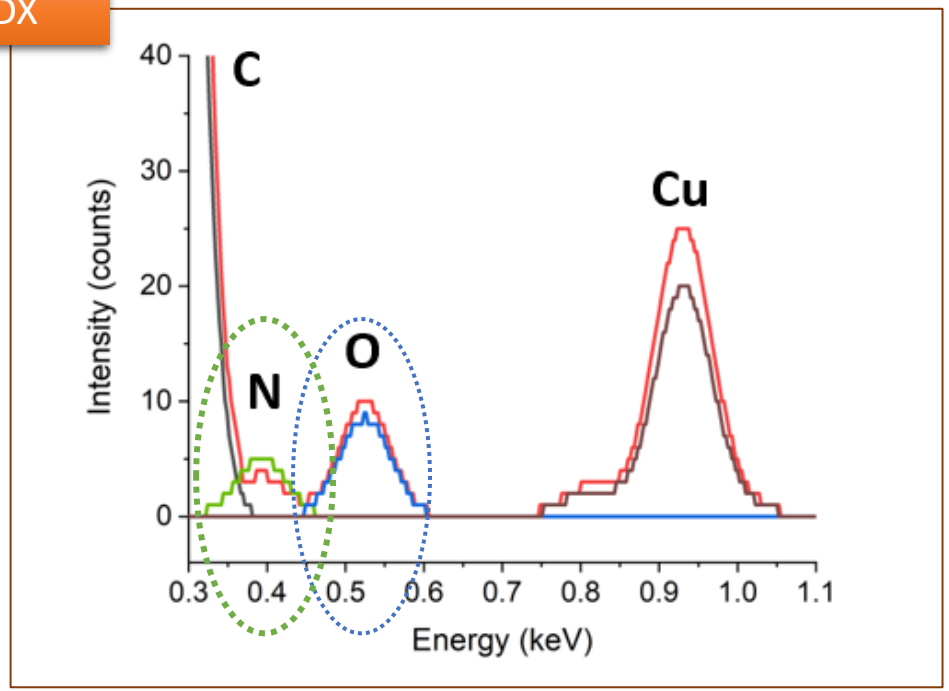
EDX – EELS

(functionalized GNS and rGO)

EDX



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EDX – EELS

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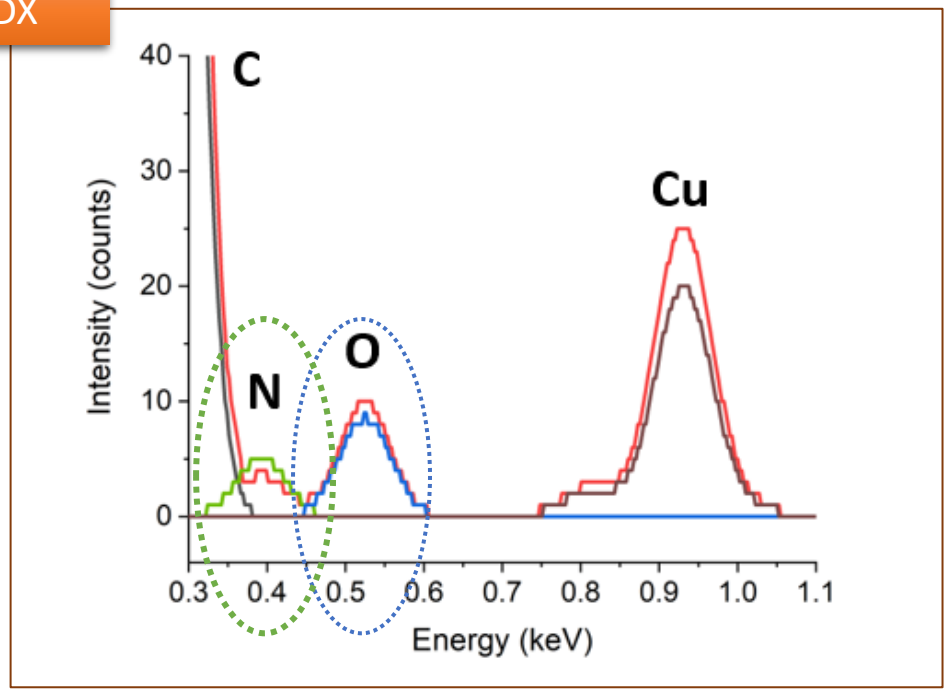
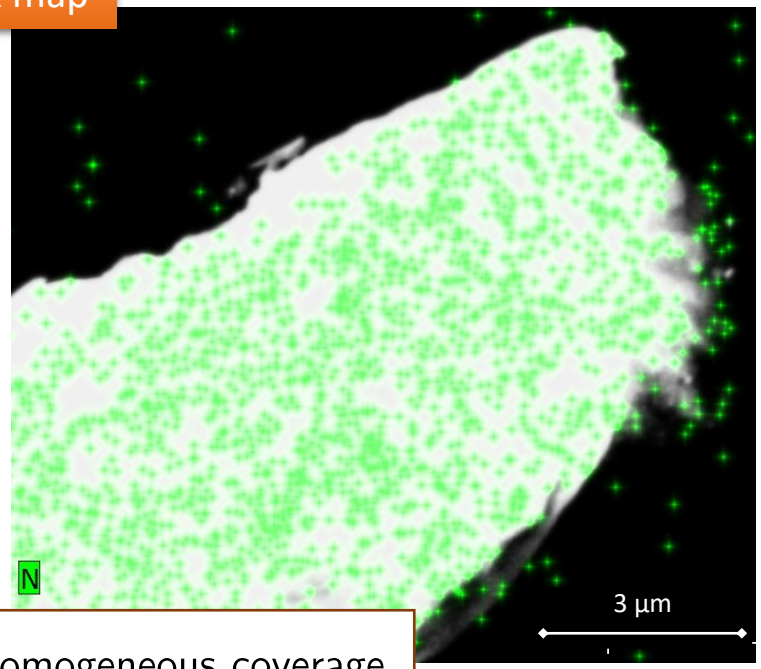


EDX map



homogeneous coverage

Carbon film-supported copper grids

[L. Basta et al., *Nanoscale Advances*, **2021**]

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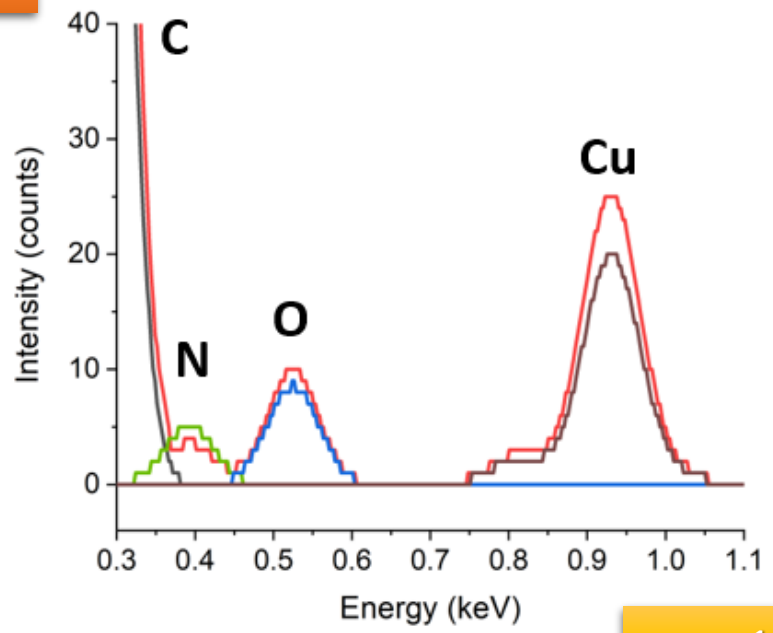
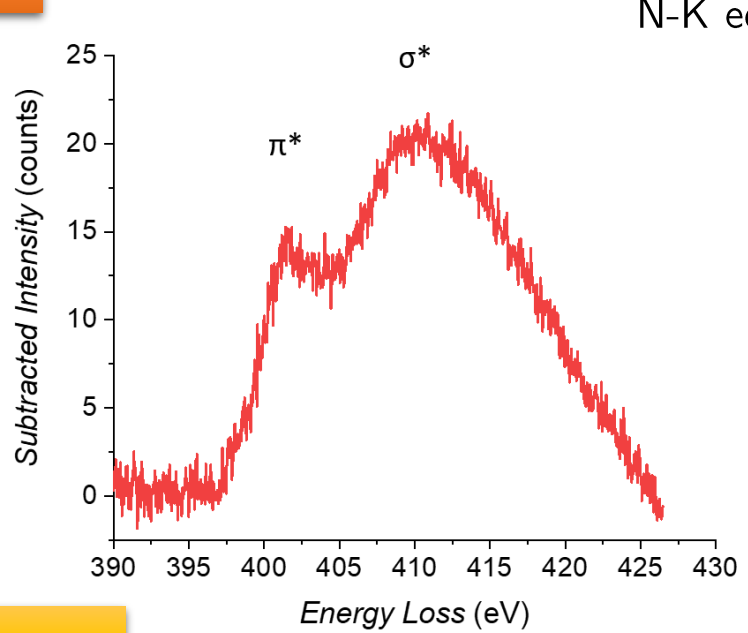
EDX – EELS

(functionalized GNS and rGO)

EDX



EELS



1,3-DC of azomethine ylide

Carbon film-supported copper grids

[L. Basta et al., *Nanoscale Advances*, **2021**]

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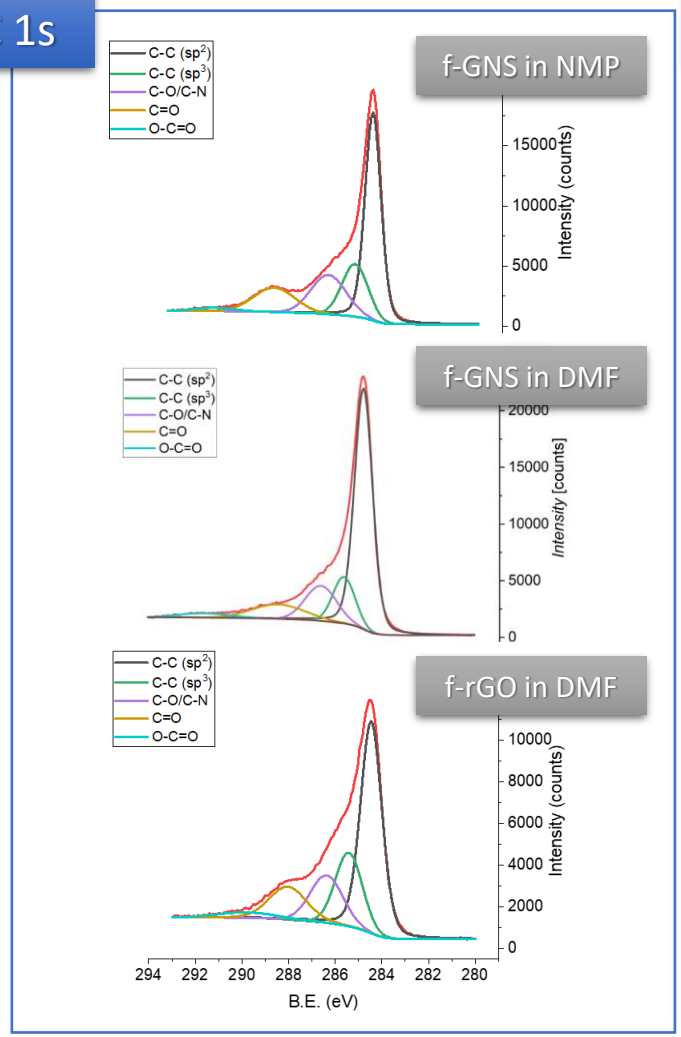
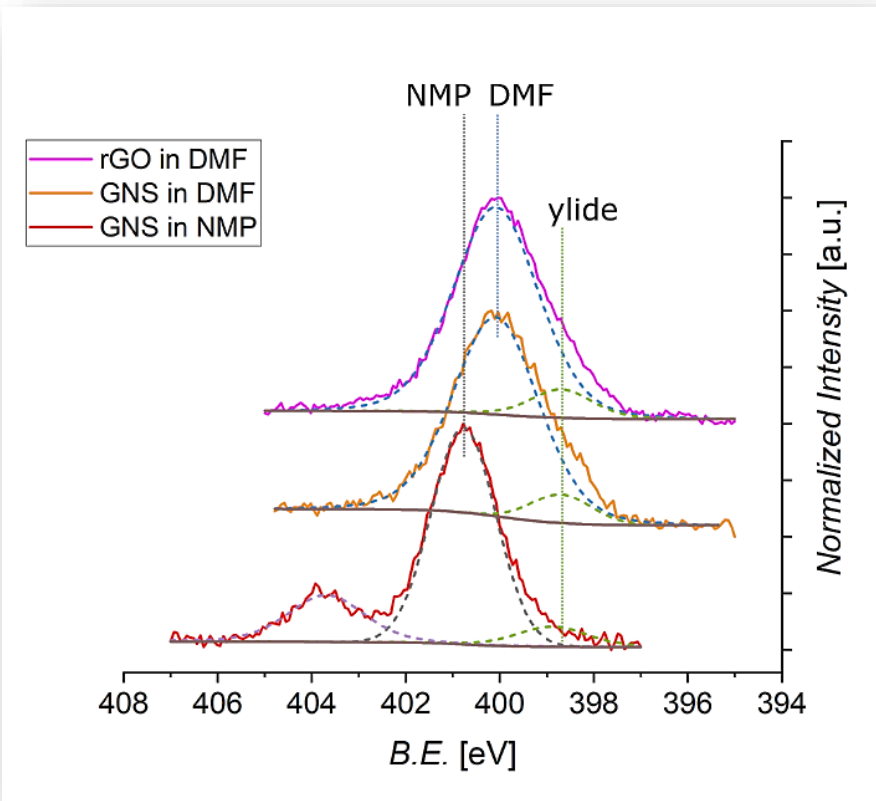
XPS

