ITINERIS

Chemical diagnostics for particulate characterization

Mario Commodo – mario.commodo@stems.cnr.it

081 7682256

IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation EU PNRR-Mission 4 "Education and Research" - Component 2: "From research to business" - Investment 3.1: "Fund for the realisation of an integrated system of research and innovation infrastructures"

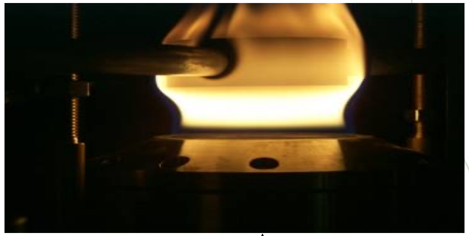
Finanziato dall'Unione europea NextGenerationEU

Ministero dell'Università e della Ricerca

Italiadomani

Some examples of different laboratory flames

Laminar premixed flames:



Fuel Air

Laminar diffusion flame:

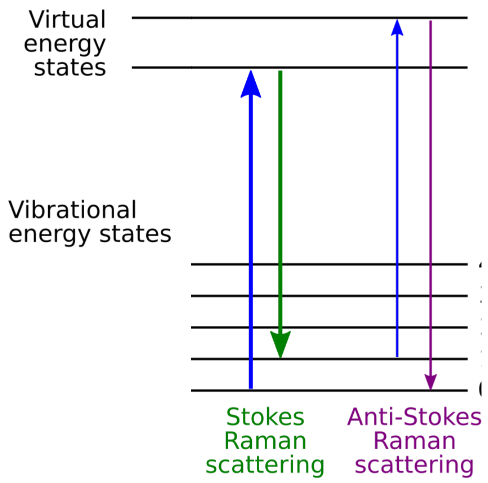
Air Air

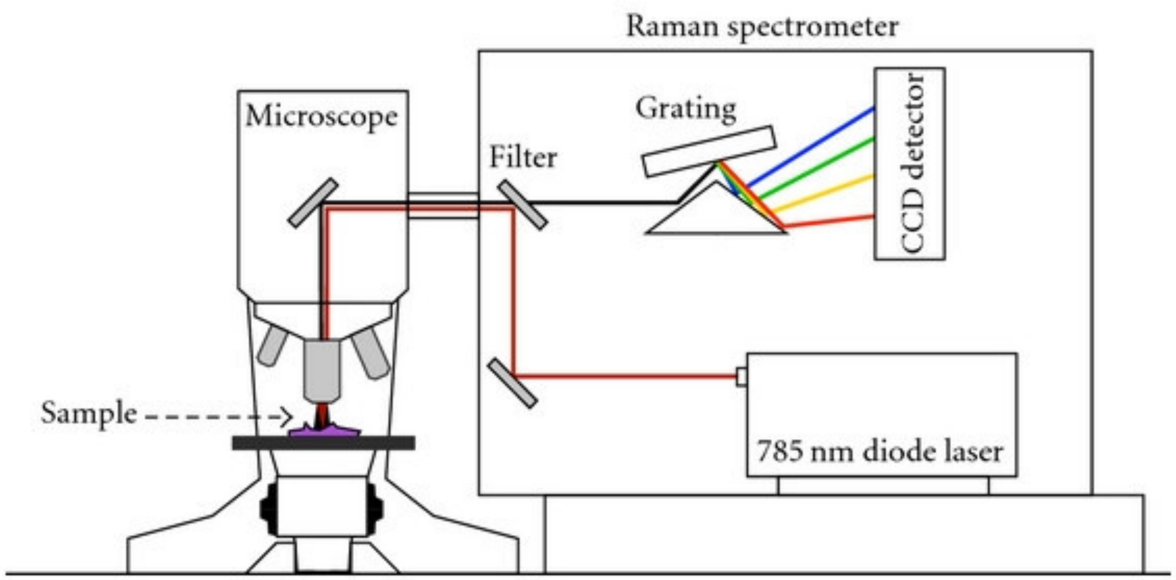
Fuel

Turbulent diffusion flame:

Fuel

Raman Spectroscopy



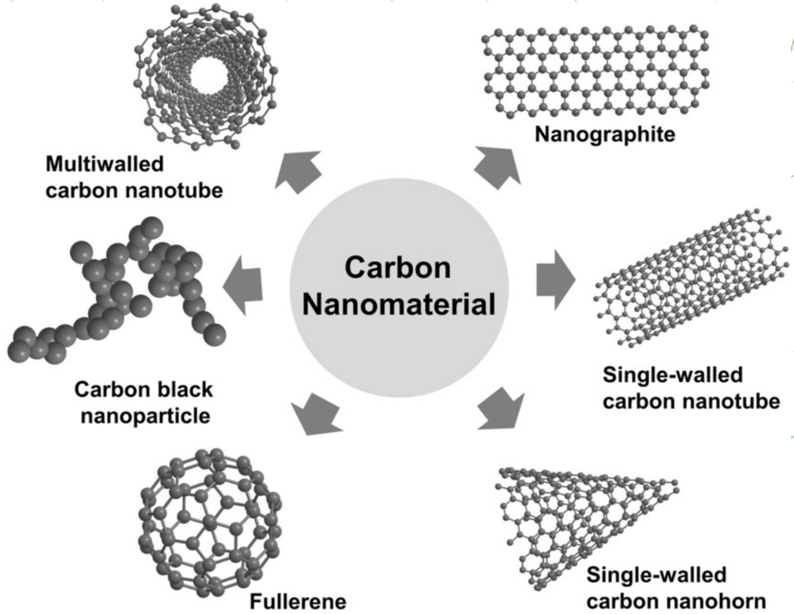


Raman Spectroscopy for Carbon Materials

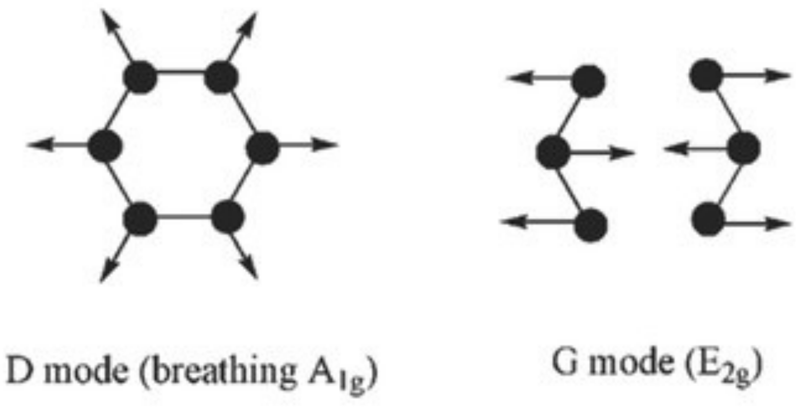
Carbon materials with **sp² hybridization,** like graphite, graphene, carbon nanotubes, and fullerenes, exhibit strong Raman scattering.

It can be used to study:

- **crystallinity**,
- presence of **defects**,
- number of **layers** (in graphene),
- **strain** in carbon nanoparticles.



