Hydrogen on Graphene: an STM study

Stefan Heun

NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore

Pisa, Italy

National Enterprise for nanoScience and nanoTechnology

NEST

NEST Pisa

- **CNR**: Vittorio Pellegrini, Valentina Tozzini, Stefan Heun
- **IIT**: Camilla Coletti, Vincenzo Piazza, Sarah Goler, Torge Mashoff
- **SNS**: Massimo Morandini, Pasquale Pingue, Fabio Beltram

SCUOLA NORMALE SUPERIORE PISA

ISTITUTO ITALIANO DI TECNOLOGIA

National Enterprise for nanoScience and nanoTechnology

Outline

- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Corrugation
- Hydrogen Storage by Functionalization

Outline

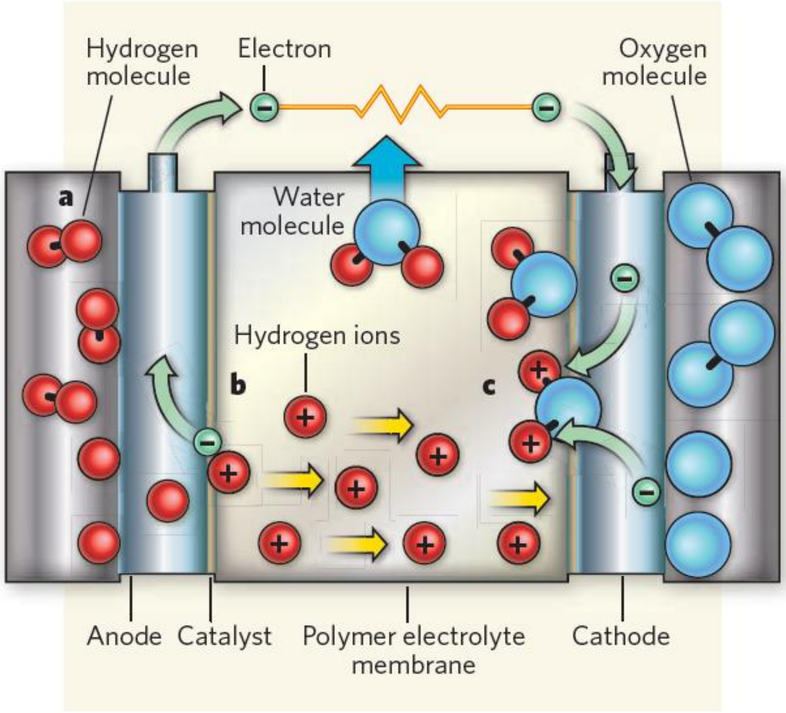
- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Corrugation
- Hydrogen Storage by Functionalization

Hydrogen & energy

As a fuel, hydrogen has advantages:

- high energy-to-mass ratio
- $H_2 + 1/2\ O_2 \rightarrow H_2O \quad \Delta H = -2.96eV$
- Non-toxic and "clean" (product = water)
- renewable

However, hydrogen is NOT an energy source: it must be produced e.g. by electrolysis, needing +2.96 eV, with zero balance with respect to energy production.

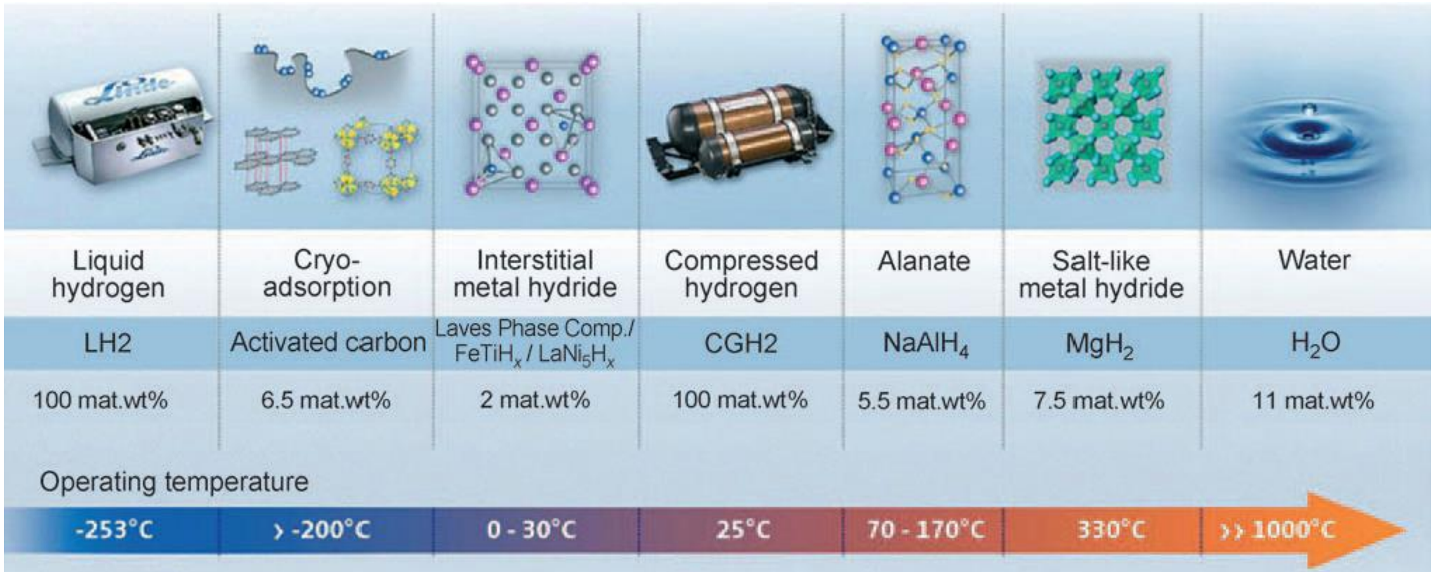


Hydrogen fuel cell

Hydrogen-fuelled vehicles

National Enterprise for nanoScience and nanoTechnology

Hydrogen Storage



Targets for **transport applications** not reached yet:

ρ_m > 5.5 wt%

ρ_V > 50 kg H_2 /m^3

P_{eq}≈1bar at T< 100°C

Compressed H_2:
High pressure and heavy container to support such pressure

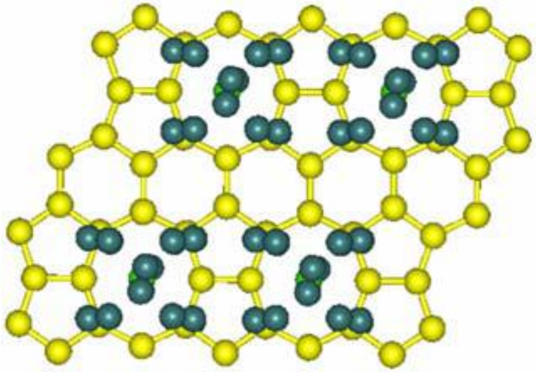
Solid State:
Physisorption
Chemisorption

Liquid H_2:
Liquefation needs energy and consumes more than 20% of the recoverable energy

National Enterprise for nanoScience and nanoTechnology

Graphene for hydrogen storage

- Graphene is lightweight, inexpensive, robust, chemically stable
- Large surface area (~ 2600 m^2/g)
- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen

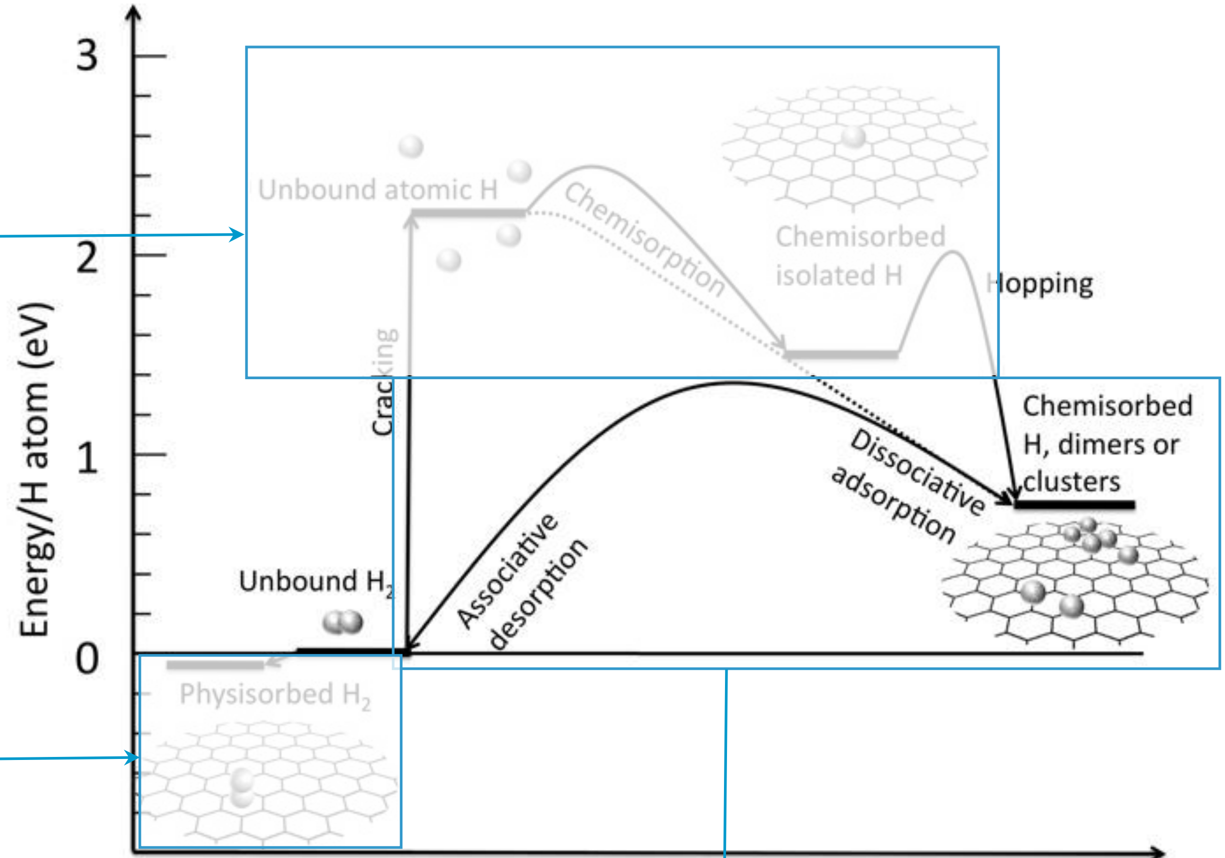


Yang et al., PRB 79 (2009) 075431

H storage in graphene

❖ Atomic hydrogen chemisorption has a small or negligible chemisorption barrier ⇒
feasible but H_2 must be cracked

❖ Physisorption weakly bounds hydrogen ⇒ acceptable storage densities only at low temperatures and/or high pressure



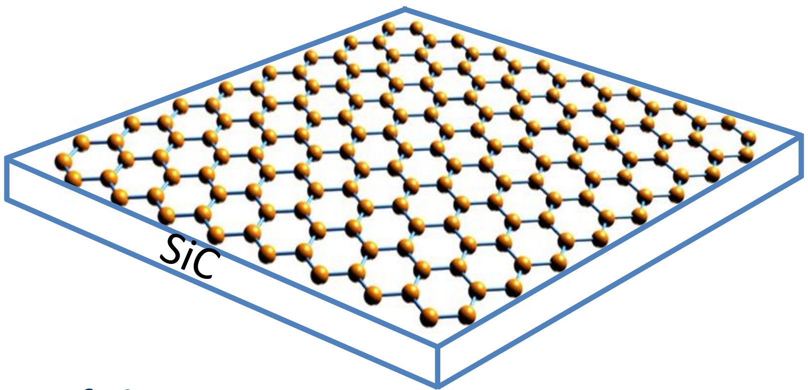
❖ Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate ~eV) ⇒ chemisorbed H is stable for transportation etc, but catalytic mechanisms are necessary in the loading-release phases