C 1s

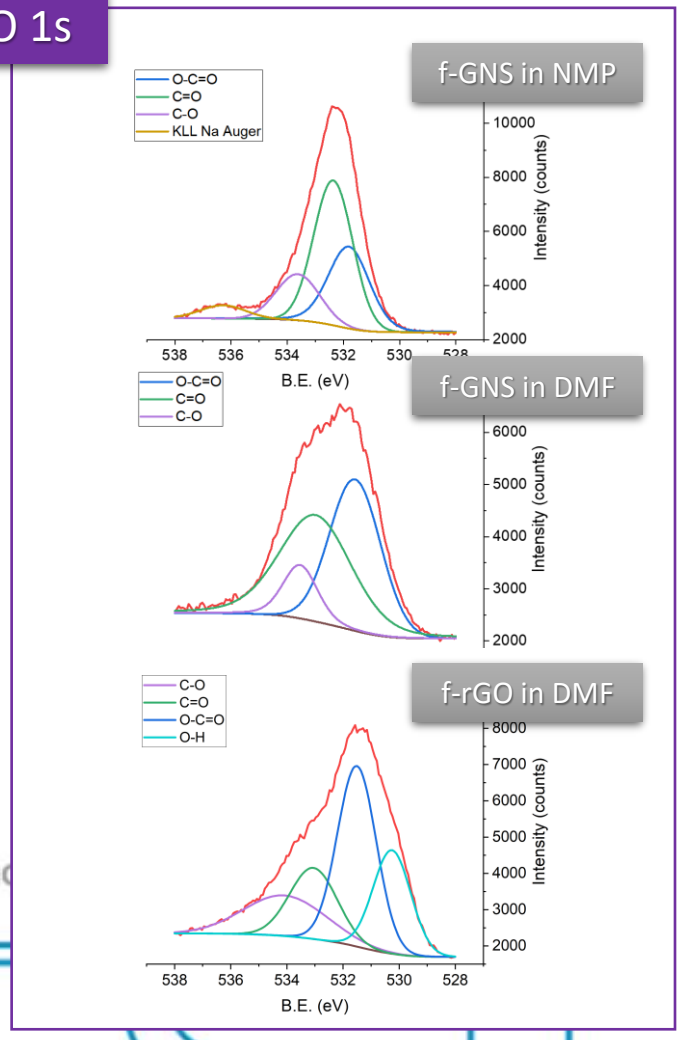


N 1s



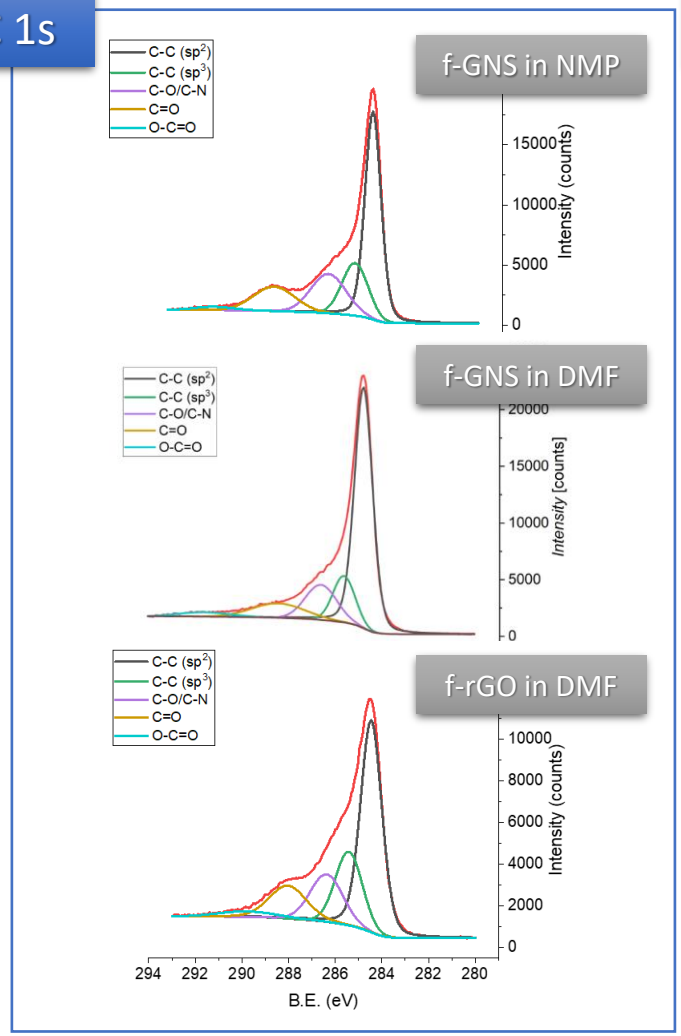
[L. Basta et al., *Nanoscale Advances*, **2021**]

