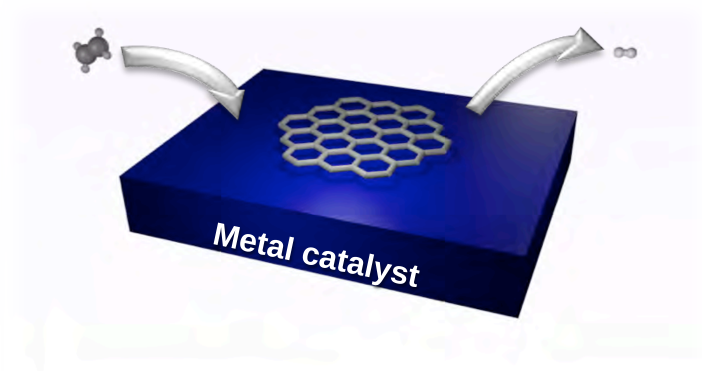
# Single Atom Catalyst at Work: Real-Time Imaging of Adatom-Promoted Graphene Growth on Nickel

L.L. Patera,[1,2] F. Bianchini,[1] C. Africh,[2] C. Dri,[1,2] G. Soldano,[3]

M.M. Mariscal,[3] **Maria Peressi**,[1,2] and G. Comelli[1,2]

[1] *Dept. of Physics, University of Trieste, Italy*
[2] *IOM-CNR, Italy*
[3] *INFIQC, CONICET and Universidad Nacional de Córdoba, Argentina*

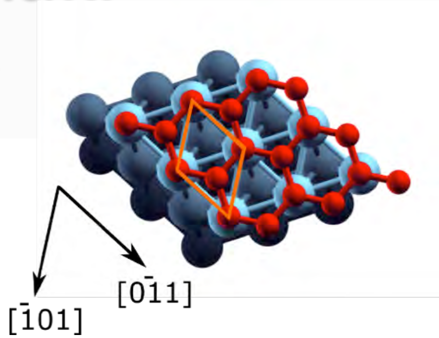
# CVD graphene growth

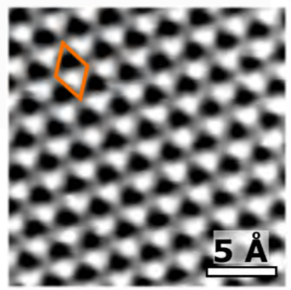



Hydrocarbon exposure → C atoms → graphene!

## Graphene/Ni

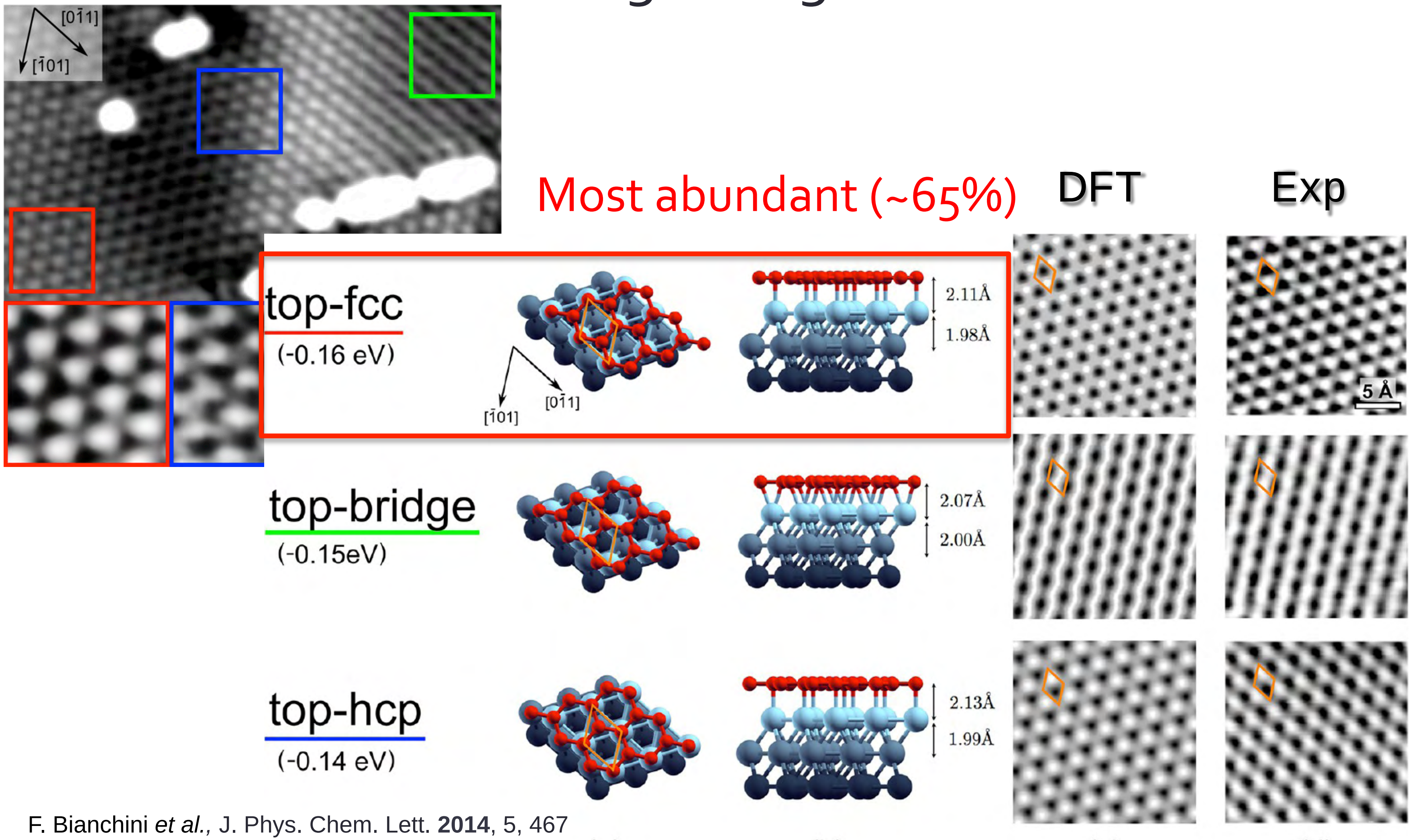
- Low temperature CVD (400-600°C)
- Subsurface C segregation
- Epitaxial growth on (111) facets