Raman Spectroscopy for Carbon Materials

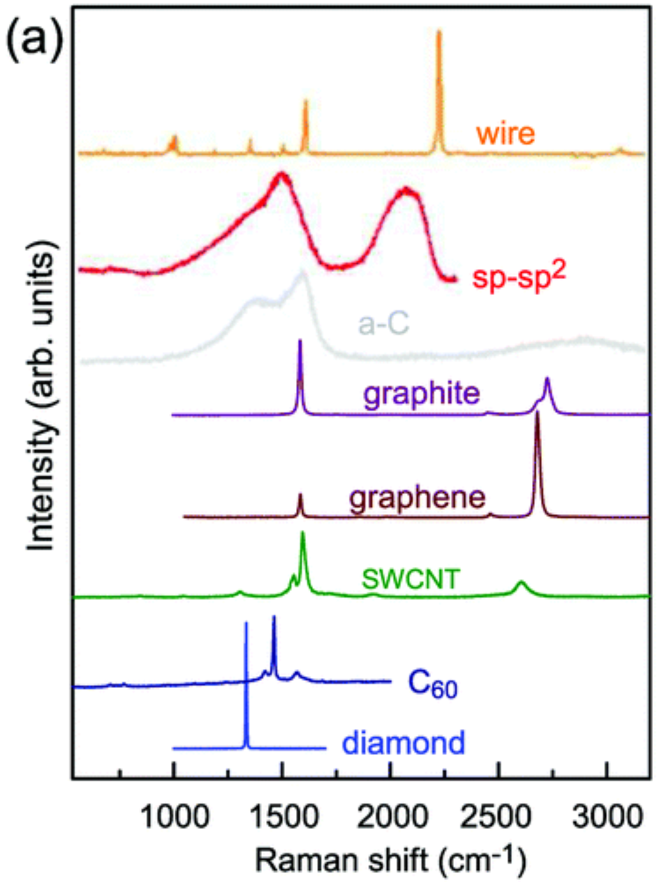


- G Band: corresponds to the in-plane vibration of sp^2 hybridized carbon atoms. Its position and shape are sensitive to **strain** and **doping**.

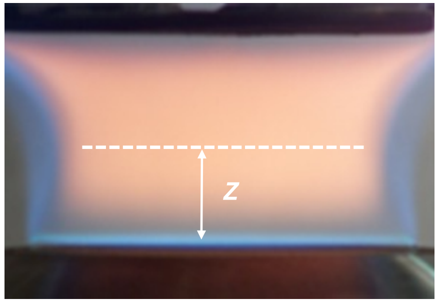
- D Band: disorder-induced and requires a **defect** to be active. Its intensity is directly related to the amount of **disorder** or **defects** in the sp^2 carbon lattice.

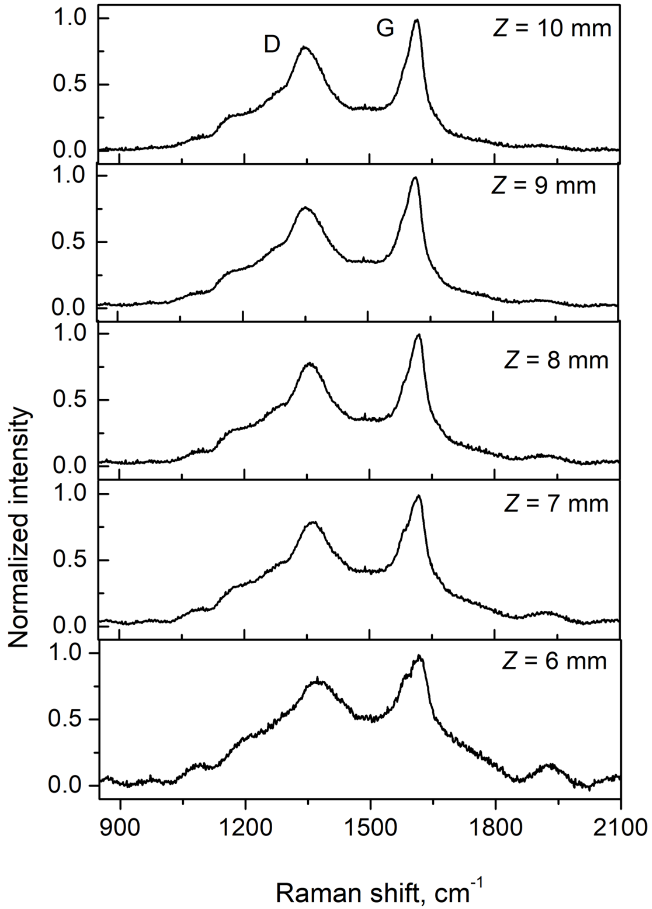
- 2D Band: second order of the D band (overtone, no defect required). Its shape, position, and intensity relative to the G band are highly sensitive to the number of **layers** in few-layer graphene, and to **strain** and **doping**.

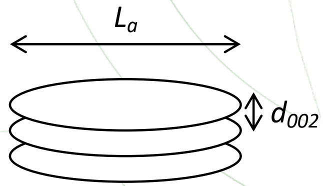
Raman Spectroscopy for Carbon Materials



Raman Spectroscopy for Carbon Nanoparticles



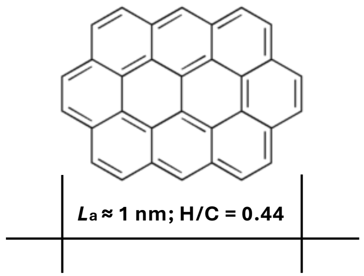




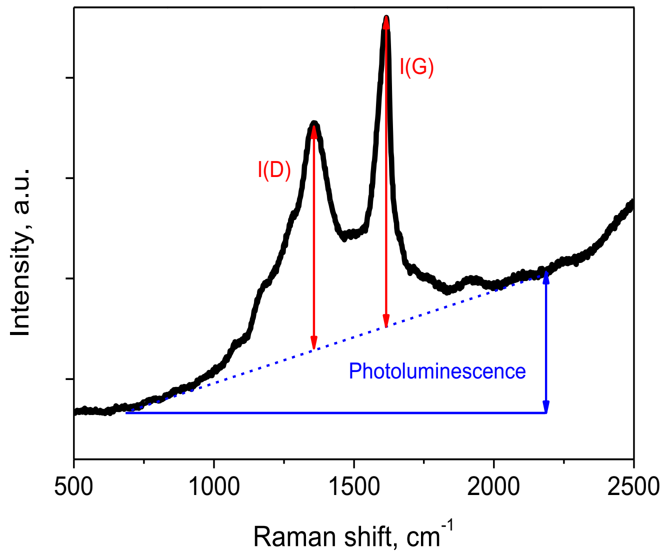
$$L_a^2(\mathrm{nm}^2) = 5.4 \cdot 10^{-2} \cdot E_L^4(\mathrm{eV}^4)\frac{I(\mathrm{D})}{I(\mathrm{G})}$$

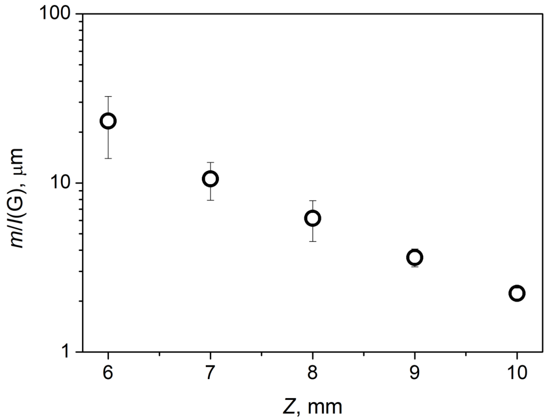
Ferrari, Basko/Nature Nanotech. (2013)

$L_a \approx 1$ **nm**

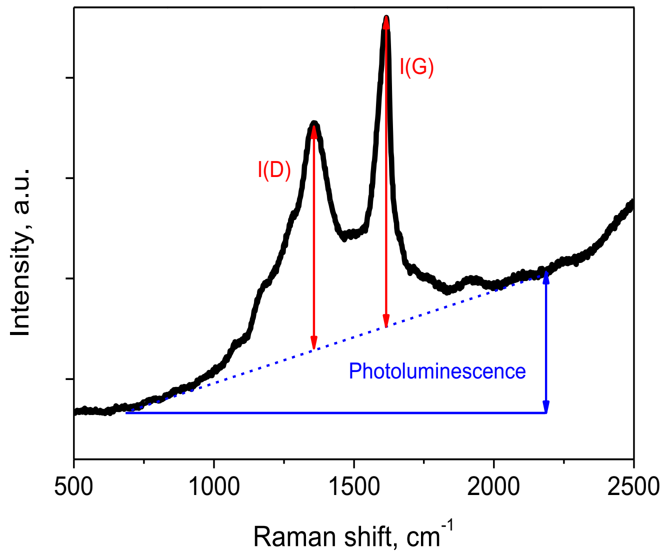


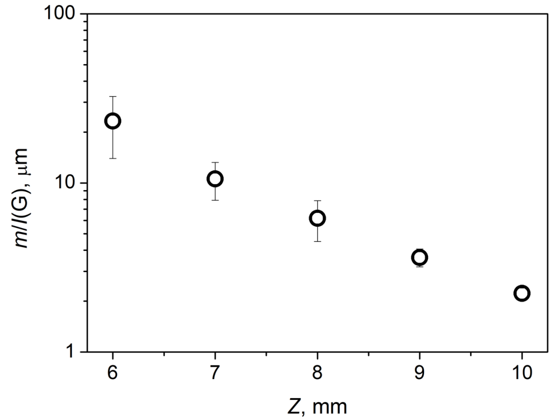
Raman Spectroscopy for Carbon Nanoparticles

