Hydrogen loading of graphene

Carlo Mariani* et aliae et alii
(Ptolemy collab. Rome)

* Università di Roma «La Sapienza» and INFN,
carlo.mariani@uniroma1.it

Ptolemy collaboration meeting, Zandvoort, The Netherlands, 6-7 October 2022

acknowledgements

Alice APPONI (Roma Tre, INFN-Ptolemy)
Maria Grazia BETTI
Elena BLUNDO (PhD student)
Gianluca CAVOTO (Sapienza, INFN-Ptolemy)
Riccardo FRISENDA
Dario MARCHIANI (PhD student)
Francesco PANDOLFI (INFN-Ptolemy)
Antonio POLIMENI
Ilaria RAGO (INFN-Ptolemy)
Alessandro RUOCCO (Roma Tre, INFN-Ptolemy)
Sammar TAYYAB (PhD student)
…, …

NPG synthesis

JEONG Samuel
ITO Yoshikazu

micro-spectroscopy

Maria Carmen ASENSIO*
José AVILA
Pavel DUDIN

*now at CSIC, Madrid

ab-initio theory

Elisa MOLINARI
Deborah PREZZI (CNR)
…
…

atomic H-bonding to graphene: graphane

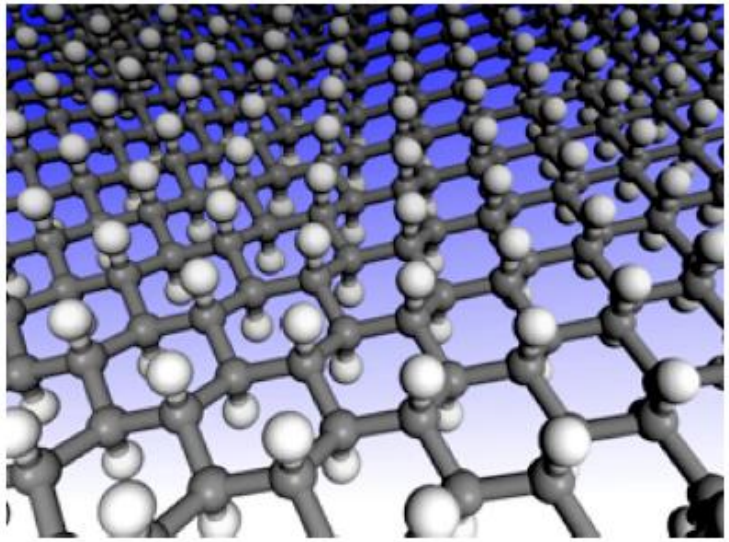
- "graphane": same structure of graphene (Gr) **BUT** semiconducting
- till now, H-Gr on Gr flakes and substrate supported-Gr
- atomic ^{1}H (H) and ^{2}H (D) chemically active as ^{3}H (T)*
- actual self-standing graphene: Nano Porous Graphene
- hydrogenation and deuteration by i) low-energy ion and ii) atom exposure: results and perspectives (high upload, cleanness, stability)

* Betti et al. (Ptolemy), Prog. Part. Nucl. Phys. **106**, 120-131 (2019);
Apponi et al. (Ptolemy), Phys. Rev. D **106**, 053002 (2022)

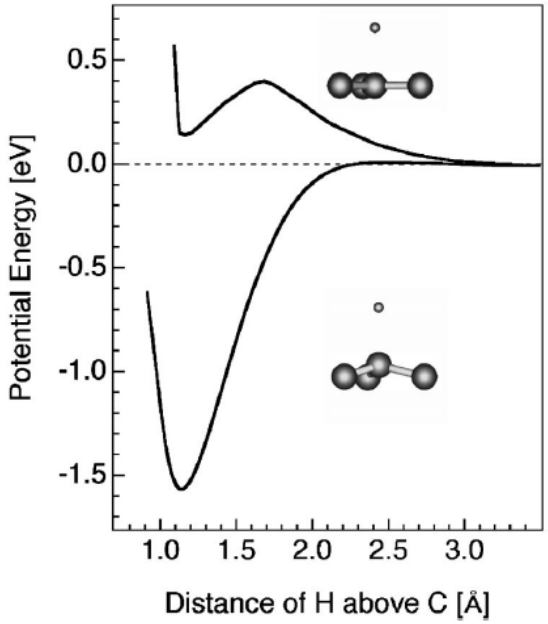
from graphene to graphane, theory

atomic H as a tool to '*pinch*' the sp^2 bonds towards an sp^3 configuration while maintaining the planar nature of graphene

"chair" conformation



Sofo et alii, Phys. Rev. B **75**, 153401 (2007)



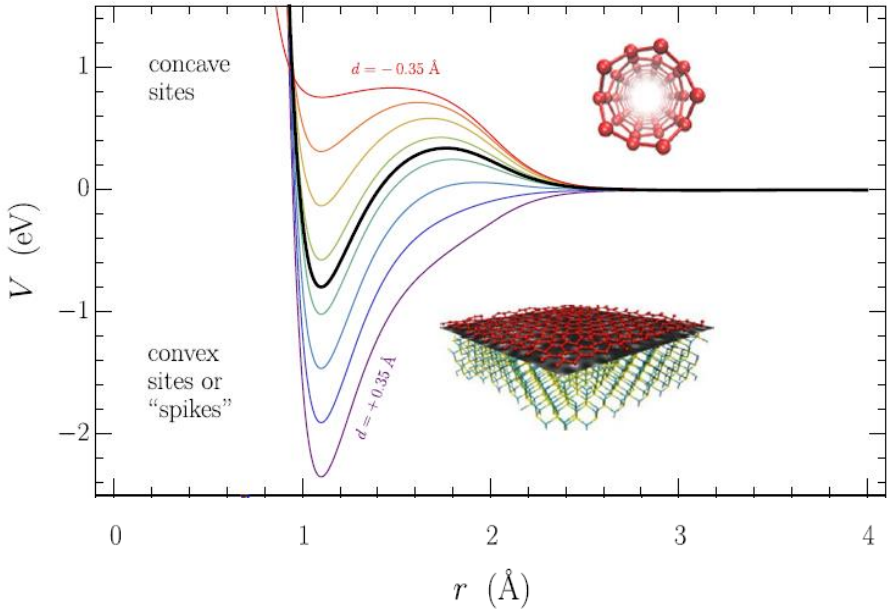
- covalent bonding, small charge transfer (~0.003 e)*

- C atom convexity (0.3 Å with respect to graphene plane) lowers H chemisorption energy barrier to ~ 0.2 eV**

H-to-C potential curve -> favoured sp^3 configuration **

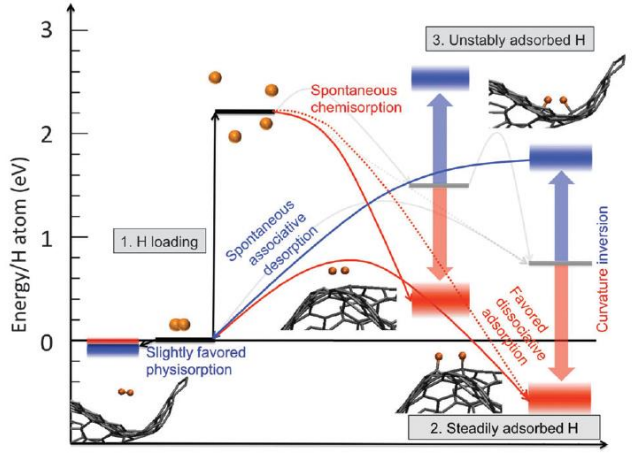
- Ryu et alii, Nano Lett. **8**, 4597 (2008); ** Ruffieux et alii, Phys. Rev. B **66**, 245416 (2002); Hornekaer et alii, Phys. Rev. Lett. **97**, 186102 (2006); Luo et alii, ACS Nano **3,** 1781 (2009)

from graphene to graphane, theory

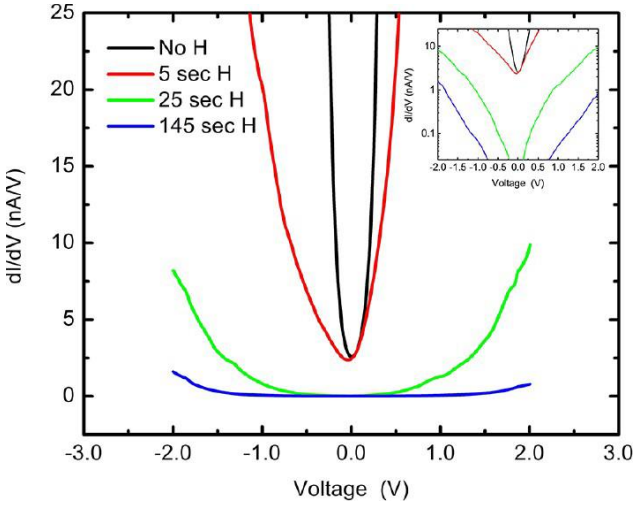


Apponi et al. (Ptolemy), Phys. Rev. D **106**, 053002 (2022)

convexity (with respect to graphene plane) **lowers H-C chemisorption energy barrier**



Tozzini and Pellegrini, Phys. Chem. Chem. Phys. **15**, 80 (2013)



Goler et al., J. Phys. Chem. **117**, 11506 (2013)

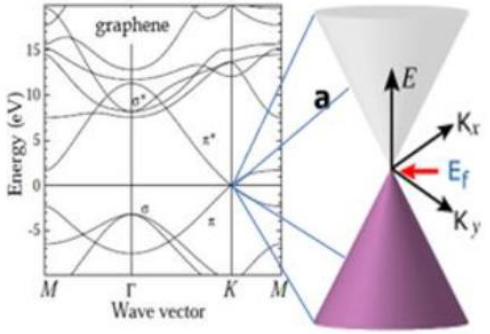
← experimental STS shows an **energy gap** at **convex Gr** zones exposed to **H**

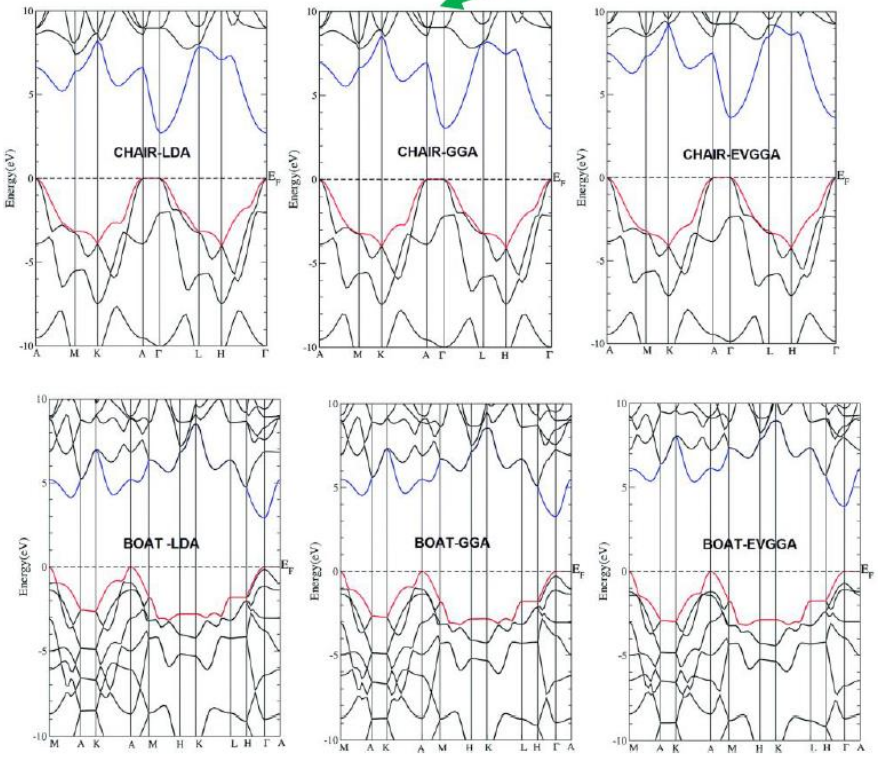
from graphene to graphane, theory

a semiconductor with ~3.5 eV energy-gap is predicted !