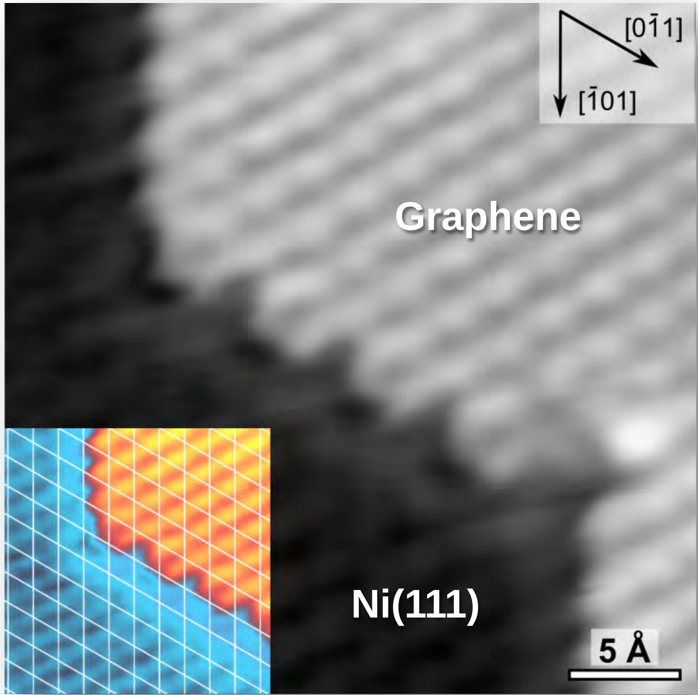

F. Bianchini *et al.*, J. Phys. Chem. Lett. **2014**, 5, 467

# Epitaxial graphene on Ni(111): cohexisting configurations

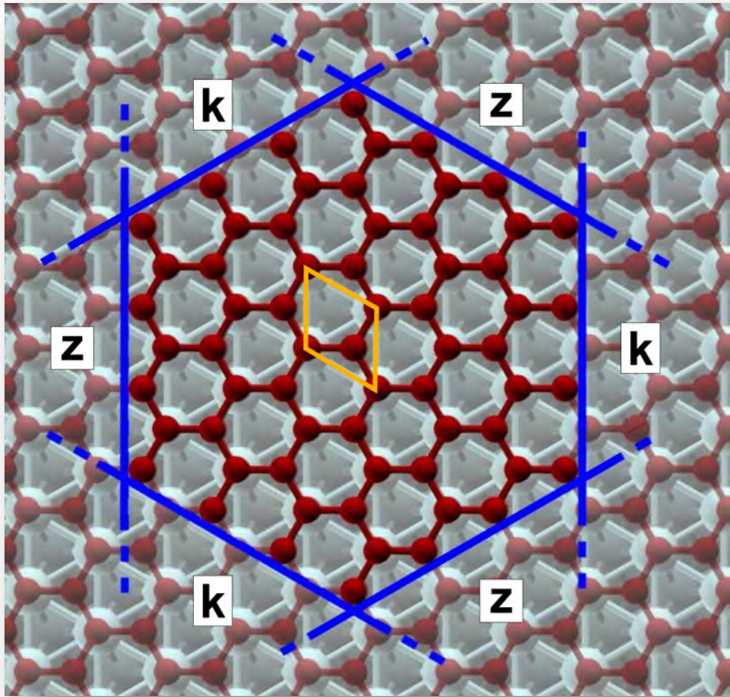



F. Bianchini *et al.*, J. Phys. Chem. Lett. **2014**, 5, 467

# Top – fcc: Edge structure




(V=-10mV, I=20 nA, RT)