O 1s

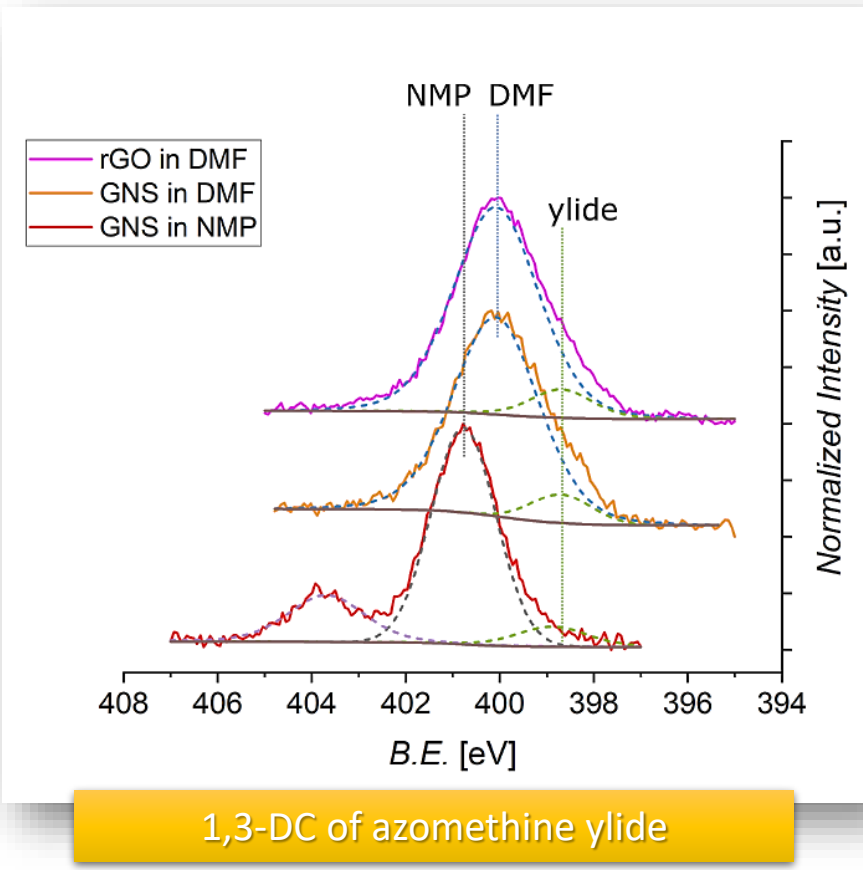


XPS

C 1s

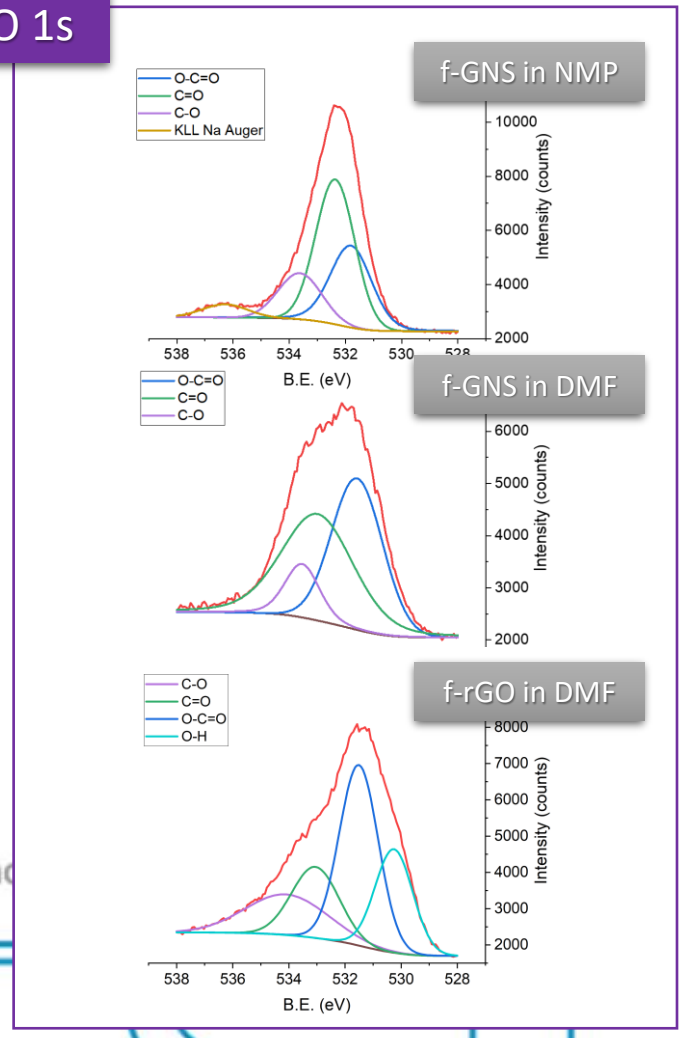


N 1s



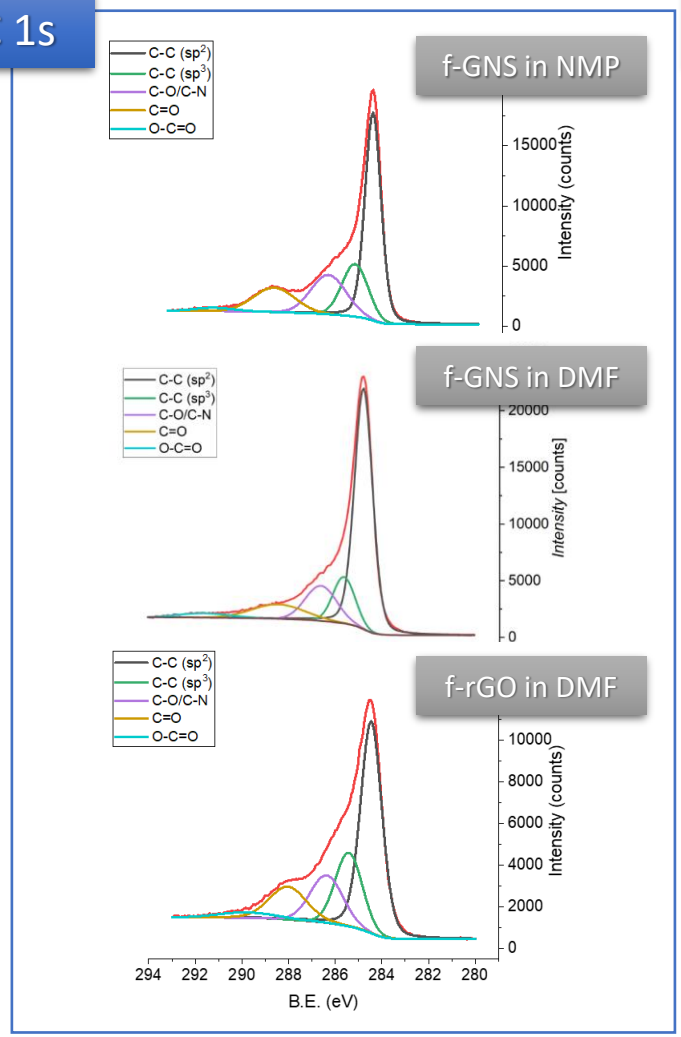
1,3-DC of azomethine ylide

O 1s

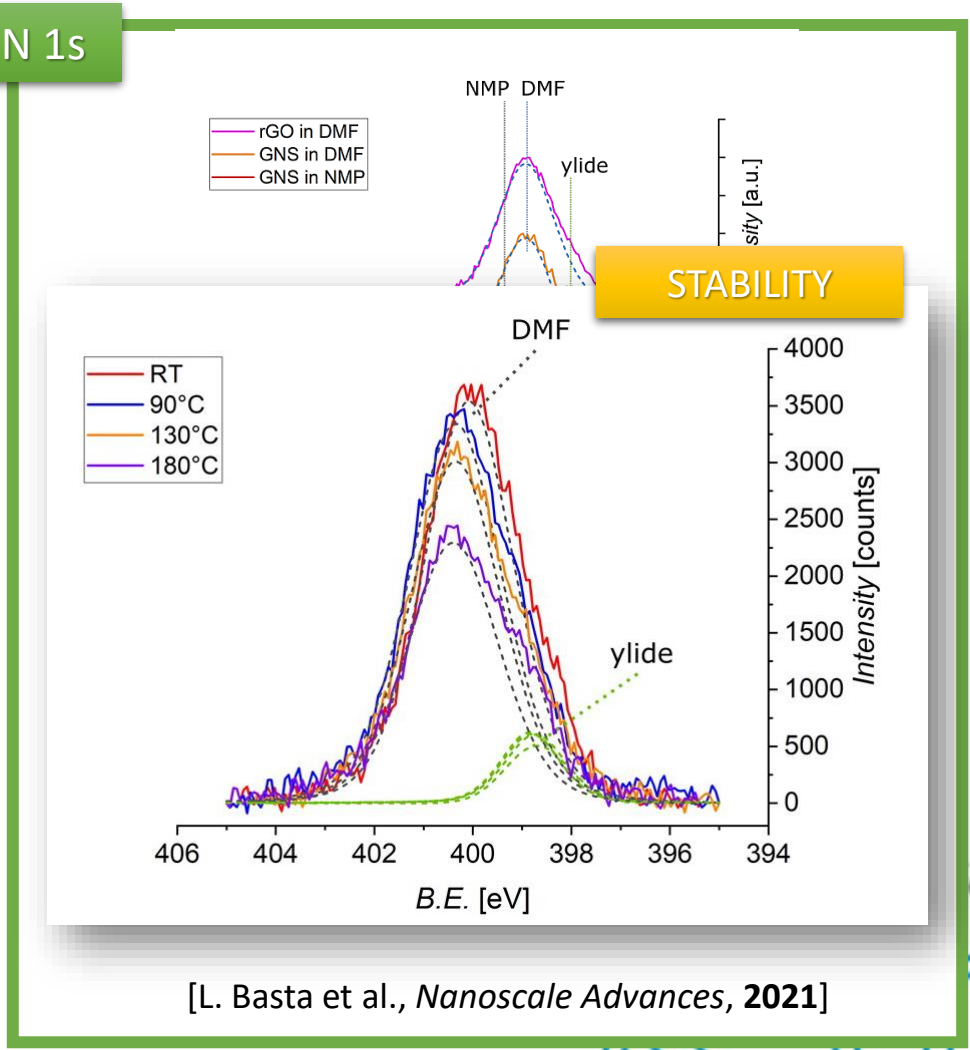


XPS

C 1s

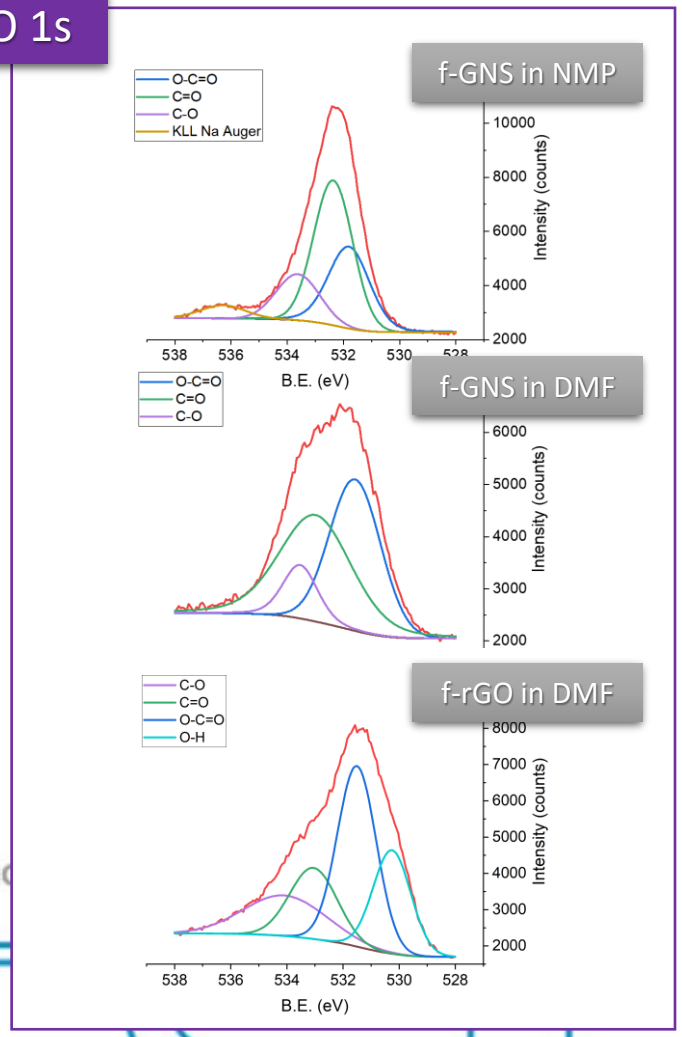


N 1s



[L. Basta et al., *Nanoscale Advances*, **2021**]

O 1s



XPS

The estimated efficiency of the functionalization is 1 azomethine ylide every *225* carbons in case of GNS in NMP, 1 ylide every *170* carbons for GNS in DMF, and 1 ylide every *110* carbons for rGO in DMF.

Elemental composition of f-GNS and f-rGO

	C (%)	N(mol) (%)	N(solv) (%)	O (%)
GNS in NMP	80.3	0.14	4.05	15.6
GNS in DMF	83.1	0.18	3.92	12.8
rGO in DMF	72.3	0.71	5.69	21.3

[L. Basta et al., *Nanoscale Advances*, **2021**]

XPS

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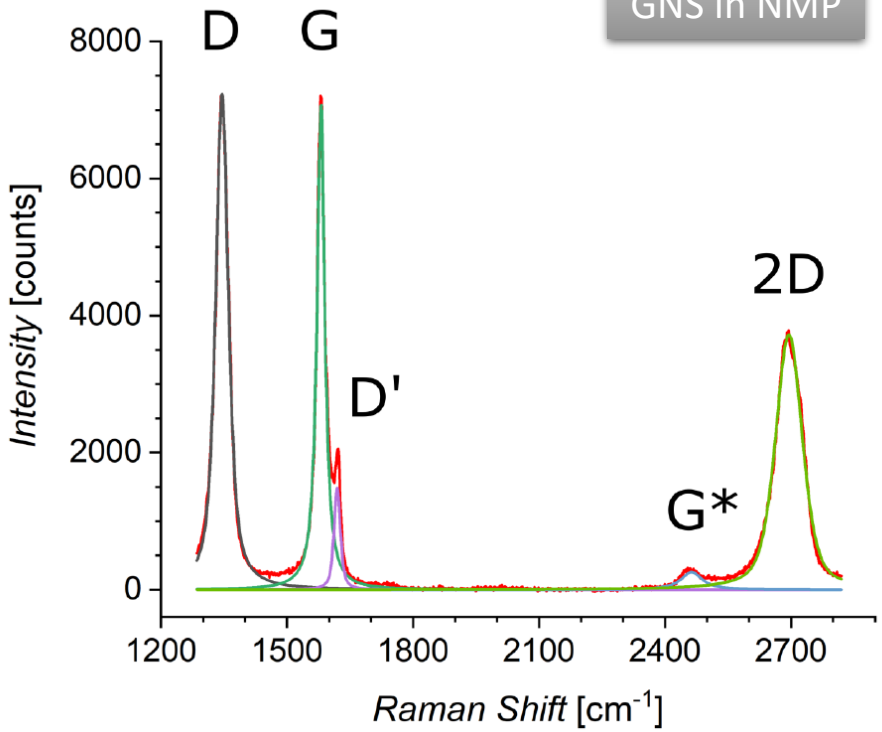
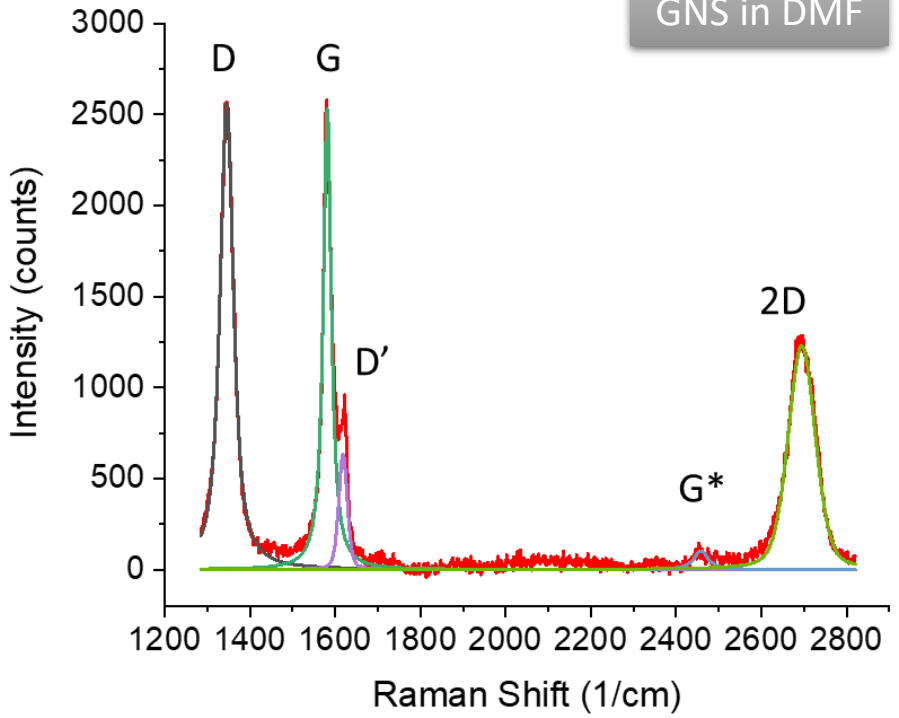
[L. Basta et al., *Nanoscale Advances*, **2021**]

Raman analysis

GNS in NMP



GNS in DMF



[L. Basta et al., *Nanoscale Advances*, **2021**]

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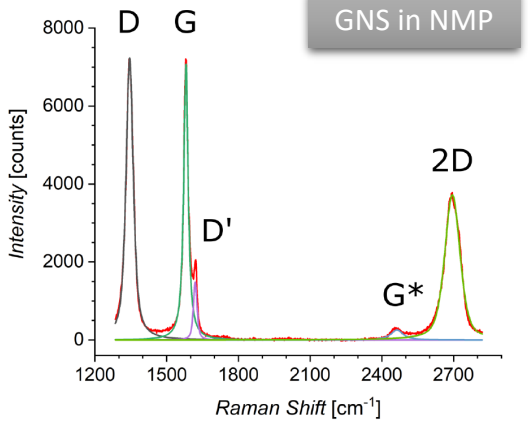
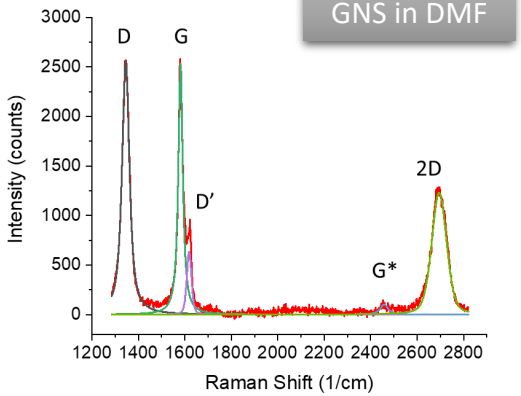
Raman analysis