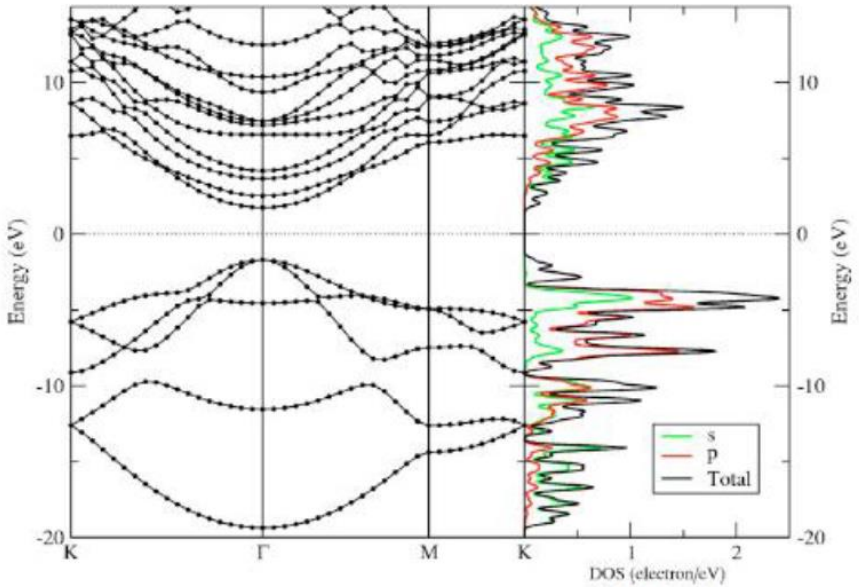
from semimetallic graphene, at K

to semiconducting "graphane", at Γ





Reshak et alii, PRCS Adv. **4**, 37411 (2014)

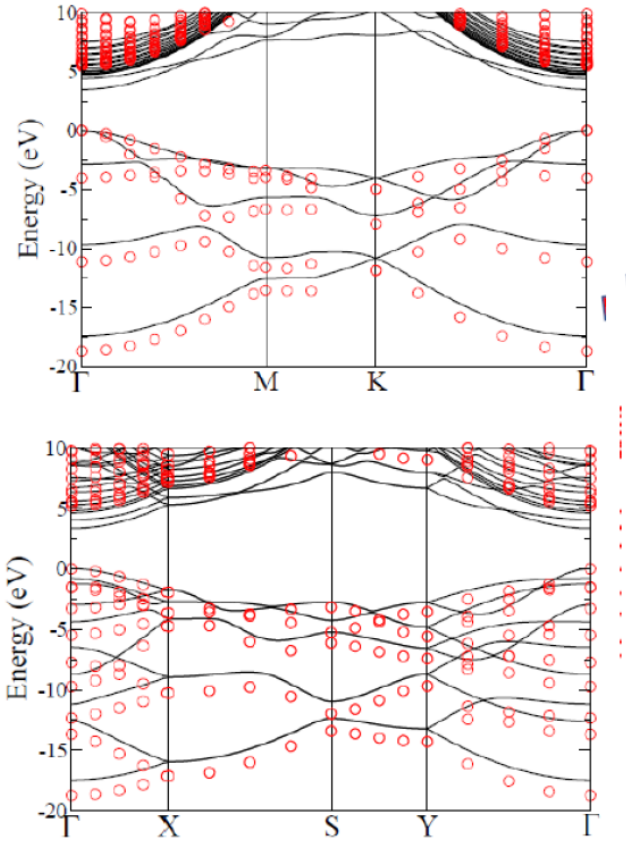


Sofo et alii, Phys. Rev. B **75**, 153401 (2007)

Samarakoon et alii, ACS Nano **4**, 4126 (2010)

from graphene to graphane, theory

calculations with GW corrections, Eg > 5 eV is predicted !



Conformation	Transition	GGA value (eV)	GW value (eV)
Chair	$\Gamma_v \rightarrow \Gamma_c$	3.5	5.4
	$M_v \rightarrow M_c$	10.8	13.7
	$K_v \rightarrow K_c$	12.2	15.9
Boat	$\Gamma_v \rightarrow \Gamma_c$	3.3	5.1
	$X_v \rightarrow X_c$	7.0	9.0
	$S_v \rightarrow S_c$	10.7	13.9
	$Y_v \rightarrow Y_c$	9.4	12.6

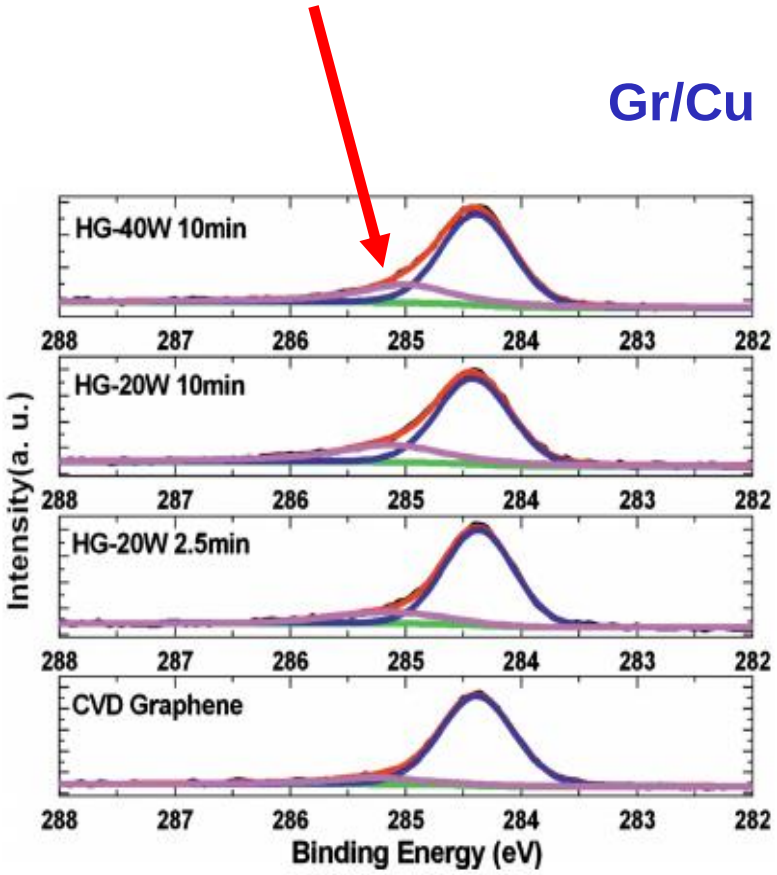
Reshak et alii, PRCS Adv. **4**, 37411 (2014)

Lebègue et alii, Phys. Rev. B **79**, 245117 (2009)

from graphene to graphane, experiments: still an open problem

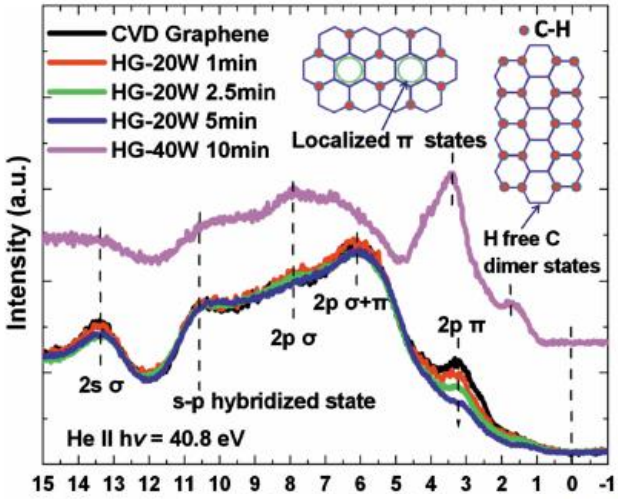
some work has been done MOSTLY on supported-graphene, and transferred Gr