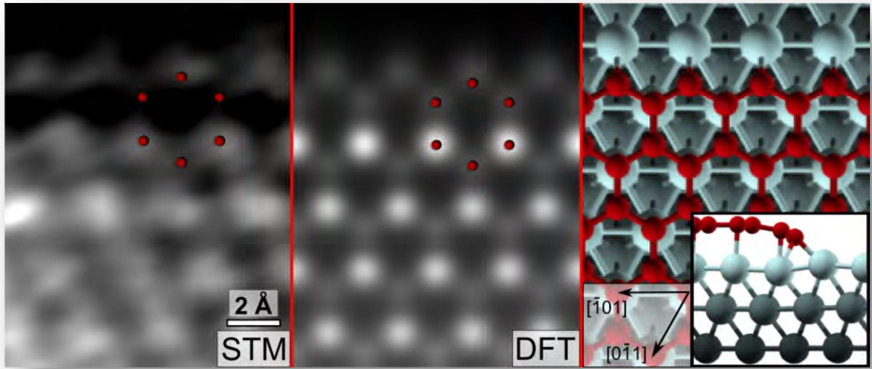

- Only two kinds of edges (zig-zag and Klein)
- fcc-hollow site termination

L.L. Patera *et al.,* Nano Lett. **2015**,15, 56-62

# Edge structure

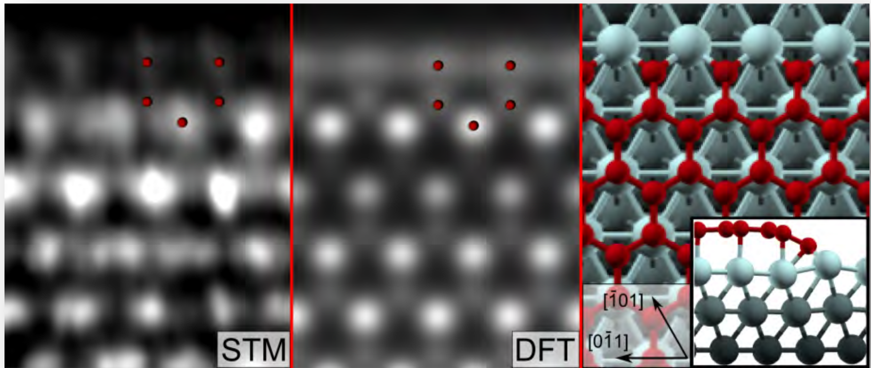
**470°C** *Substrate passivated edges*

z



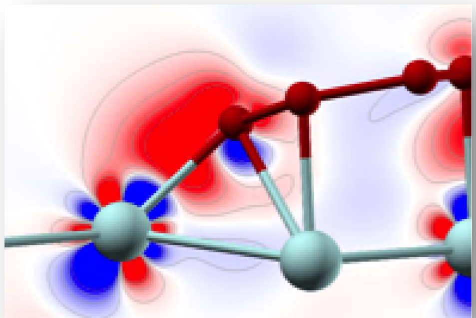

(9 mV, 1.3 nA)

k




(9 mV, 1.3 nA)

- High speed STM is needed (*250 ms/frame*)
- Single periodicity on both the edges
- Edges seem to be bent toward the substrate

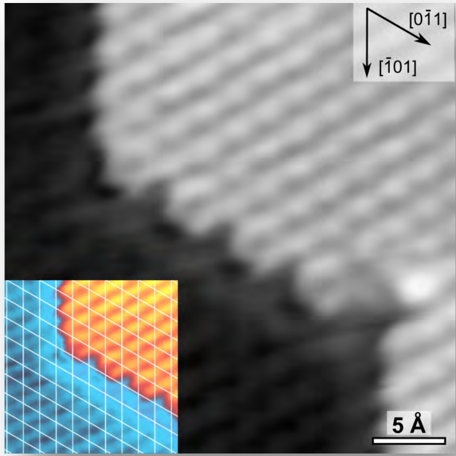


Edges are anchored to the metal (**covalent bond**)

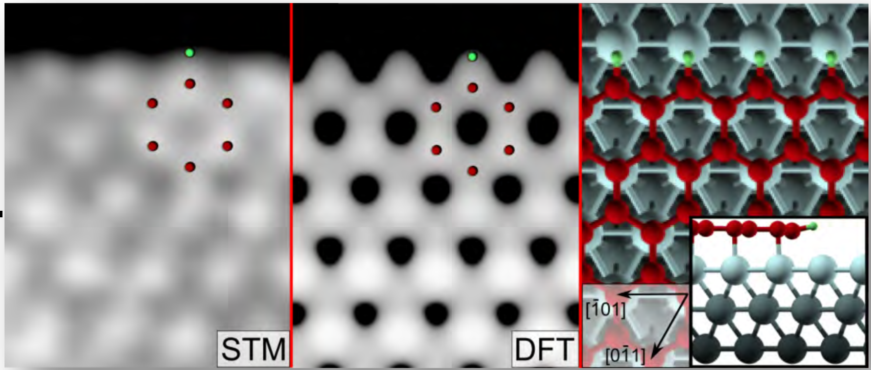
L.L. Patera *et al.*, Nano Lett. **2015**,15, 56-62

# Edge structure

**RT** *H-terminated edges*

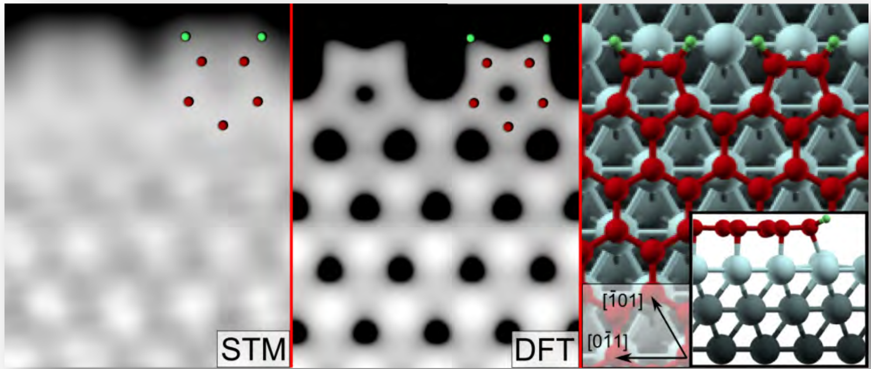



z1



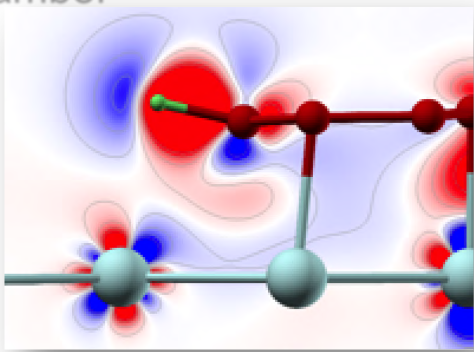

(0.2 V, 20 nA)

