UNIVERSITÀ DI PISA

Master's Degree in Materials and Nanotechnology

Master's Thesis

Functionalization of 3D Graphene with Metal Nanoparticles:

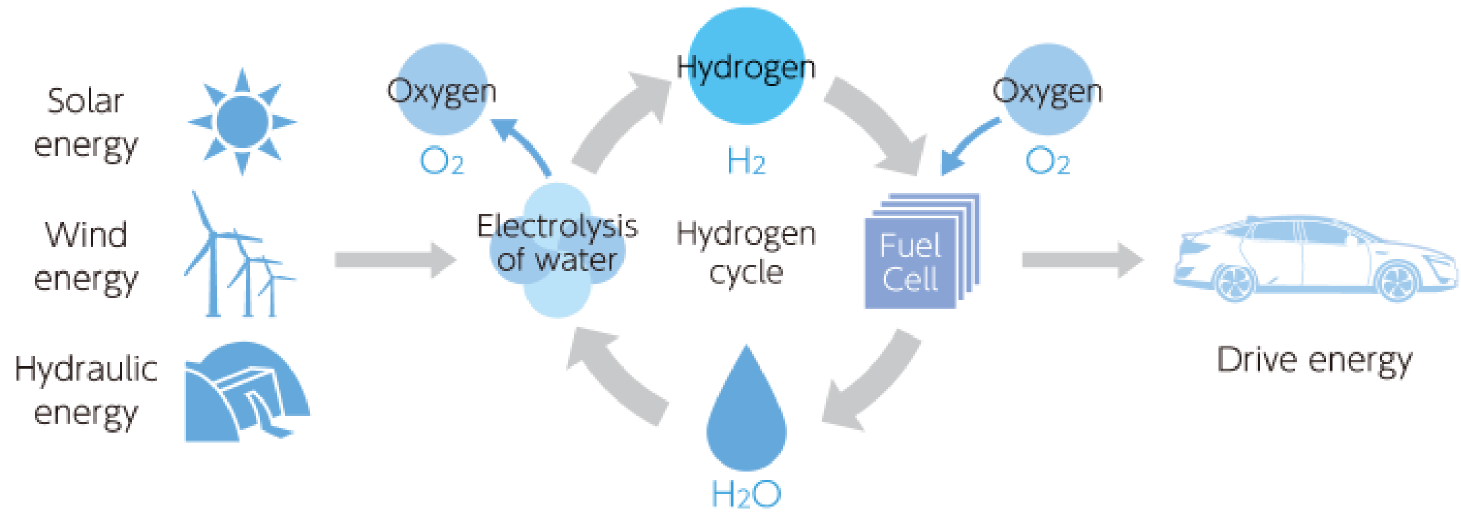
Perspectives for Hydrogen Storage

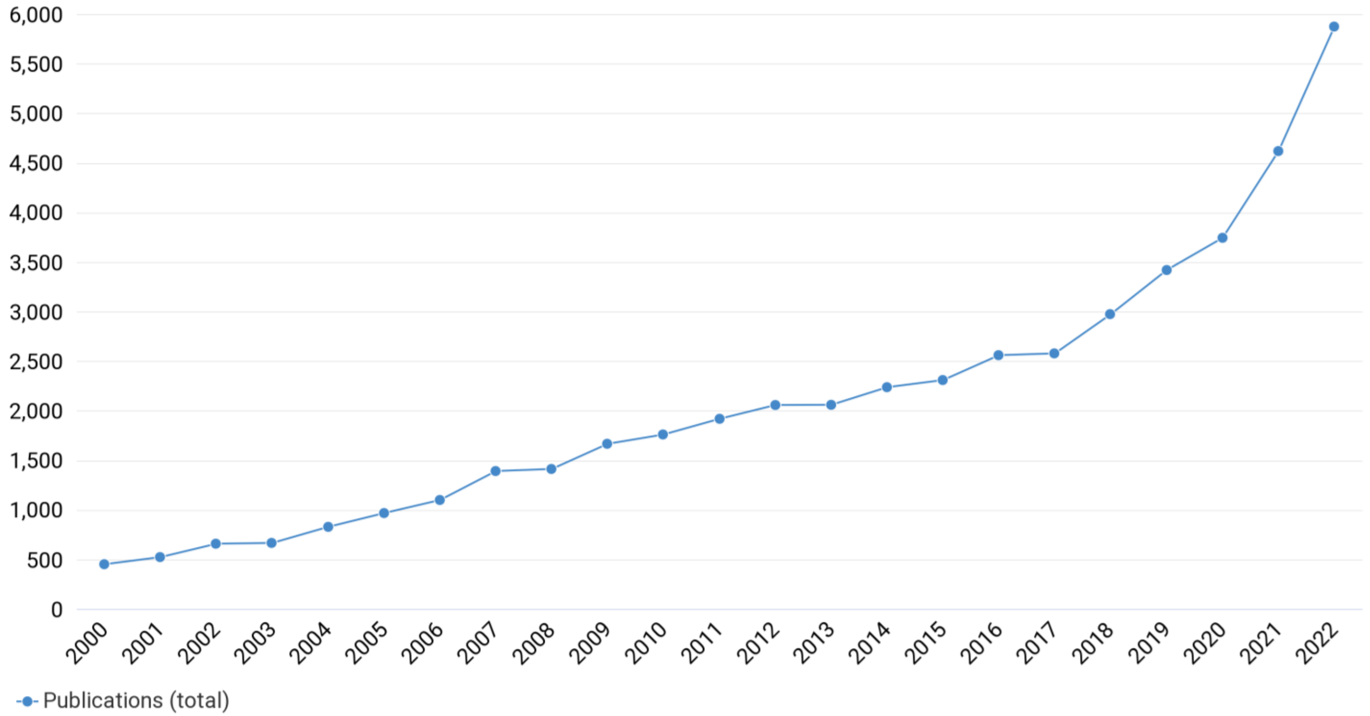
Candidate:
Emanuele Pompei

Supervisors:
Dr. Stefano Veronesi
Dr. Stefan Heun

Academic Year 2021-2022

Sustainable Renewable Energy





Hydrogen Economy

- Decarbonization → Renewable Energy Sources

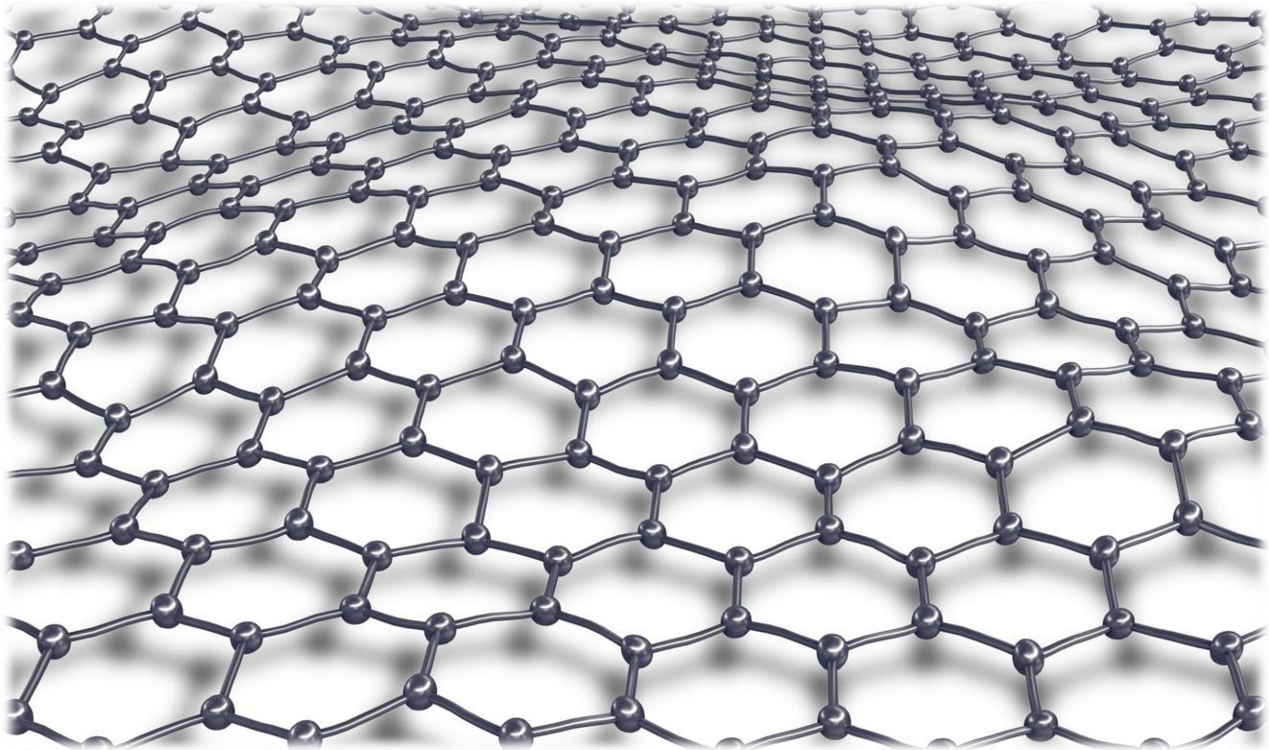
- Renewable sources are intermittent

→ Energy storage

- Chemical energy storage under form of Hydrogen

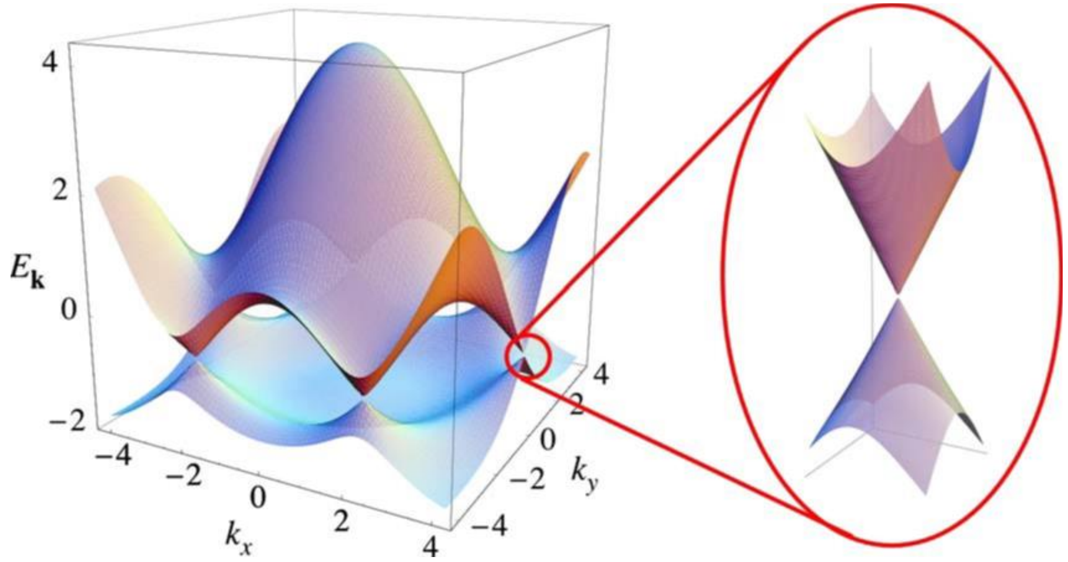
→ Hydrogen storage

www.dimensions.ai



Graphene

- First 2D material discovered
- Carbon allotrope
- Astonishing properties
  - High specific surface area (2630 m^2/g)
  - High strength ($\sim 10^3$ times more than Steel or Kevlar)
  - High charge carriers mobility ($\sim 200000\ \mathrm{cm^2/Vs}$)
  - High conductivity both electric and thermal (up to $\sigma \sim \frac{\mathrm{MS}}{\mathrm{m}}$ and $\kappa \sim 4000 \frac{\mathrm{W}}{\mathrm{mK}}$)
  - Linear band dispersion at K and K’ points