Gr/Cu



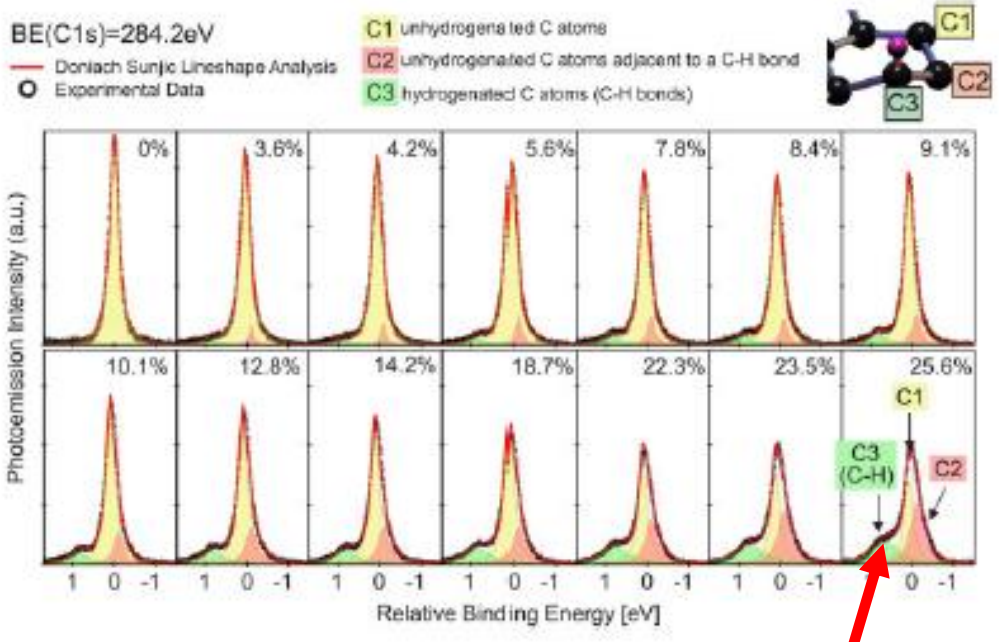
C1s core level photoemission

valence band photoemission



C1s core level photoemission

Gr/Au



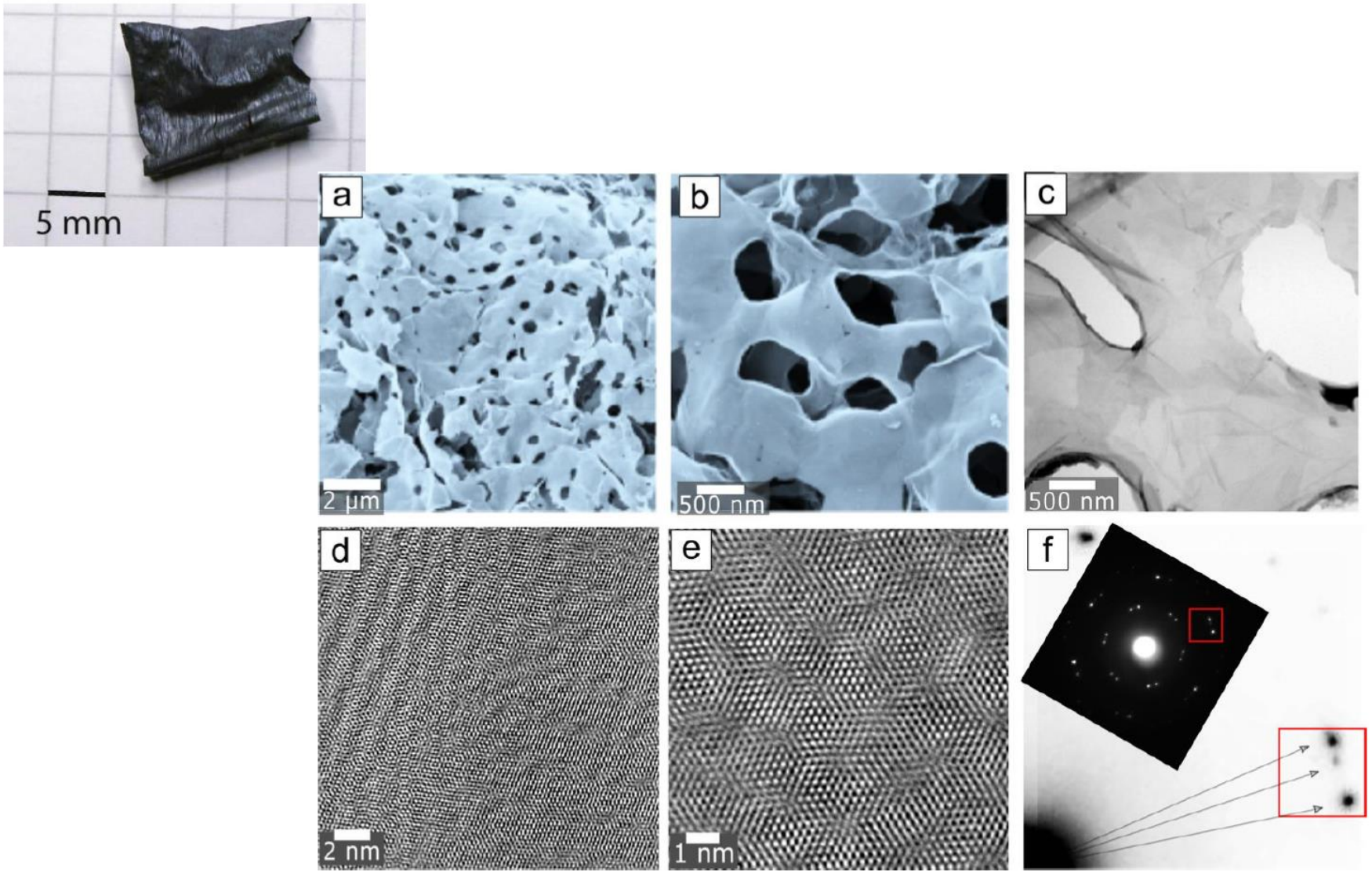
Luo et alii, Appl. Phys. Lett. **97**, 233111 (2010)

Haberer et alii, Phys. Stat. Sol. B **248**, 2639 (2011)

i) fully freestanding and high-quality graphene (nanoporous graphene, NPG)

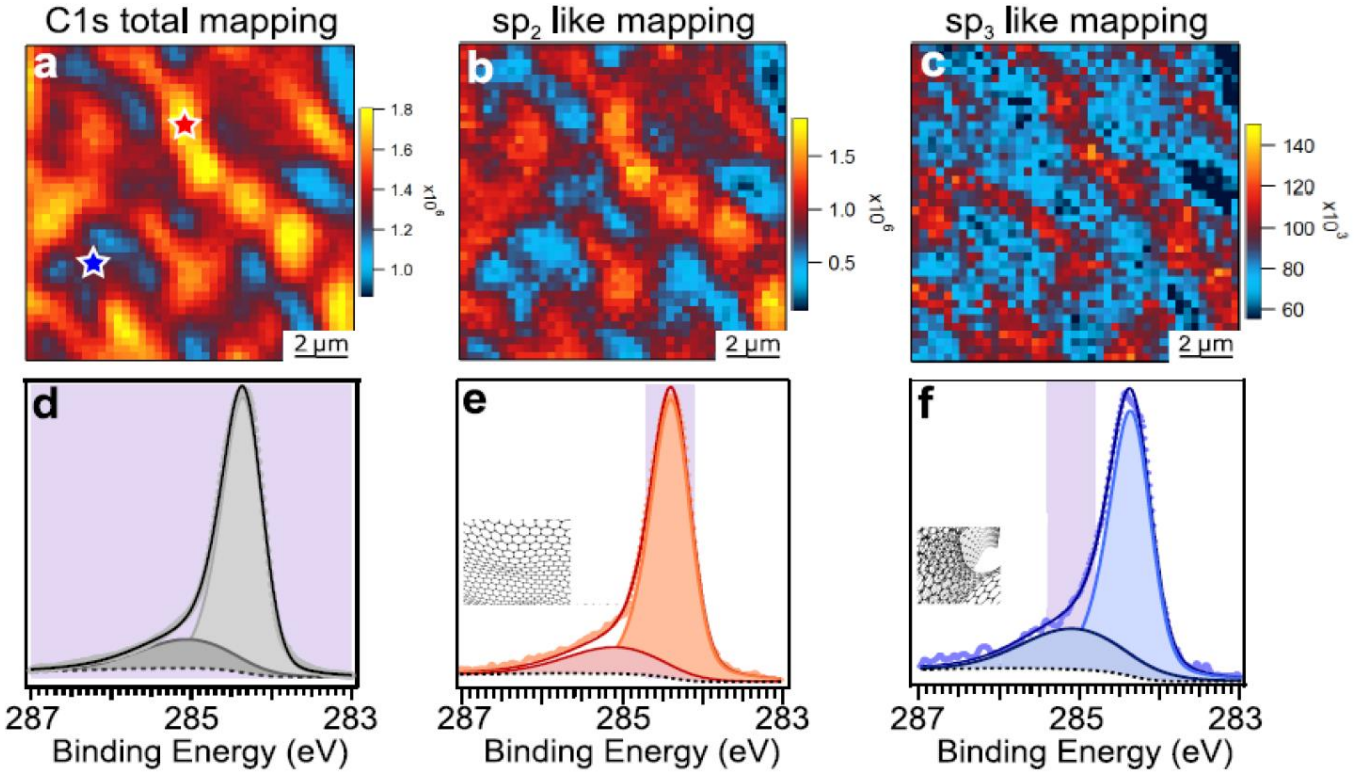
ii) its functionalisation with H and D (atomic H and D as chemically active as T)

NPG: microscopy and diffraction analysis



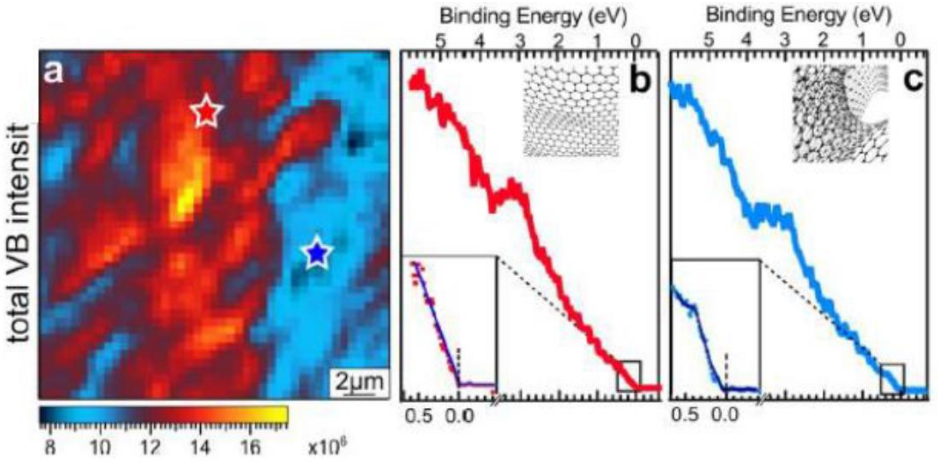
Di Bernardo et alii, ACS Omega **2**, 3691 (2017); Carbon **131**, 258 (2018)

NPG: spatially-resolved photoelectron spectroscopy



C 1s
core level

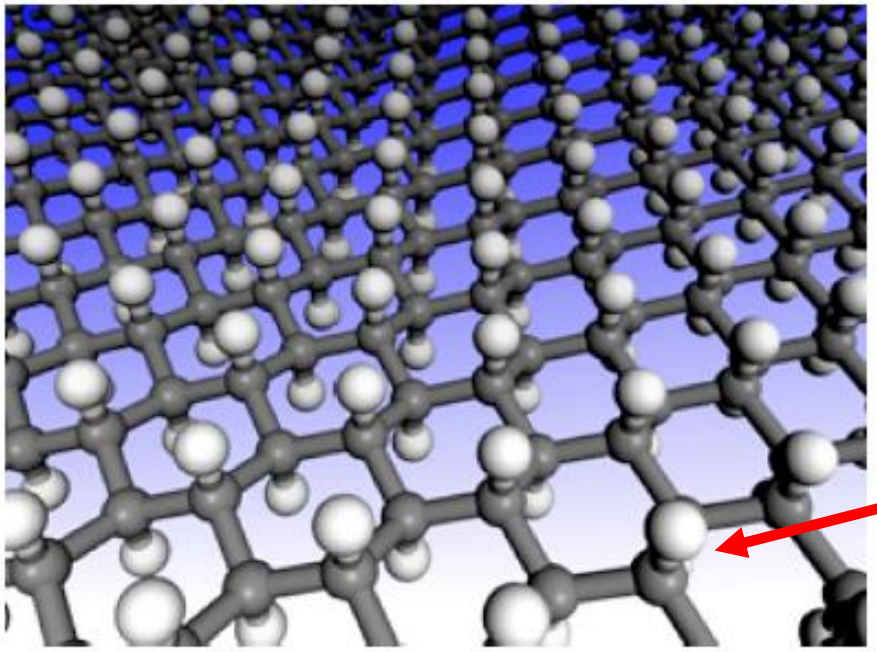
Valence Band: linear spectral density towards E_F (Dirac cone)