rk1



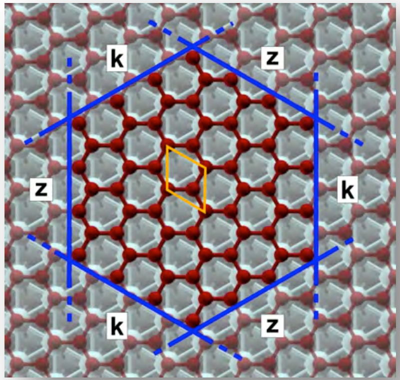

(0.2 V, 20 nA)

- Sharp step-edge contrast
- Single periodicity on z edge
- Double periodicity on Klein edge
- $H_2$ is the most abundant gas in the UHV chamber



Hydrogenation breaks the edge-metal bond

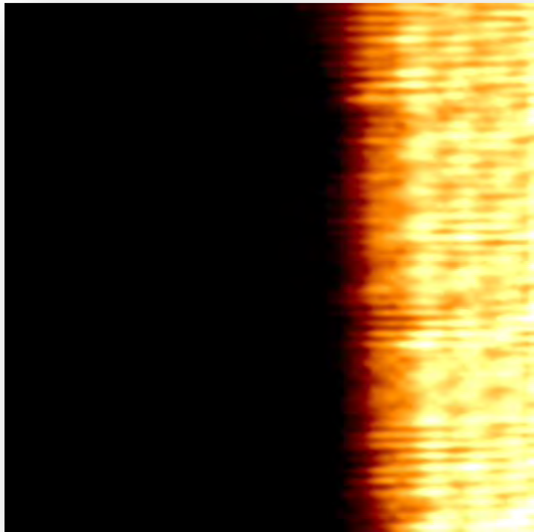
L.L. Patera *et al.,* Nano Lett. **2015**,15, 56-62



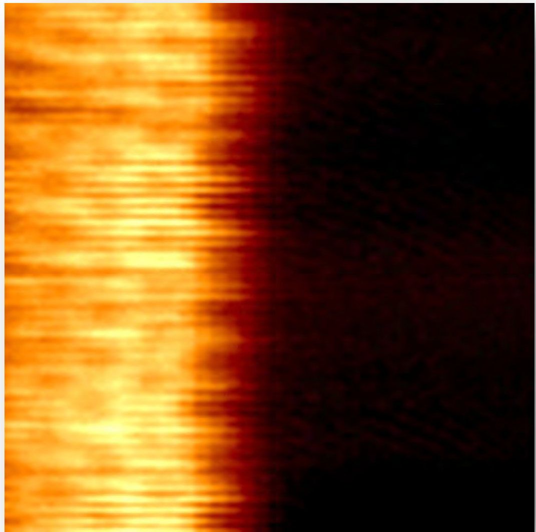

# Edge growth at 440°C

STM movies with high spatial and temporal resolution
image acquisition rates up to **100 frame/s**
with FAST module added on commercial STM
https://fastmodule.iom.cnr.it/