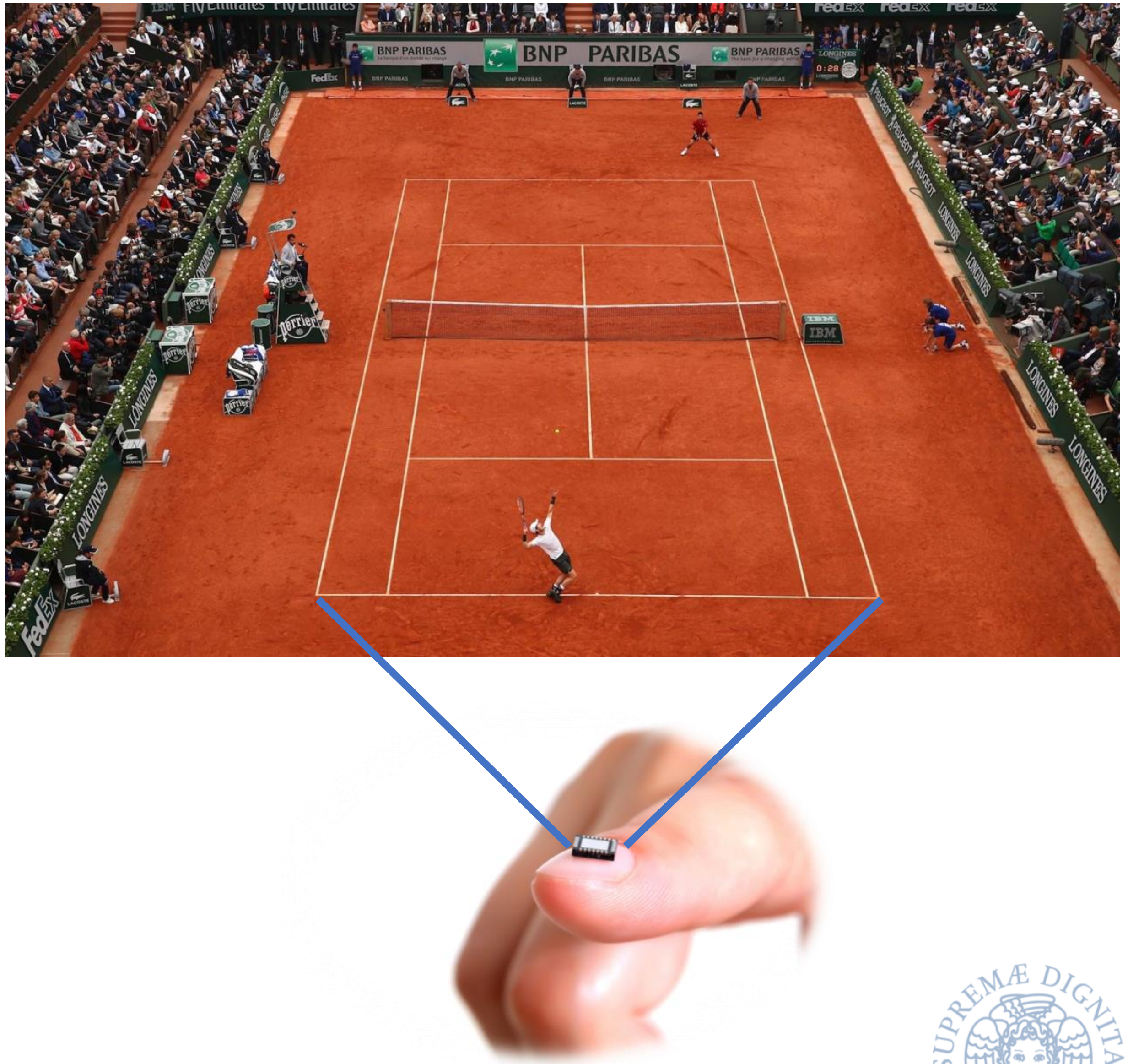


Why 3D?

- The adsorption of $1\ \mathrm{mg}$ of H_2 on monolayer graphene would need $\sim 260\ \mathrm{m}^2$ of graphene

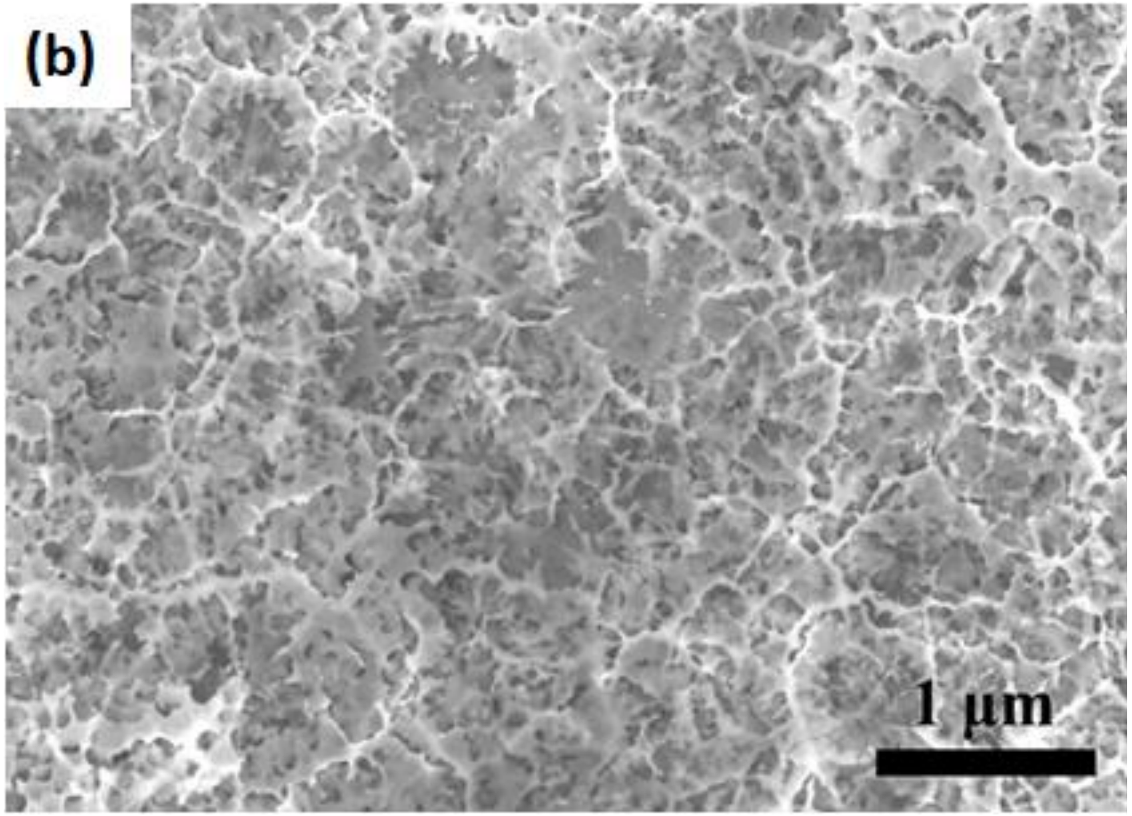
- For fit large area into a small volume the 3^d dimension is needed

→ 3D Graphene

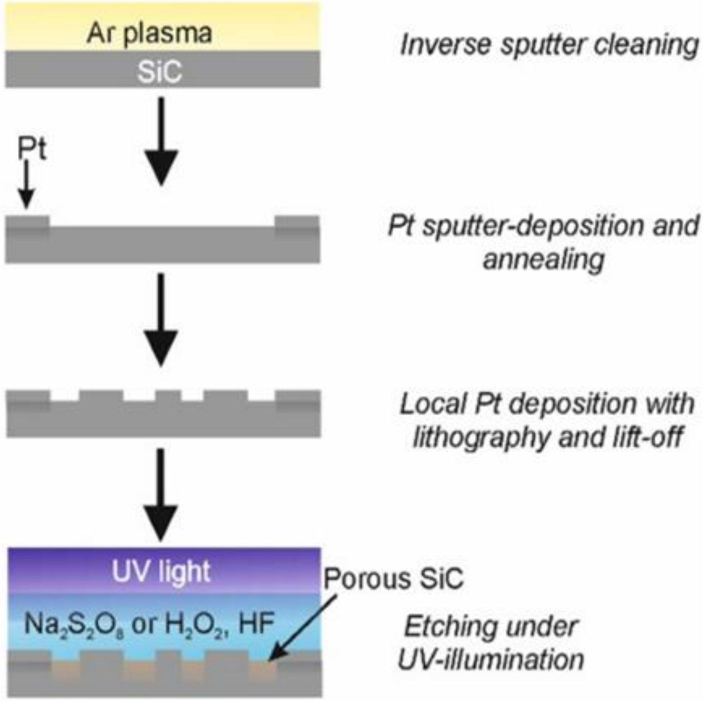


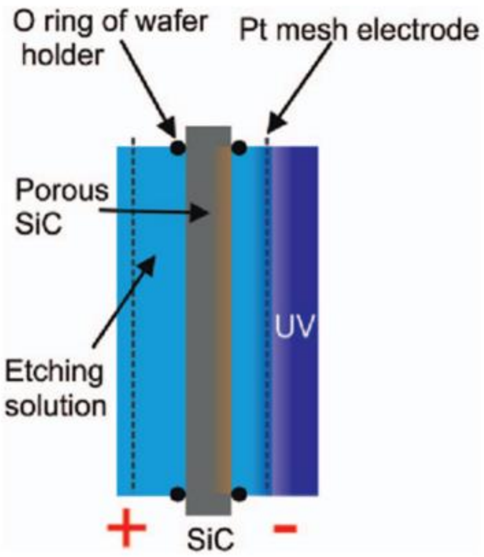
Porous Silicon Carbide

- New 3D Carbon-based material
- Electrochemically porousified Silicon Carbide (SiC) wafer

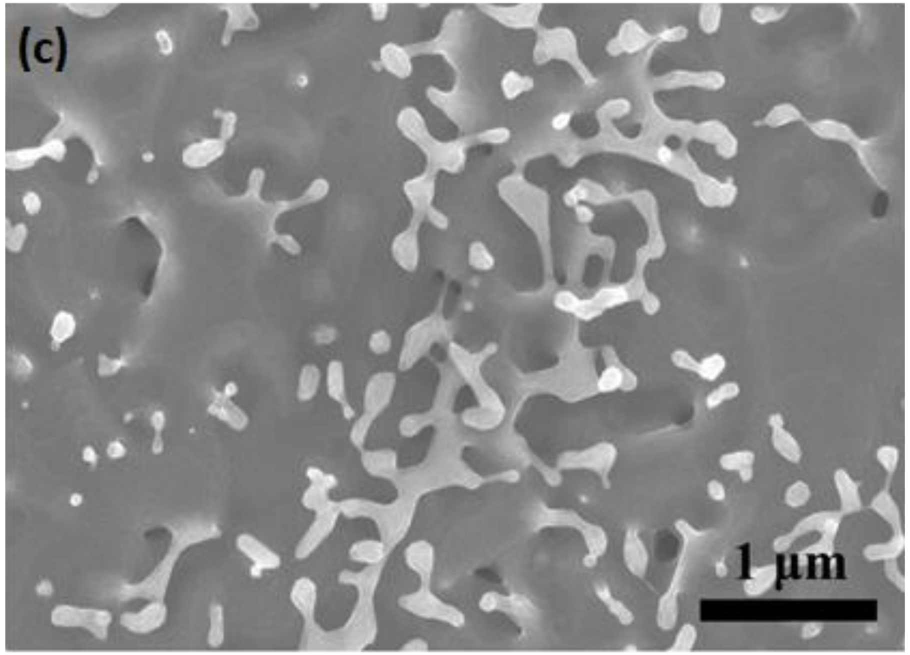


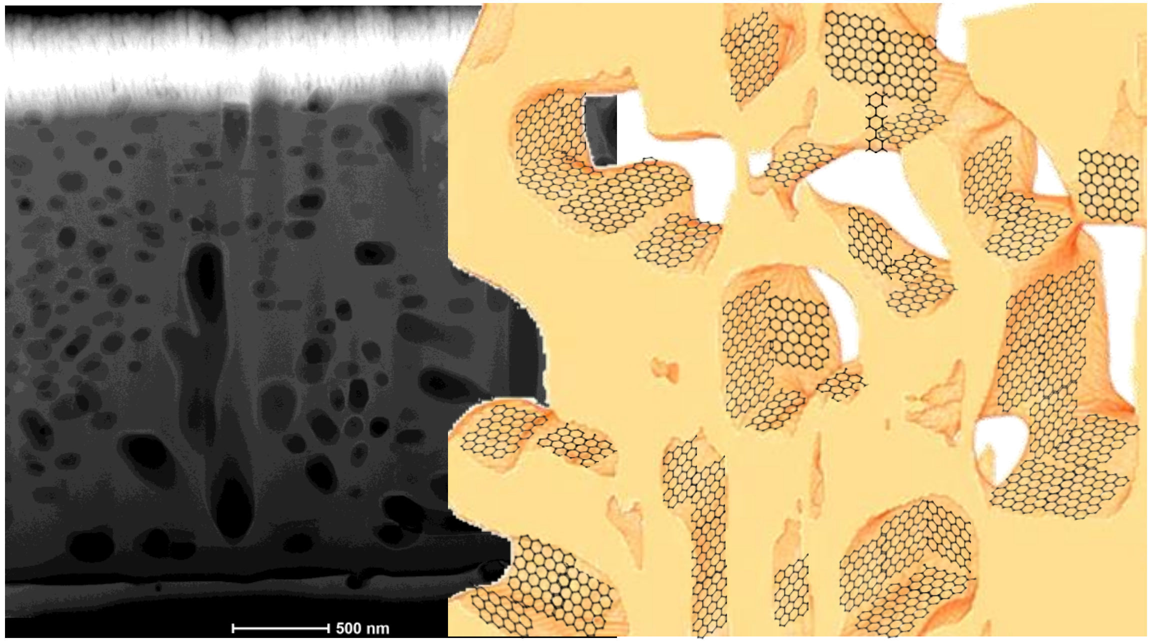
- Metal Assisted Photochemical Etching (MAPCE)
- PhotoElectroChemical Etching (PECE)





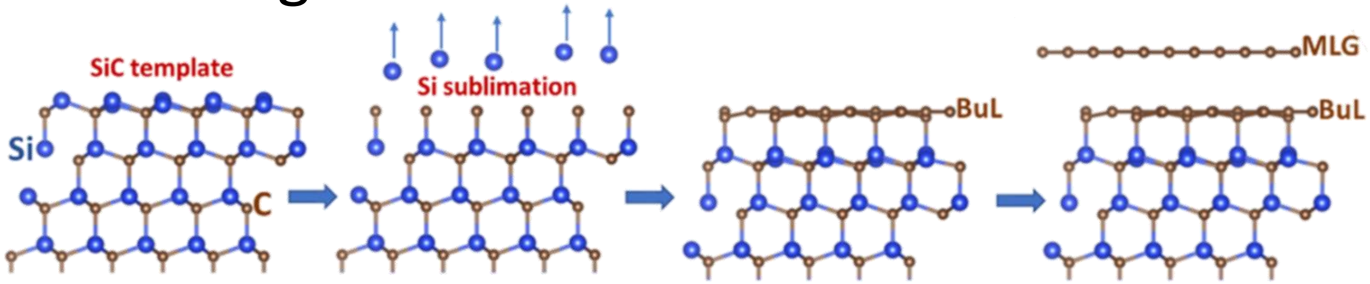
S. Veronesi et al. Carbon 189 (Apr. 2022), pp. 210–218.
M. Leitgeb et al. ECS Journal of Solid State Science and Technology 5.10 (2016), P556–P564