Di Bernardo et alii, ACS Omega **2**, 3691 (2017); Carbon **131**, 258 (2018)

from graphene to graphane

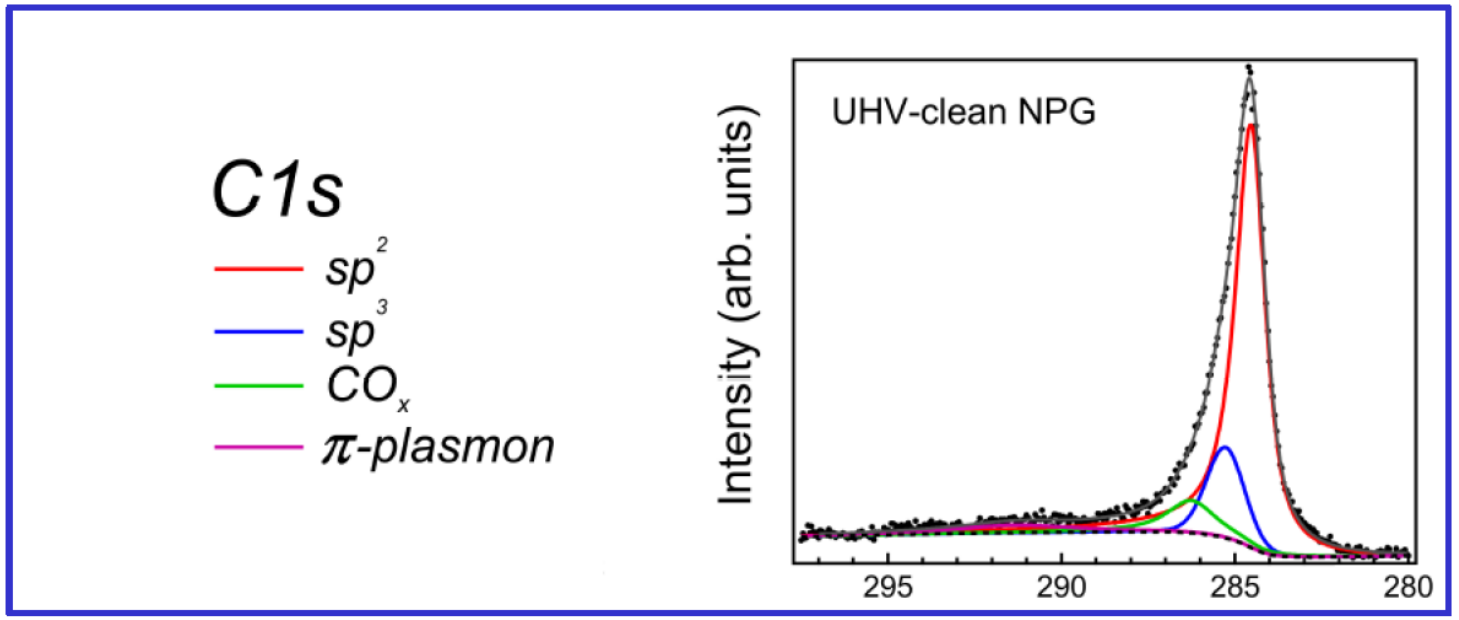
atomic H as a tool to '*pinch*' the sp2 bonds towards an sp3 configuration while maintaining the planar nature of graphene



sp3 H-C bond

how to estimate the H (or D):C upload → directly from a quantification of the sp3 bond spectroscopic signal from the XPS C 1s core level:

$$\%H/C = I_{sp3} / (I_{sp3} + I_{sp2}) = \Theta$$



Abdelnabi et alii, Nanomat. **11**, 130 (2021)

from graphene to graphane, experiments: the cold plasma approach (Princeton group)

Carbon 177 (2021) 244–251

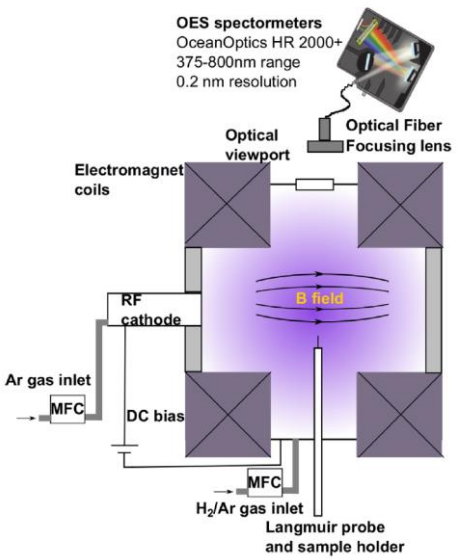
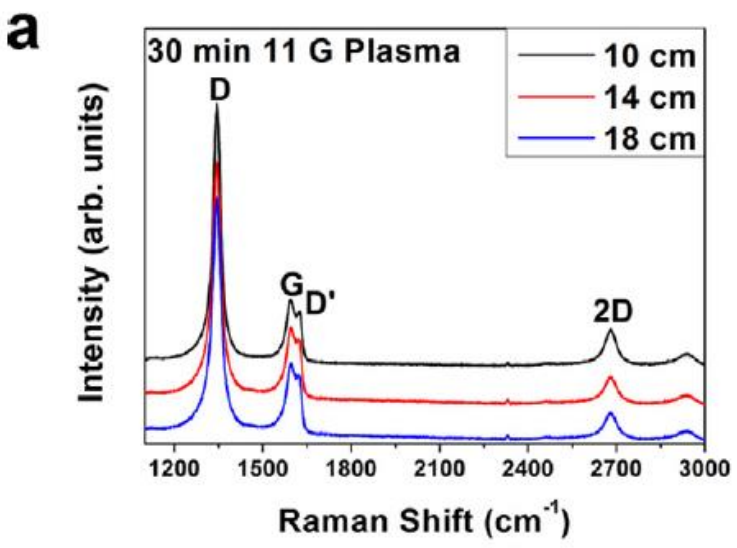
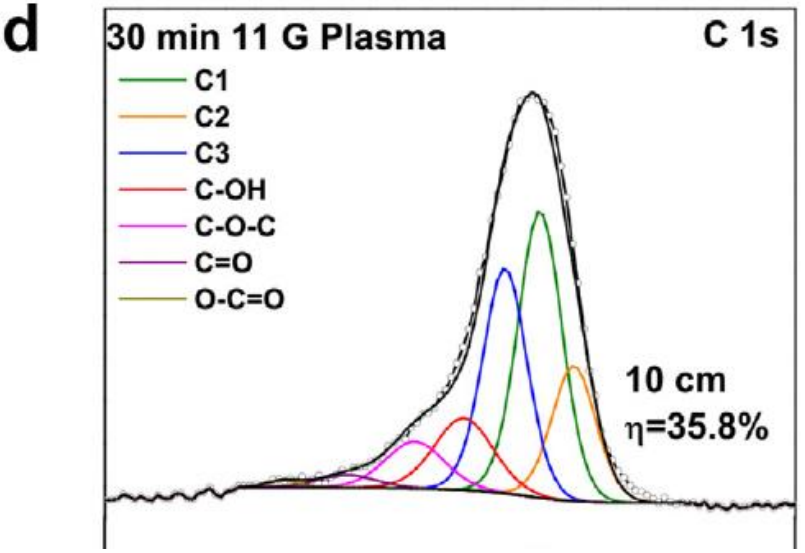


Fig. 1. Low-temperature crossed-field plasma discharge system setup. (A colour version of this figure can be viewed online.)

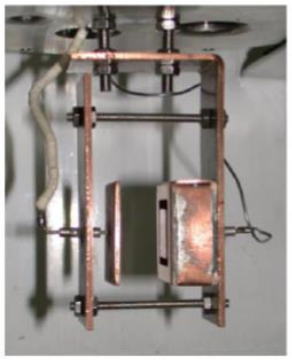
sp3 content of ~36%





Zhao et alii, Carbon **244**, 2639 (2021)

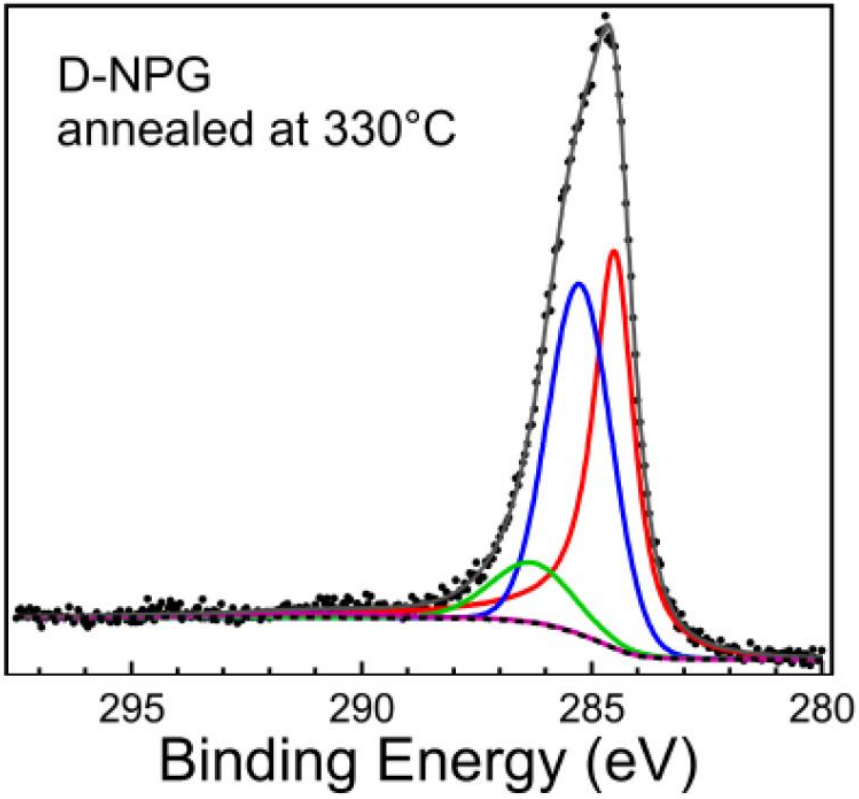
second method: thermal-energy (**<0.1 eV**) **H^+ ions**



very low-energy (thermal energy, <0.1 eV) D+ source at atmospheric pressure (Madrid collaboration)

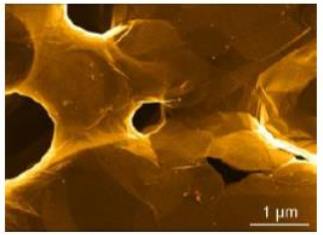
Θ_D ~ 50%

not any dangling bond defect

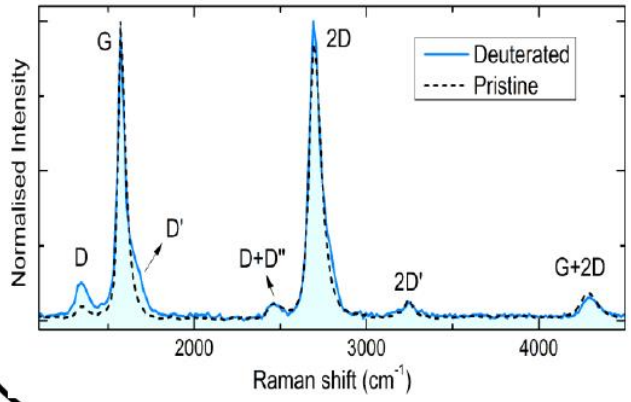


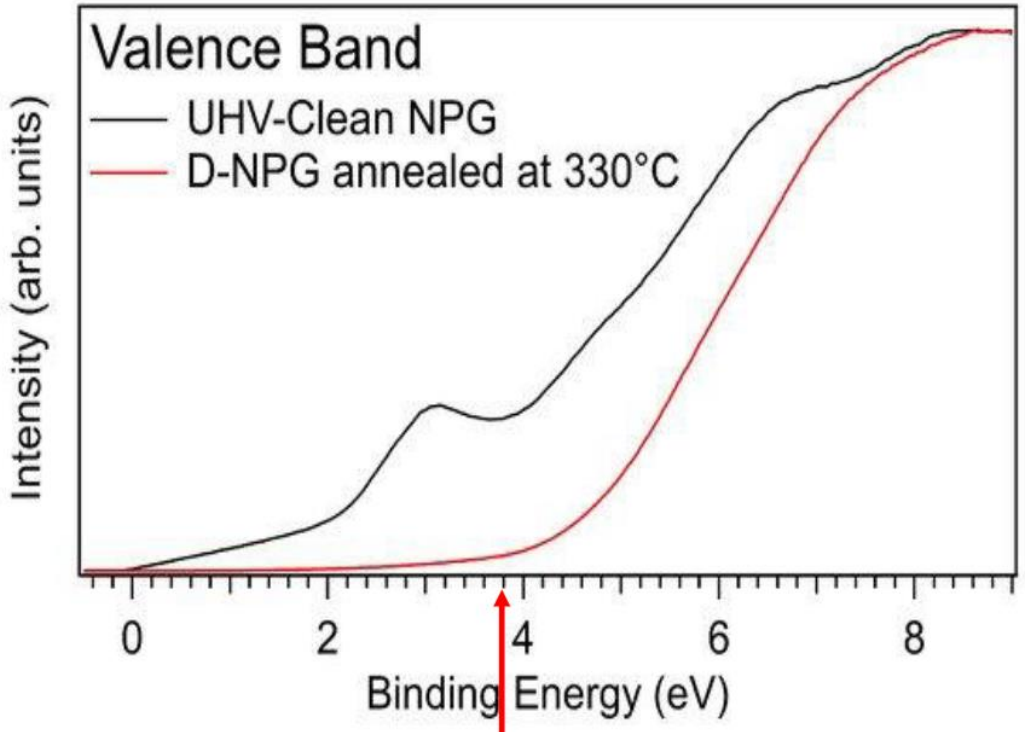
Abdelnabi et alii, Nanomat. **11**, 130 (2021)

experimentally achieved «graphane»



excellent D-NPG lattice quality (Raman)