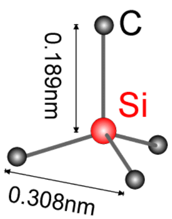
Outline

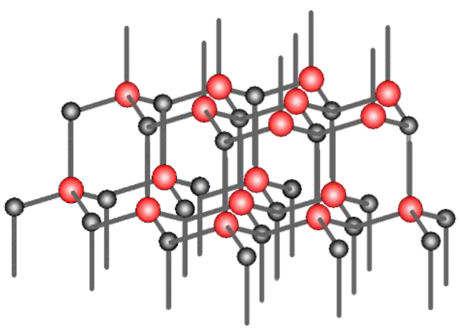
- Presentation of NEST
- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Corrugation
- Hydrogen Storage by Functionalization

Graphene growth on SiC

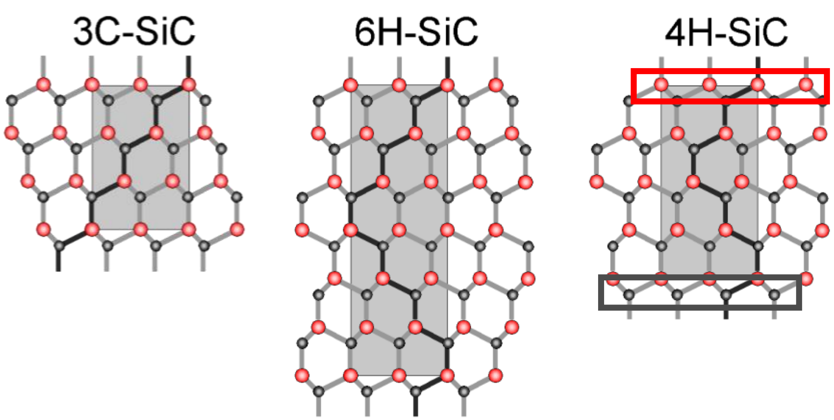
Graphene or thin graphite films form on SiC surfaces upon annealing at high temperatures as a result of SiC decomposition.







Bilayer of Si-C tetrahedra

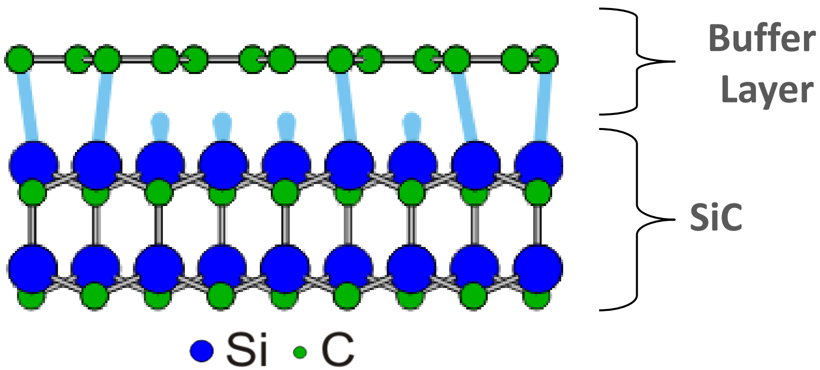


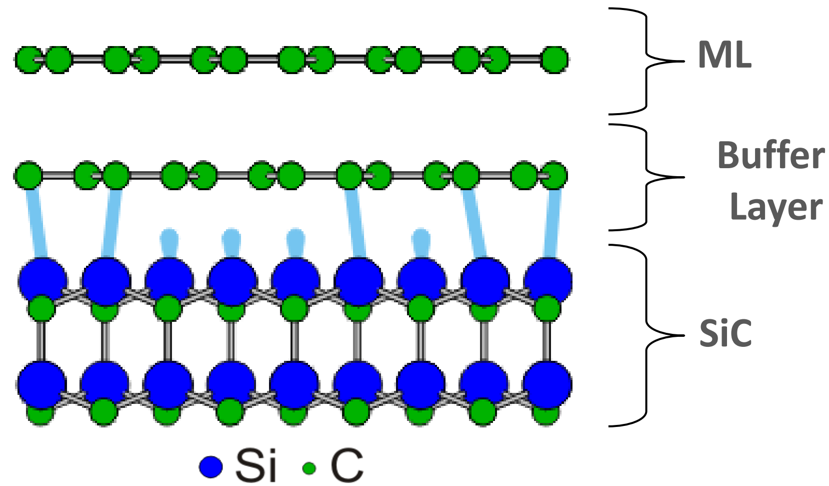
Si(0001) face → **Graphene:**
Ordered stacking
Good thickness control

C(000$\bar{1}$) face → **Graphene:**
Rotational disorder
Poor thickness control

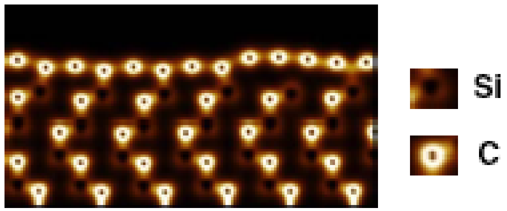
CNRNANO PISA NEST

Graphene growth on SiC(0001)



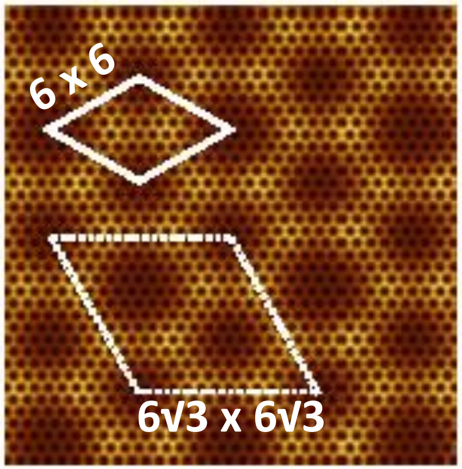


Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp^3 C-Si bonds.