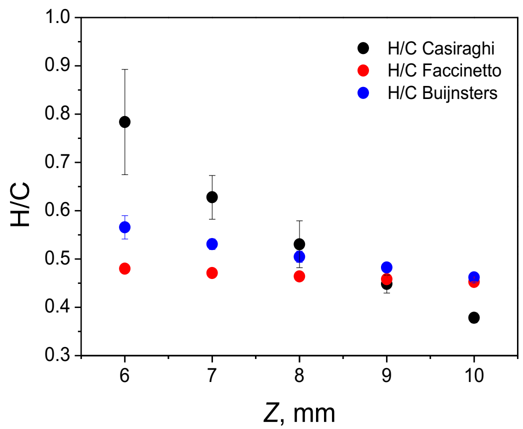




Raman Spectroscopy for Carbon Nanoparticles







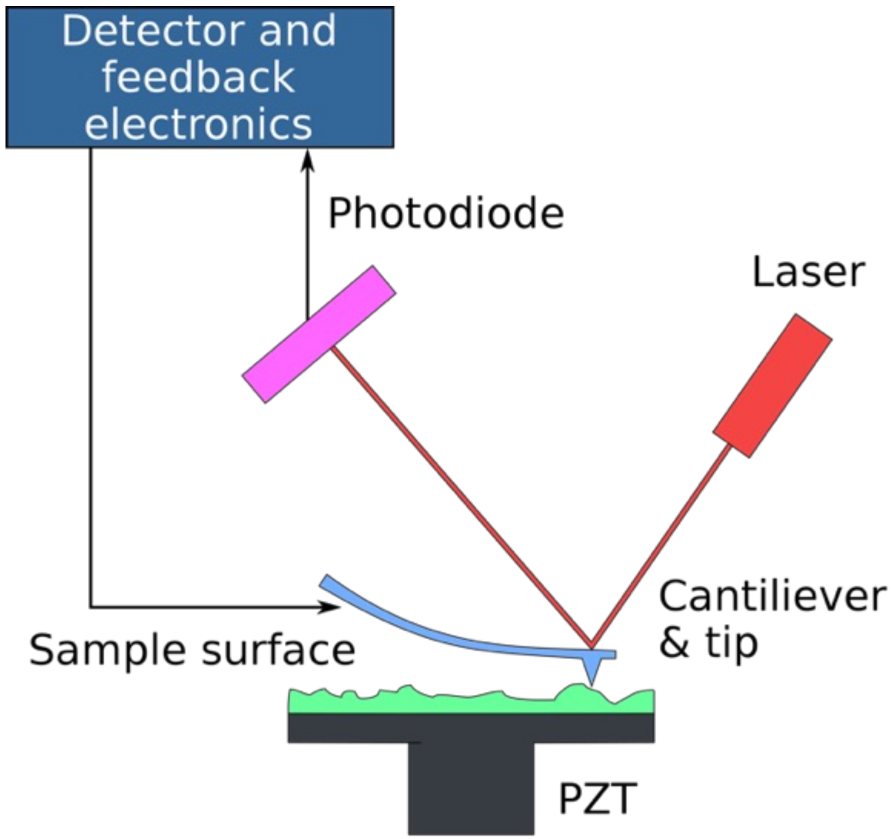
$$H\ [at.\%] = a + b * \log(\frac{m}{I(G)})$$

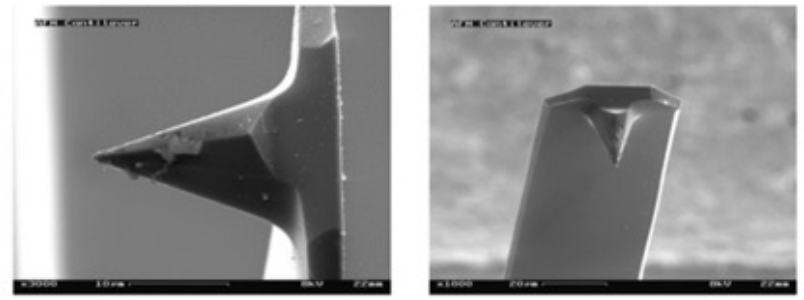
Casiraghi et al. Diam. Relat. Mater. 14 (2005)
(Hydrogenated amorphous carbon - a-C:H)

Buijnsters et al. J. Appl. Phys. (2009)
(Hydrogenated amorphous carbon - a-C:H)

Faccinetto et al. Comm. Chem. (2020)
(soot from diffusion flame)

Atomic Force Microscopy

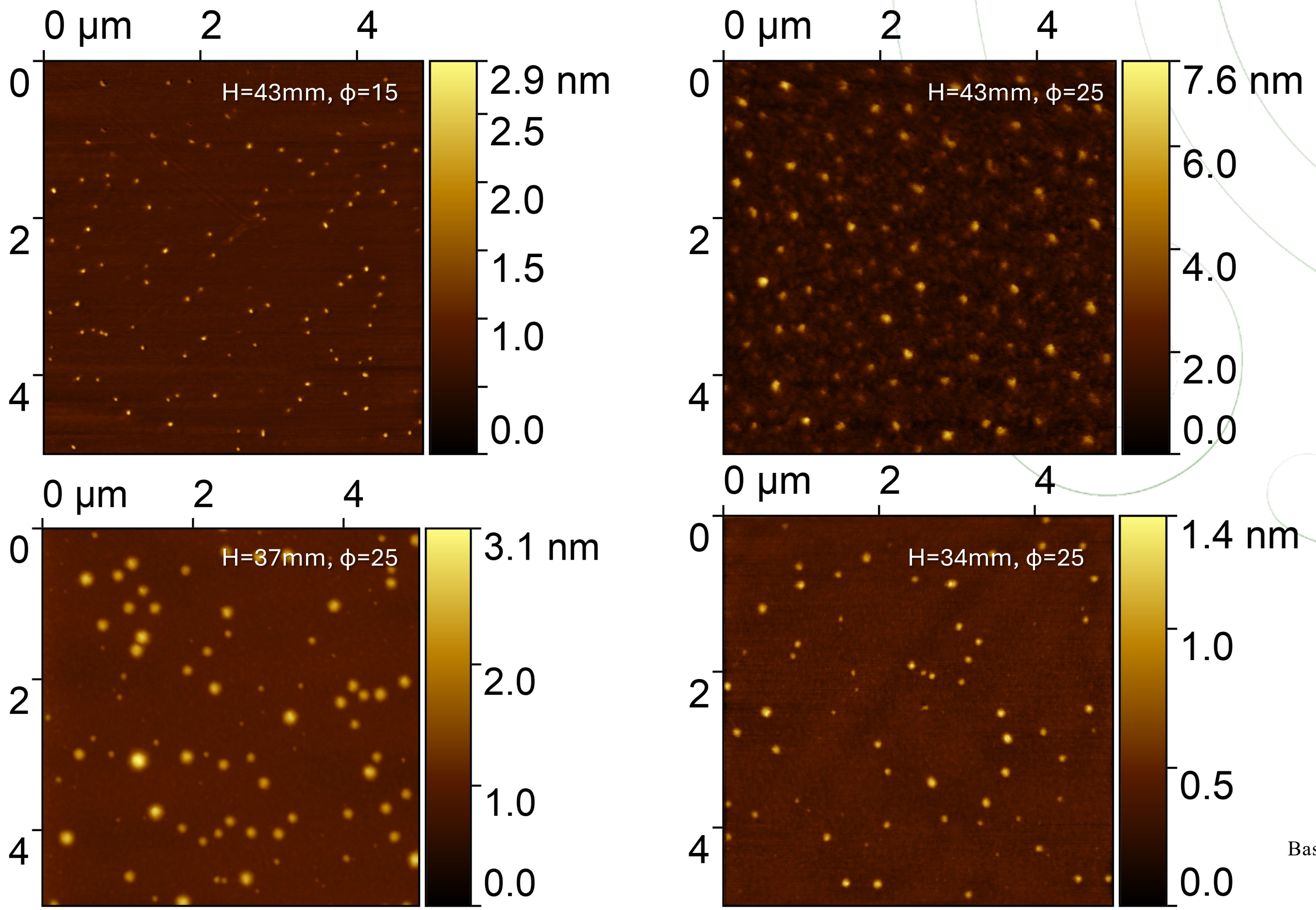




Tip radius 2 – 150 nm:

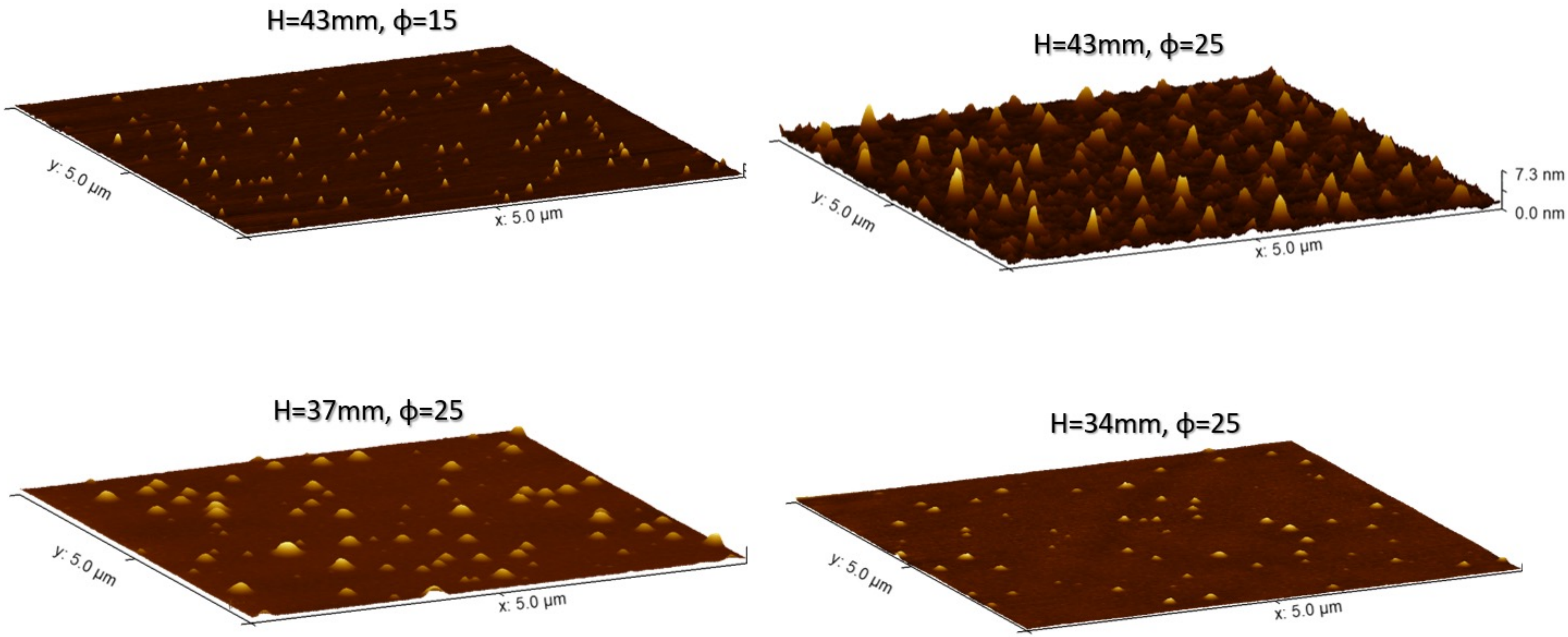
- super sharp;
- conductive coatings;
- magnetic coatings;
- diamond-like.

AFM for Carbon Nanoparticles



Basta et al. 2024: 10.1016/j.fuel.2024.132342

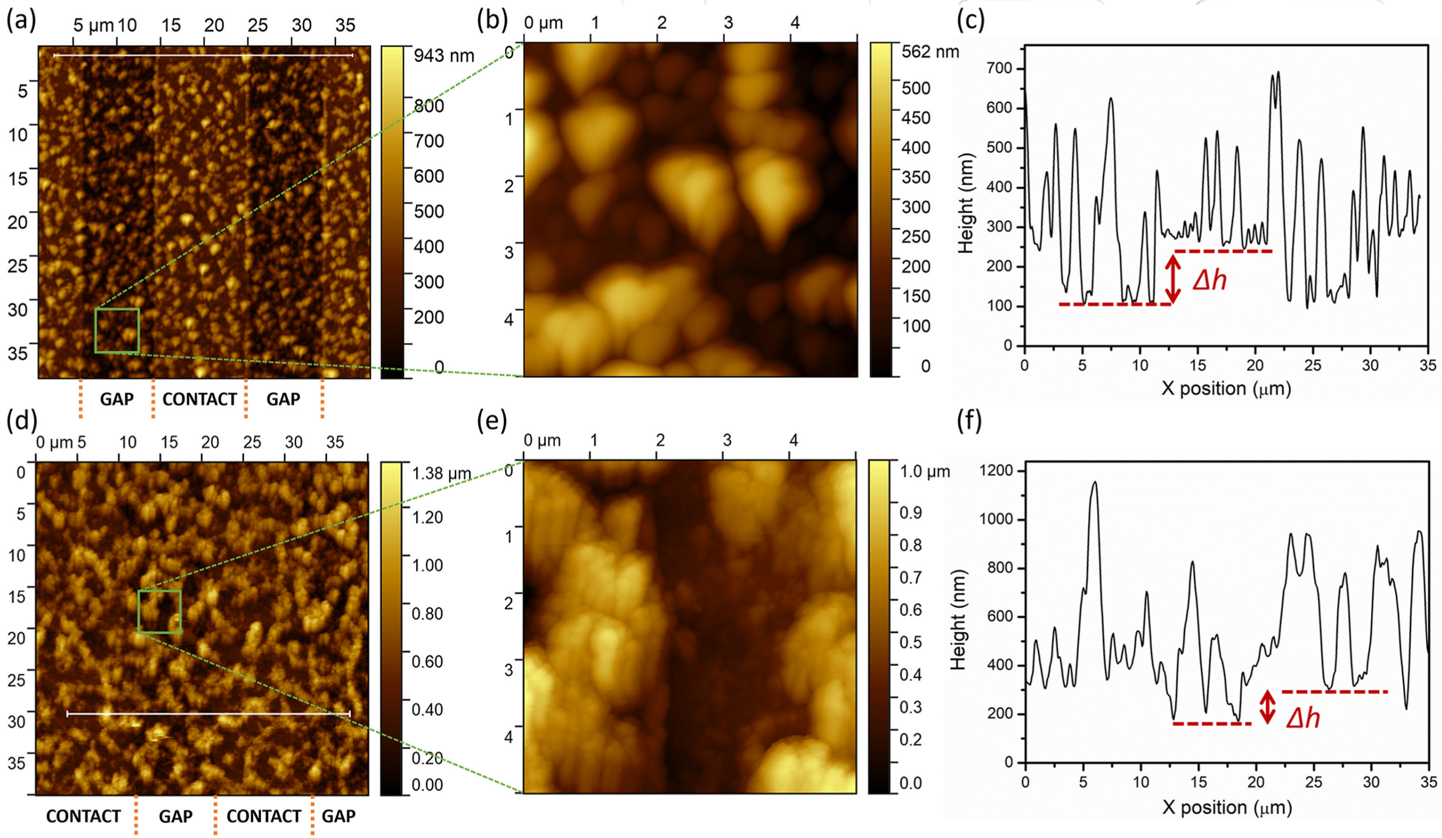
AFM for Carbon Nanoparticles



Basta et al. 2024: 10.1016/j.fuel.2024.132342

AFM for Carbon Nanoparticles

AFM images of samples with 20 and 50 insertions. CNPs are clearly visualized both inside the glass gaps (the lower ribbons) and on the gold contacts (the higher ribbons).