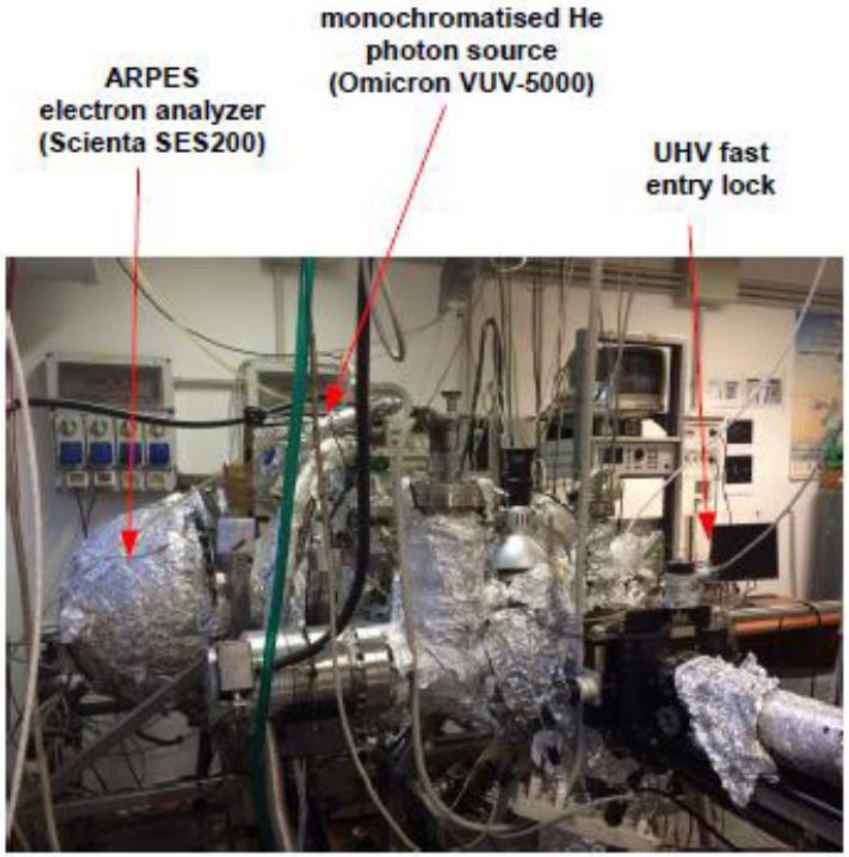


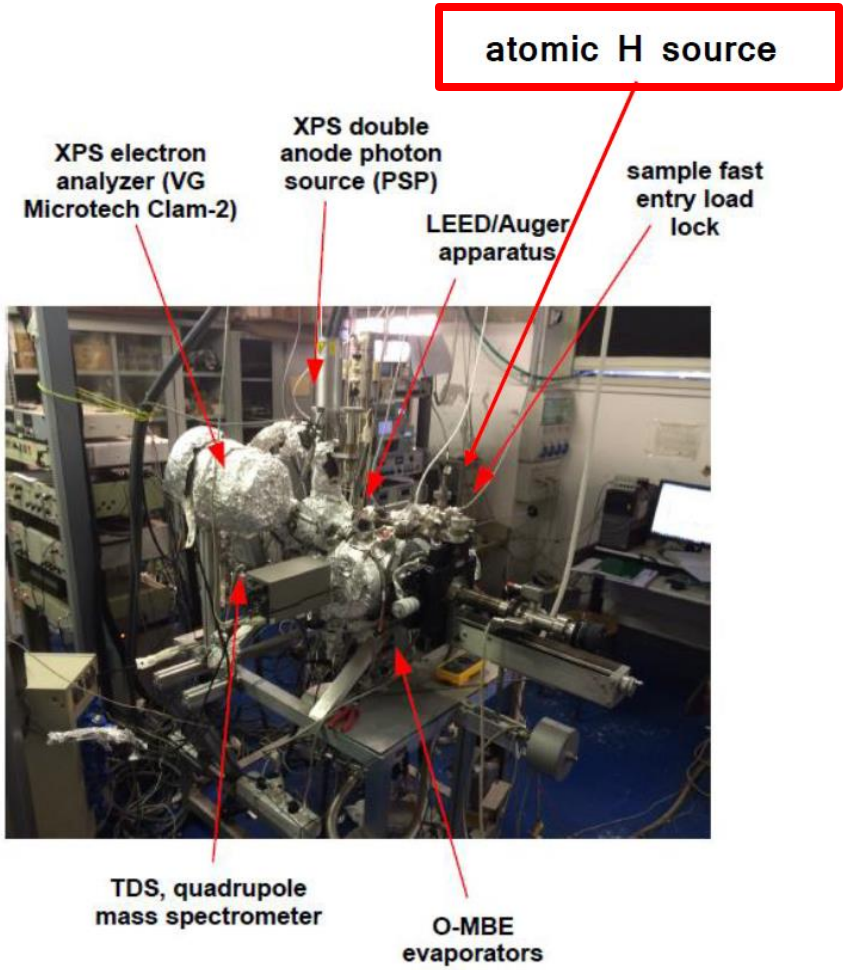


opening of the energy band gap (UPS)

Abdelnabi et alii, Nanomat. **11**, 130 (2021)

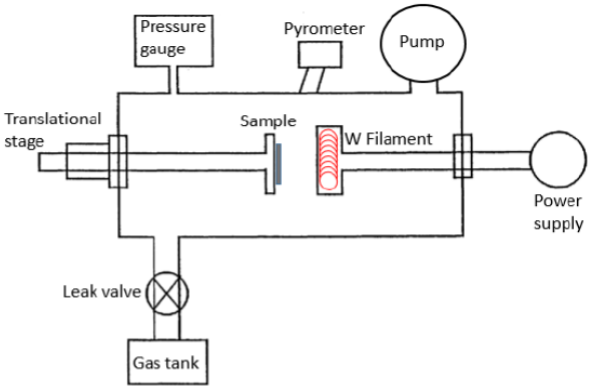
Nanostructures at Surfaces Laboratory @ Sapienza





https://sites.google.com/uniroma1.it/nano-surface-physics/home

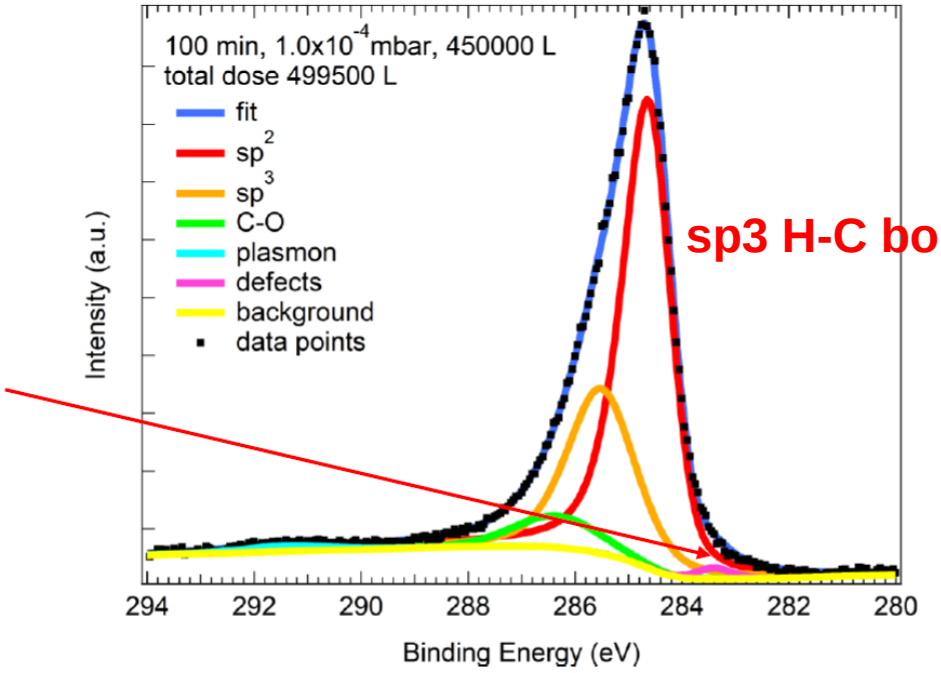
third method, first attempt: **hot W filament** in vacuum, atomic **H at ~0.2 eV** kinetic energy