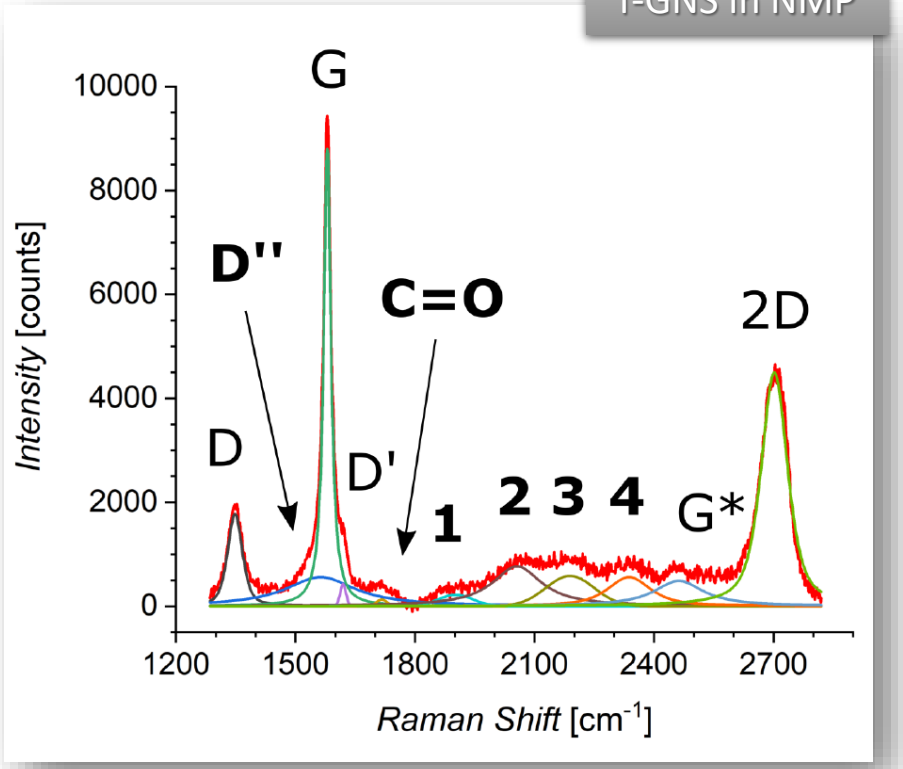
GNS in NMP



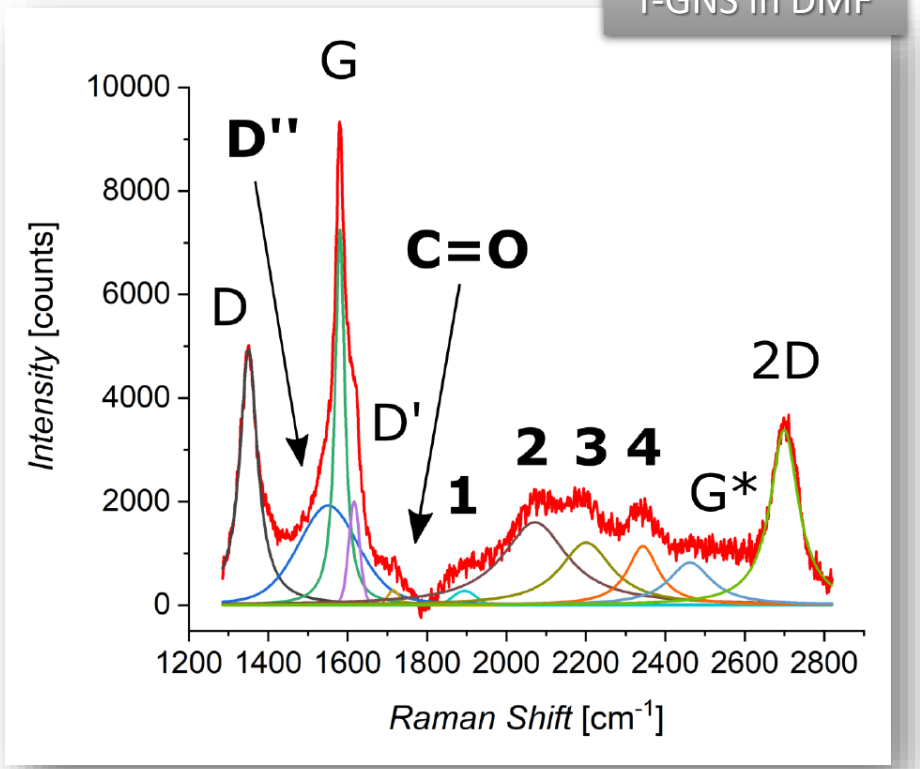
GNS in DMF



f-GNS in NMP



f-GNS in DMF



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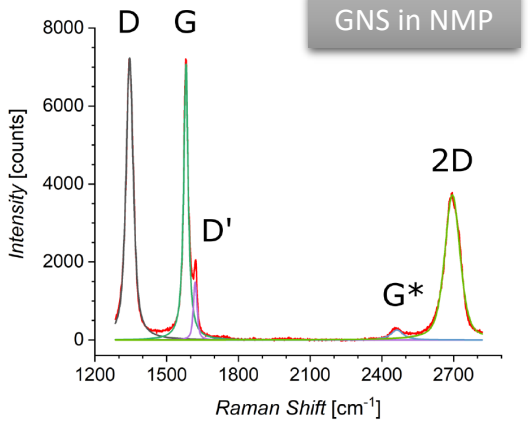
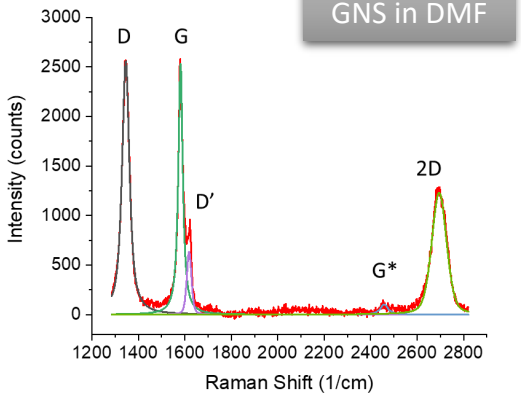
[L. Basta et al., *Nanoscale Advances*, **2021**]

Raman analysis

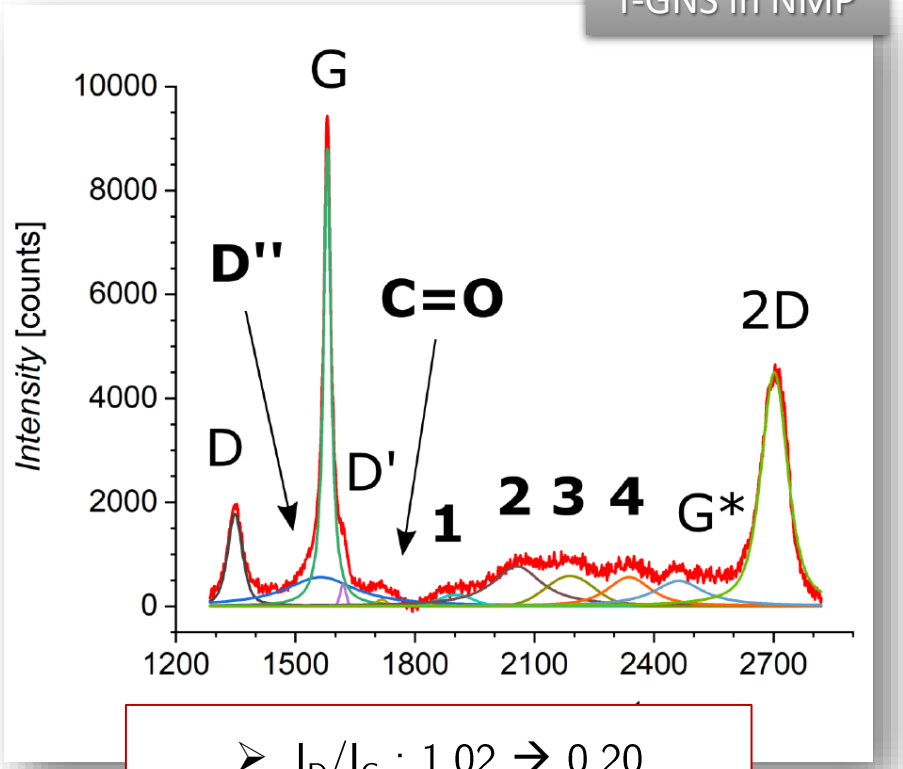
GNS in NMP



GNS in DMF

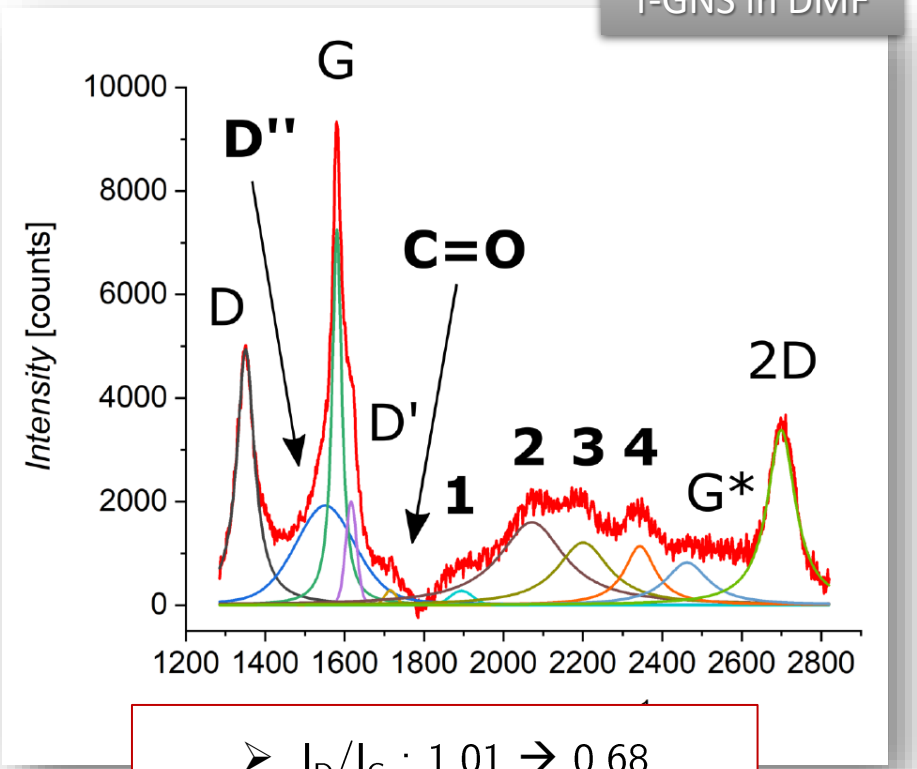


f-GNS in NMP



➢ I_D/I_G : 1.02 → 0.20

f-GNS in DMF



➢ I_D/I_G : 1.01 → 0.68

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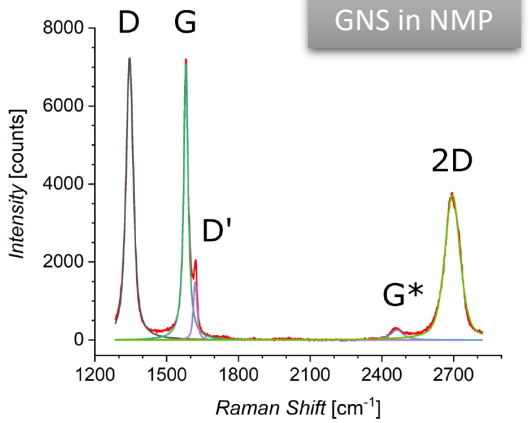
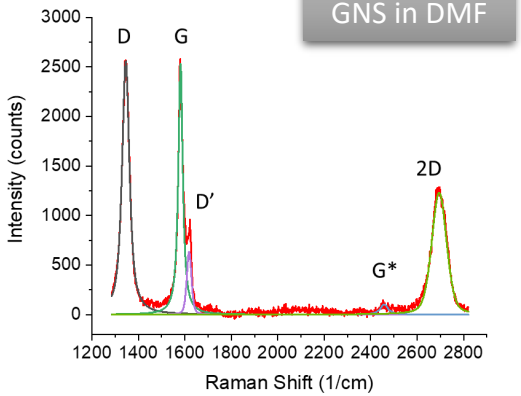
[L. Basta et al., *Nanoscale Advances*, **2021**]

