GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO

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10 ANNIVERSARY

Atomic Force Microscopy Assisted Graphene 3D-Modification

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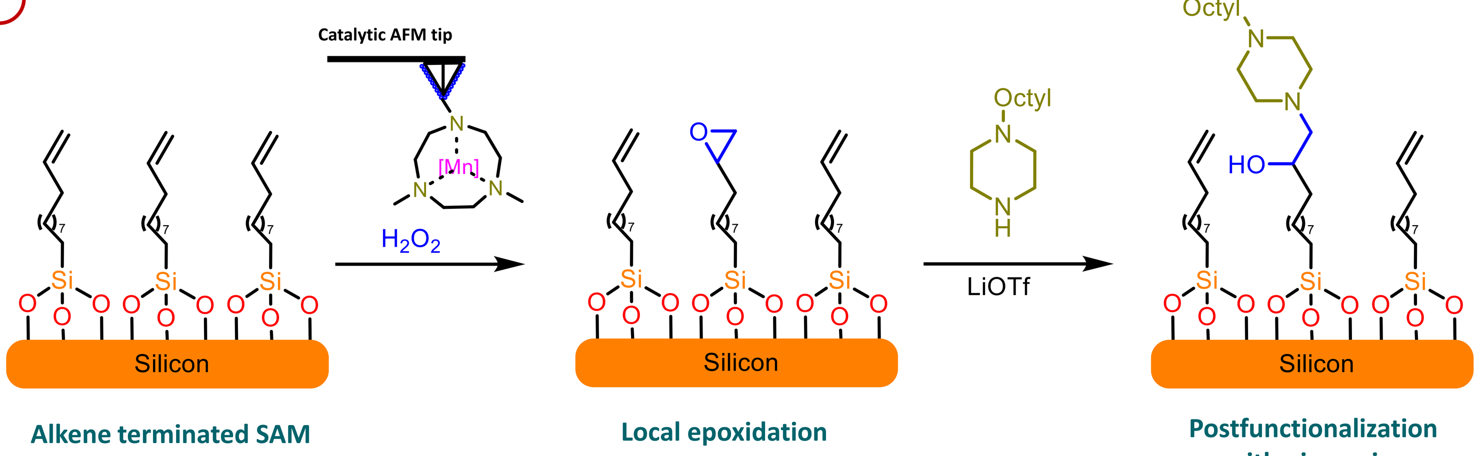
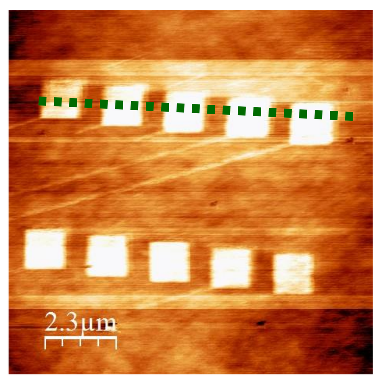
Methodology background.
Catalytic Scanning Probe Lithography (cSPL) validated on SAMs

Objective: to perform cSPL assisted epoxidation on a supported graphene layer.

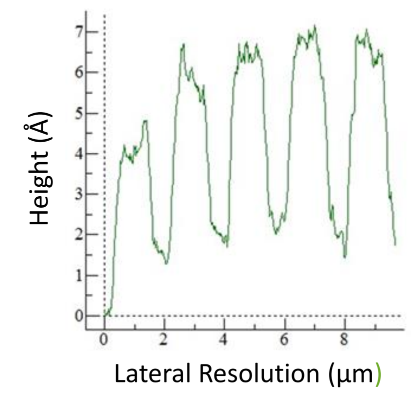
- Organometallic catalyst grafted on a silicon AFM tip.
- AFM tip provides a local catalytic chemical reaction.
- Epoxidation reaction optimized on alkene-terminated self-assembled monolayers (SAMs).
- Spatial resolution up to 40 nm. [1-3]



Alkene terminated SAM — Local epoxidation — Postfunctionalization with piperazine