atomic H source by hot filament-induced thermal cracking of H2

Θ ~ 30%

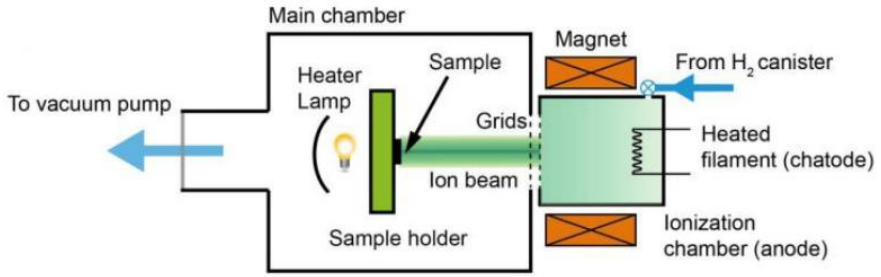
but defects arise at low binding energy



sp3 H-C bond

fourth method: low-energy
(~6 eV) H^+ ions

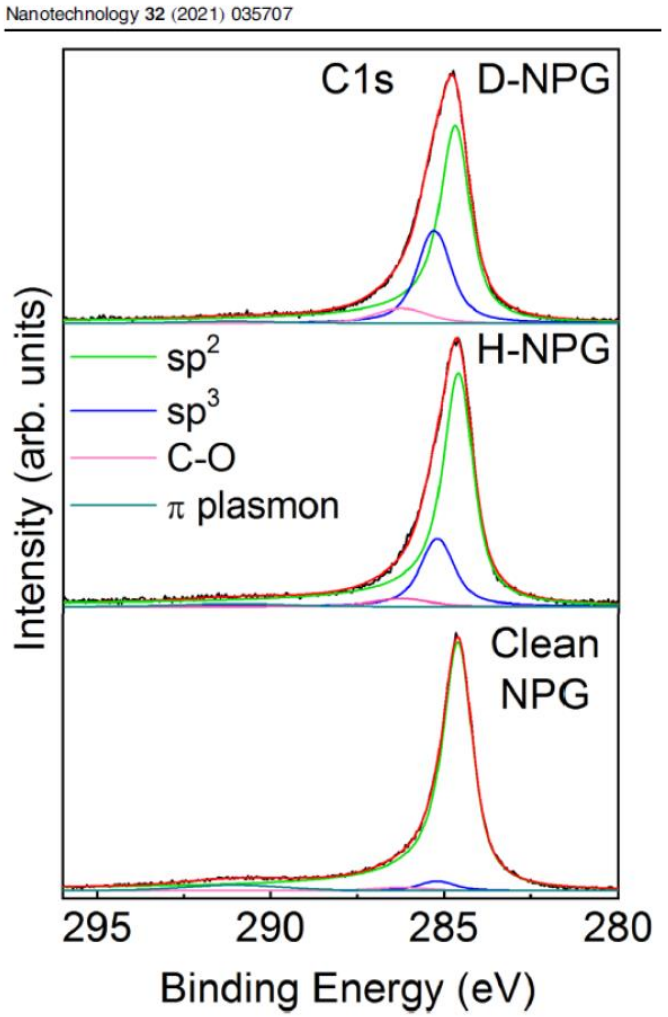
low-energy (6 eV) H+ Kaufmann source



$\Theta_H = 25\%$

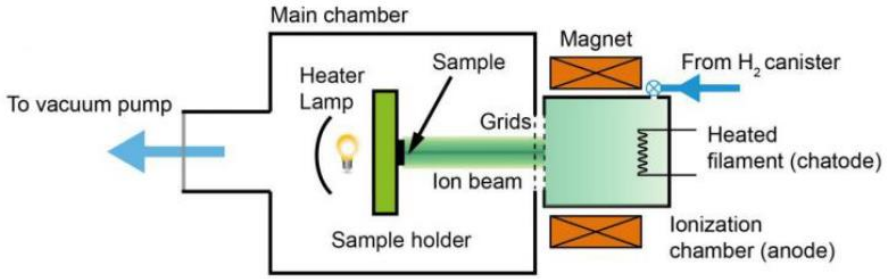
$\Theta_D = 36\%$

no dangling bond defect states

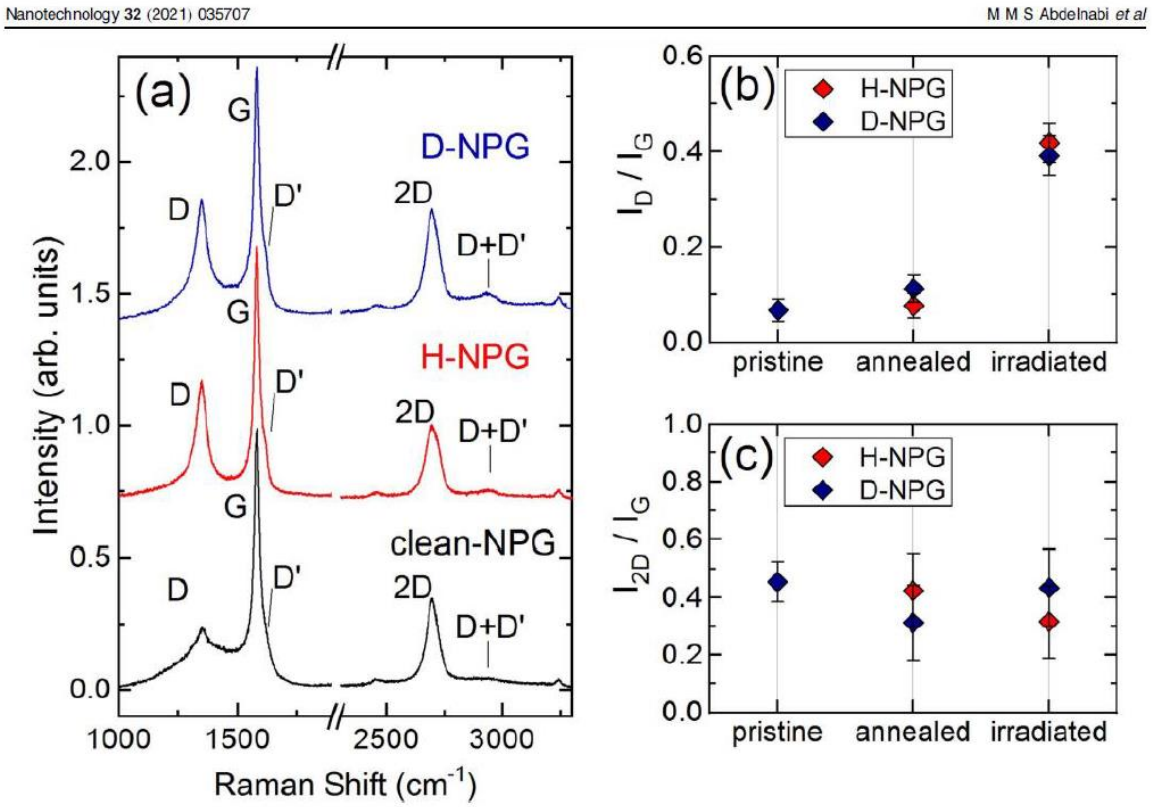


Abdelnabi et alii, Nanotechnology **32**, 035707 (2021)

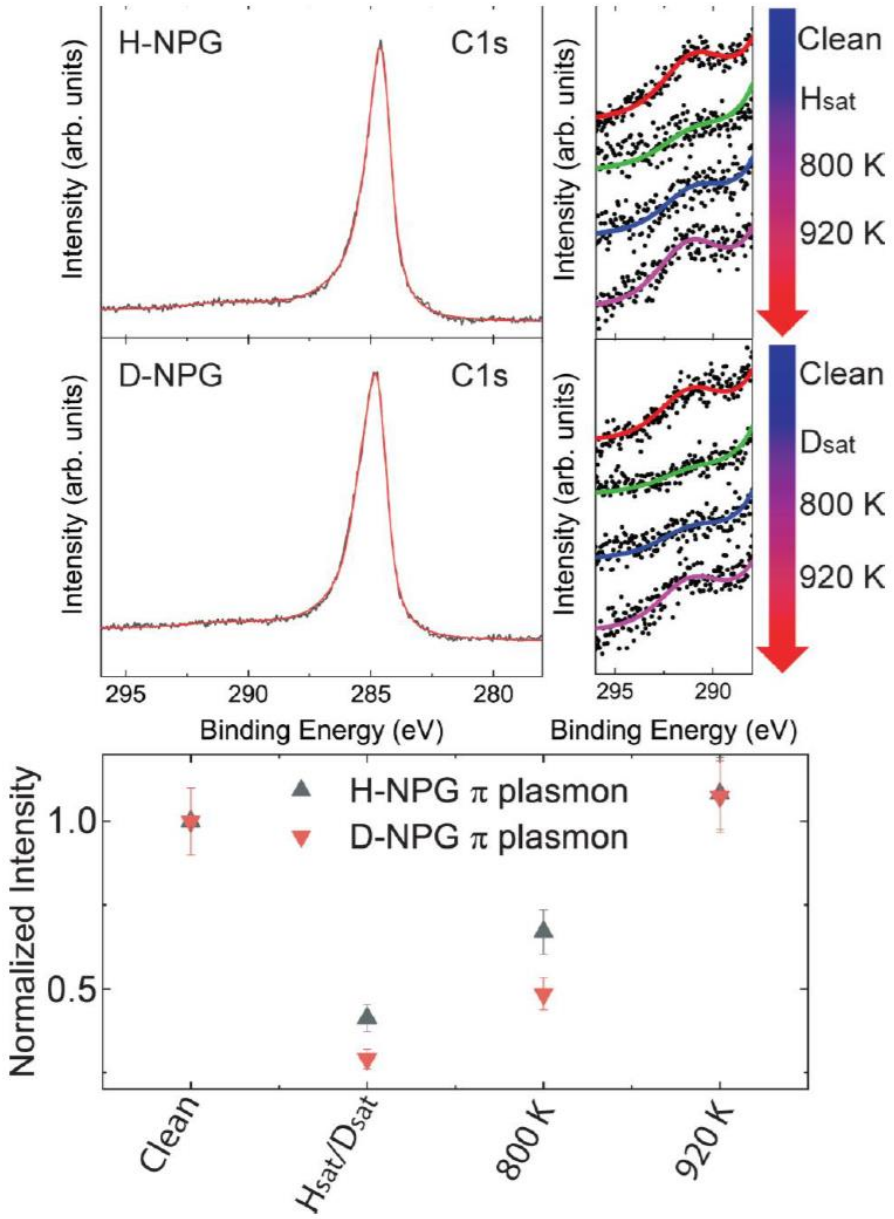
low-energy (6 eV) H+ Kaufmann source



Raman spectroscopy



Abdelnabi et alii, Nanotechnology **32**, 035707 (2021)



the π-plasmon, further fingerprint of sp^2 bond reduction

Very high thermal stability

H-C and D-C bonding found to be much more stable than in previous works → here desorption does not start below 530°C and complete recovering of sp^2-graphene only at 650 °C!

Abdelnabi et alii, Nanotechn. **32**, 035707 (2021)

fifth (third improved) method:
atomic **H at ~0.2 eV** kinetic energy
by hot-capillary in vacuum