z



3.5 x 3.5 nm$^2$, **36.5 Hz**



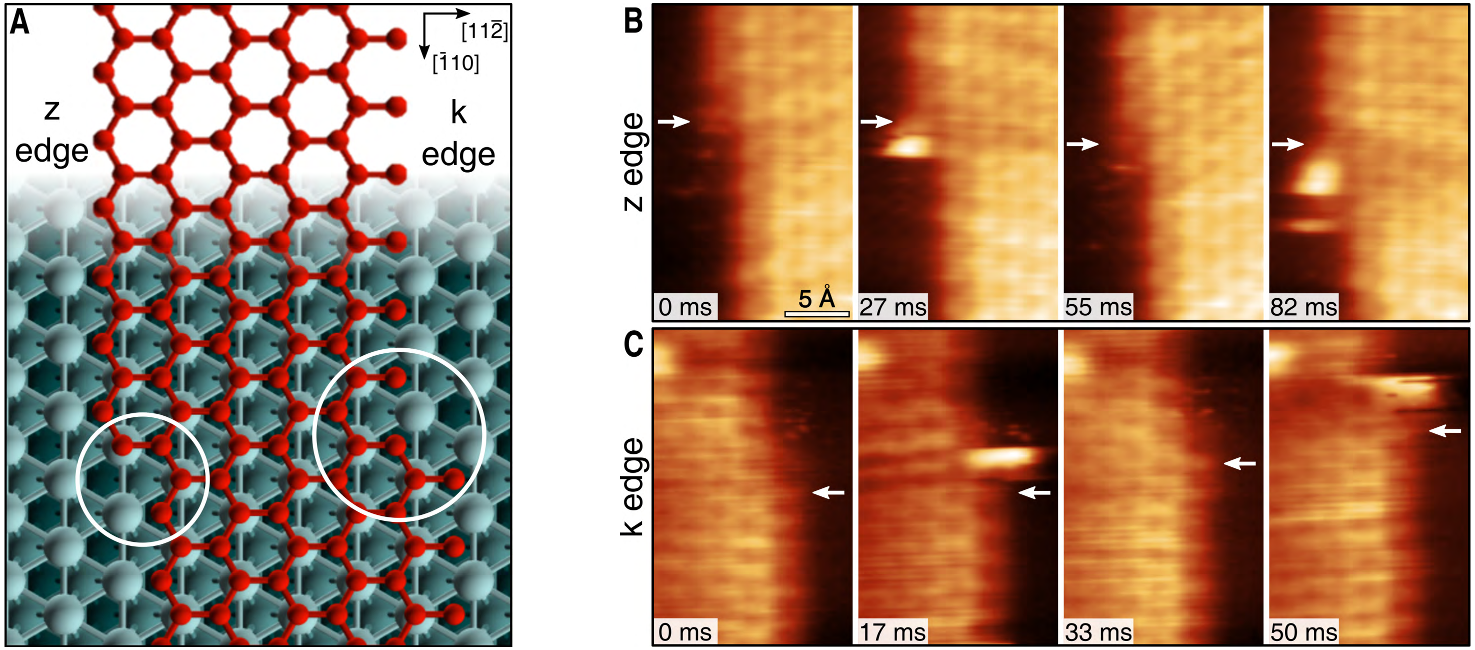
k

2.5 x 2.5 nm$^2$, **60 Hz**

- Fast C attachment mechanism
- Row-by-row growth on both z and k edges

L.L. Patera et al., *Science* **2018**, 359, 1243

# Edge growth at 440°C

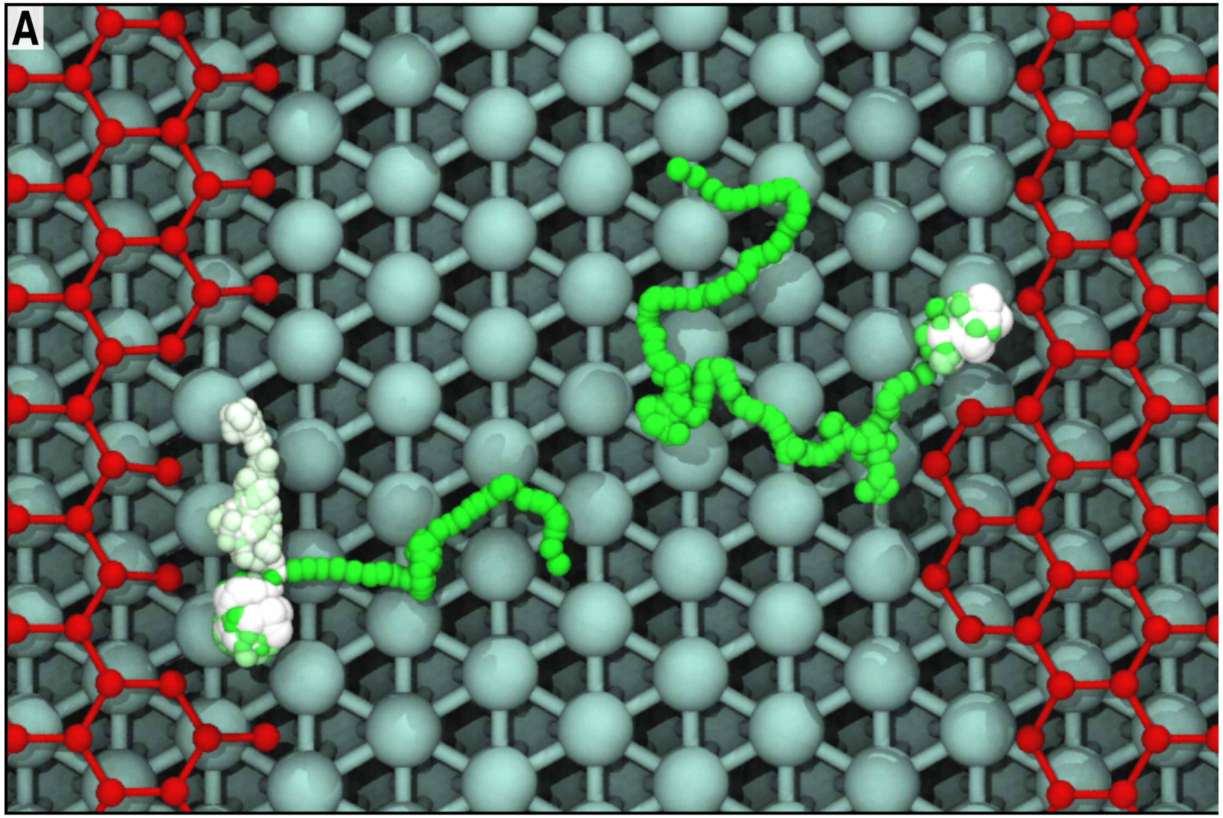



- Bright features at kink sites
- Based on appearance and DFT calculations for static point defects after CVD graphene growth on Ni(111) : Ni adatoms ?