AFM topography image



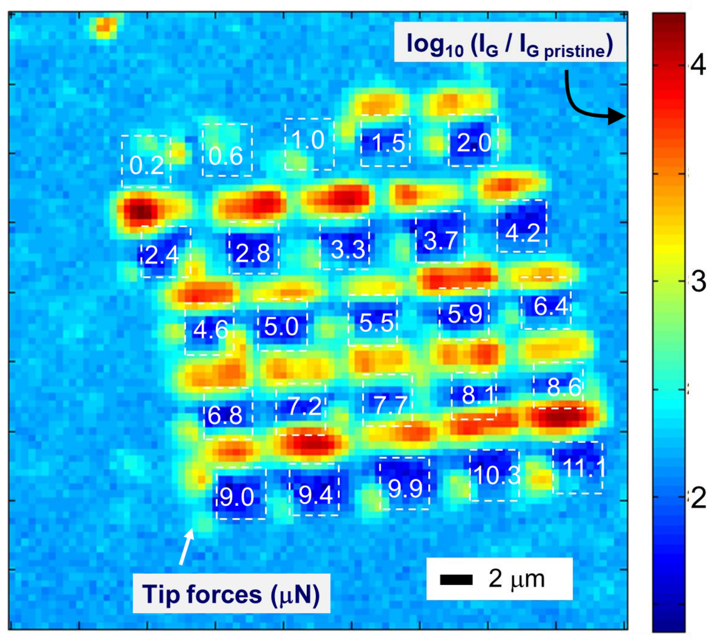
Topography line profile

AFM tip assisted graphene folding

Experiments with catalytic Si AFM tip

During the optimization of tip force **in reaction conditions** (H_2O_2, acetonitrile, catalytic AFM tip), the graphene in a series of treated square zones was **cut and pushed** on top and on sides (**a**,**b**).[4]

c)

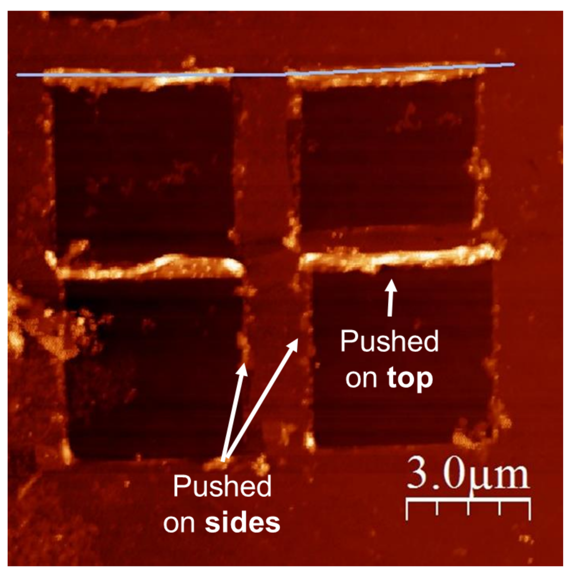


Raman mapping of the G band intensity

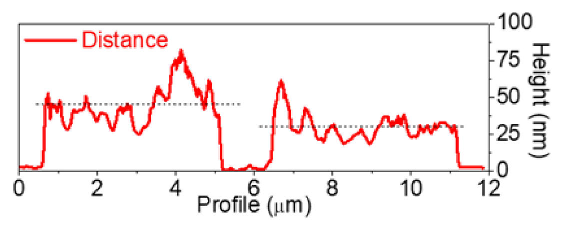
Raman analysis of pushed graphene (c-e):

- **G- and 2D-bands** remain principal.
- **G-band** 100-fold intensification (**c**).
- Small **D-band** – limited defects introduced.
- **2D-band (e)**: neither bi-, tri-, quadrilayer graphene nor graphite, but SLG with a single or a bimodal Lorentzian shape;
- stacking misorientation and weaker Raman interaction between planes.

a)

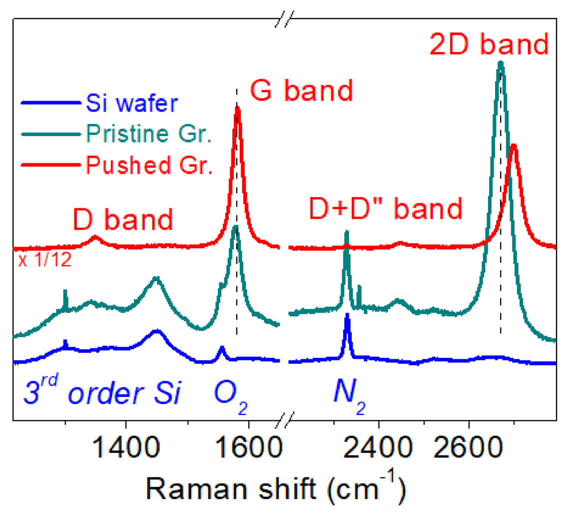


b)

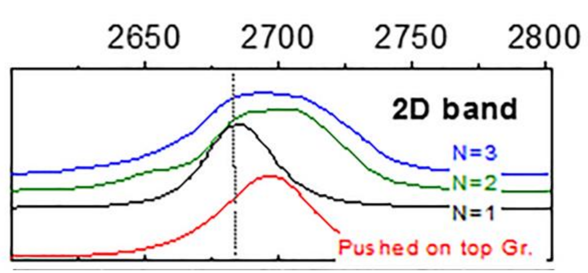


AFM topography (a) and profile (b) of the folded zones

d)



e)