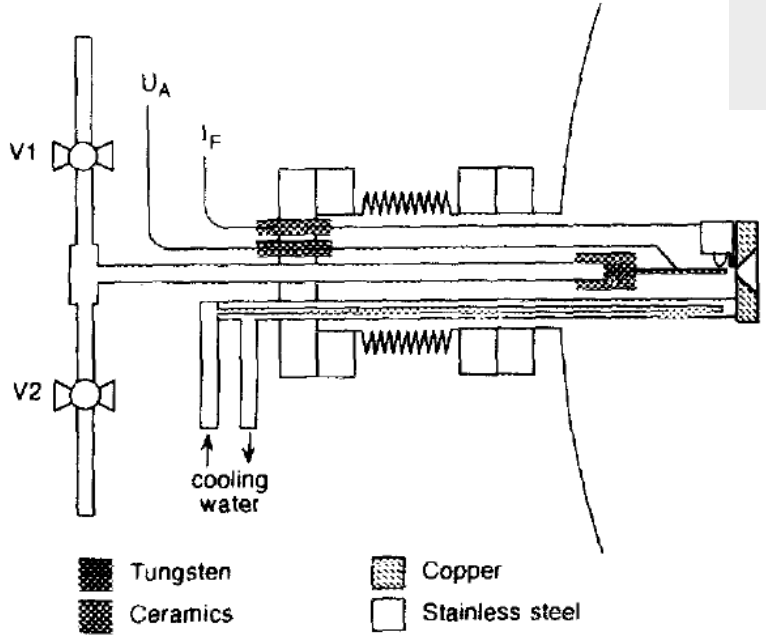


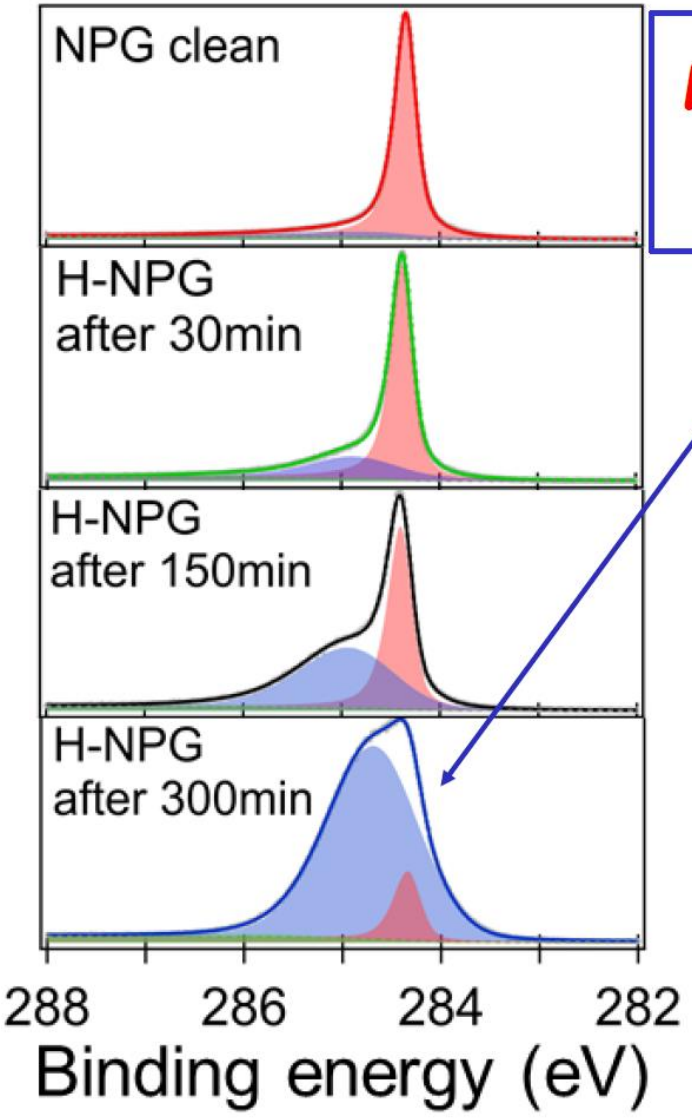
FIG. 1. Schematic drawing of the atomic hydrogen source.

H_2 flow into a capillary with hot-spot (~2100 C) in UHV → more than 95% molecules cracked in **atomic H** concentrated onto the sample

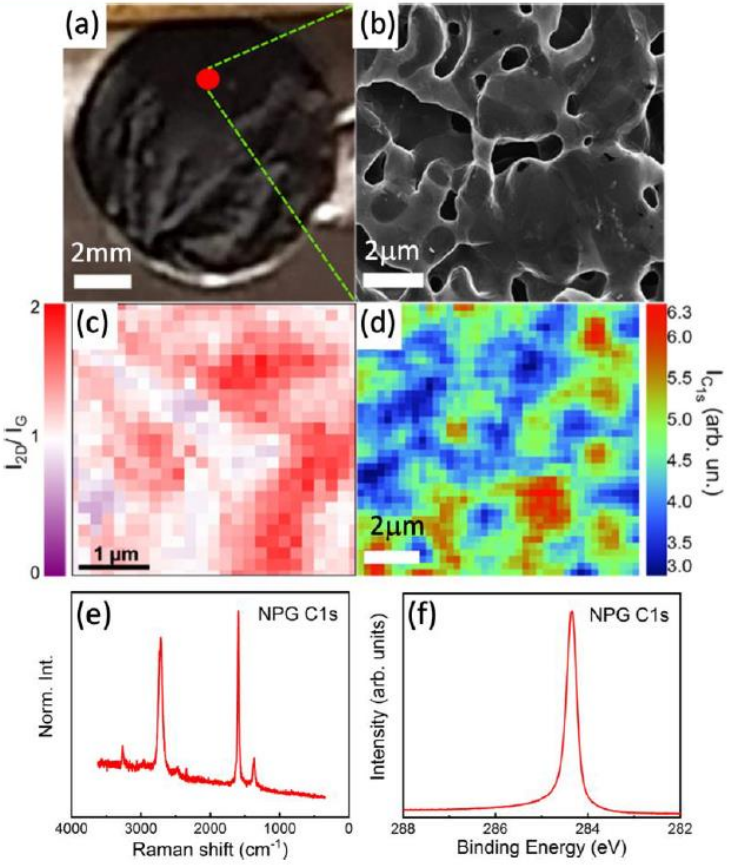
Bischler and Bertel, J. Vac. Sci. Technol. A **11**, 458 (1993)

high-quality atomic H cracking through capillary in UHV

H-NPG with spatial resolution, Soleil (Paris)



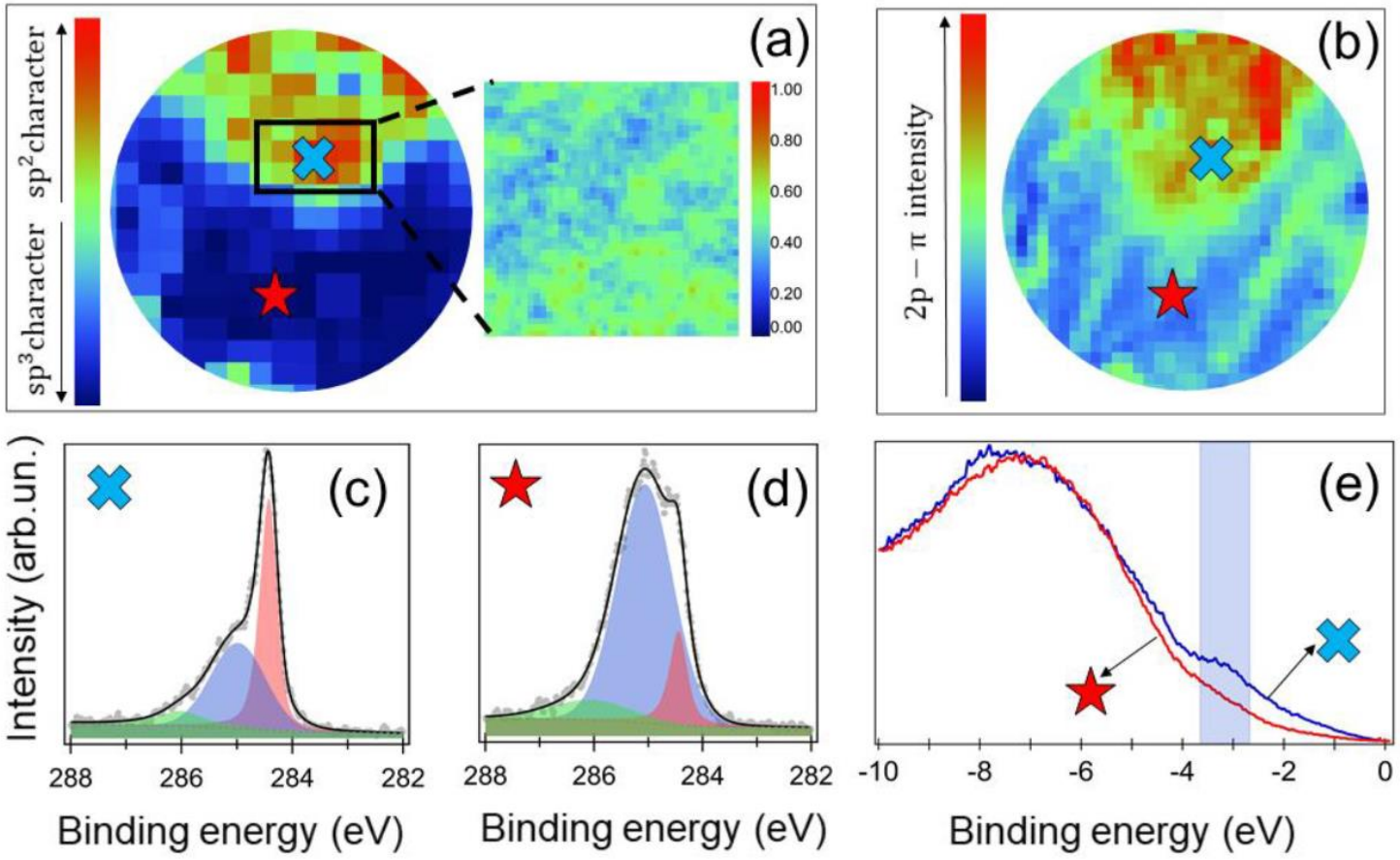
reached ~90% H-upload!



Betti et alii, Nano Lett. **22**, 2971 (2022)

H-NPG with spatial resolution

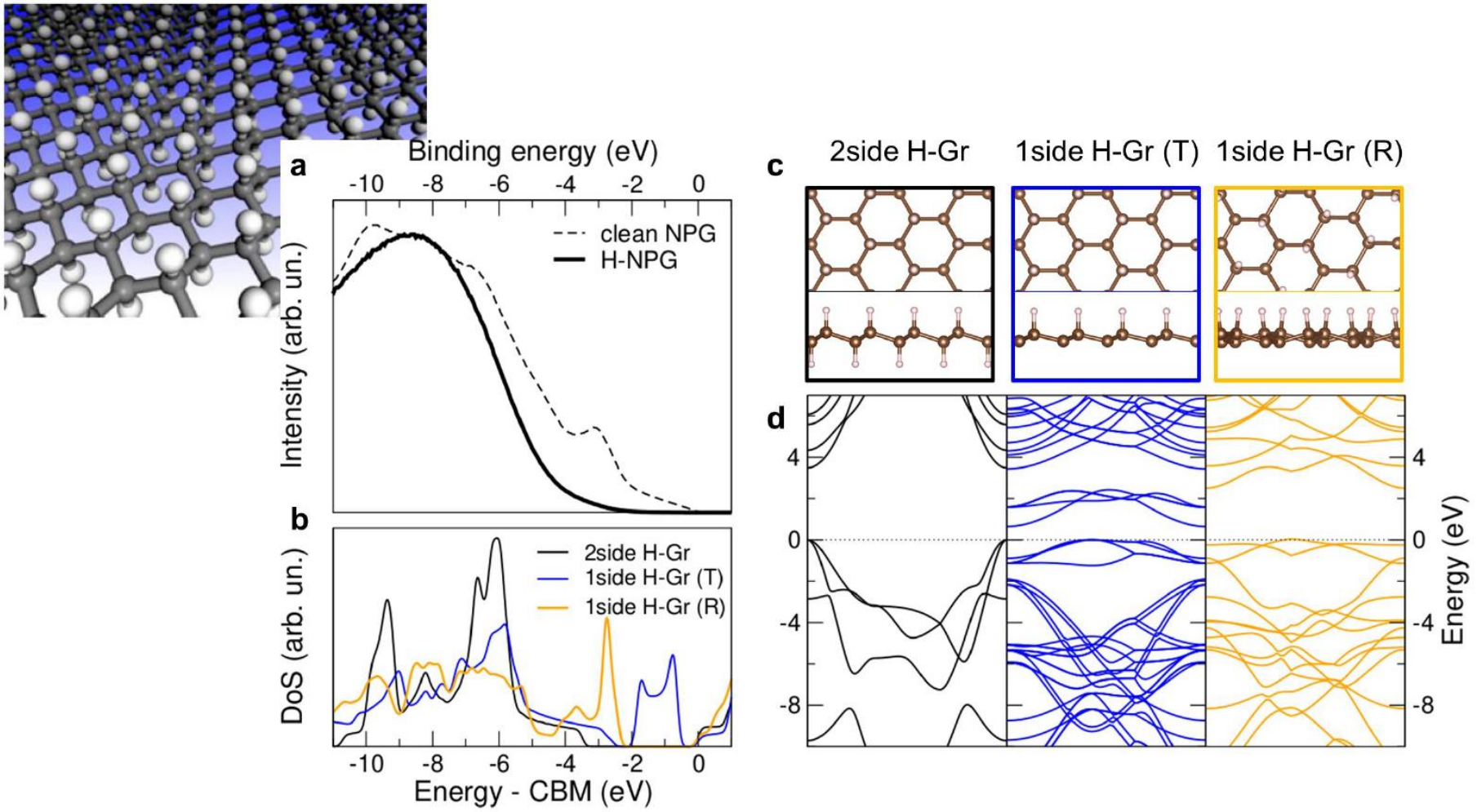
H-C spatial distribution: highest sp3 signal → valence band energy gap opening