L.L. Patera et al., *Science* **2018**, 359, 1243

# Molecular Dynamics (ReaxFF)

k edge

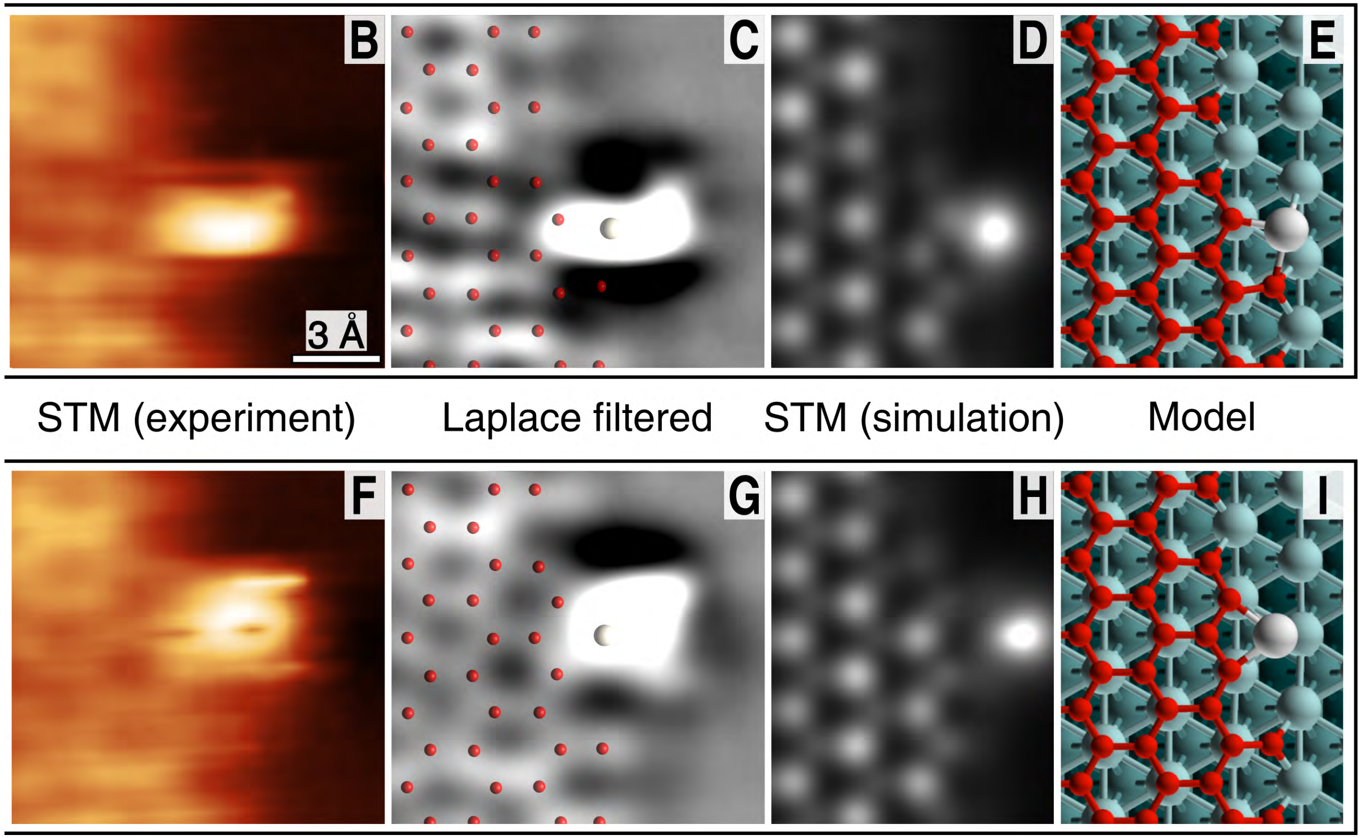



z edge

- At 710 K diffusing Ni adatoms are trapped by kinks at both graphene edges (trajectories from green to white)