Raman analysis

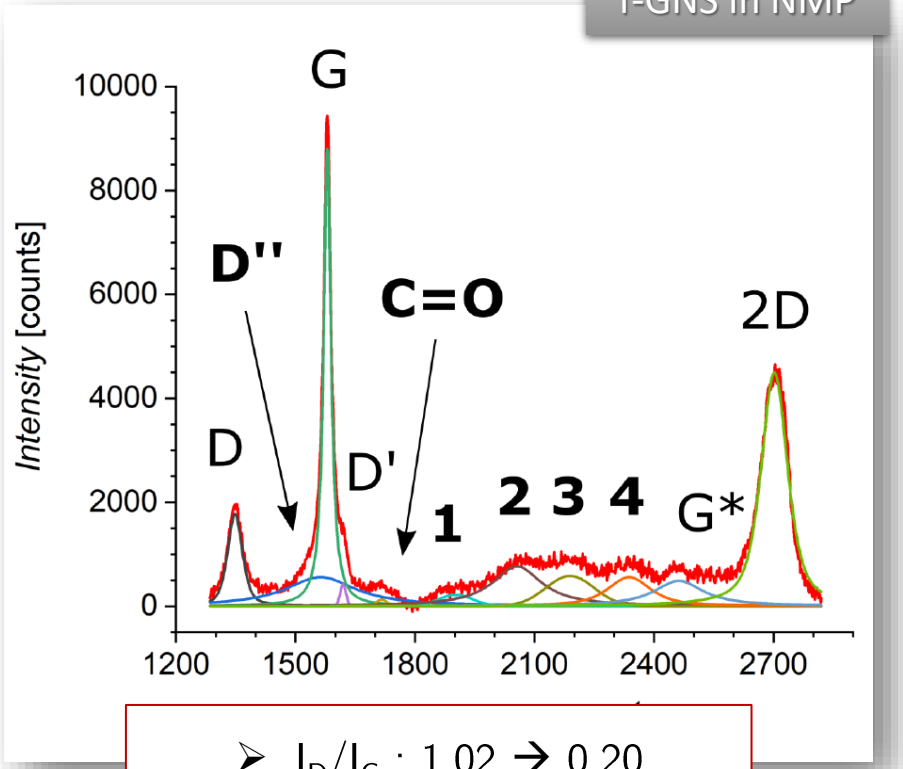
GNS in NMP



GNS in DMF

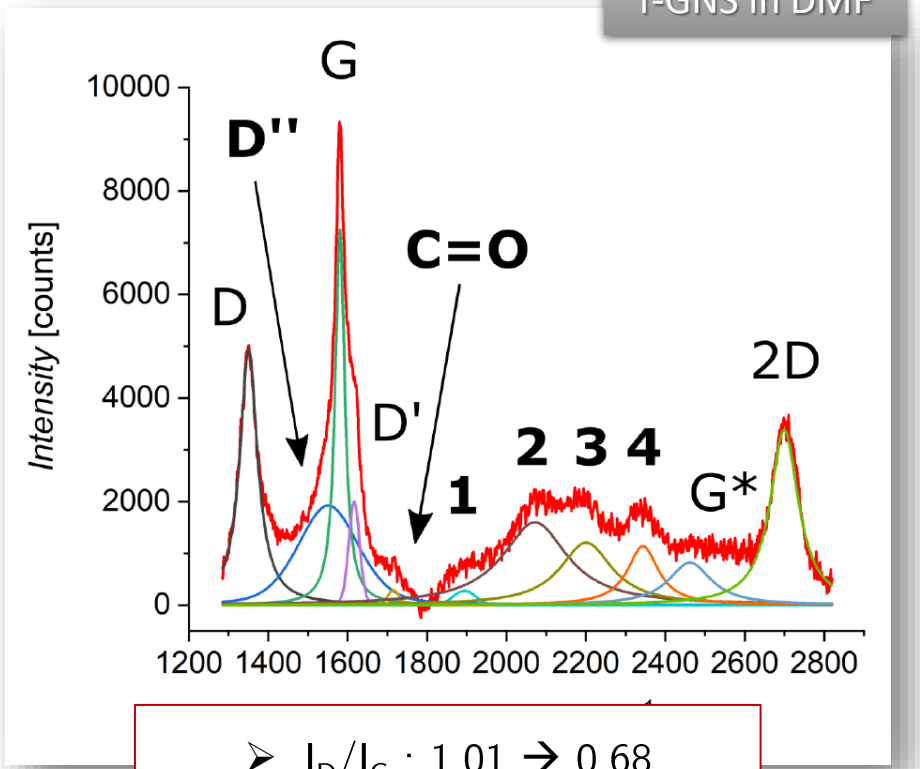


f-GNS in NMP



- I_D/I_G : 1.02 → 0.20
- I_{2D}/I_G : 0.53 → 0.51

f-GNS in DMF

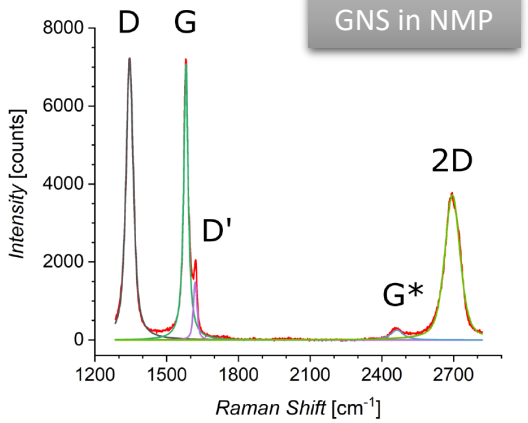


- I_D/I_G : 1.01 → 0.68
- I_{2D}/I_G : 0.49 → 0.49

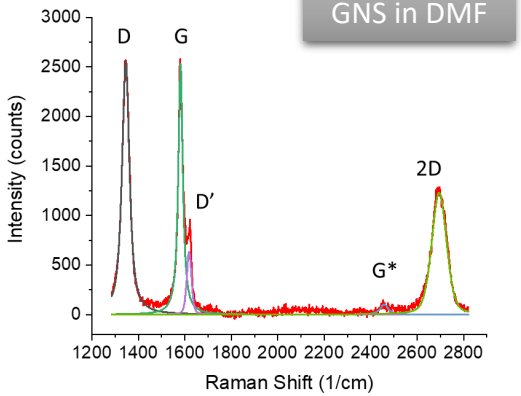
[L. Basta et al., *Nanoscale Advances*, **2021**]

Raman analysis

GNS in NMP

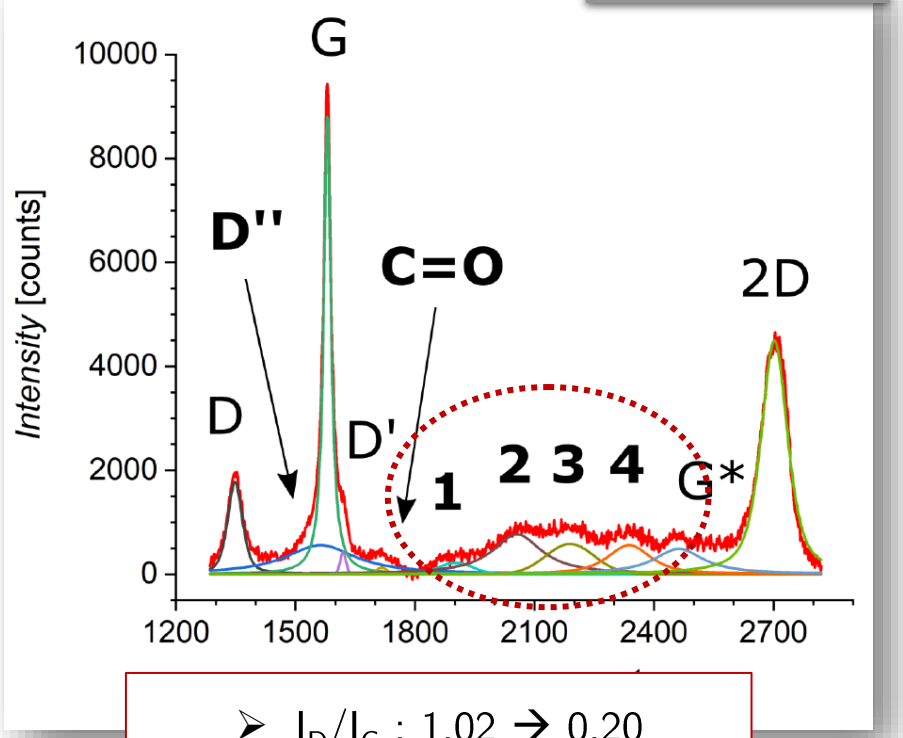


GNS in DMF



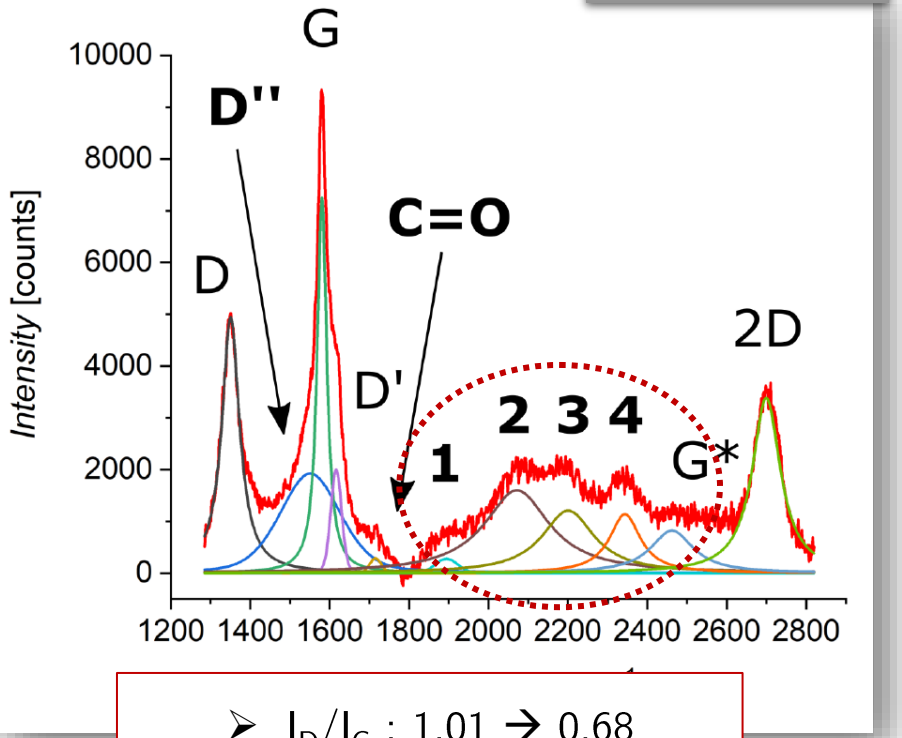
[L. Basta et al., *Nanoscale Advances*, **2021**]

f-GNS in NMP



- I_D/I_G : 1.02 → 0.20
- I_{2D}/I_G : 0.53 → 0.51
- New peaks!