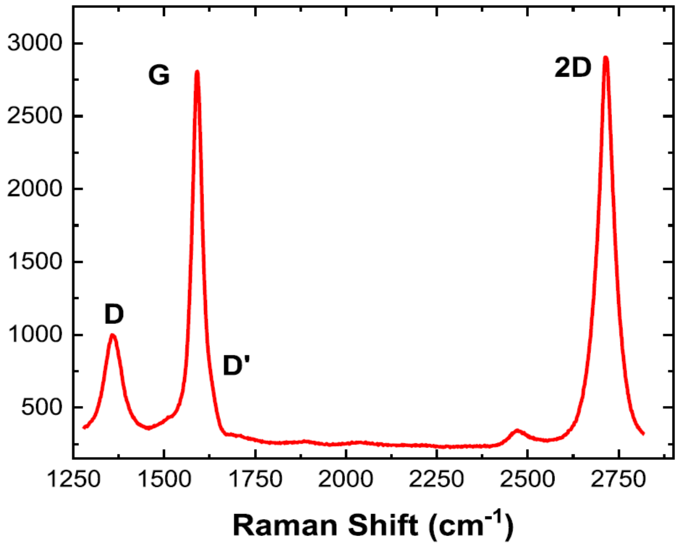
3D Graphene

- Graphenization of the SiC porous structure via thermal decomposition at 1650 K under Ultra High Vacuum condition



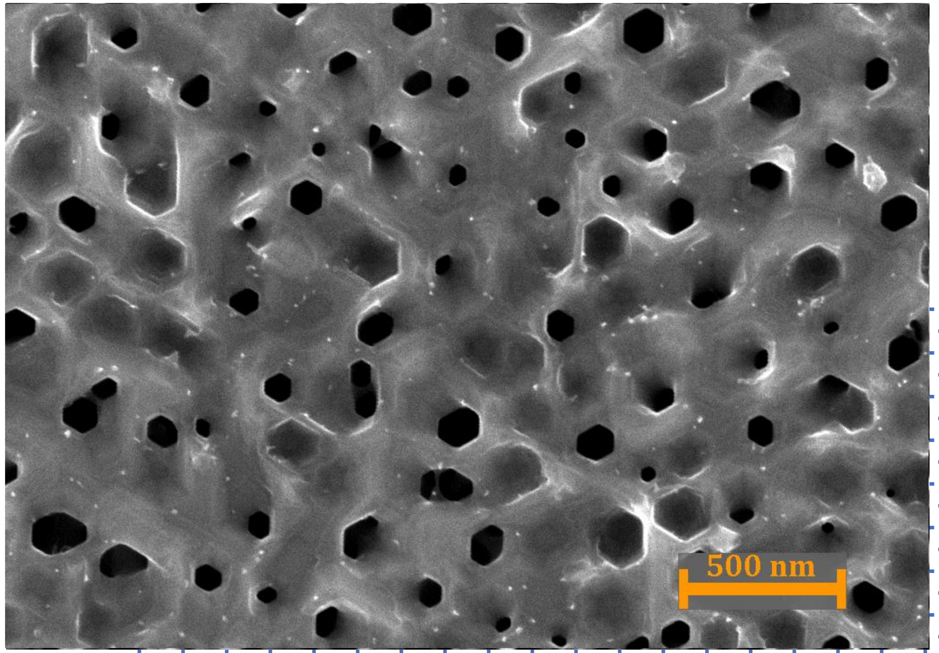
- 200 times more available surface

- Raman spectroscopy
  - High quality graphene

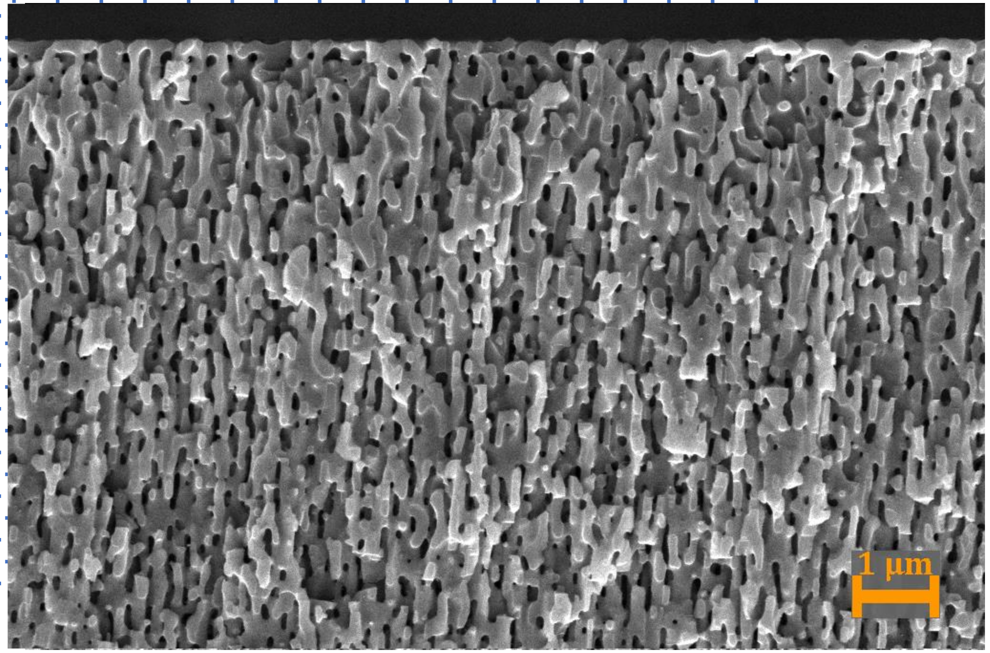


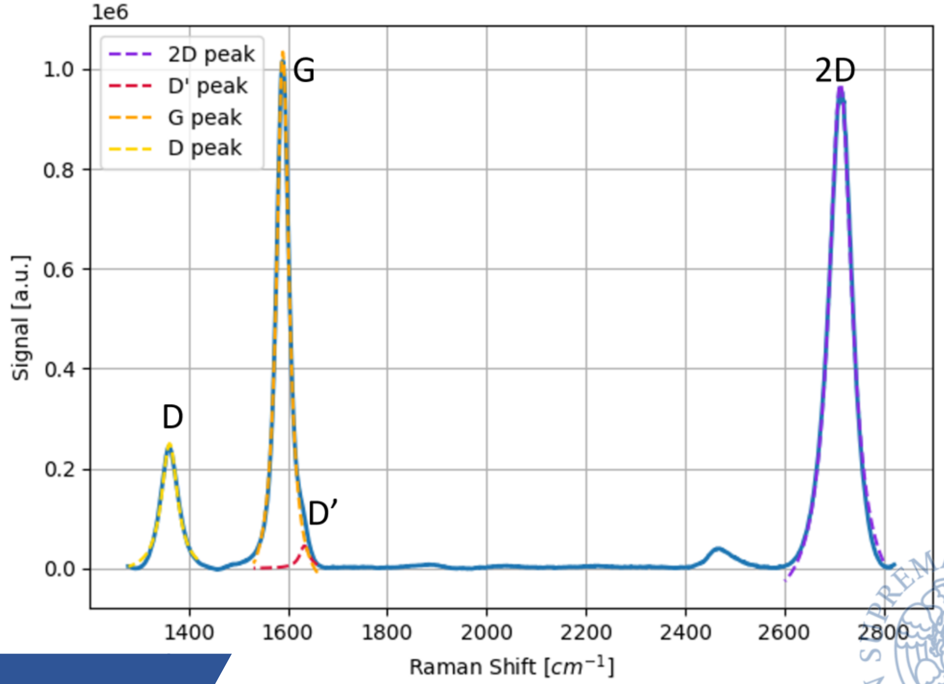
S. Veronesi et al. Carbon 189 (Apr. 2022), pp. 210–218.

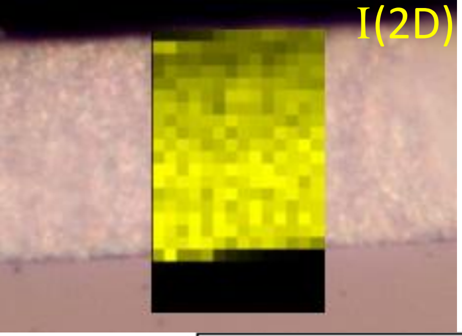
3D Graphene – New Generation



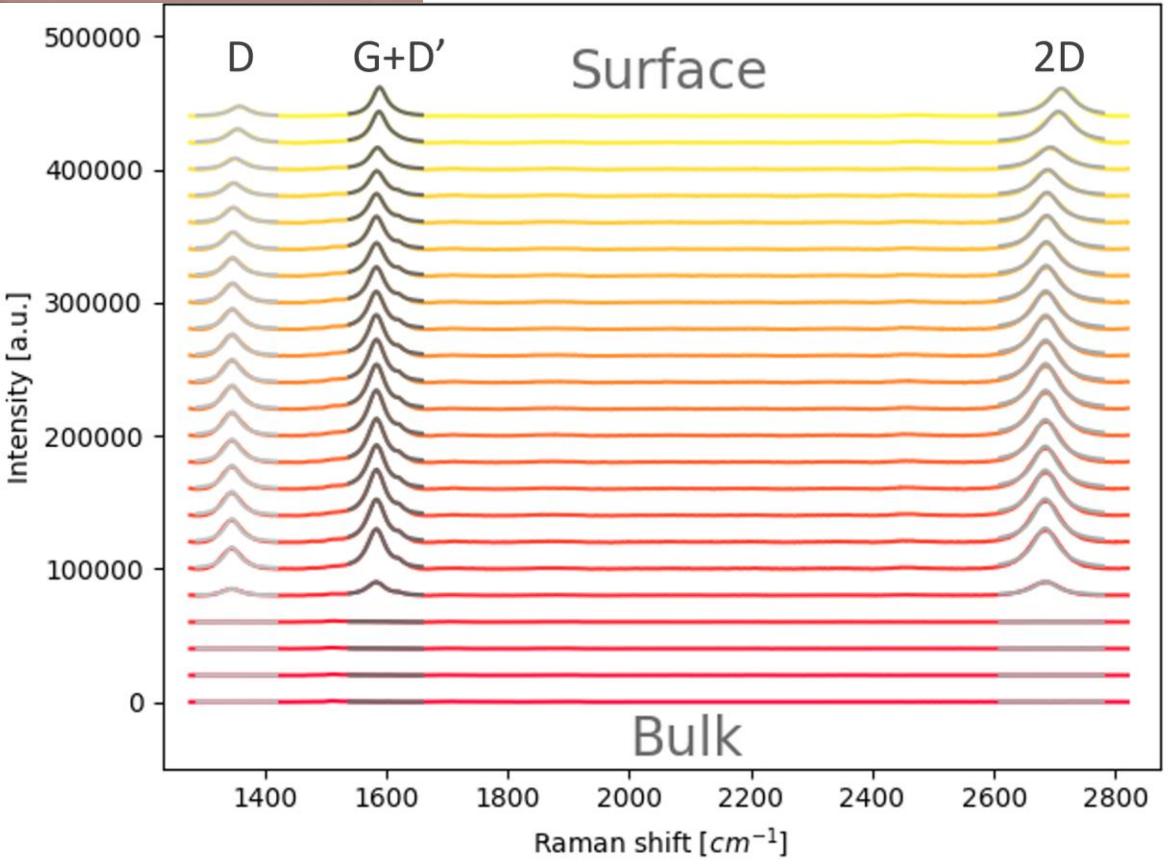
- New etching procedure
MAPCE → PECE → MAPCE
- Same graphene growth condition
- High quality Graphene

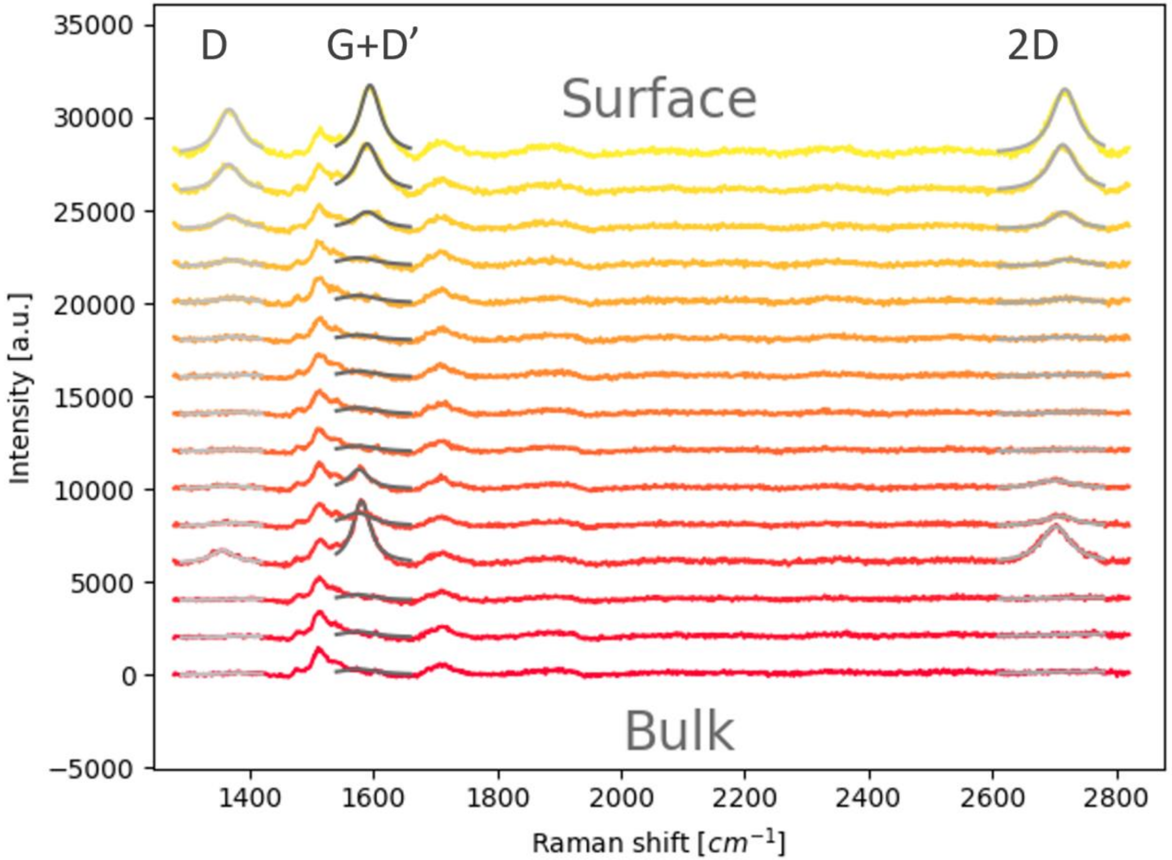






New vs. 1st Gen.