F. Varchon, et al., PRB 77, 235412 (2008).

Theoretical Calculations



F. Varchon, et al., PRB 77, 235412 (2008).

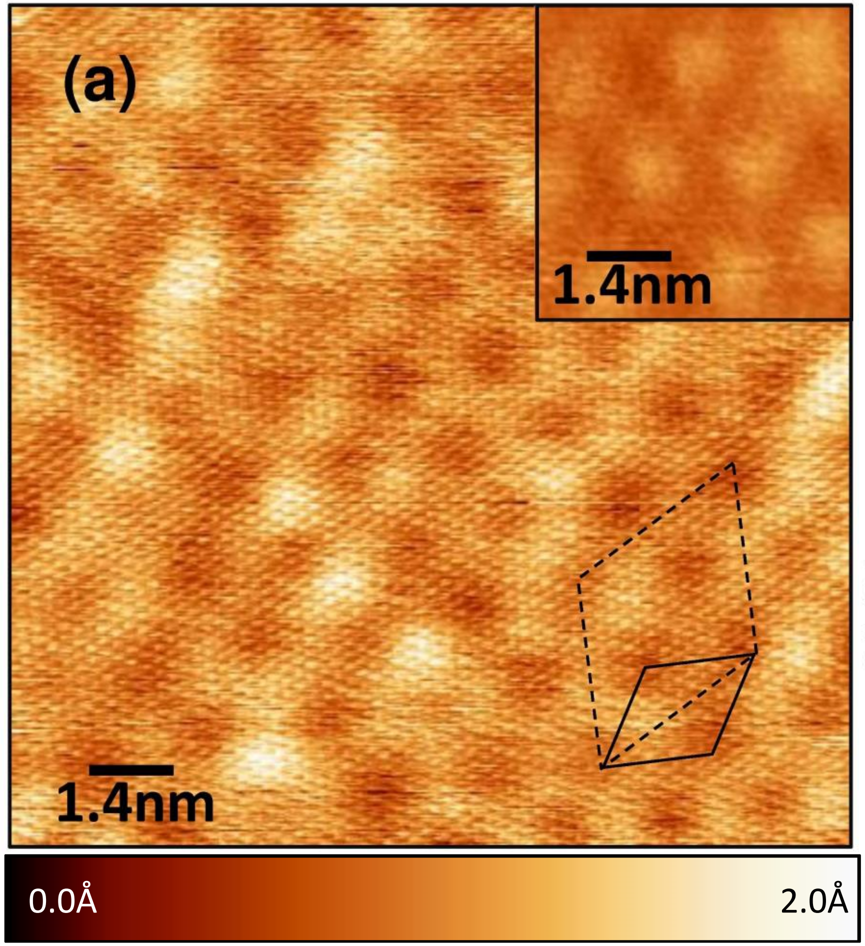
Superstructure of both the buffer layer and monolayer graphene on the Si face from the periodic interaction with the substrate.

National Enterprise for nanoScience and nanoTechnology
NEST

Buffer Layer

Bias: +1.7V
Current: 0.3nA

$6\sqrt{3} \times 6\sqrt{3}$ - - - - -
quasi-(6x6) ——



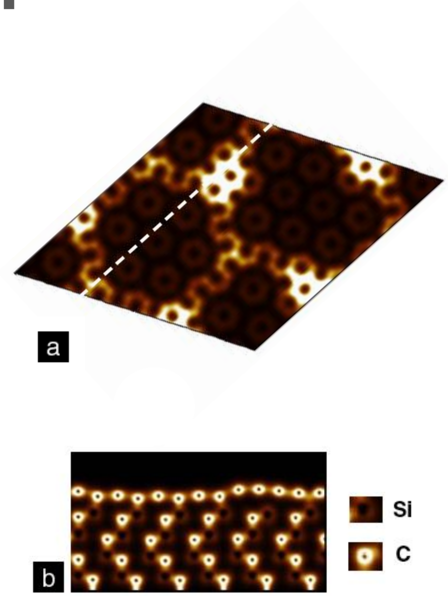


FIG. 2. (Color online) Total charge density of the buffer layer on SiC(001). (a) total charge density in the 6*R*3-SiC unit cell. (b) cross section of the total charge density along the line defined in (a). The black dots that appear when the cross section goes through the middle of an atom are due to the use of pseudopotentials (no core electrons).