Betti et alii, Nano Lett. **22**, 2971 (2022)

H-NPG with spatial resolution

DFT-GW calculations: "graphane" as 2-side H-graphene



Betti et alii, Nano Lett. **22**, 2971 (2022)

conclusions and…

- **Excellent hydrogenated (~90%)* free-standing "graphane"**

- Best methods:

i) **thermalised ions** at atmospheric pressure
ii) exposure to low-energy **atomic H** (D) in ultra-high-vacuum

* apparent discrepancy of D upload: ~50% D content measured by XPS on-campus, ~90% H upload with XPS at lower photon energy with SR → different sampling mean free path (due to photoelectron kinetic energy)

…perspectives →

perspectives

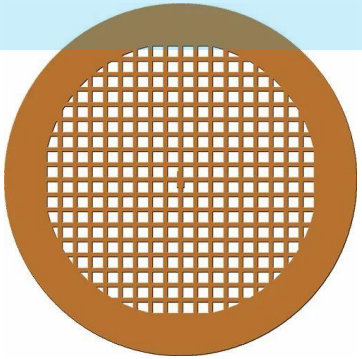
achieved: **Gr** deposited on a **TEM grid** (Pisa) and characterized in Roma Tre →Talk Apponi (Thursday)

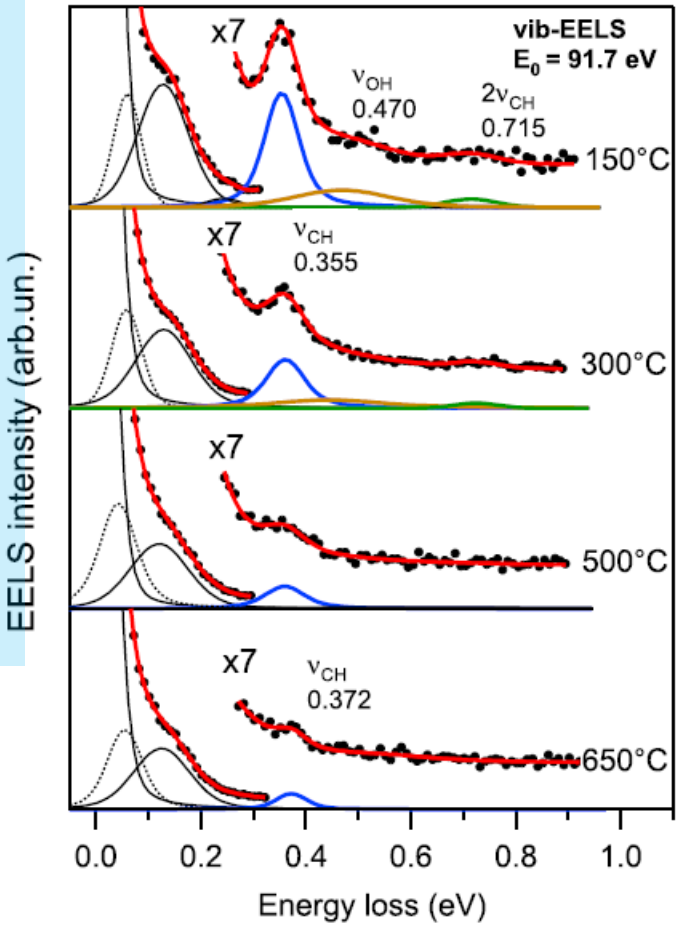
Next steps (2022-23):

i) e^--**transmittance** through H-Gr (on TEM grid)

i) SR **spectromicroscopy** comparison of H upload (all-in-UHV) on **flat Gr** and on **metal-supported Gr**, few micron-sized areas (Roma Tre)

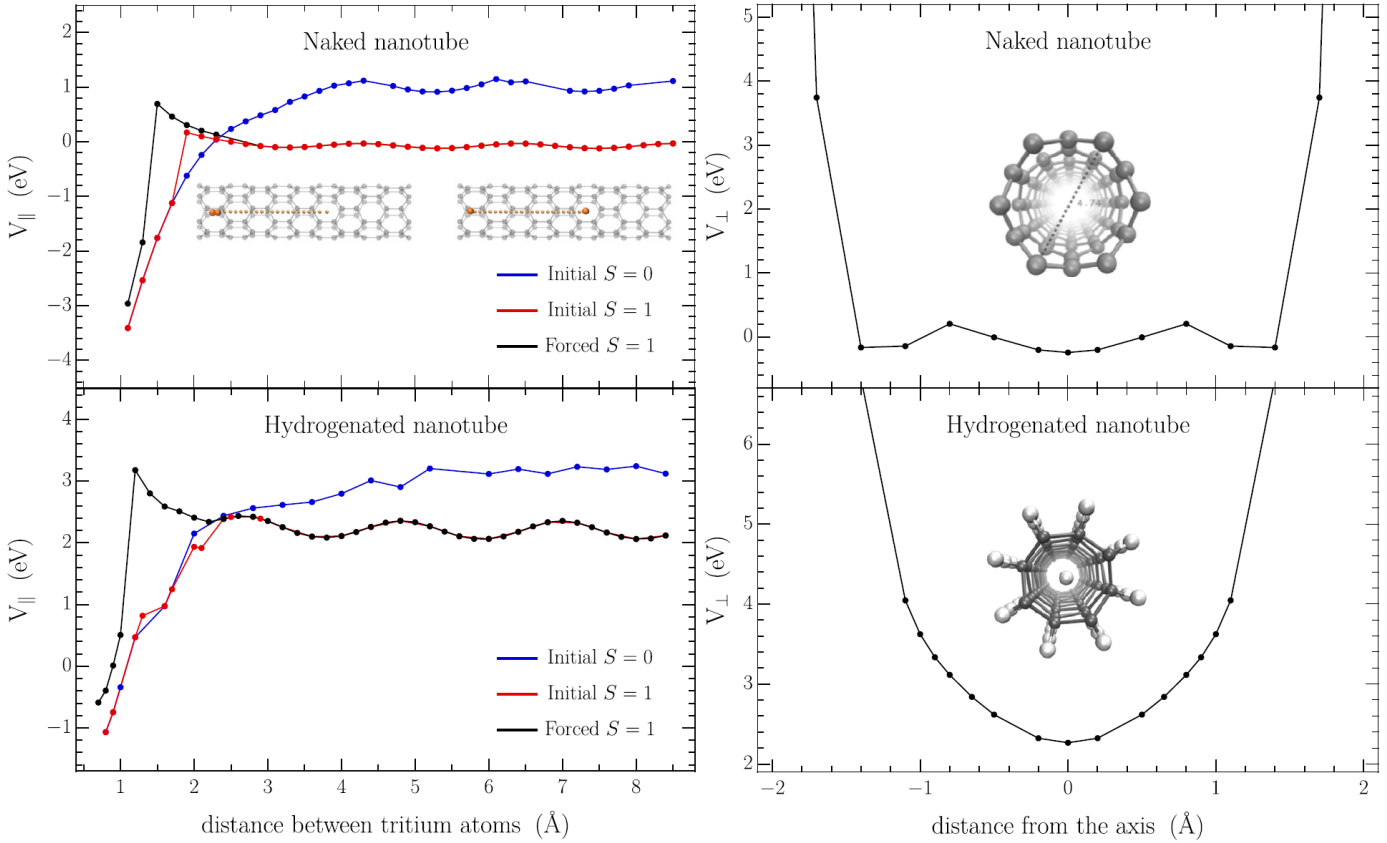
ii) on-campus investigation of H upload (all-in-UHV) on **flat Gr** and on **metal-supported Gr** by XPS, vib-EELS





G. Di Filippo, A. Liscio, A. Ruocco,, Applied Surface Science. **512** (2020) 145605. https://doi.org/10.1016/j.apsusc.2020.145605.

perspectives



given the **proposed CNT interior** as **host** for **free H** atoms

more **stable** once its **external** wall is **passivated by H**

Apponi et al. (Ptolemy), Phys. Rev. D **106**, 053002 (2022)

calculations by Esposito, Tozzini et al.

Next steps (2022-2023):

i) H (D) upload (all-in-UHV) **external** surfaces of **highly aligned vertical CNT**

ii) XPS estimation of **H (D) upload** on the **external** wall surface

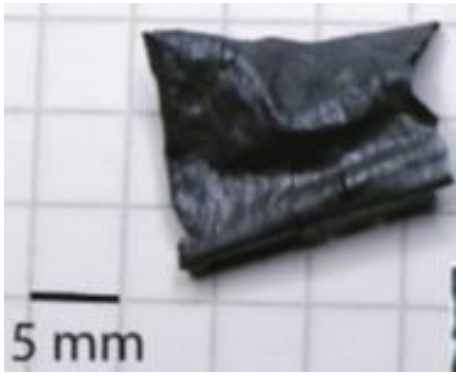
perspectives

Next steps (2023 ?) → Cavoto talk (Thursday)**:**

i) New vacuum set-up for high-temp. molecular cracker at SRNL, USA

ii) T upload of **NPG** and of **Gr**-on-TEM grid (all-in-vacuum) at SRNL (collab. Princeton)

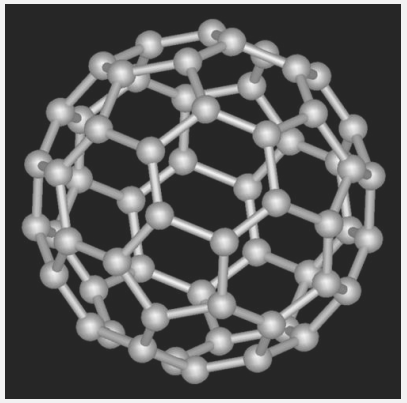
iii) XPS estimation of **T upload** after transfer in the UHV chamber in Rome

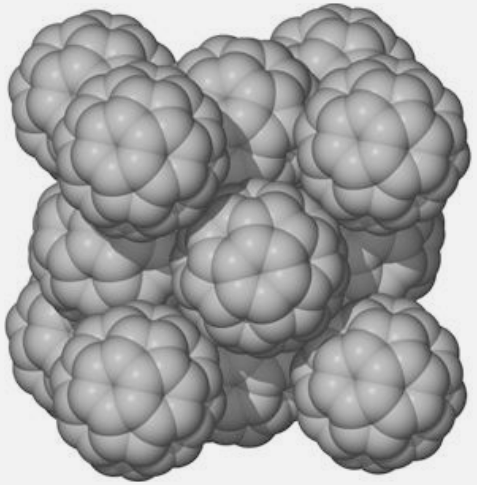


typical NPG sample

perspectives

fullerene (C60)





fulleride (C60 crystal)

internal cages as hosts for H atoms…

(on-going calculations by Esposito, Tozzini et al.)

Further steps (or GedankenExperiment)**?**

i) H (D) upload (all-in-UHV) on **external** surfaces of **fullerene/fulleride**

ii) XPS estimation of **H (D) upload** on the **external** surface

thank you for your attention