L.L. Patera et al., *Science* **2018**, 359, 1243

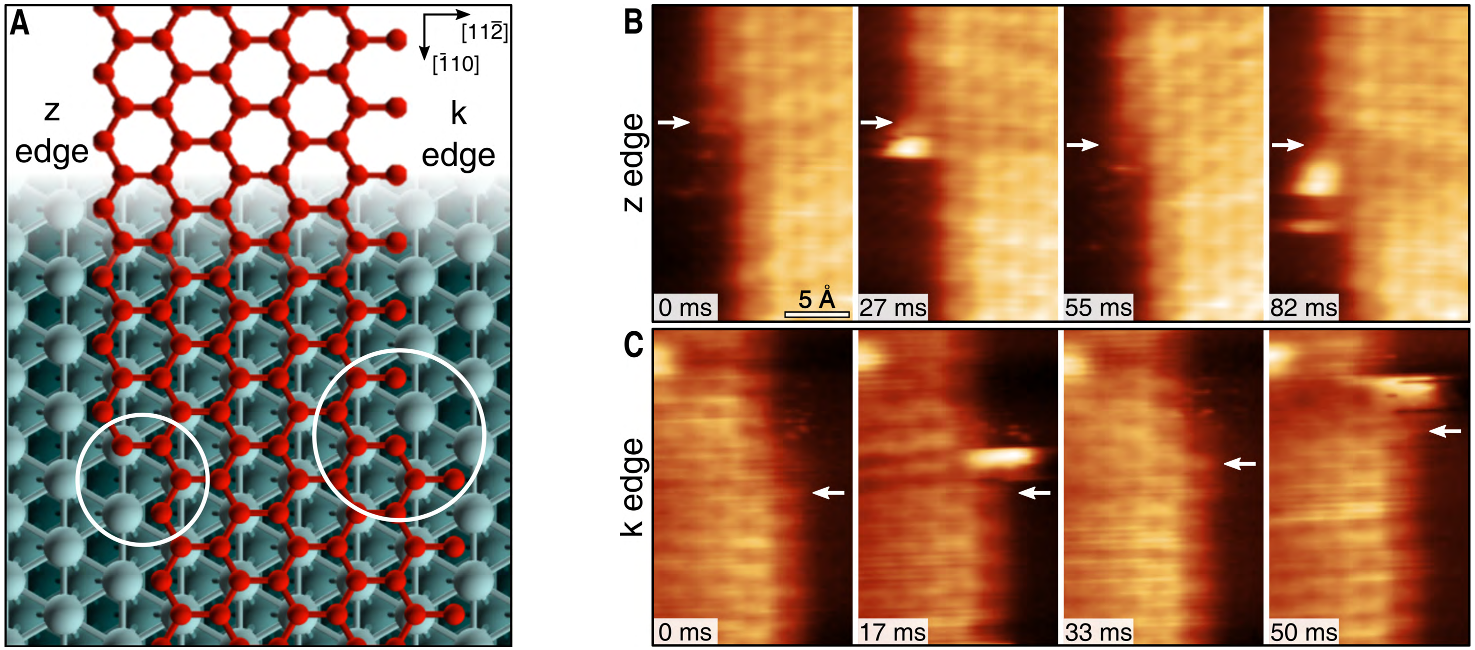
# Along the k edge




- Two short-lived bound states
- DFT confirms presence of Ni adatoms

L.L. Patera et al., *Science* **2018**, 359, 1243

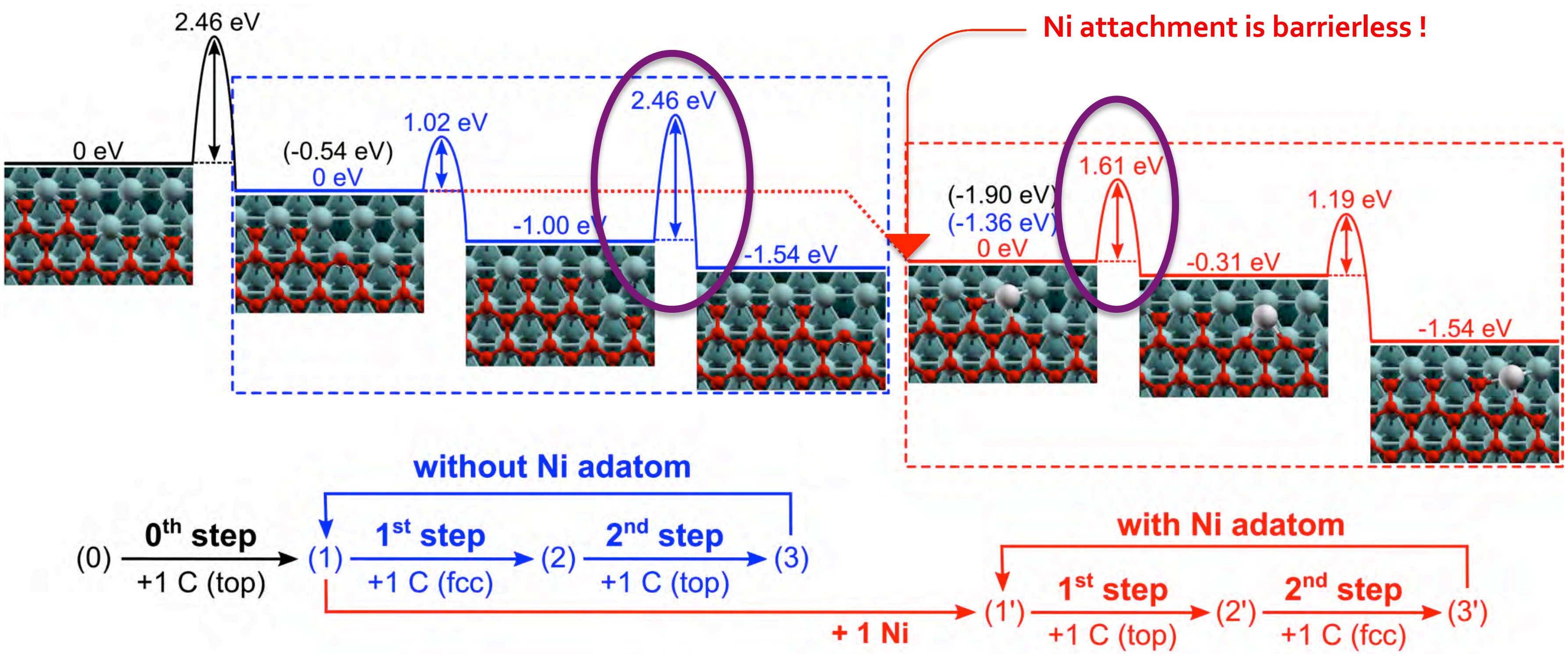
# Edge growth at 440°C




- Bright features at kink sites
- Based on appearance and DFT calculations for static point defects after CVD graphene growth on Ni(111) : Ni adatoms ? YES ! Confirmed by MD+DFT
- Presence of Ni adatoms correlated to growth events