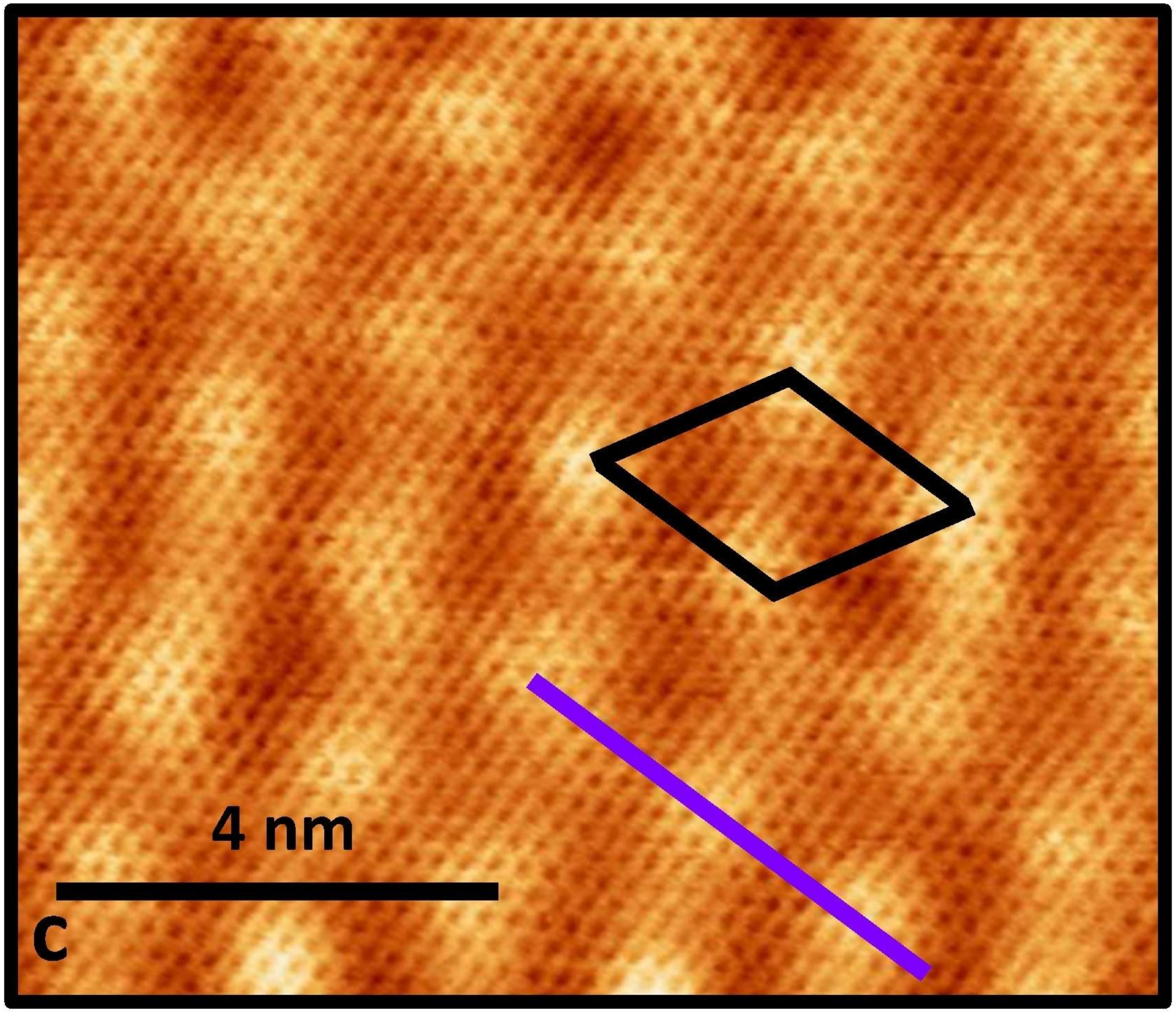
F. Varchon, et al., PRB 77, 235412 (2008).

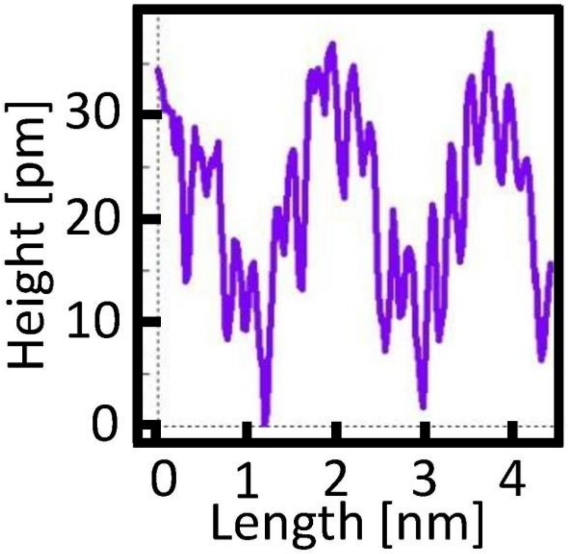
S. Goler *et al.*: Carbon **51**, 249 (2013).