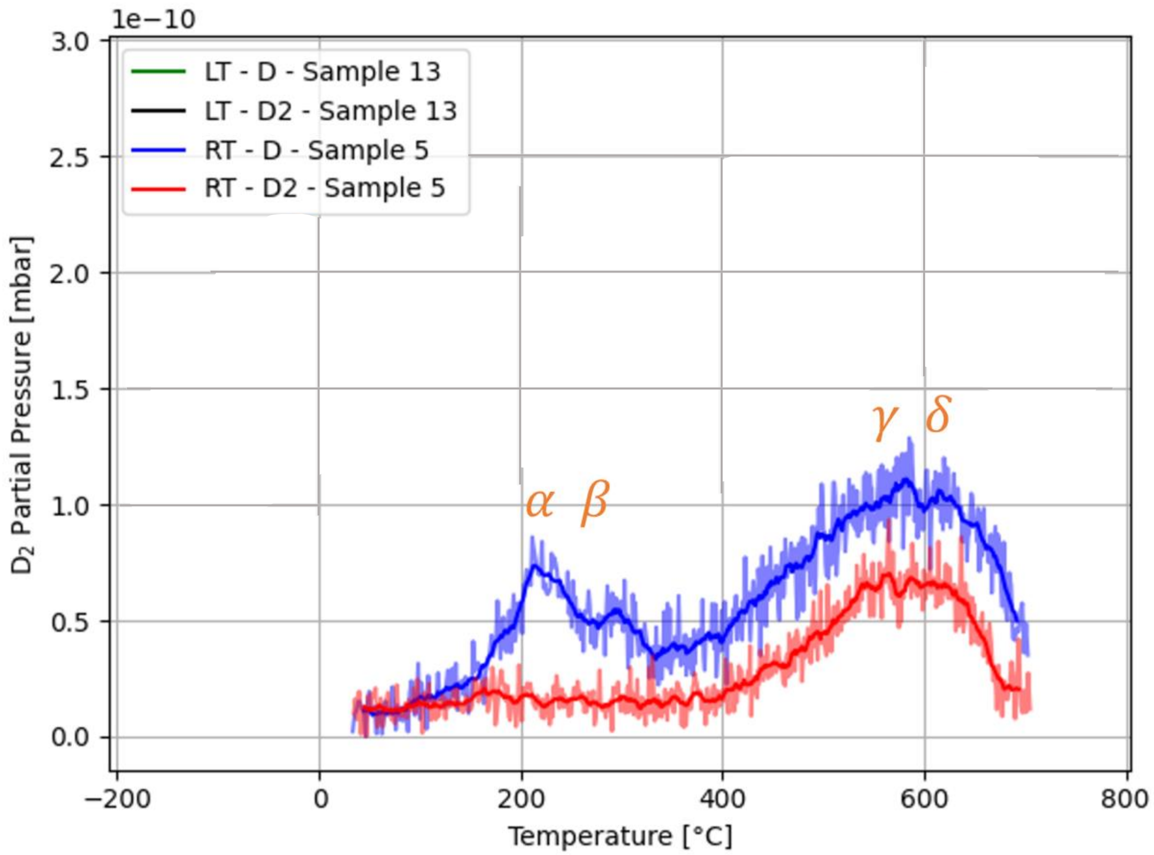


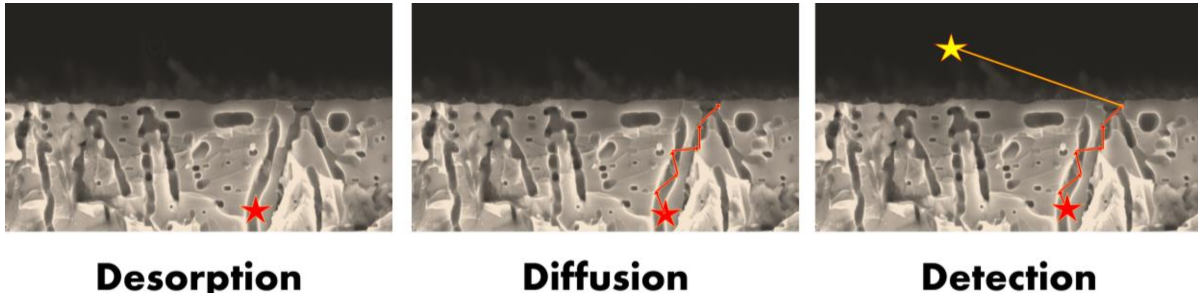
Large improvement in the graphene homogeneity, quality and quantity along the porous layer

New Gen. – Hydrogen Storage

TDS measurements

- α and β peaks
  - 216°C and 314°C (1.2 and 1.5 eV)
  - Only upon D exposure
- γ and δ peaks
  - 535°C and 641°C (2.0 and 2.3 eV)
  - Catalytic splitting of D_2
- P peak
  - Physisorption
  - "Fast" delayed emission: from τ ~15 min to τ ~70 s





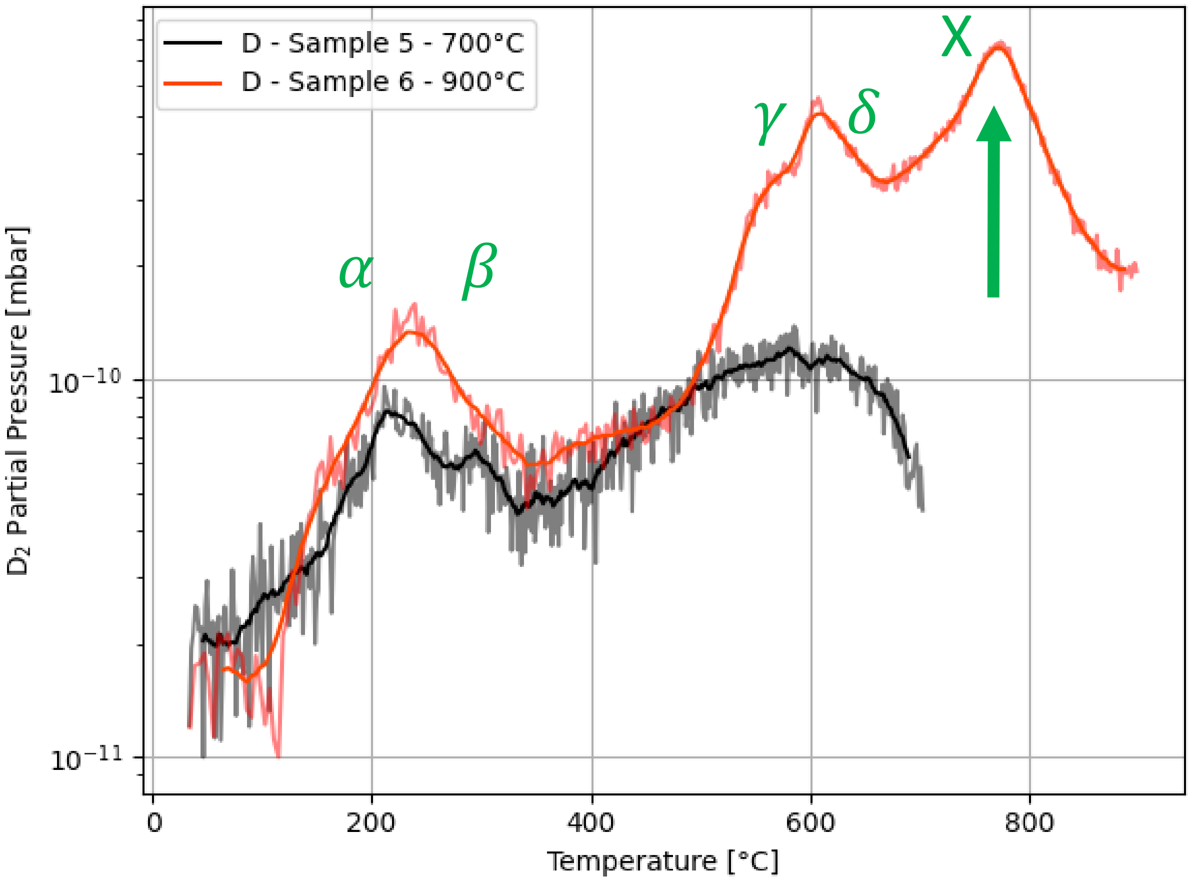
A. Macili et al. Applied Surface Science 615 (Apr. 2023), p. 156375

New Gen. – Hydrogen Storage

Uptake Comparison

Sample	Uptake - D_2	Uptake - D
1^{st} gen.	$2 \cdot 10^{-12}$ mol	$7 \cdot 10^{-12}$ mol
New gen.	$3 \cdot 10^{-11}$ mol	$9 \cdot 10^{-11}$ mol
New gen. - 900	$2 \cdot 10^{-10}$ mol	$4 \cdot 10^{-10}$ mol

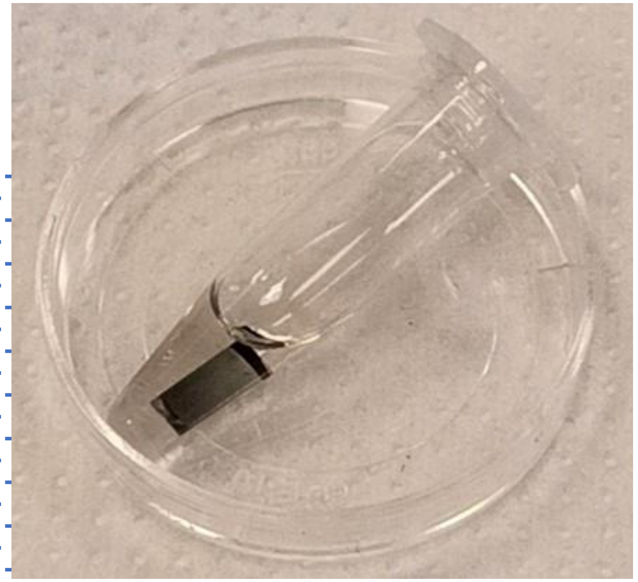
- Higher Temperature Degassing
  - Appearance of the X peak at 778°C (2.7eV)
  - Observed also after D_2 exposure
  - About 100 times higher uptake

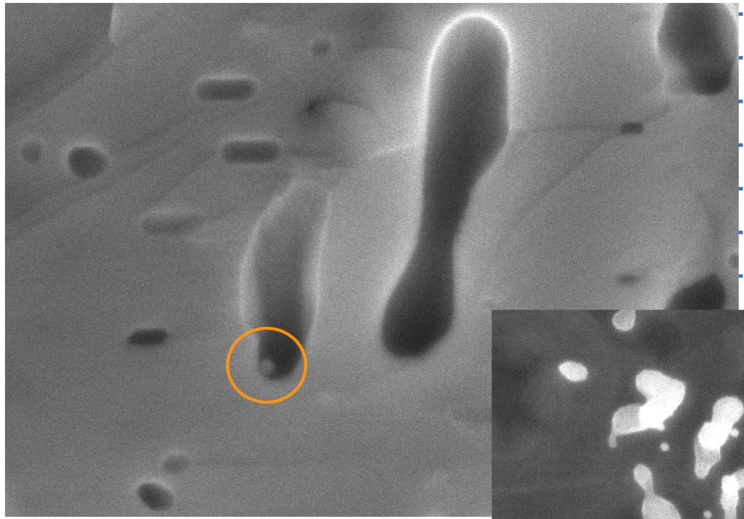


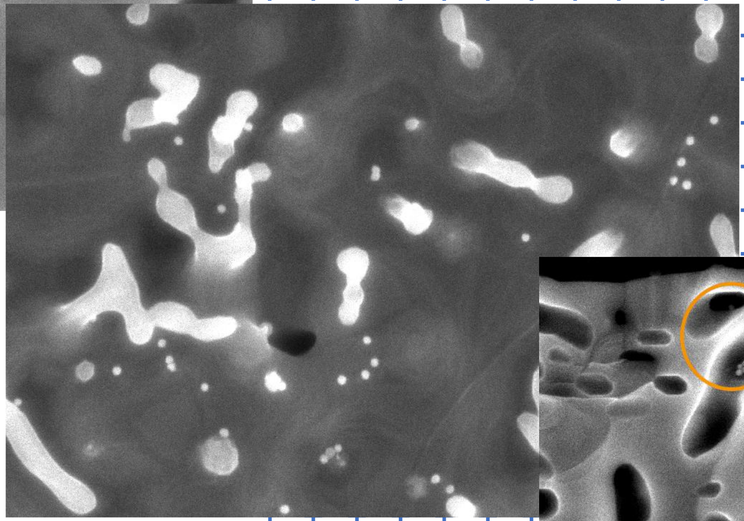
A. Macili et al. Applied Surface Science 615 (Apr. 2023), p. 156375