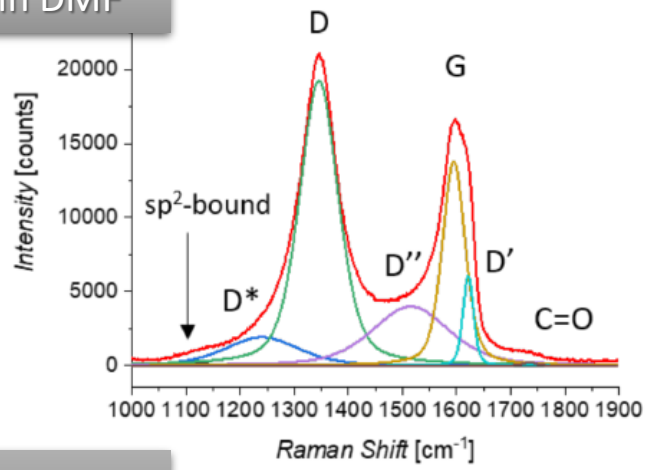
f-GNS in DMF

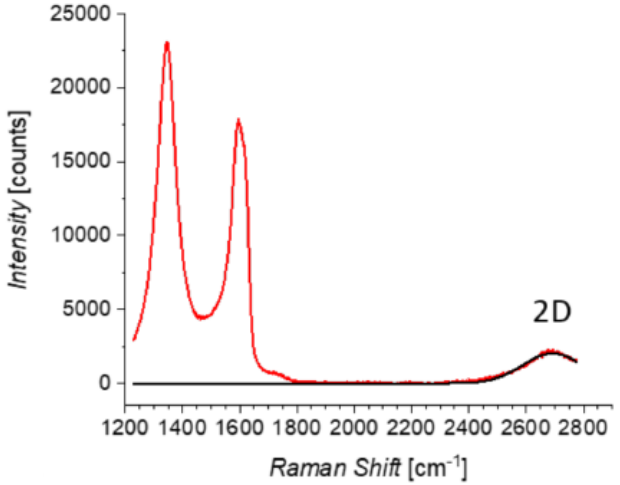


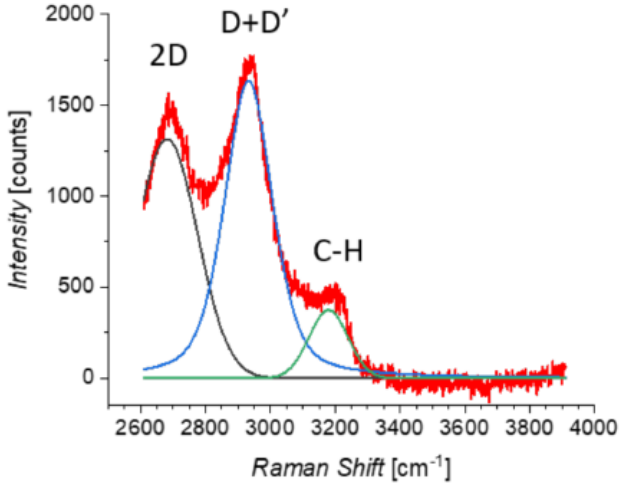
- I_D/I_G : 1.01 → 0.68
- I_{2D}/I_G : 0.49 → 0.49
- New peaks!

Raman analysis

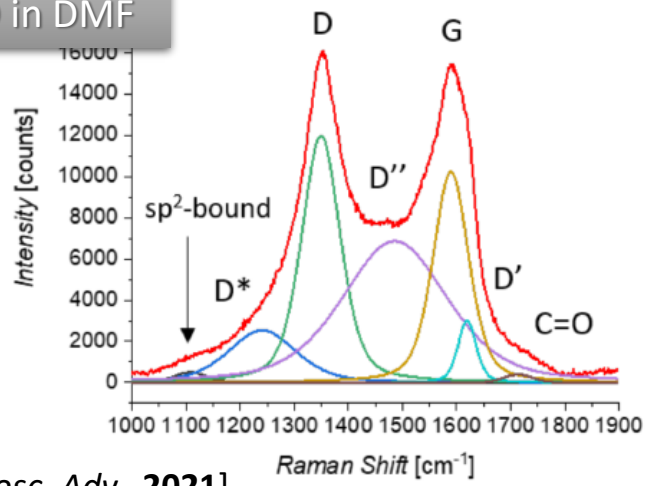
rGO in DMF

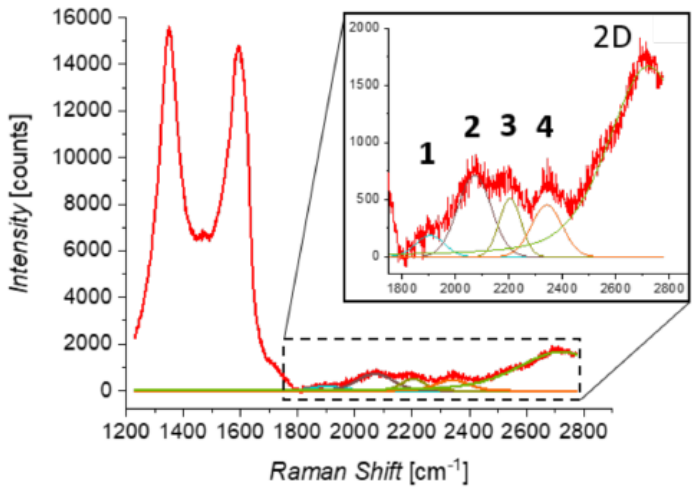


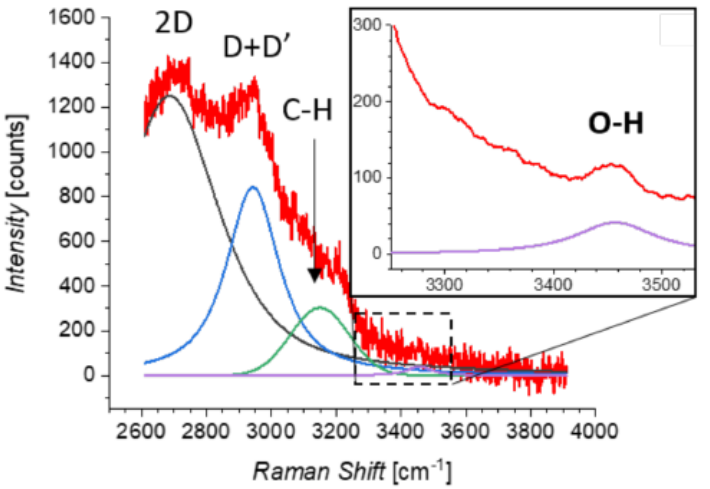




f-rGO in DMF





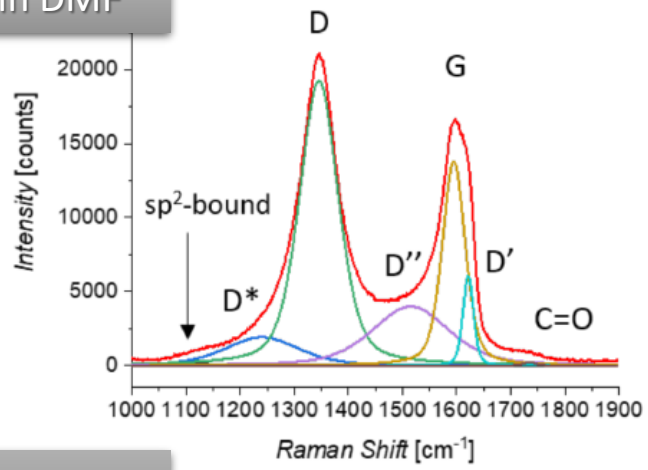


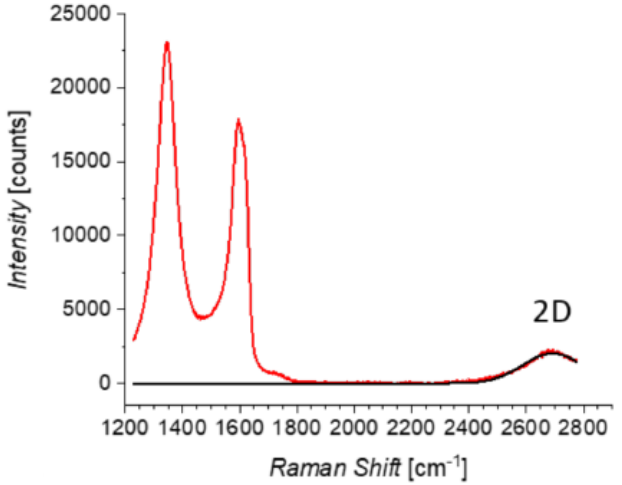
[L. Basta et al., *Nanosc. Adv.*, **2021**]

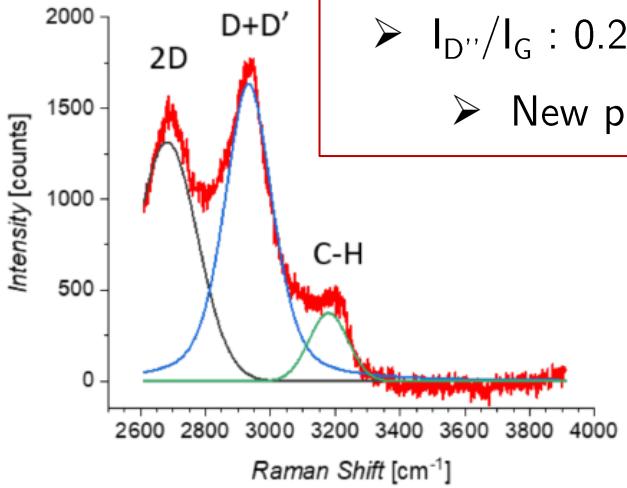
Raman analysis

- I_D/I_G : 1.39 → 1.17
- $I_{D''}/I_G$: 0.29 → 0.67
- New peaks!

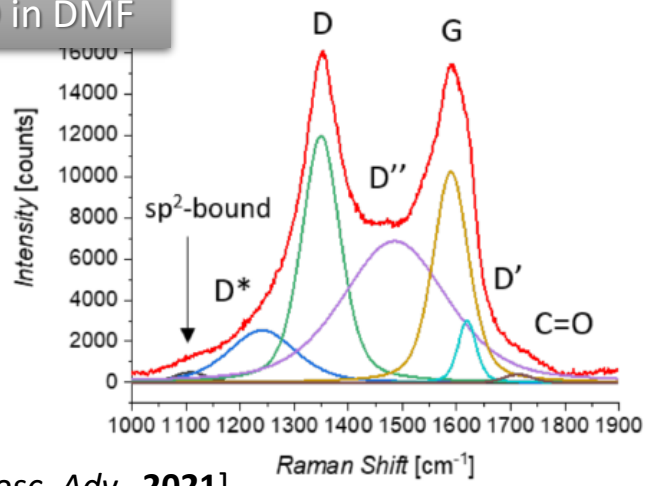
rGO in DMF

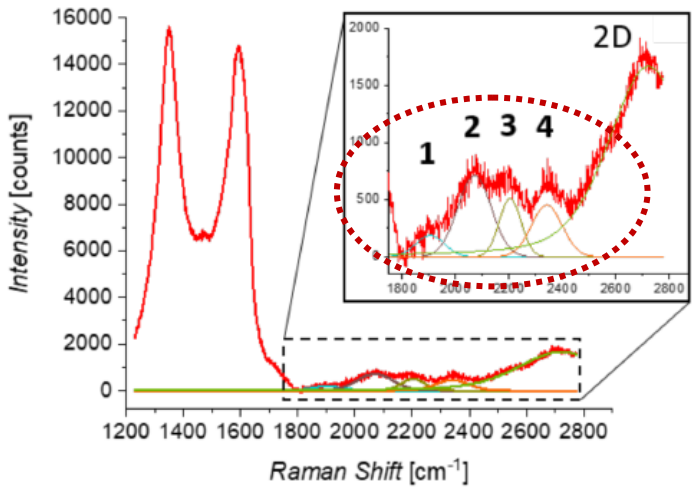


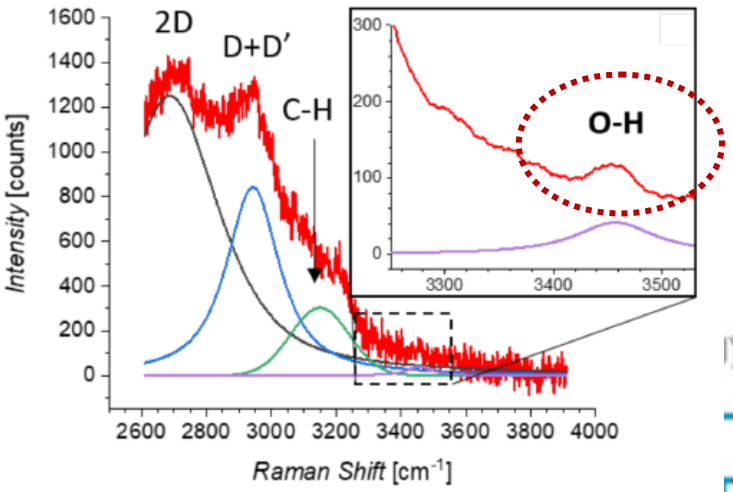




f-rGO in DMF

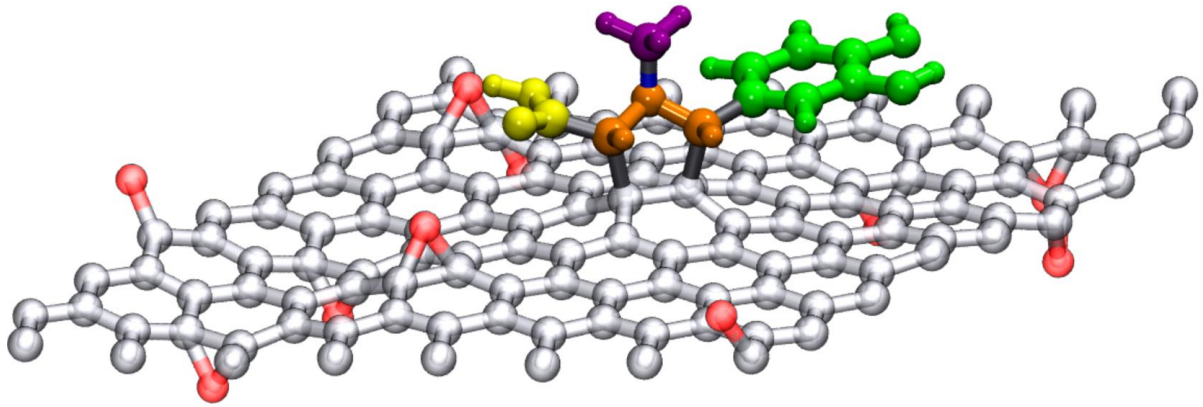






[L. Basta et al., *Nanosc. Adv.*, **2021**]