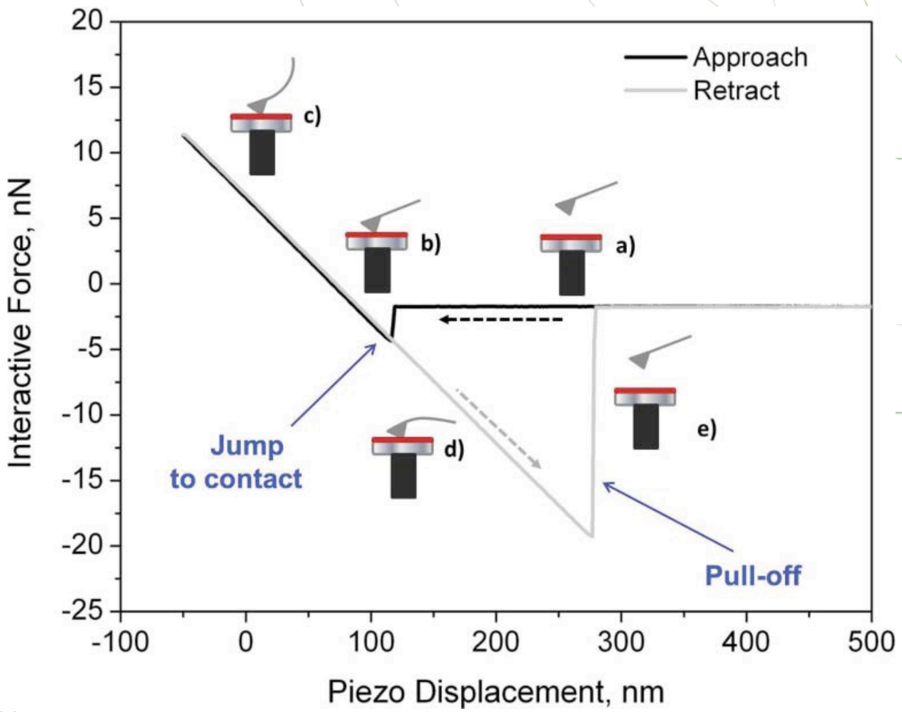


Basta et al. 2024: 10.1016/j.fuel.2024.132342

AFM for Carbon Nanoparticles

Nano mechanical properties (**hardness**, **Young's modulus**, etc…) can be investigated via Force Spectroscopy measurements.

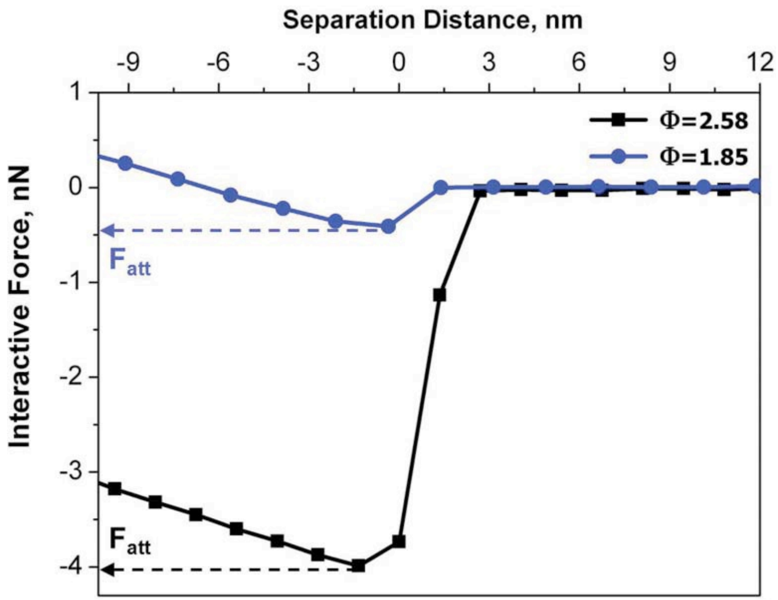
A typical experimental **force–distance** curve measured by AFM. The black line refers to the **approach** of the cantilever to the sample surface, while the grey line refers to **retraction** from the sample surface.

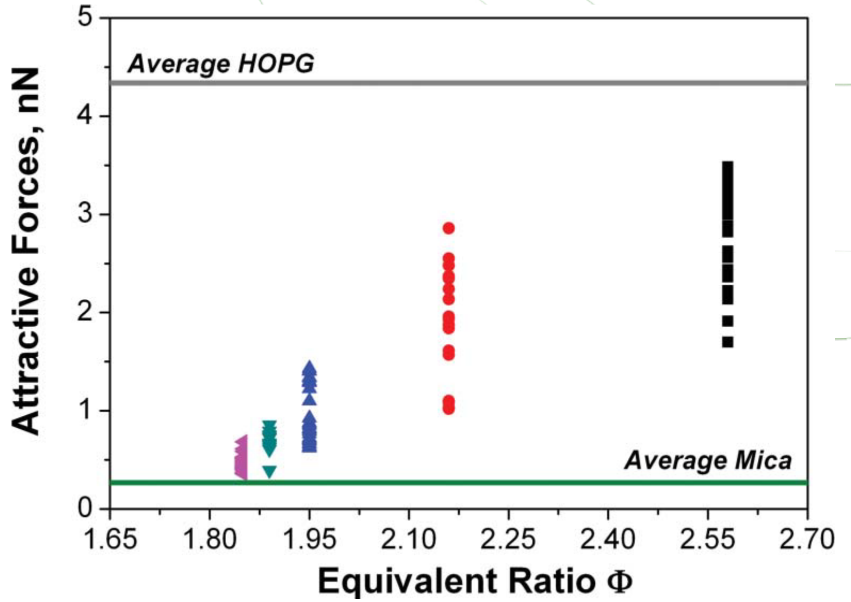


De Falco et al. 2015:10.1080/02786826.2015.1022634

AFM for Carbon Nanoparticles

Attractive forces between particle and probe-tip measured on various particles as a function of flame equivalence ratio. The average values measured on mica and HOPG are also reported by the lower horizontal (green) and the higher horizontal (grey) line, respectively.





AFM for Carbon Nanoparticles

The van der Waals forces between a sphere and a flat plane in the Derjaguin approximation:

$$F_{vdW} = -\frac{A_{tip-particle} R_{tip}}{6D^2}$$

R_{tip} is the radius of the tip, D is the tip–particle separation distance, and $A_{tip–particle}$ is the Hamaker constant corresponding to the system tip–particle.

The Hamaker constant trend confirms a continuous increase of particle **graphitization** by increasing the **size of the aromatic domains** and/or the three-dimensional **internal ordering** by increasing the flame-equivalent ratios.

	Hamaker constant A, 10^{-19} J
HOPG	4.7 ± 0.3 [a]
Particles at $\Phi = 2.58$	3.5 ± 1.6[b]
Particles at $\Phi = 2.16$	2.2 ± 0.9[b]
Particles at $\Phi = 1.95$	1.5 ± 0.5[b]
Particles at $\Phi = 1.89$	0.98 ± 0.01[b]
Particles at $\Phi = 1.85$	0.95 ± 0.01[b]
Benzene	0.5[c]
Aliphatic	0.1[c]

[a]Lee et al. (2002); [b]this study; [c]Israelachvili (2011).