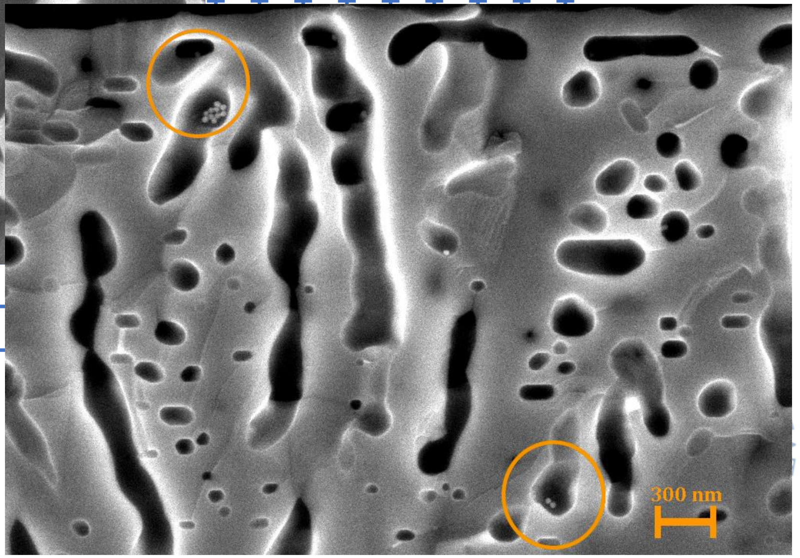
3D Graphene – Metal Functionalization

- Gold NPs
  Water → Ethanol
- Gold 1.1
  - 1 drop of solution
- Gold 1.2
  - 3 drops of solution
- Gold 1.3
  - 45 min immersion under sonication
- Gold 1.4
  - 24h immersion
  - Surface NPs density, $\sigma \sim 4\ \mathrm{NPs}/\mu\mathrm{m}^2$
  - Pores NPs density, $\rho \sim 1.5\ \mathrm{NPs}/\mu\mathrm{m}^2$



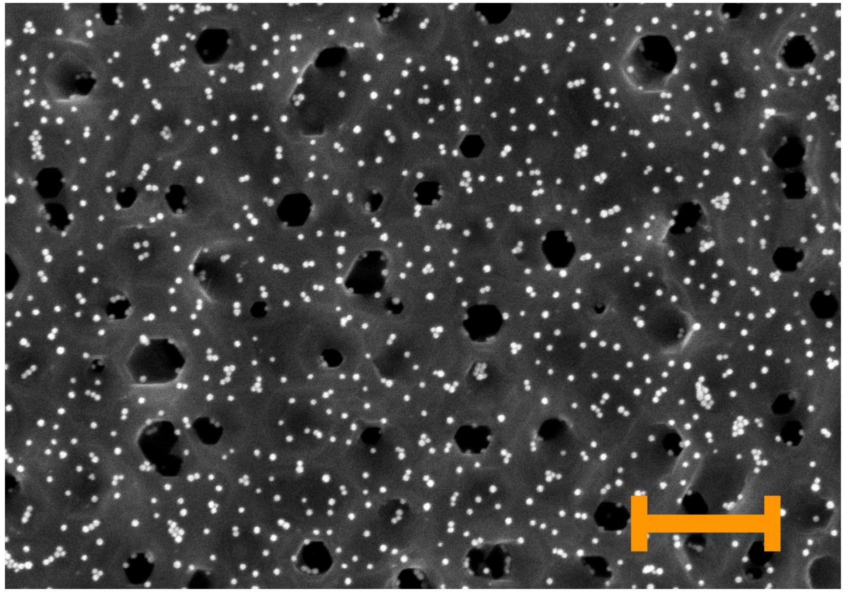


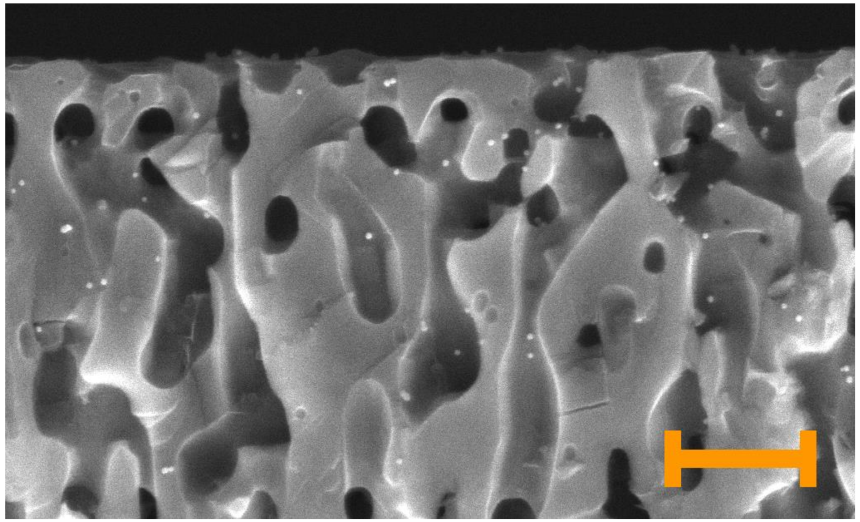


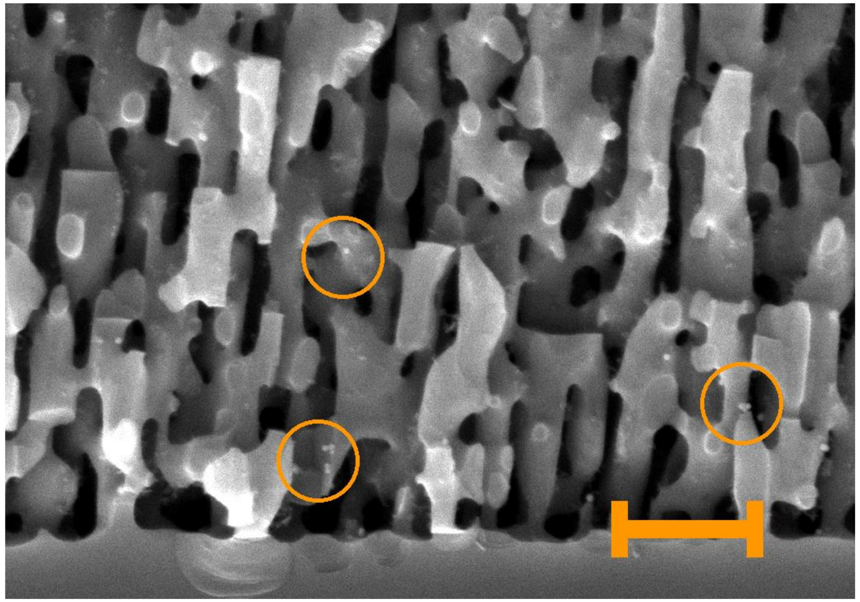


AuNPs Functionalization

- AuNPs on New gen.
  - 24h immersion
  - $\sigma = 220 \pm 25$ NPs/μm^2
  - $\rho = 15 \pm 1$ NPs/μm^2
  - NPs high diffusion length



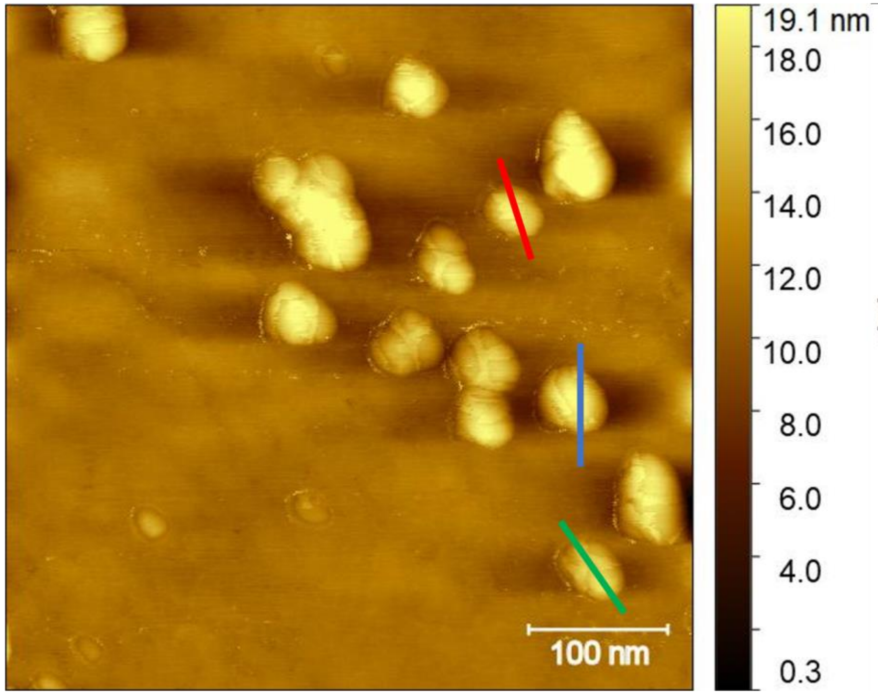


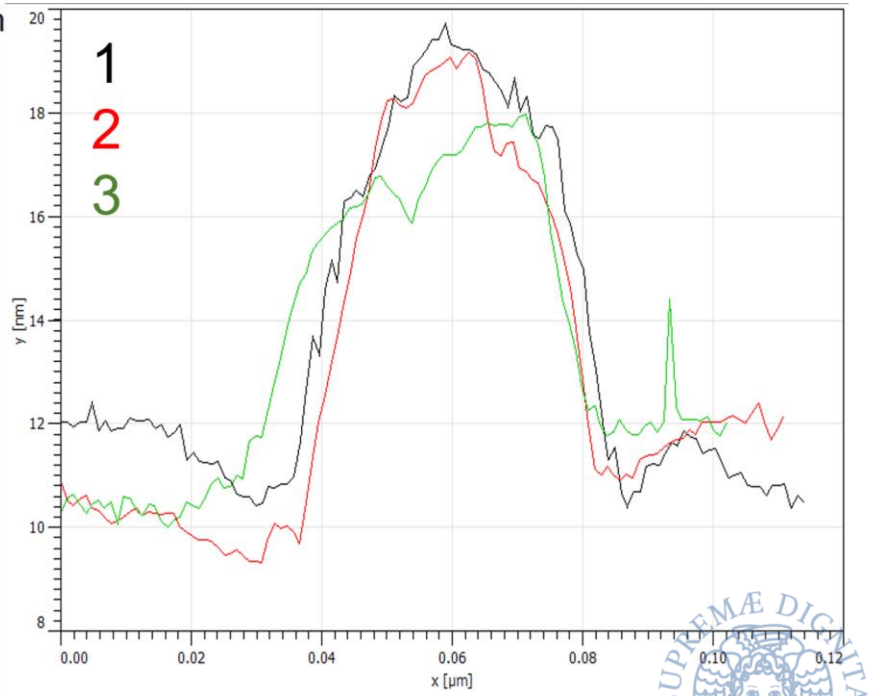


- Further experiments:
  - Longer immersion
  - Higher concentration

Palladium NPs 1st Synthesis

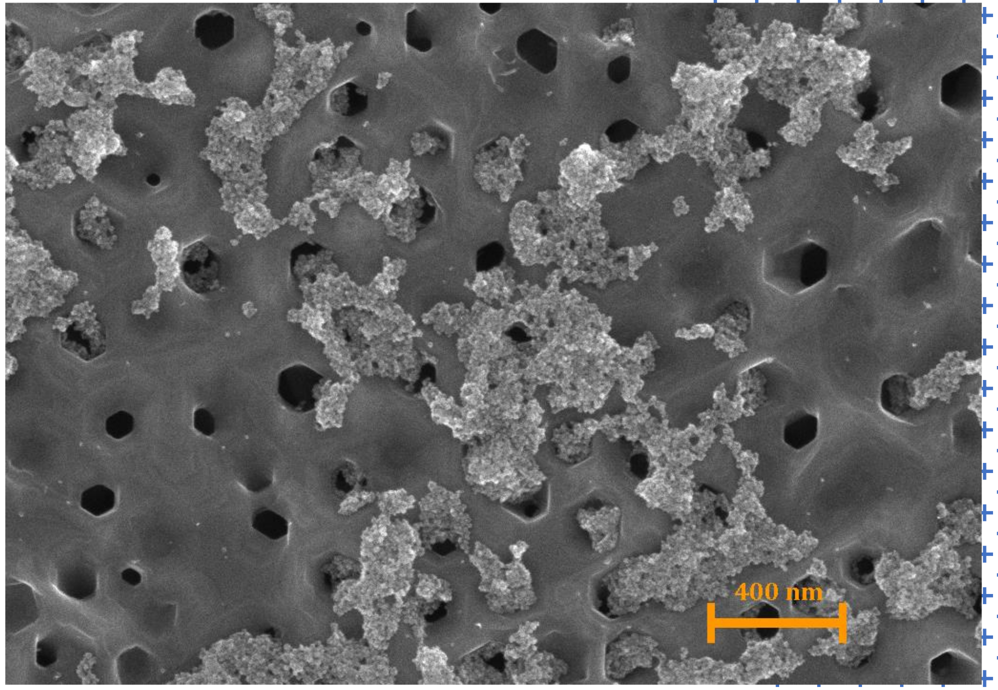
- Palladium Acetate, $Pd(OAc)_2$, in Sodium Dodecyl Sulphate, SDS, refluxed at 100°C under magnetic stirring → SDS-PdNPs
- NPs collection by ultra-high speed centrifugation
- NPs dispersion in ethanol
- AFM measurements
  - Monodispersed NPs
  - Tendency to cluster