DFT – Power Spectrum



[*L. Bellucci* @ NEST]

[L. Basta et al., *Nanoscale Advances*, **2021**]

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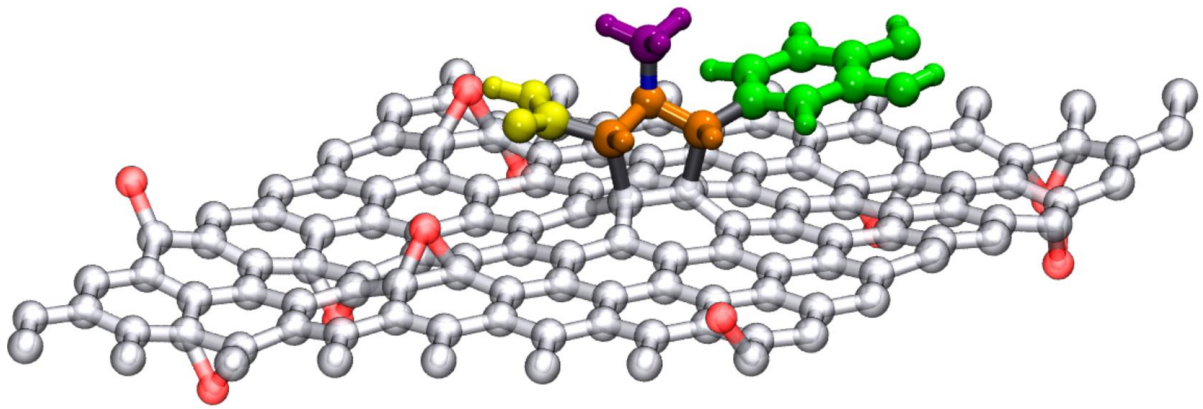
DFT – Power Spectrum



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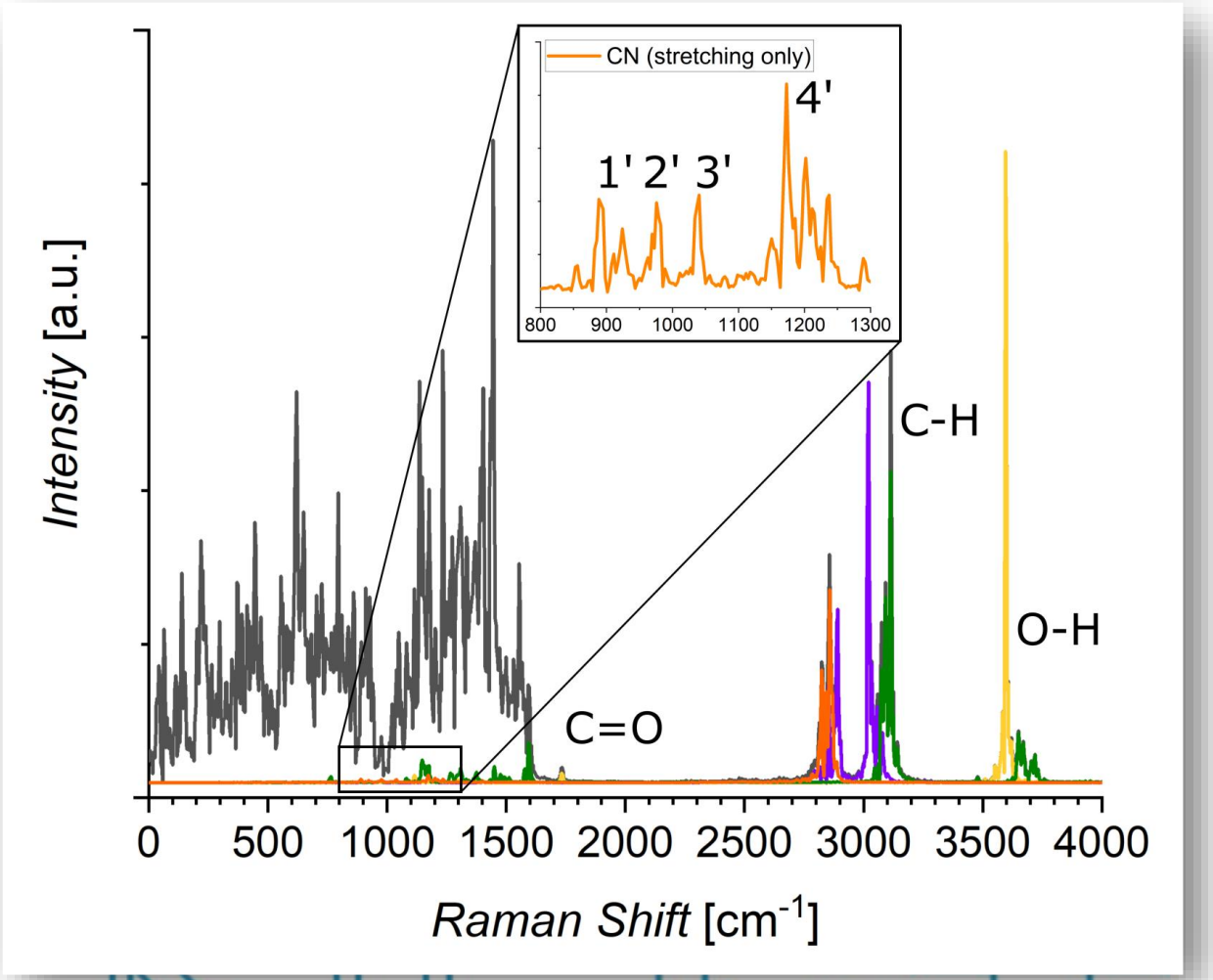
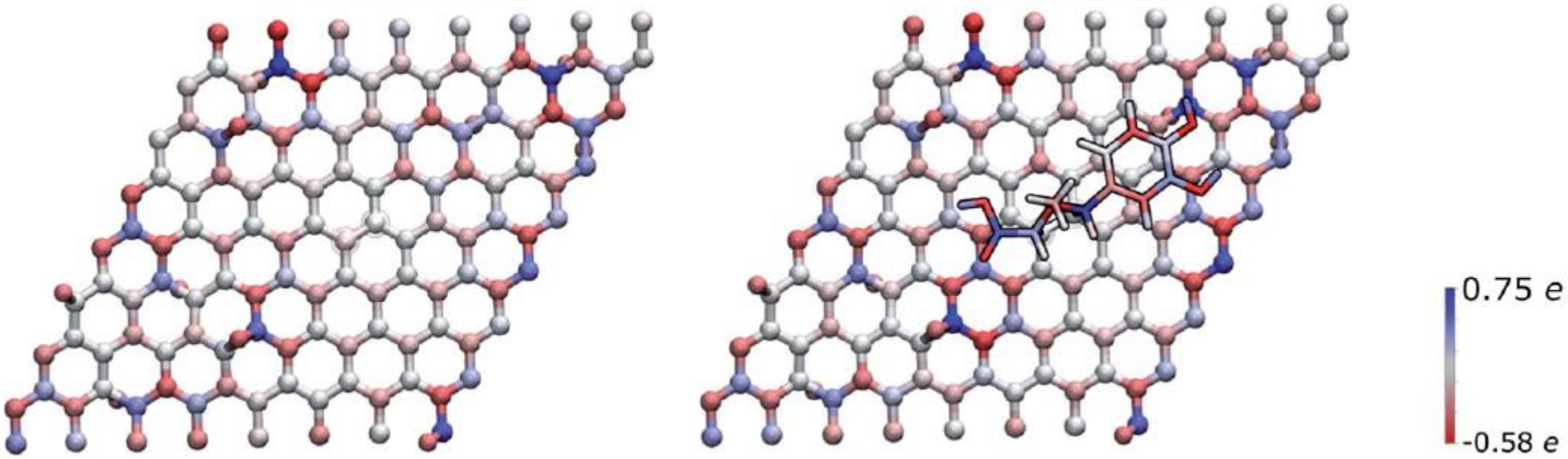
[L. Basta et al., *Nanoscale Advances*, **2021**]



DFT – CHARGE LOCALIZATION

pristine rGO

f-rGO



RESP (restrained electrostatic potential) derived partial atomic charges

[L. Basta et al., *Nanoscale Advances*, **2021**]

Conclusions

- 1,3-DC of GNS and rGO in the liquid phase

Conclusions

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- Solvent comparison:
  - NMP → better dispersion
  - DMF → higher functionalization

Conclusions

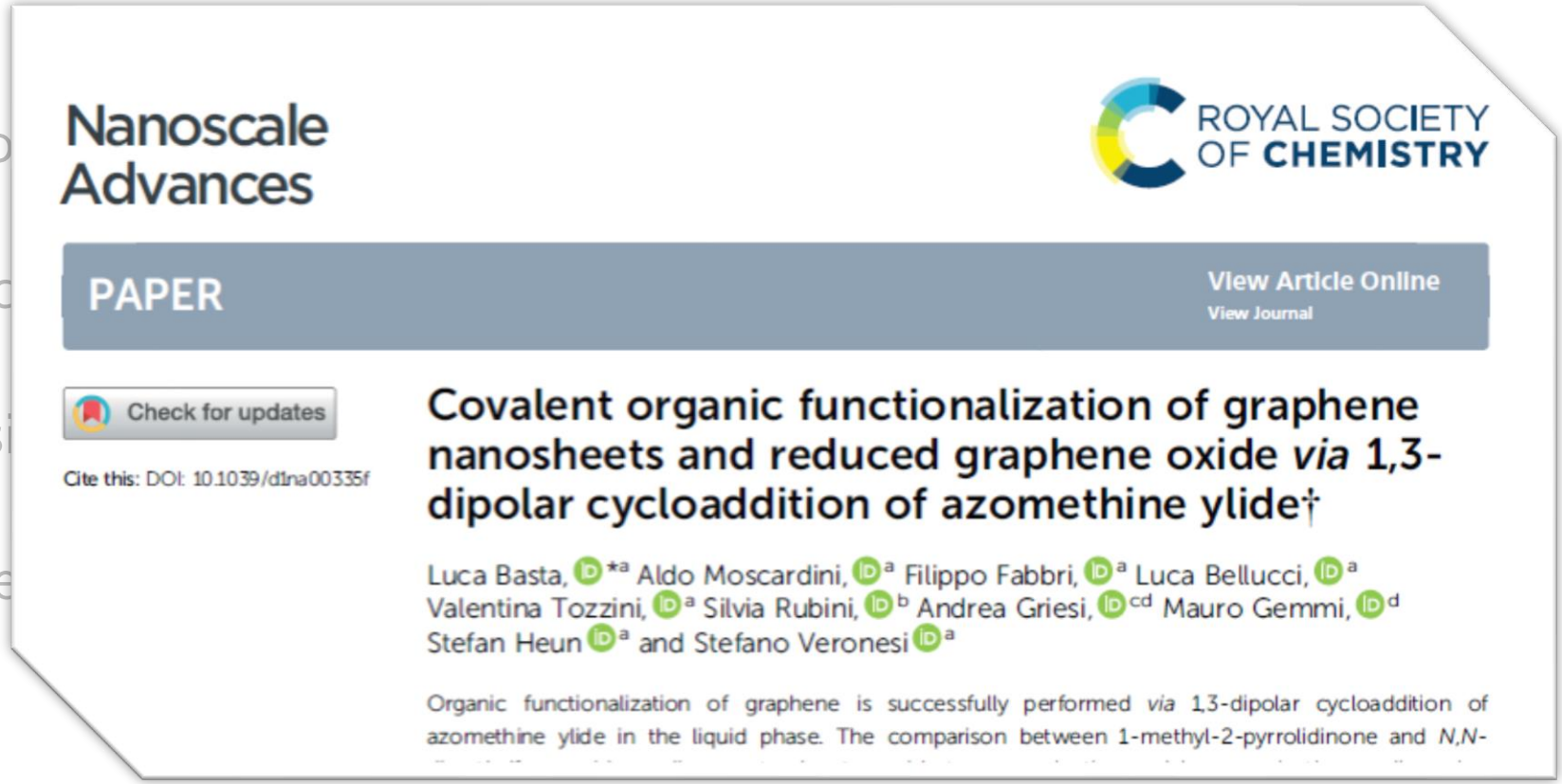
- 1,3-DC of GNS and rGO in the liquid phase
- Solvent comparison (NMP vs DMF)
- Raman signature of the functionalization