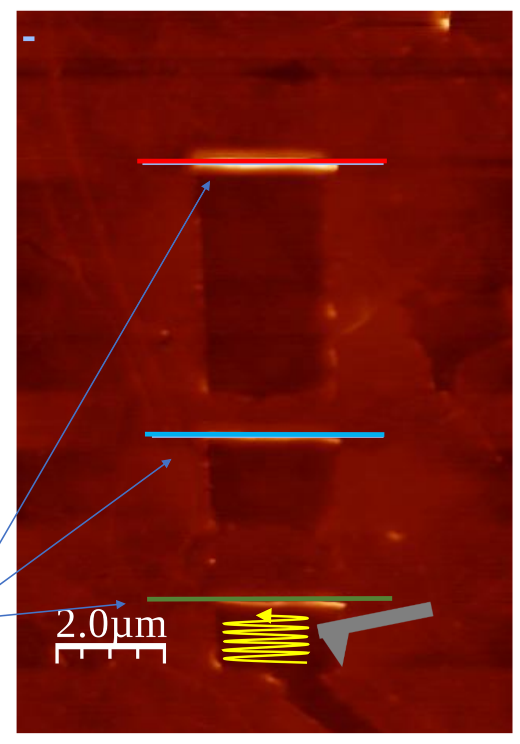
Raman spectrum before (green) and after (red) the tip scan (d), 2D-band analysis (e)

Experiments with non-catalytic Si AFM tip

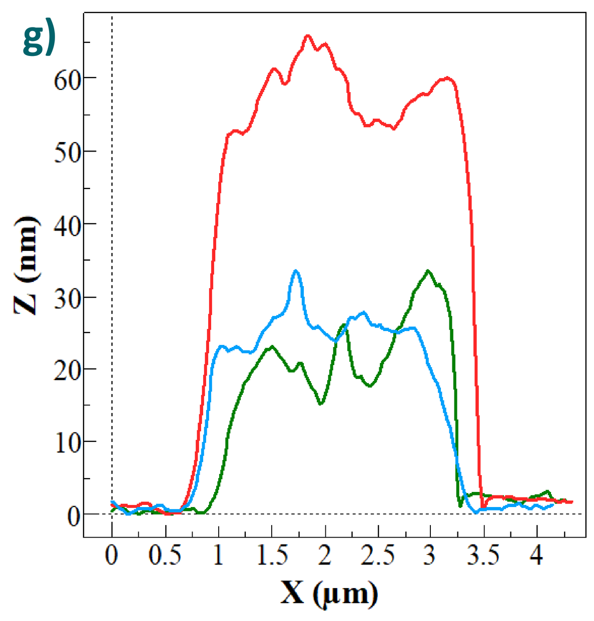
Study of AFM tip induced graphene folding:

- non-catalytic AFM tip;
- atmospheric conditions (no reaction solution);
- series of **rectangular zones** treated with AFM tip **zig-zag movements** (**f**): 2x1, 2x2, 2x4 µm;
- AFM mesured **profiles** of folded structures from 20 to 60 nm (**g**).

f)



g)



AFM topography (f) and profile (g) of the folded zones

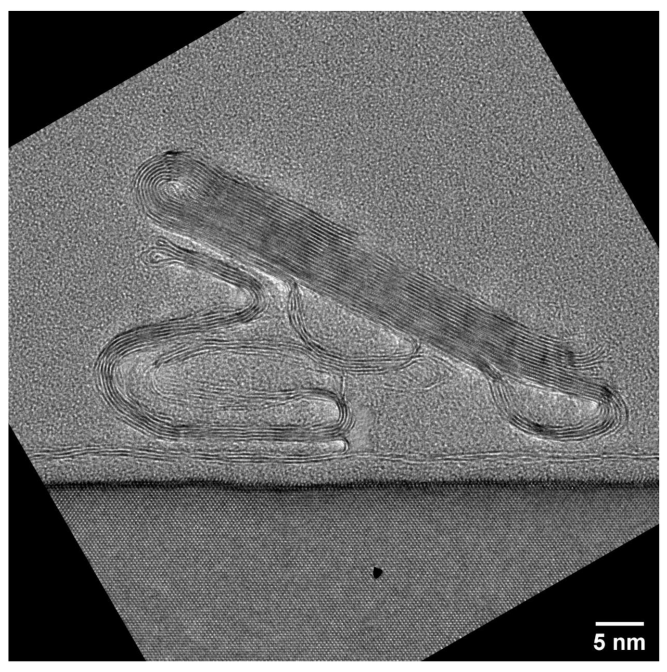
Technical and operational details:

- AFM tip: ACT «AppNano », Silicon.
- Graphene sample: CVD «Graphenea «Easy tranfer», Si substrate «Siltronix», 500 µm thick.
- Lithography: contact mode, 512 lines per 4 µm, 1 line/s, tip force 6 µN.
- Topography: «tapping» mode, 0,2 line/s.

TEM analysis:

- A transverse cross-section of the folded structure prepared by FIB method.
- TEM analysis revealed enrolled and well-stacked graphene layers (**h**).
- Average Interlayer distance 0,33 nm (close to graphite).

h)



TEM image of the cross-section of the folded structure

Région Provence Alpes Côte d'Azur

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Conclusions and Perspectives

- A versatile cSPL technique for high-resolution SAM functionalization was developed.
- cSPL essays on supported graphene layers lead to the graphene folding and stacking.
- Raman and TEM analysis of the folded structures revealed well-stacked misoriented multilayer formations, further characterizations are envisaged.
- Spacially resolved covalent cSPL graphene functionalization experiments are on-going.

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