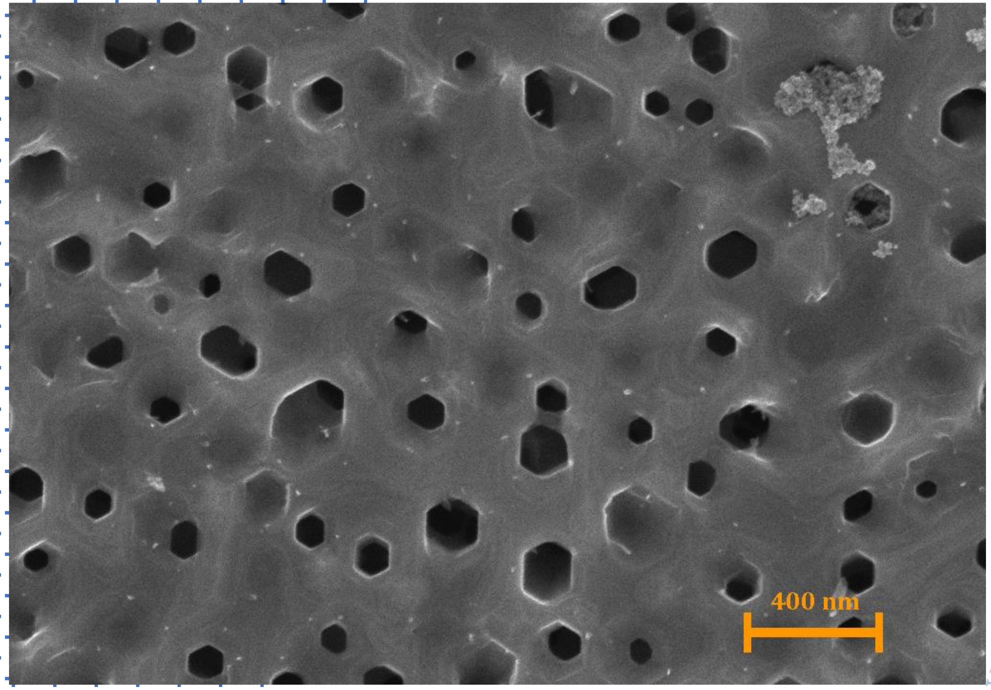




SDS-PdNPs Functionalization

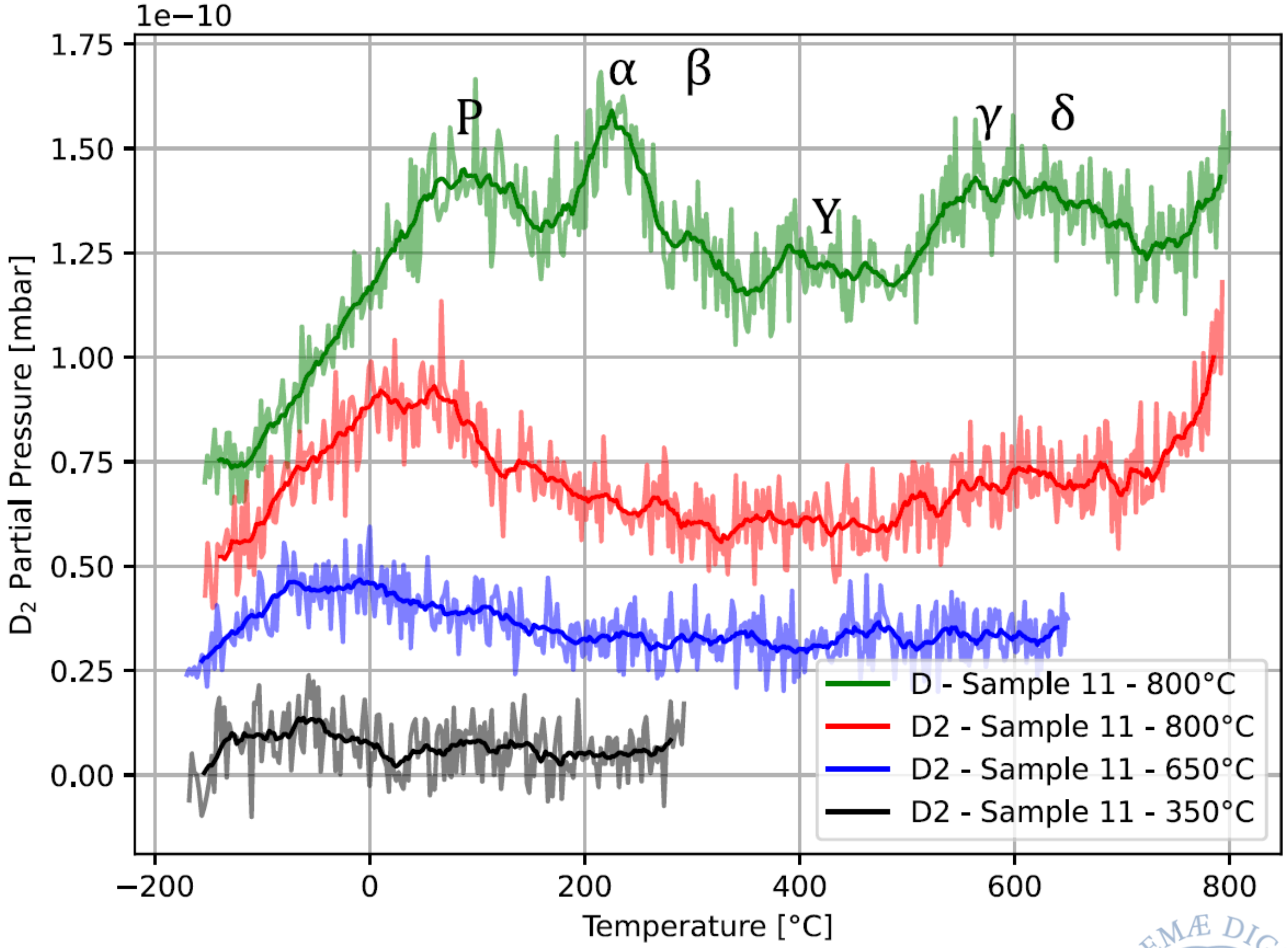
- Immersion in the SDS-PdNPs colloidal solution for 24h
- Successful functionalization
- NPs clustering





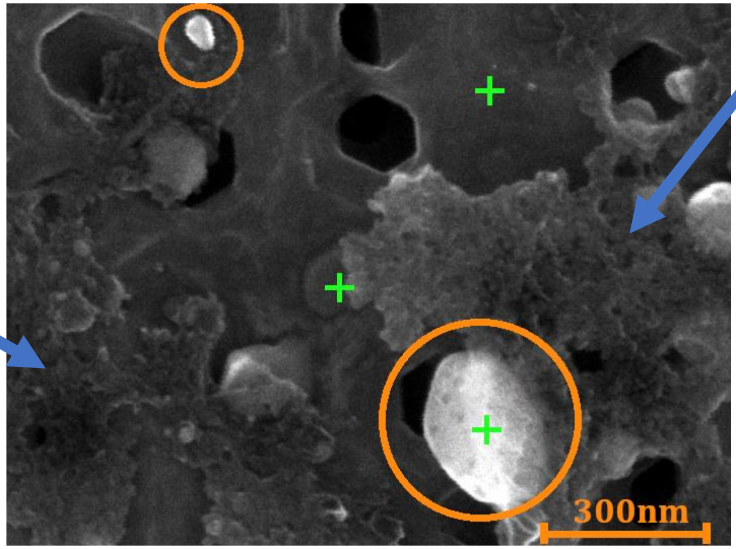
SDS-PdNP-Functionalized 3D Graphene – Hydrogen Storage

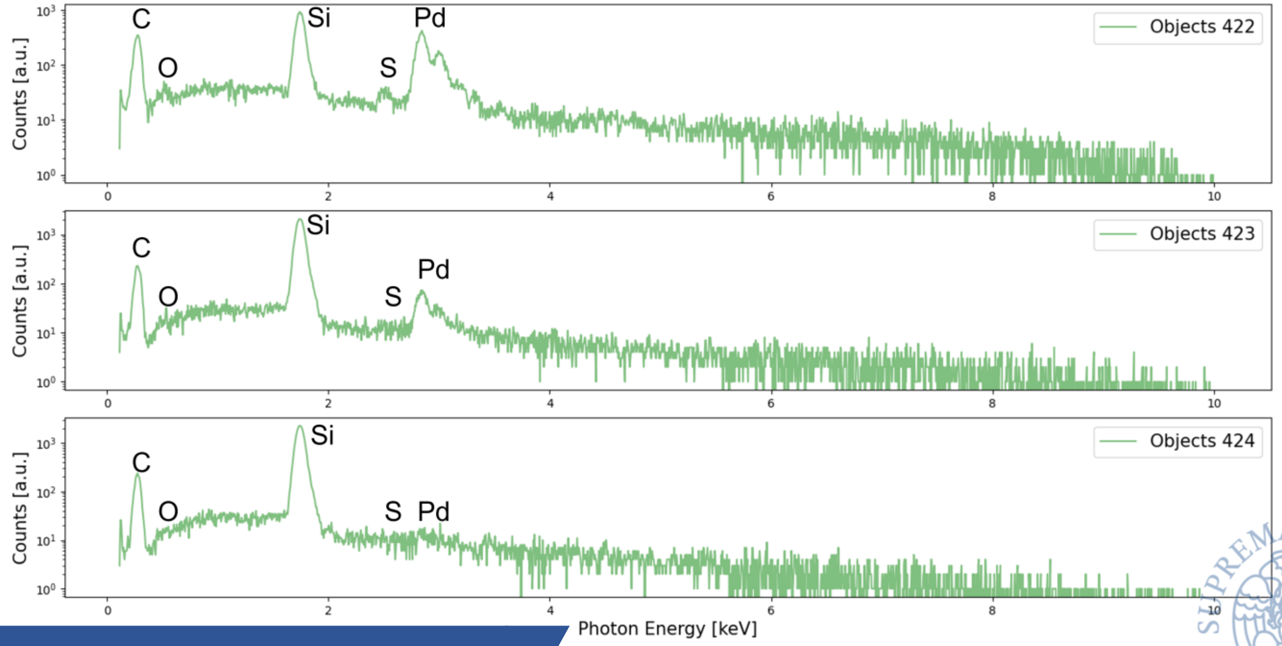
- Annealing from 350°C to 800°C
- 800°C needed to restore the chemisorption
- Lower temperature is needed for Physisorption
- 30 min D_2 exposure doesn't lead to an uptake increase
  - "Fast" delayed emission



SDS-PdNP-Functionalized 3D Graphene – SEM/EDX

- SEM-EDX analysis
  - Clustering
  - Amorphous carbon residuals
  - Sulfur poisoning