Conclusions

- 1,3-DC of GNS and rGO in the liquid phase
- Solvent comparison (NMP vs DMF)
- Raman signature of the functionalization
- Higher reactivity of rGO due to the presence of “defects”

Conclusions

- 1,3-DC o
- Solvent c
- Raman si
- Higher re



Nanoscale Advances

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/d1na00335f

Covalent organic functionalization of graphene nanosheets and reduced graphene oxide *via* 1,3-dipolar cycloaddition of azomethine ylide†

Luca Basta, *[a] Aldo Moscardini, [a] Filippo Fabbri, [a] Luca Bellucci, [a] Valentina Tozzini, [a] Silvia Rubini, [b] Andrea Griesi, [cd] Mauro Gemmi, [d] Stefan Heun [a] and Stefano Veronesi [a]

Organic functionalization of graphene is successfully performed *via* 1,3-dipolar cycloaddition of azomethine ylide in the liquid phase. The comparison between 1-methyl-2-pyrrolidinone and *N,N*-

[L. Basta et al., *Nanoscale Advances*, **2021**]

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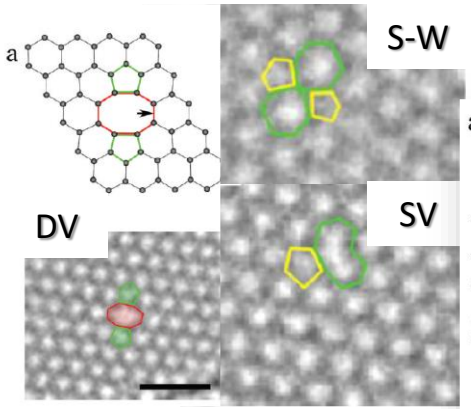
Outlooks

Investigation on defects



[*ACSNano*, **2015**, 9, 4, 3428
ACSNano, **2011**, 5, 1, 26]

[*L. Basta*, *arXiv*, **2021;**
L. Bellucci, F. Bianco @ NEST]

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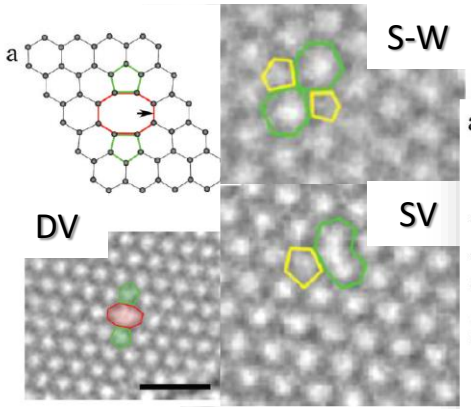

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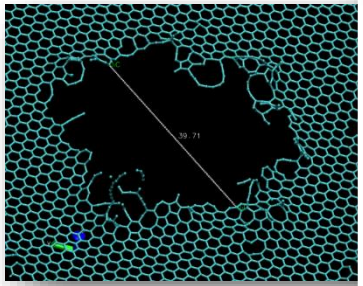

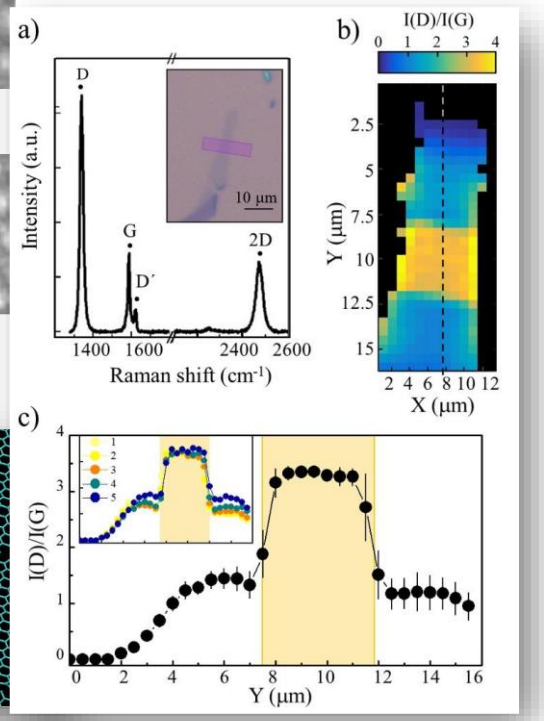

[*L. Basta*, *arXiv*, **2021;**
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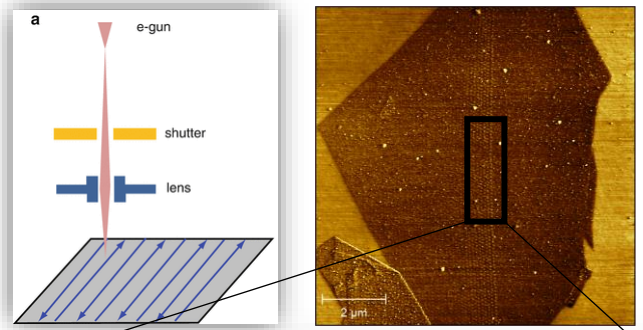
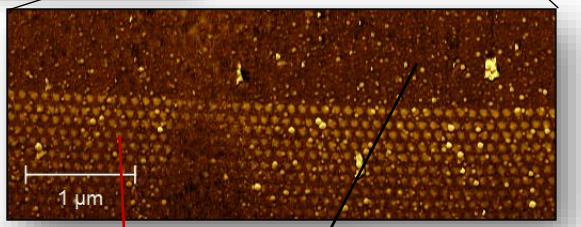
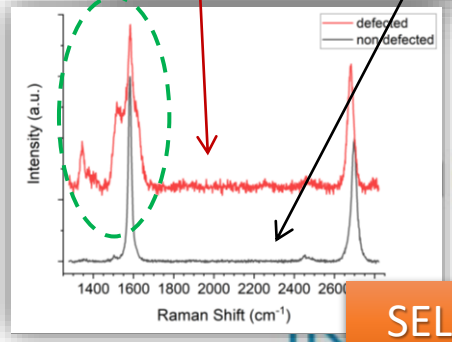
Patterned graphene flakes







SELECTIVITY

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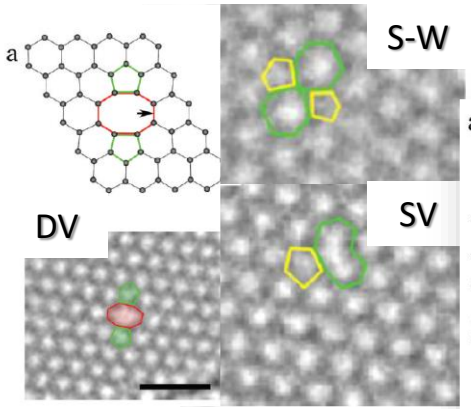
Outlooks

Investigation on defects



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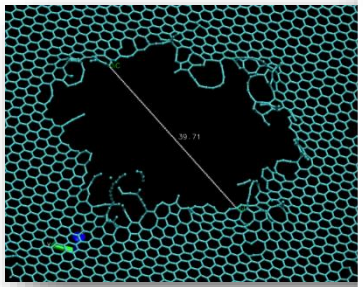

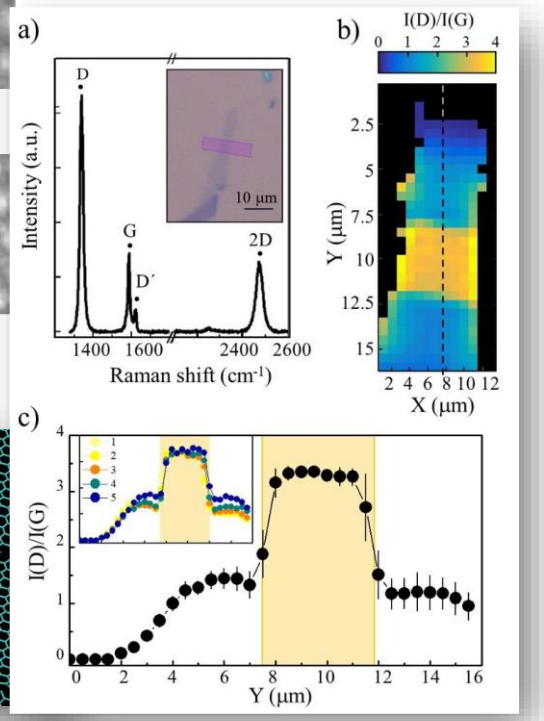

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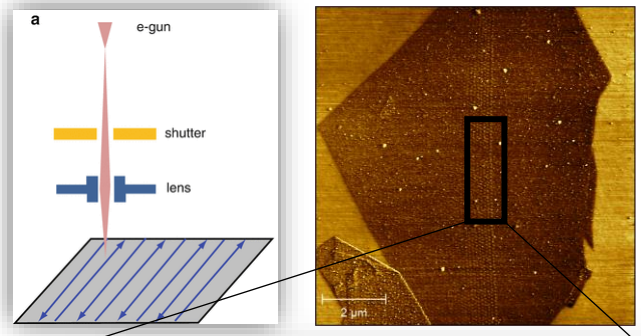
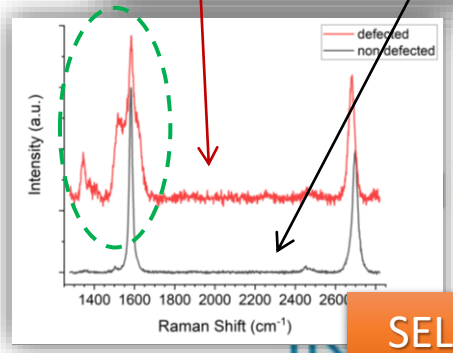
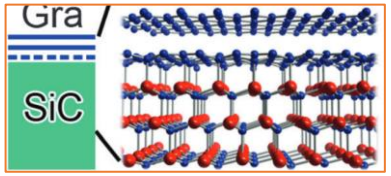


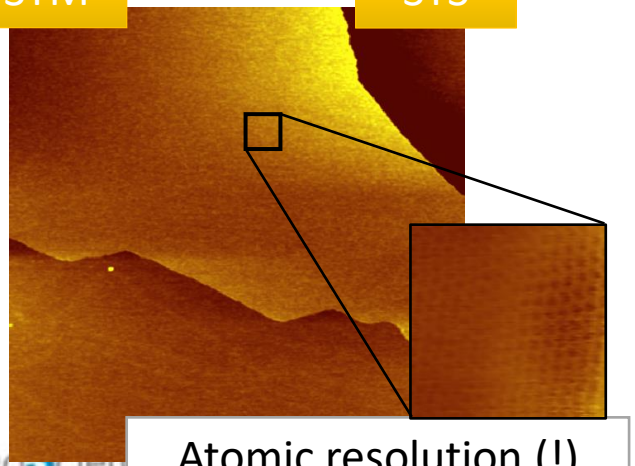


SELECTIVITY

Epitaxial ML Graphene



STM STS



Atomic resolution (!)

People

Aldo Moscardini

Filippo Fabbri

Silvia Rubini

Andrea Griesi

Mauro Gemmi

Luca Bellucci

Valentina Tozzini

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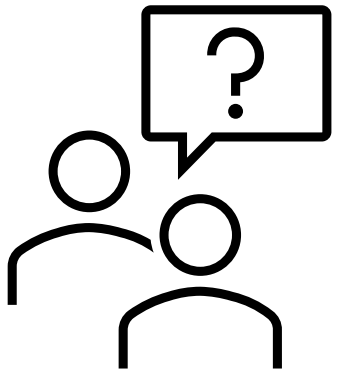
Thank You

For Your Attention



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