National Enterprise for nanoScience and nanoTechnology

Monolayer Graphene

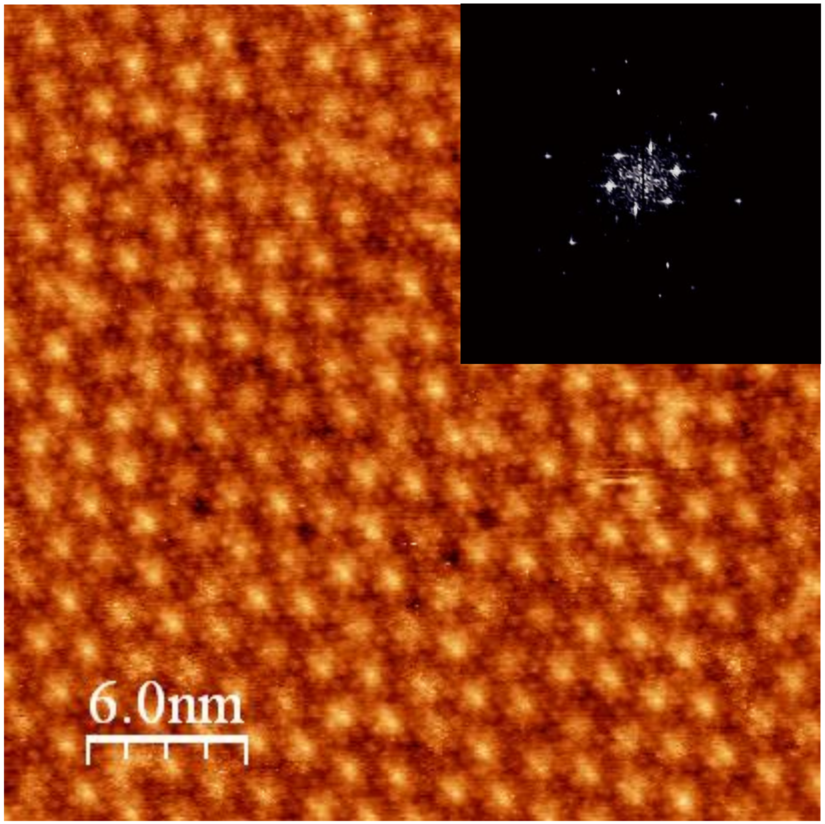
STM



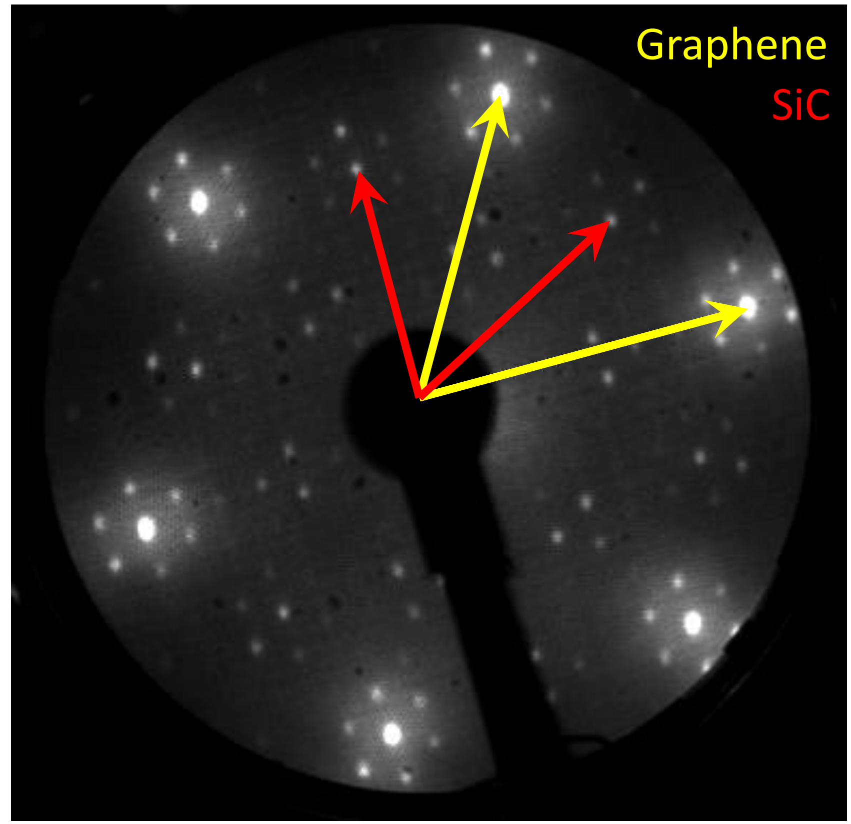


S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

6√3x6√3-Superstructure

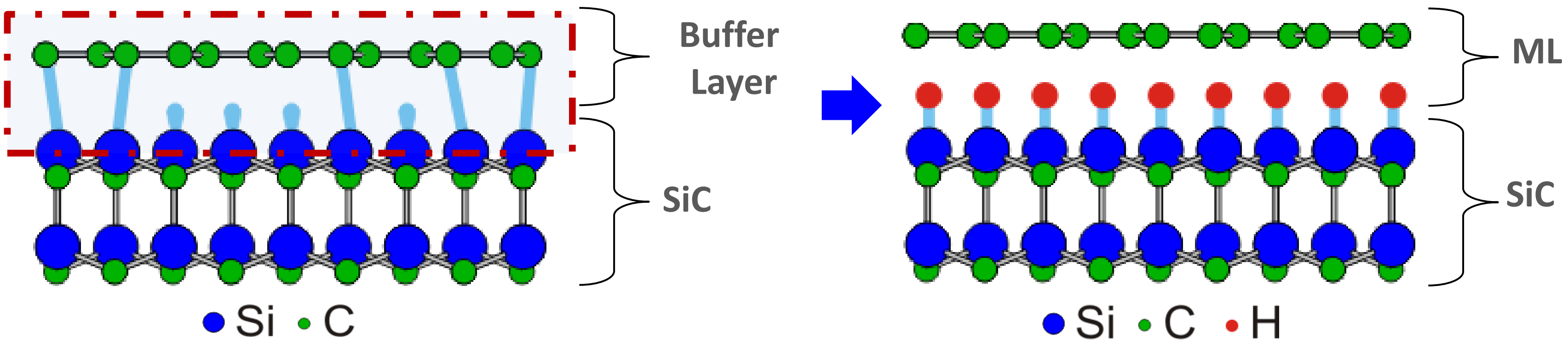


30 nm, 1V, 100 pA



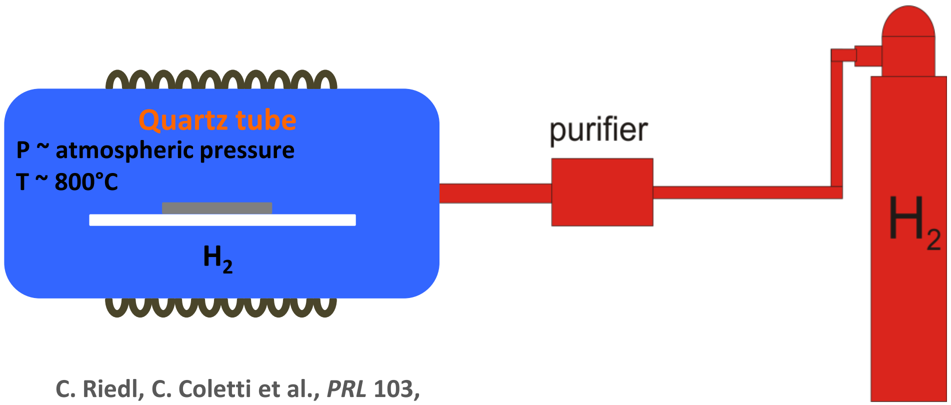
E= 75 eV