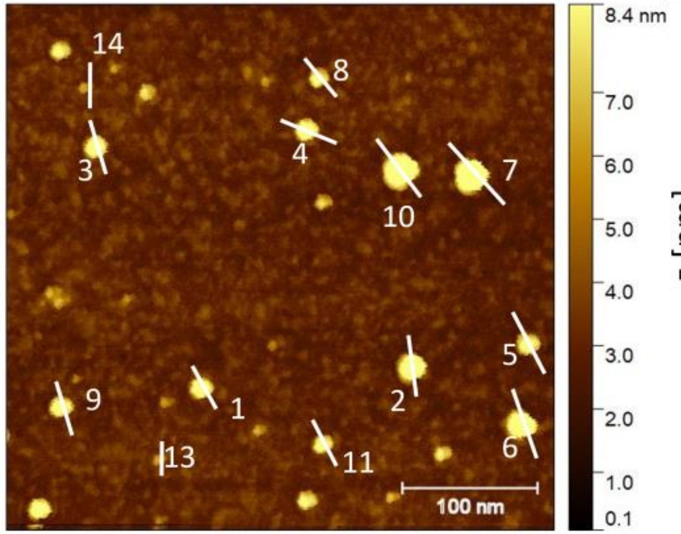


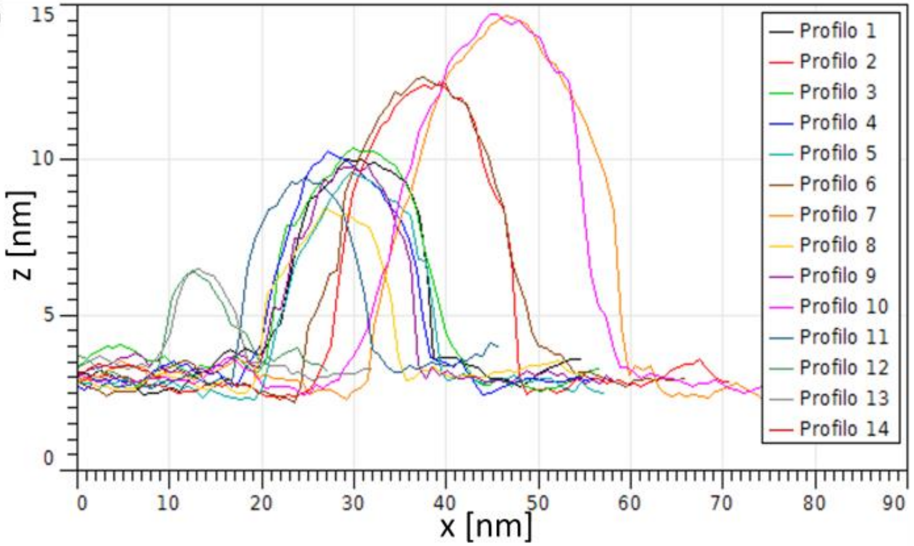


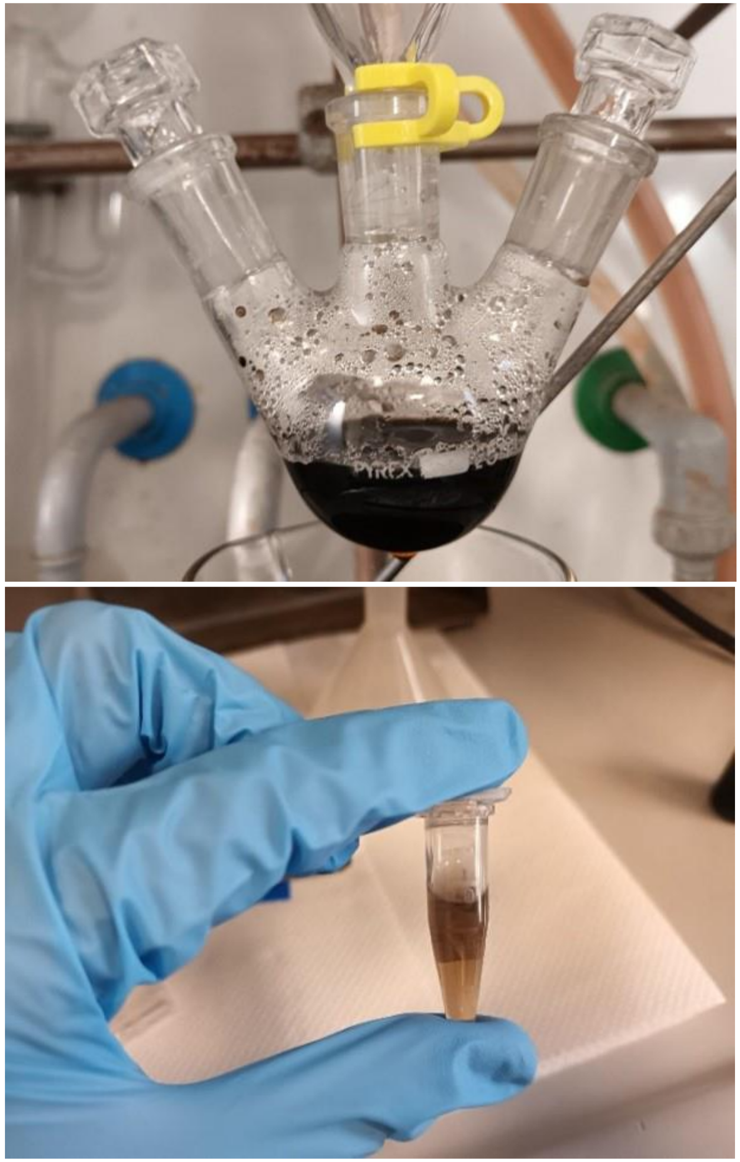
L.J. Hoyos et al. *J. Chem. Soc., Faraday Trans.*, 1992,88, 3367-3373

Palladium NPs 2nd Synthesis

- Palladium Acetate, $Pd(OAc)_2$, and Poly(NVinyl-2-Pyrrolidone), PVP, in Ethylene Glycol, EG, heated under magnetic stirring → PVP-PdNPs
- Smaller cap layer molecules → less amorphous carbon
- AFM measurements
  - Less monodispersed
  - Clustering is absent



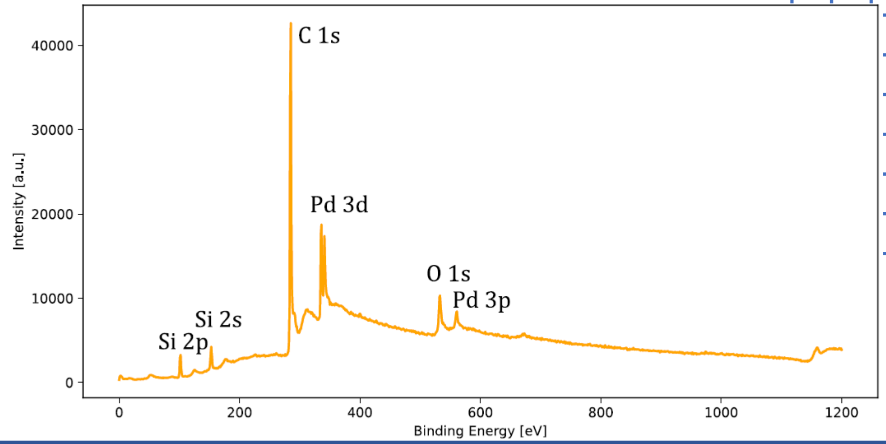


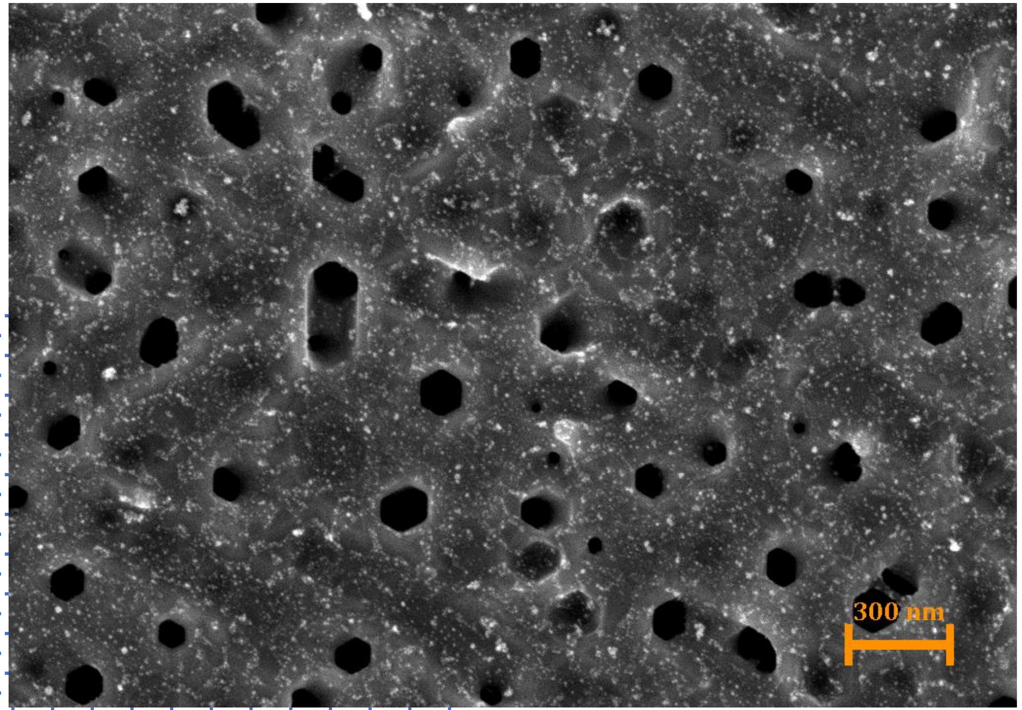


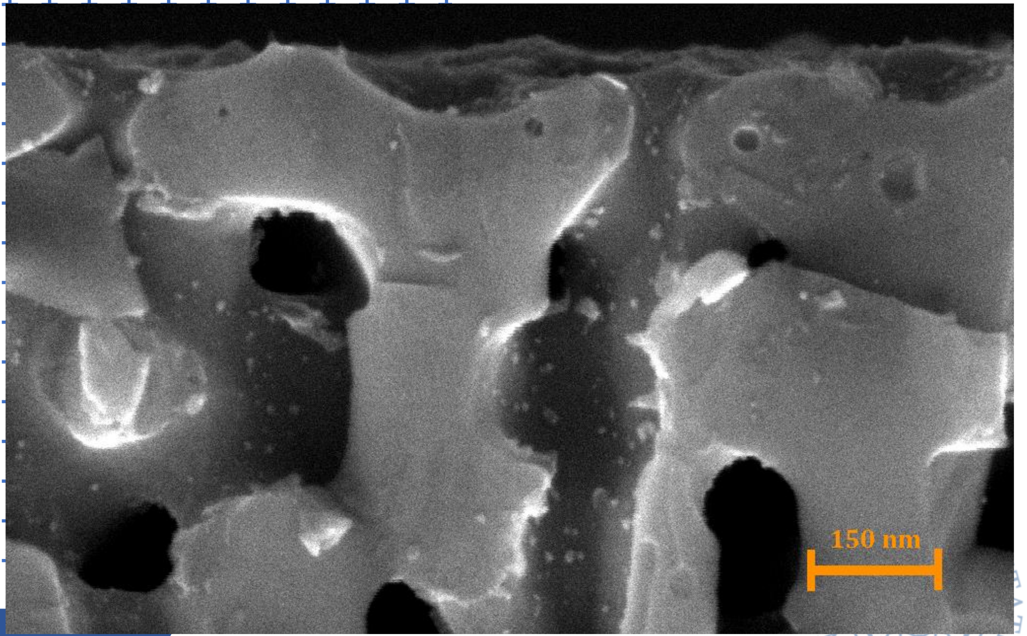
PVP-PdNPs Functionalization

- Immersion in the PVP-PdNPs colloidal solution for 24h

- Successful functionalization
- No clusters
- Diffusion inside the pores
- Large amount of deposited Pd is confirmed by XPS