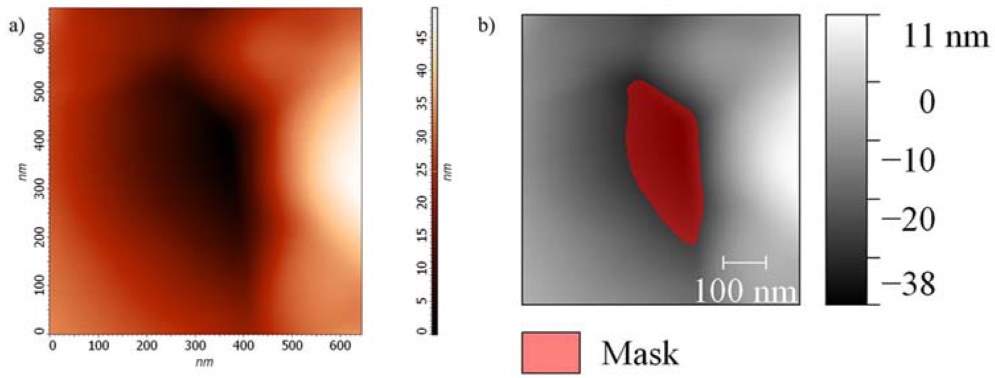
De Falco et al. 2015:10.1080/02786826.2015.1022634

AFM for Carbon Nanoparticles

A continuum elastic theory can be used to derive the mechanical properties of the sample, based on the Hertz theory: spherical tip indenting a semi-infinite plane, neglecting adhesion forces.

$$F = \frac{4}{3}E^{*}\sqrt{R(d-d_0)^3} + F_{adh}$$

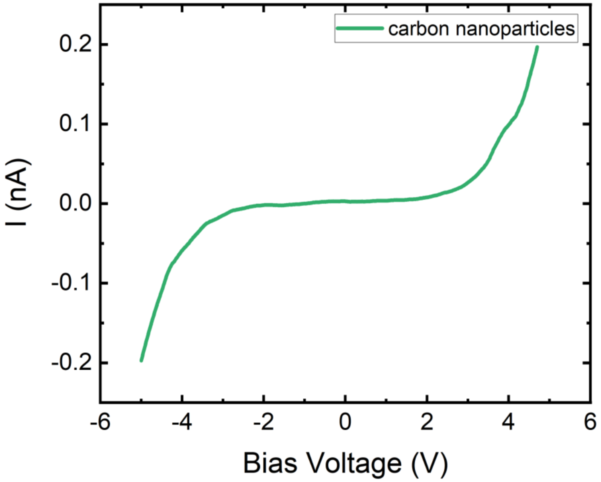
$$H = \frac{F_{max}}{A_p}$$



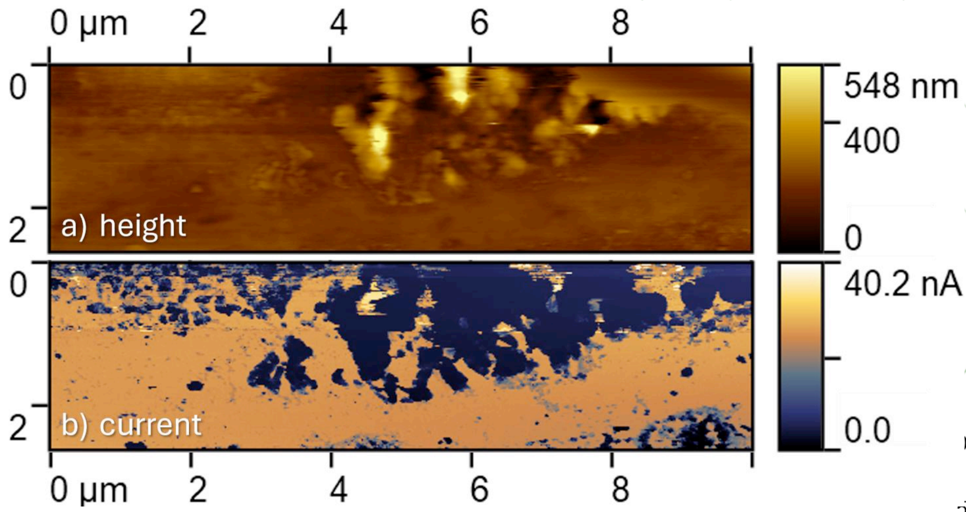
Sample	Hardness *H*, GPa	Young's Modulus *E*, GPa
Sample #1	0.75 ± 0.05	4.2 ± 0.3
$\Phi = 2.01$	0.90 ± 0.05	7.2 ± 0.4
$\Phi = 2.55$	0.70 ± 0.05	3.8 ± 0.3
HOPG	2.40 ± 0.10	7.5 ± 0.3

De Falco et al. 2021: 10.3390/app11188448

C-AFM for Carbon Nanoparticles

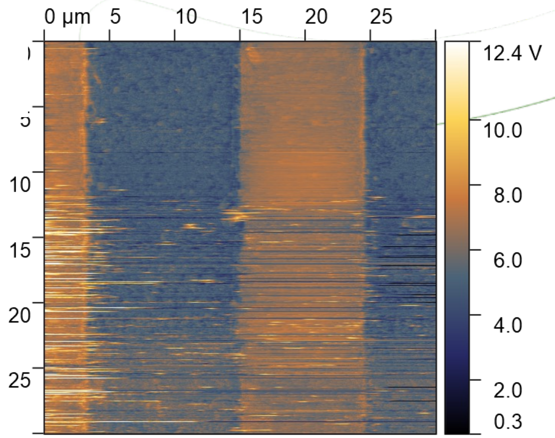


I-V curve showing typical **semiconductor** behaviour

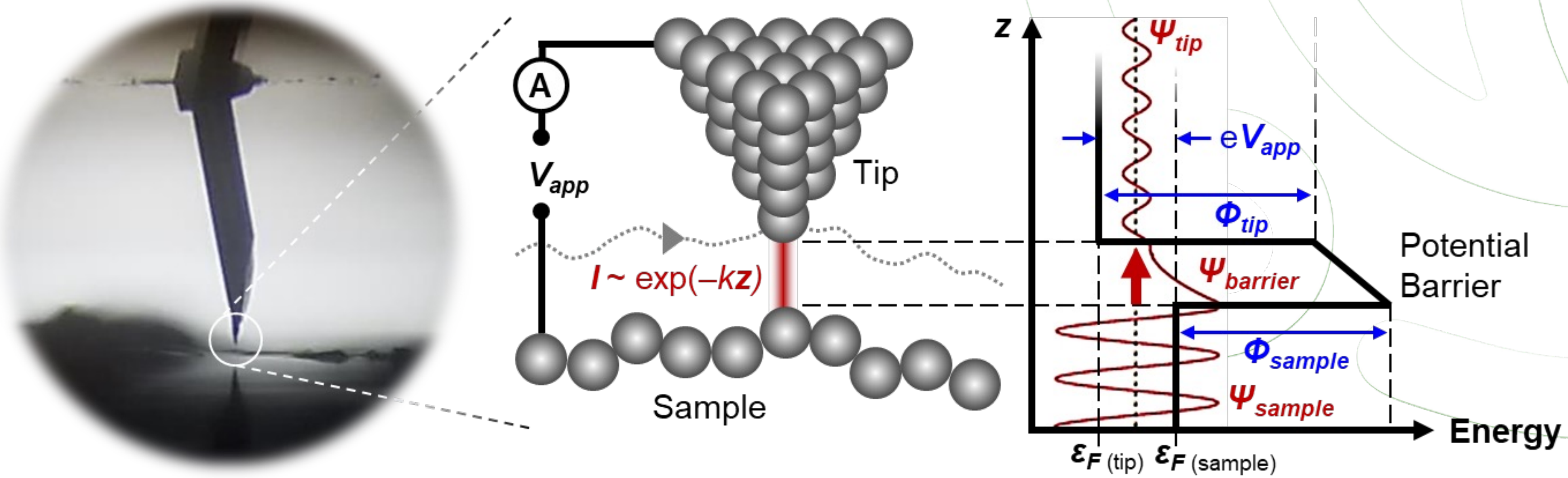


Morphology and **spreading current** acquired from the carbon nanoparticles and gold substrate.