L.L. Patera et al., *Science* **2018**, 359, 1243

# Alternative growth pathways

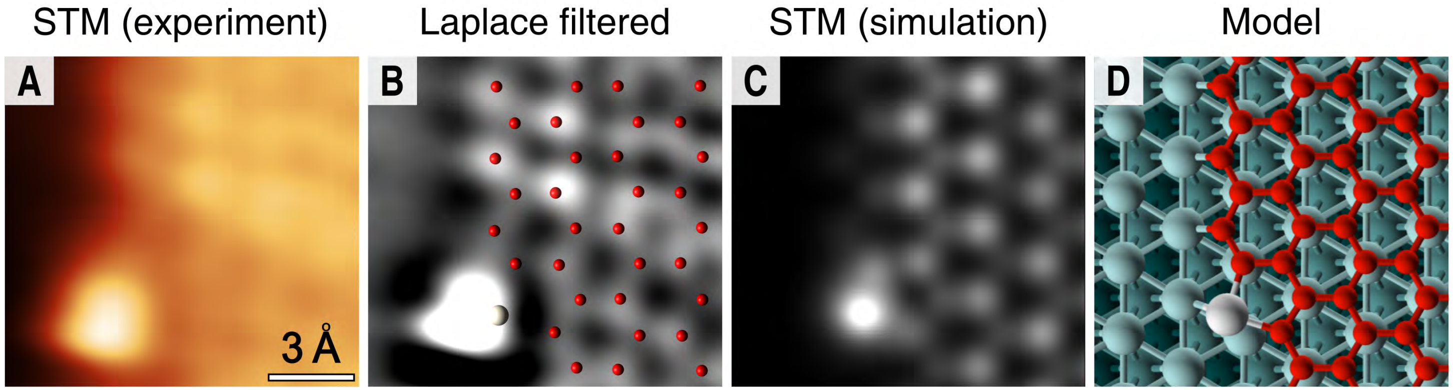



With Ni adatom reduction of ~35% of the rate limiting energy barriers of the cycling process

➡ **Ni adatom catalyses the growth process!**

L.L. Patera et al., *Science* **2018**, 359, 1243

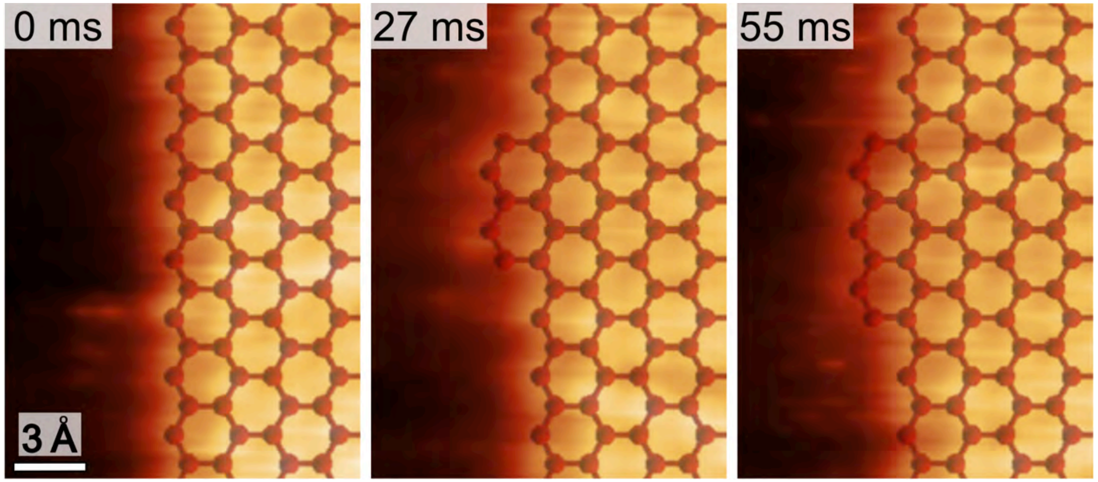
# Along the z edge




- One bound state
- Again compatible with DFT barriers for Ni detachment

L.L. Patera et al., *Science* **2018**, 359, 1243

# Formation of kink sites along the z edge




➢ Dashes along the stright edge: weakly bound adatoms (not Ni!)

L.L. Patera et al., *Science* **2018**, 359, 1243

# Conclusions

## Graphene growth on Ni(111):

- High spatial and temporal resolution STM measurements of growing graphene islands at technologically relevant T
- Ordered line-by-line growth at graphene edges
- Ni adatoms temporarily trapped at kink sites
- Atomic structure of intermediate short-lived (ms scale) configurations
- Complete reaction path from DFT calculations

→ Ni adatoms catalyse C incorporation at the edges

→ first real-time observation and complete characterization of the catalytic role of single atoms during a technologically relevant process

More details:

Patera L.L., Bianchini F., Africh C., Dri C., Soldano G., Mariscal M.M., Peressi M., Comelli G., *Science* **2018**, 359, 1243

Theory:

*M.P.*

*F. Bianchini (University of Trieste - now at University of Oslo)*

QUANTUMESPRESSO

*G. Soldano and M. Mariscal (INFIQC-CONICET and Universidad Nacional de Córdoba)*

*MD-ReaxFF*

STM experiments:

*C. Africh (CNR-IOM)*

*G. Comelli (University of Trieste & CNR-IOM)*

*L.L. Patera (University of Trieste & CNR-IOM - now at University of Regensburg)*

*C. Dri (Univ. of Trieste & CNR-IOM – now at Elettra Sincrotrone Trieste - Fast-STM)*

*Funding:*

*MIUR (Prin project)*

*EU (H2020 R&I programme, grant agreement NFFA-Europe)*

*Italian Ministry of Foreign Affairs and International Collaboration*

*University of Trieste*