Hydrogen Intercalation



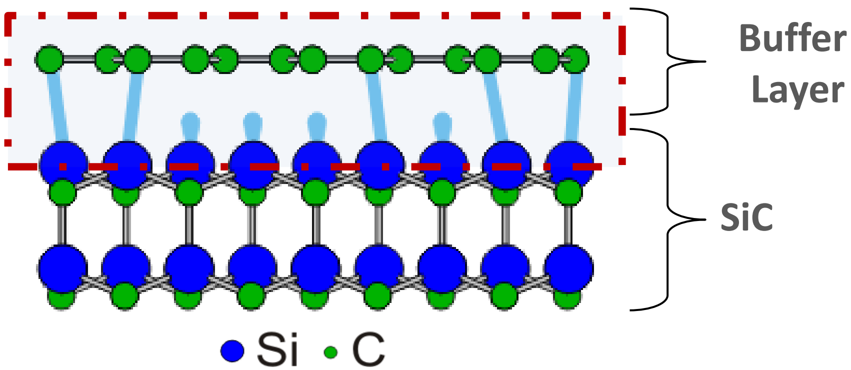
Buffer Layer (BL)

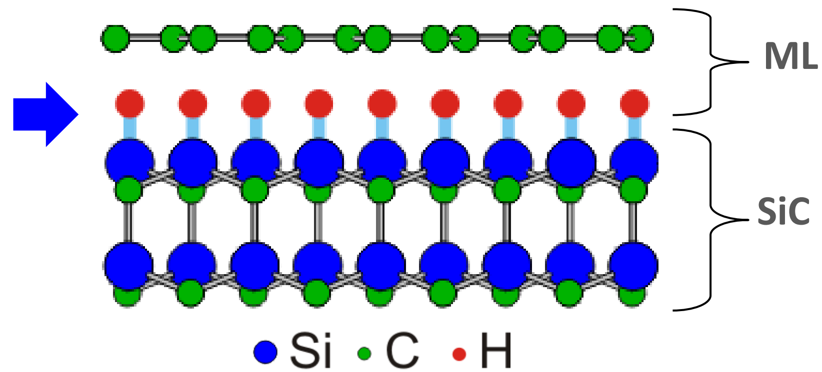
Quasi-free standing monolayer graphene



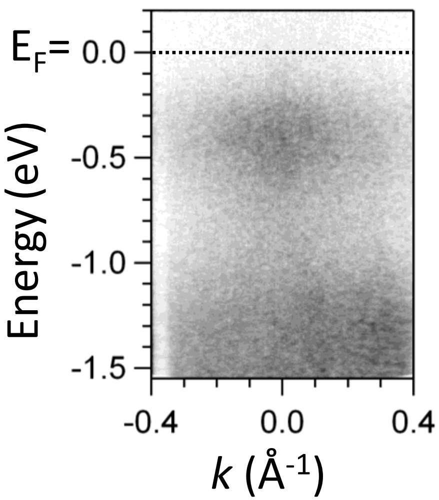
C. Riedl, C. Coletti et al., *PRL* 103, 246804 (2009)

Hydrogen Intercalation

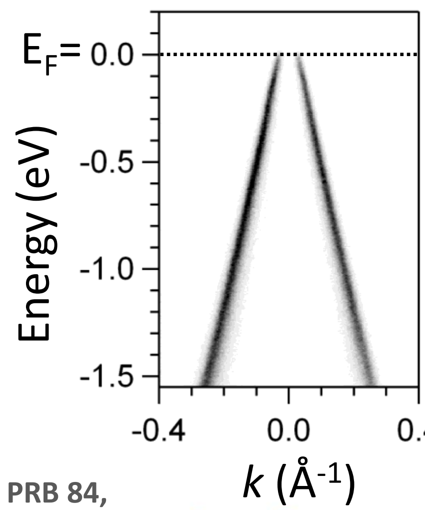




Buffer Layer (BL)