Kelvin Probe Force Microscopy
SURFACE POTENTIAL



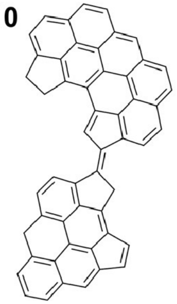
Scanning Tunneling Microscopy (STM)

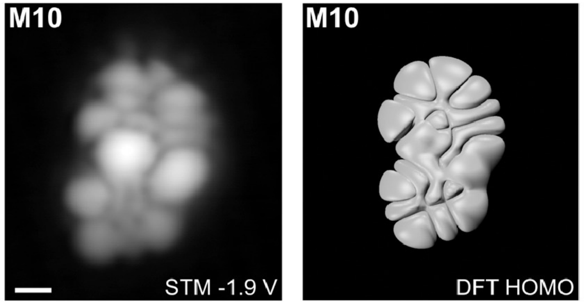


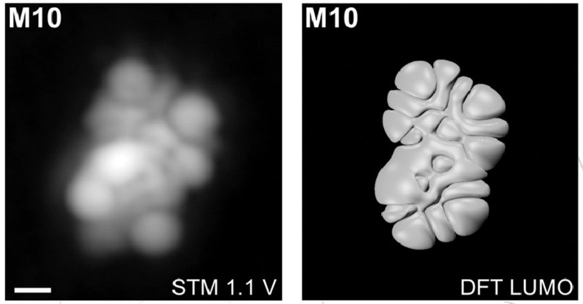
Non-contact investigation:

- morphology (extremely sharp conductive tip),
- electronic properties.

STM for Carbon Nanoparticles

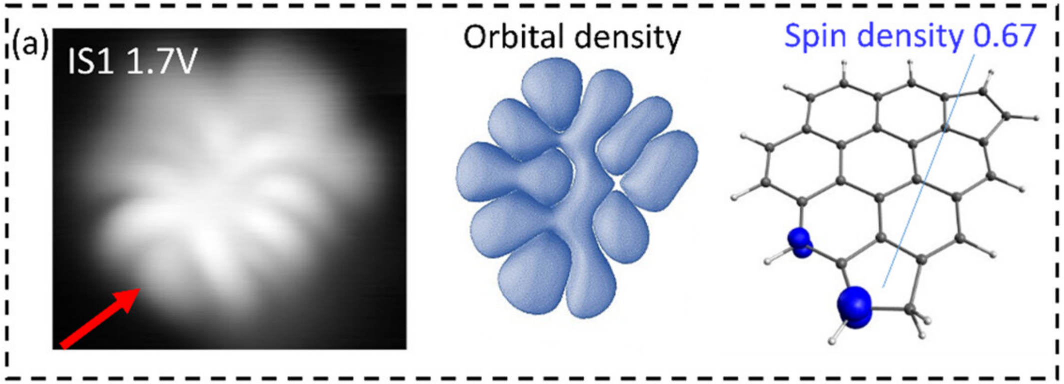






Scale bars are 5 Å

Strongly localized π-radicals

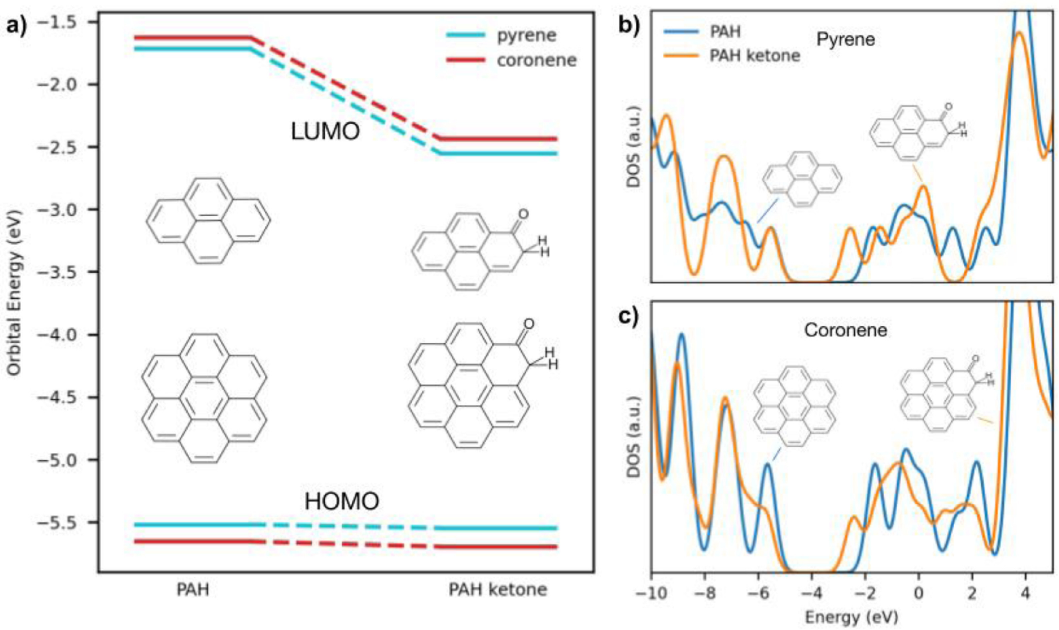


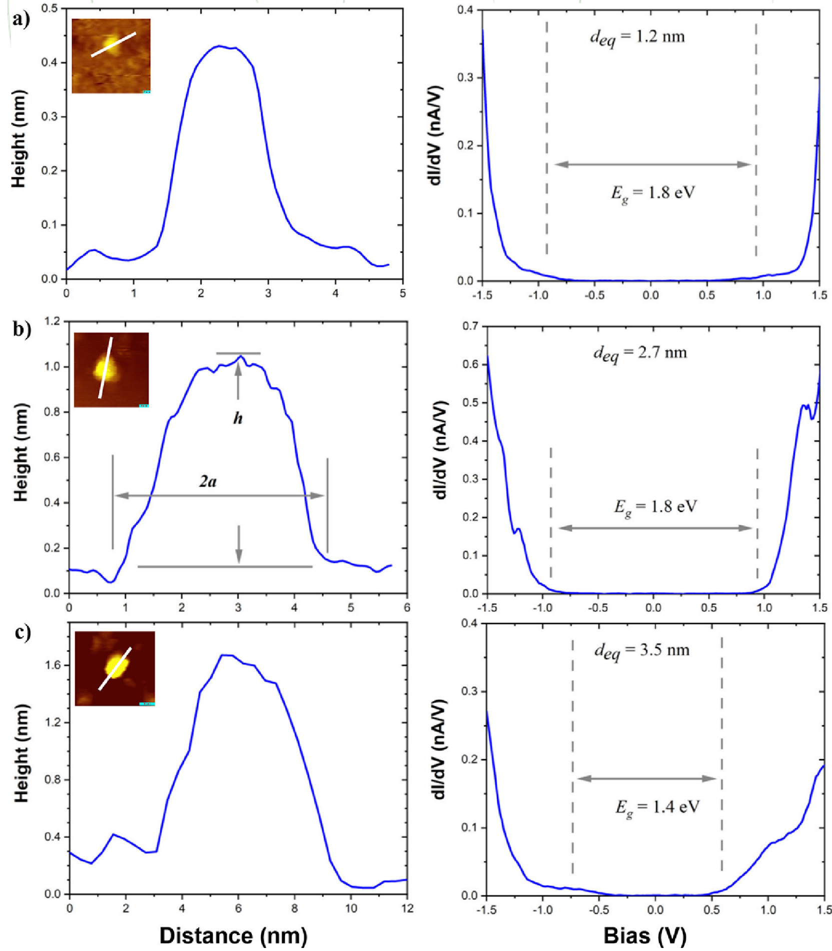
- molecular **orbital densities**,
- localized **radicals**.