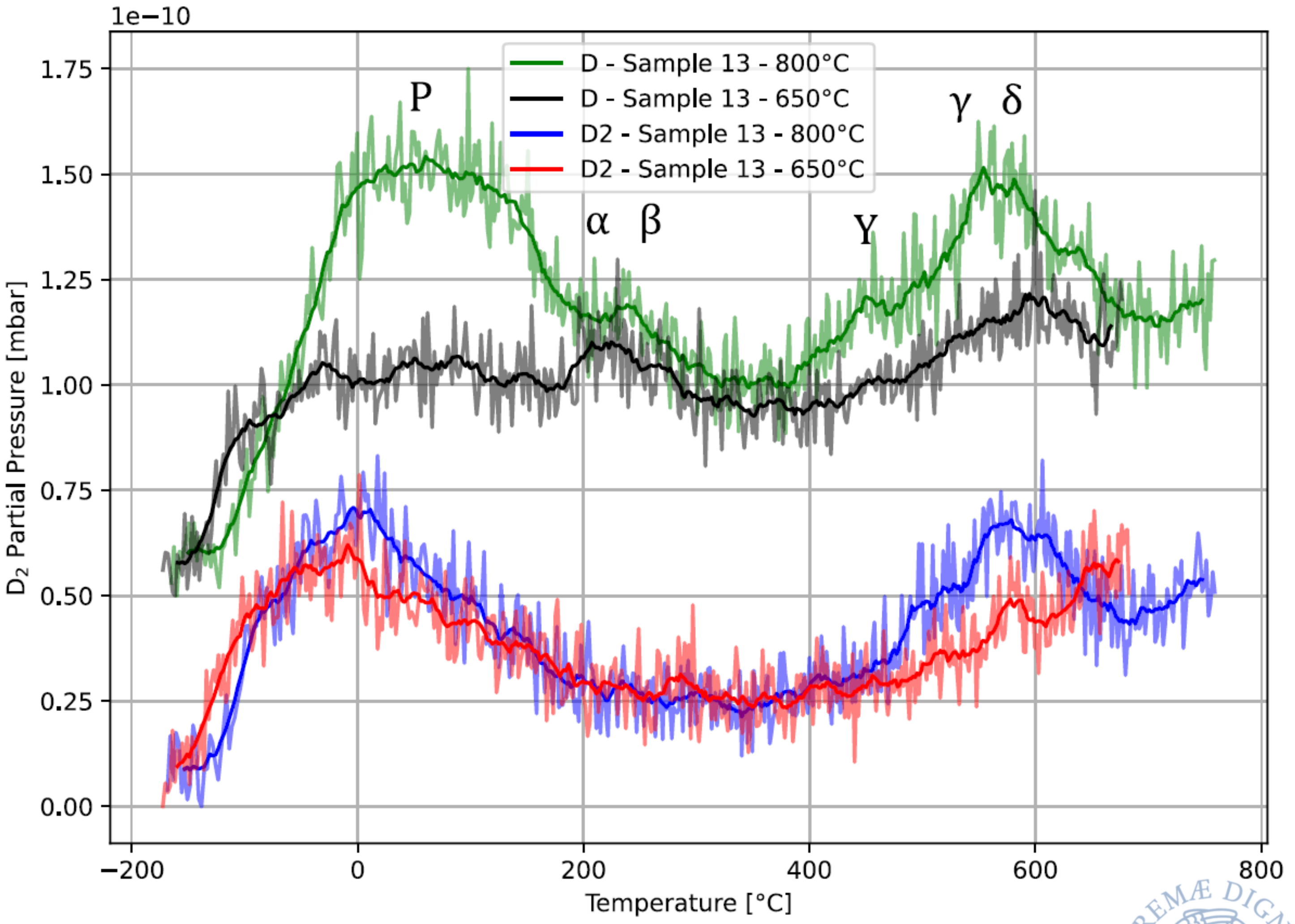






PVP-PdNP-Functionalized 3D Graphene – Hydrogen Storage

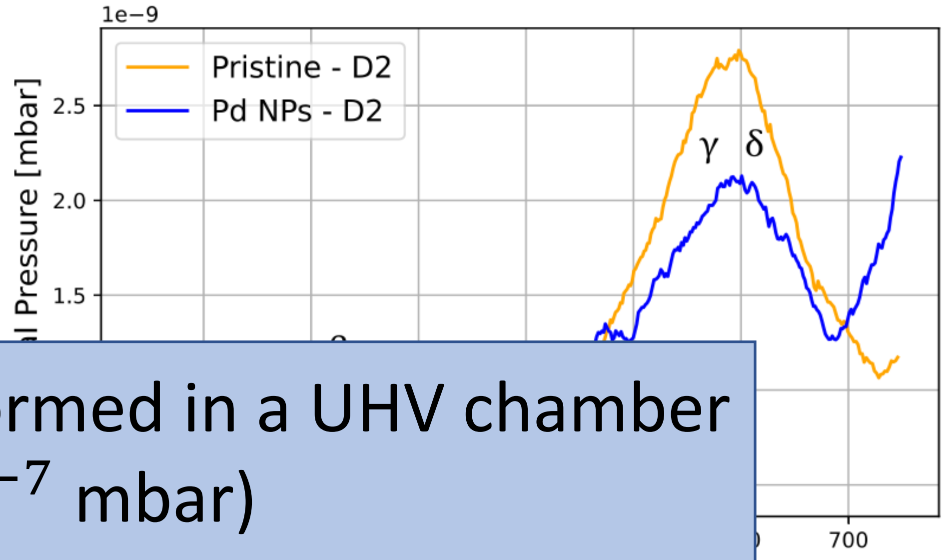
- Annealing from 600°C to 800°C
- Much larger chemisorption signal compared to SDS-NPs
- Physisorption less affected (uptake similar to pristine)

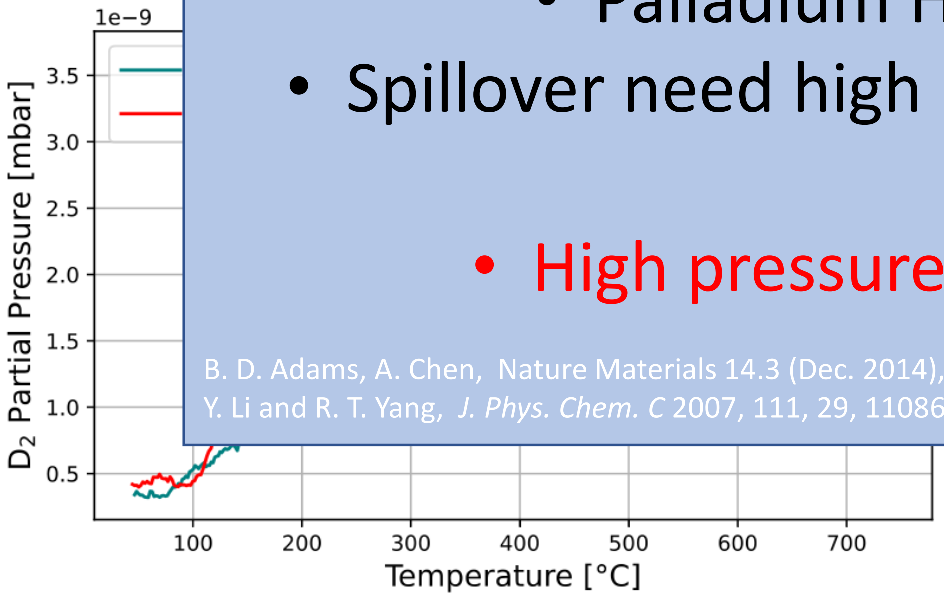


Pristine vs. Functionalized

D exposure

- Com
- Spe





peak at 118°C (1 eV)

- All Hydrogenation experiments were performed in a UHV chamber (Hydrogenation pressure 10^{-7} mbar)

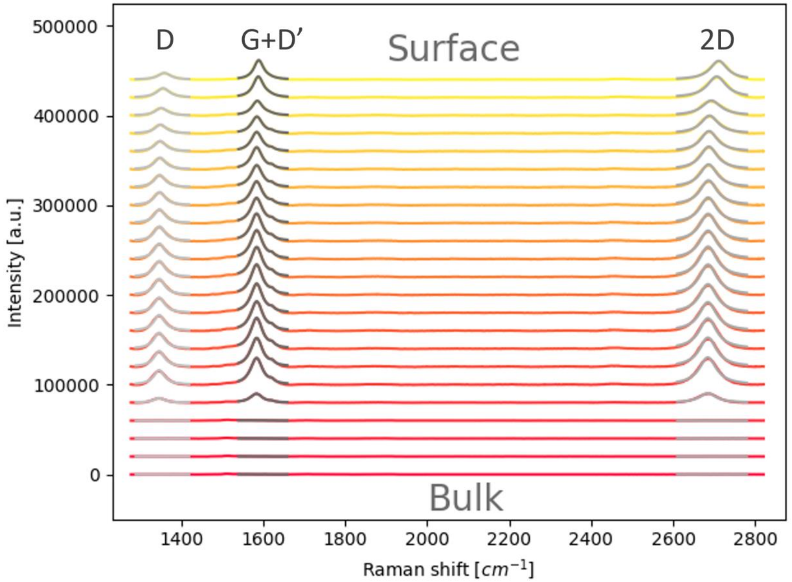
- Palladium Hydride need $P > 10$ mbar (at RT)
- Spillover need high pressure to be effective (even tens of bar)

- High pressure experiments have to be performed

B. D. Adams, A. Chen, Nature Materials 14.3 (Dec. 2014), pp. 271–279
Y. Li and R. T. Yang, *J. Phys. Chem. C* 2007, 111, 29, 11086–11094

Main Results

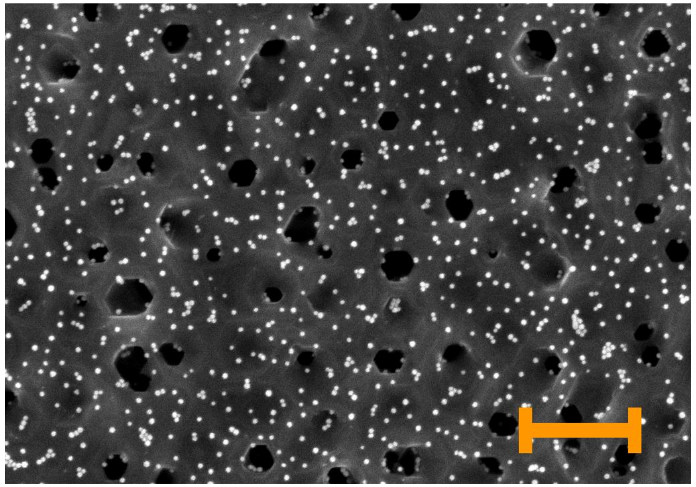
- Large improvement in the 3D graphene homogeneity, quality and quantity along the porous layer



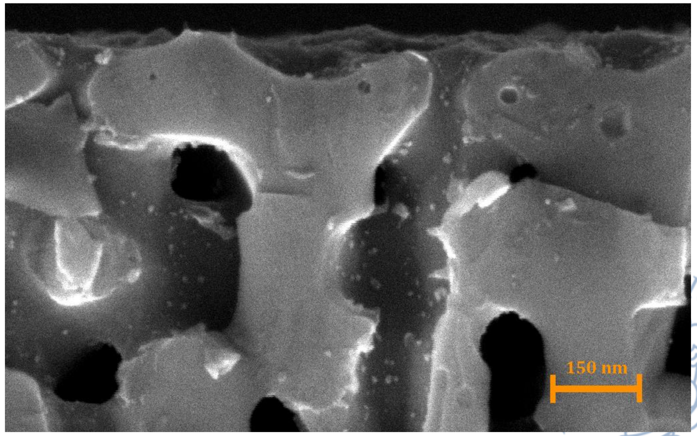
- 100 times larger uptake of molecular deuterium on 3D graphene

Sample	Uptake - D_2	Uptake - D
1st gen.	$2 \cdot 10^{-12}$ mol	$7 \cdot 10^{-12}$ mol
New gen.	$3 \cdot 10^{-11}$ mol	$9 \cdot 10^{-11}$ mol
New gen. - 900	$2 \cdot 10^{-10}$ mol	$4 \cdot 10^{-10}$ mol

- Found an effective metal NP functionalization procedure (demonstrated both with Au and Pd, and which should apply for every metal)

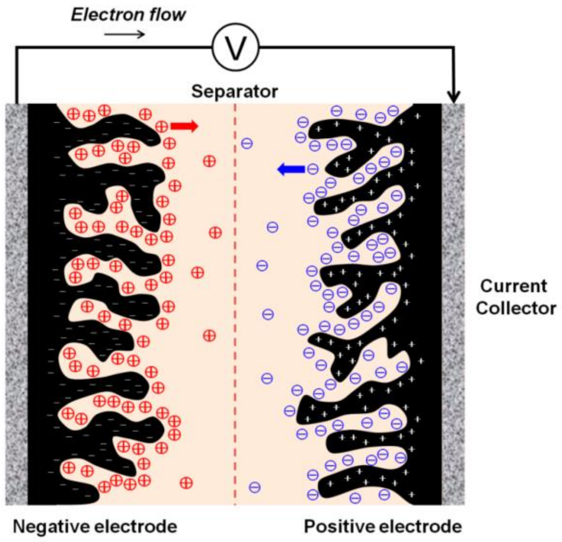


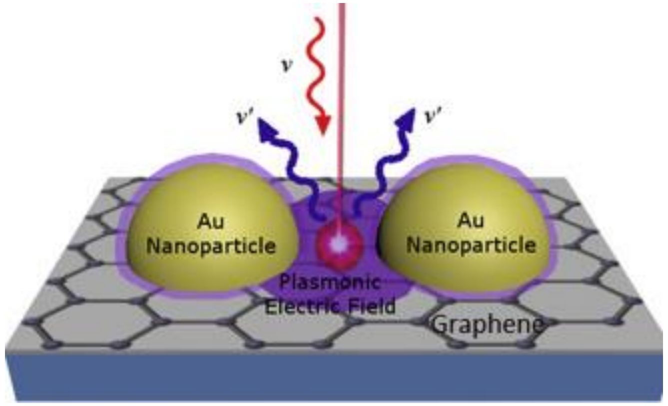
- Found optimal condition for PdNP functionalization



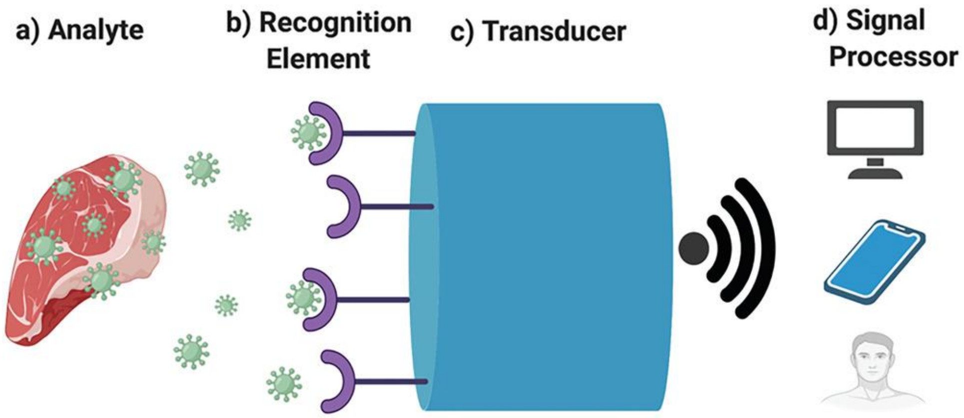
Outlook

- Ongoing studies
  - Higher pressure Hydrogenation experiments
  - Computational simulations
  - TEM measurements





- Possible applications
  - Supercapacitors
  - Surface Enhanced Raman Spectroscopy
  - Sensors (Hydrogen, Food, etc.)



Thank you for your attention!

Acknowledgments

- Ylea Vlamidis
  @ CNR-NANO, Pisa
  (Raman Spectroscopy and AFM measurements, and PdNPs synthesis)

- Silvia Rubini
  @ CNR-IOM, Trieste
  (XPS measurements)

- Valentina Zannier
  @ CNR-NANO, Pisa
  (SEM measurements)

- U. Schmid, C. Zellner,
  M. Leitgeb and M. Schneider
  @ TU Wien
  (porousified Silicon Carbide samples)