Shulz et al. 2019: 10.1016/j.proci.2018.06.100

STS for Carbon Nanoparticles

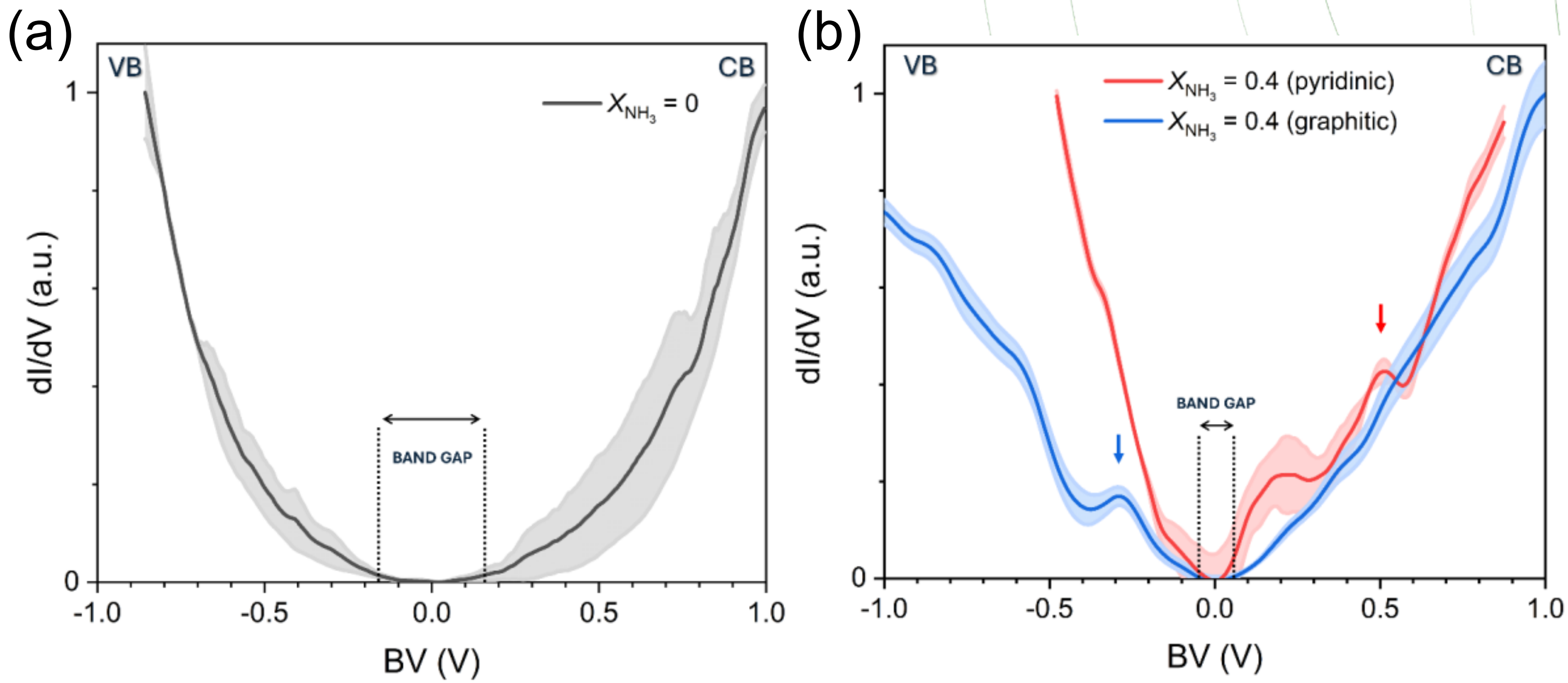
By measuring the tunneling current as a function of the applied voltage (I-V curves), STS can probe the local electronic **density of states** (LDOS) → **band gap**





Veronesi et al. 2022: 10.1016/j.combustflame.2021.111980

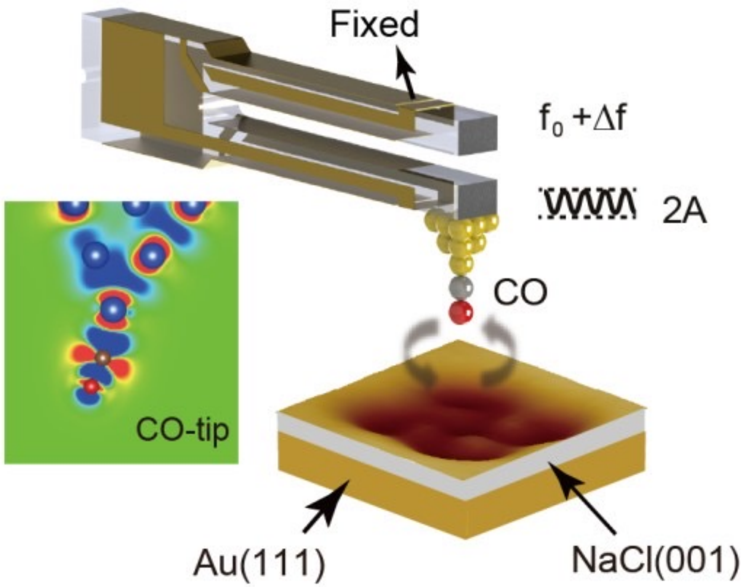
STS for Carbon Nanoparticles

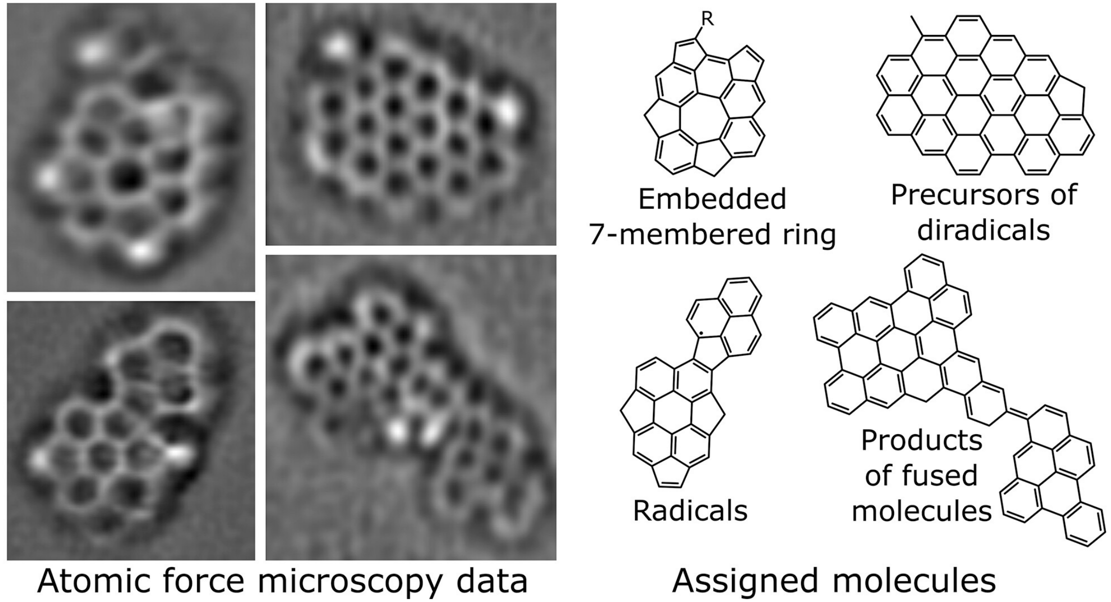


The STS spectra of collected soot from the **ammonia-diluted** flame show characteristic features of **nitrogen** doping. Some spectra (blue curve) present a peak for negative bias, showing graphitic-N, others show a peak for positive bias, revealing pyridinic-N.

Oner et al. 2025: MCS13 – Corfu

HR-AFM for Carbon Nanoparticles





True **atomic resolution** and localized defects.

Lieske et al. 2023: 10.1021/acsnano.3c02194

ITINERIS

THANKS!

IR0000032 – ITINERIS, Italian Integrated Environmental Research Infrastructures System
(D.D. n. 130/2022 - CUP B53C22002150006) Funded by EU - Next Generation EU PNRR-Mission 4 “Education and Research” - Component 2: “From research to business” - Investment 3.1: “Fund for the realisation of an integrated system of research and innovation infrastructures”

Finanziato dall'Unione europea NextGenerationEU

Ministero dell'Università e della Ricerca

Italiadomani