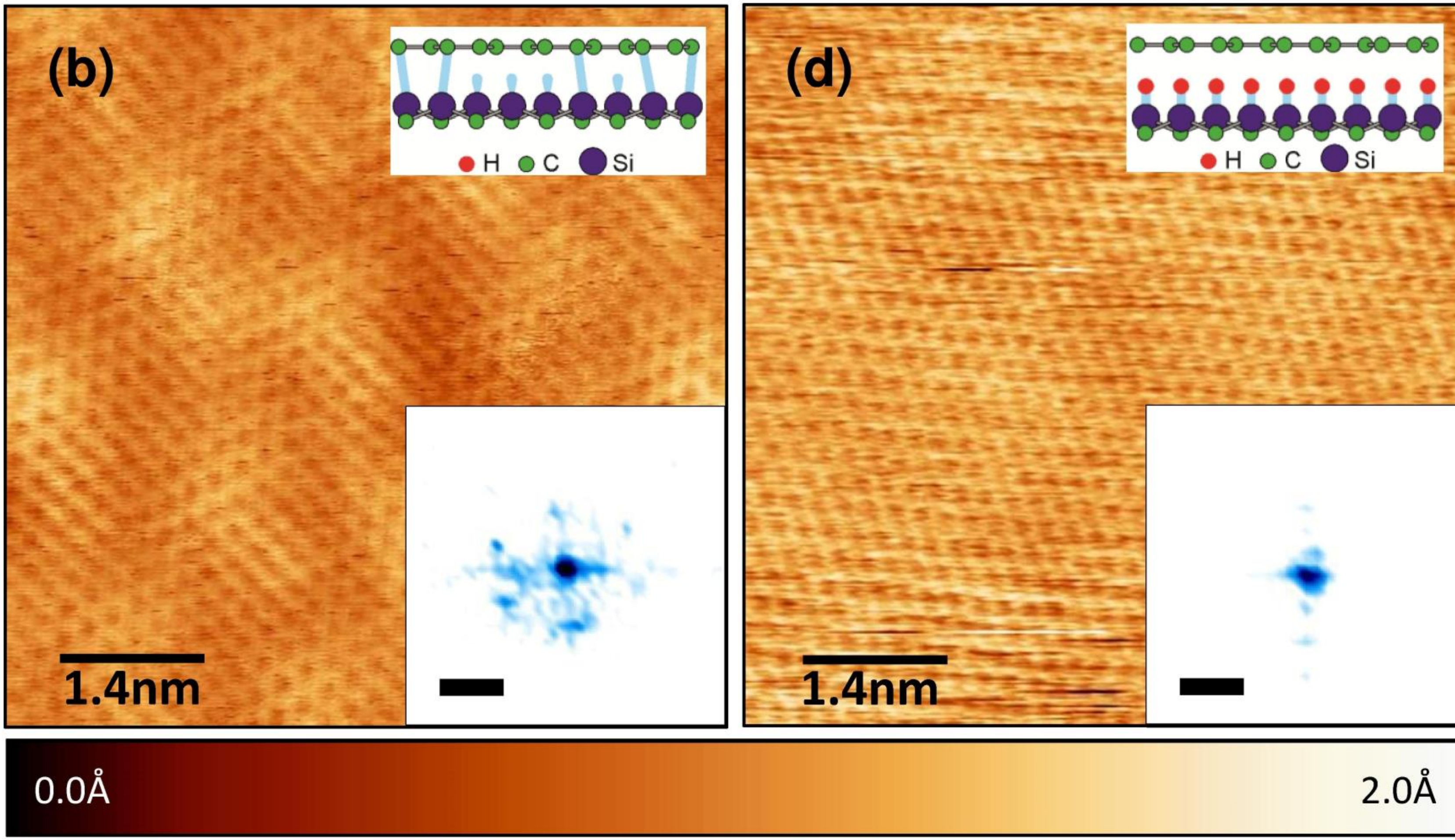
Quasi-free standing monolayer graphene



$p=2.6\cdot10^{12}$ cm^{-2}

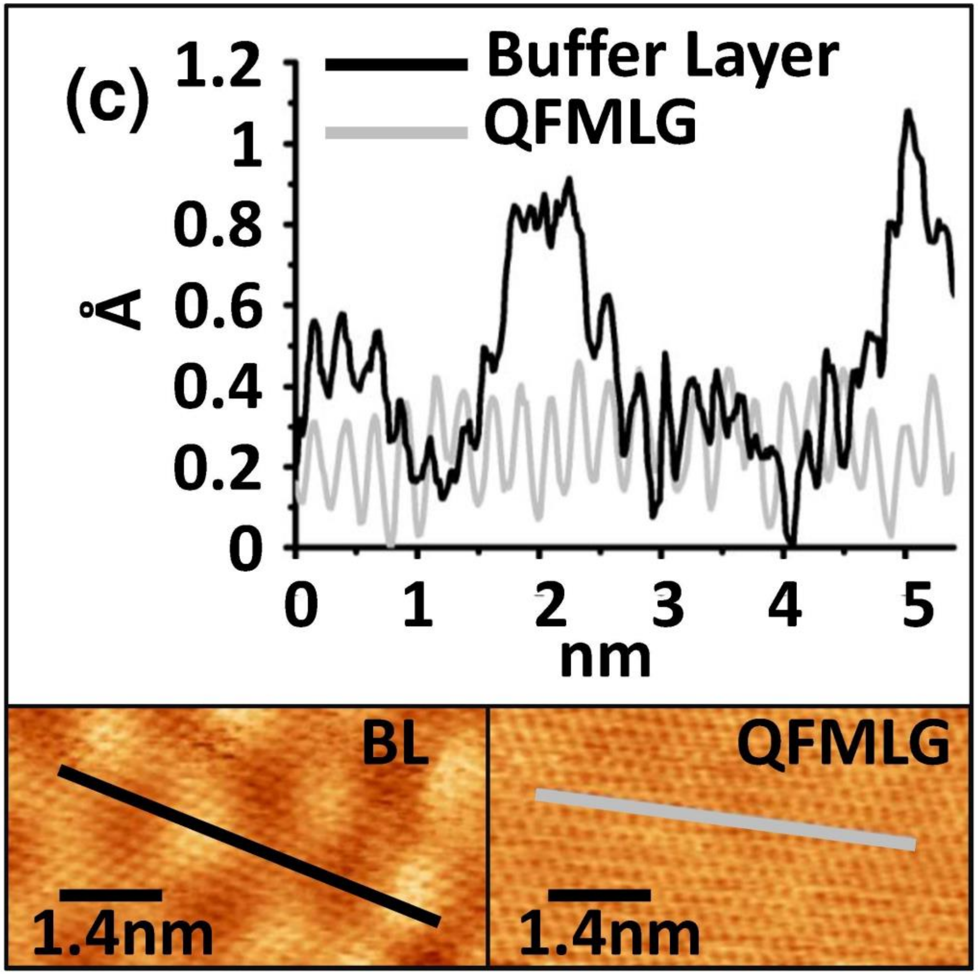
S. Forti, et al., PRB 84, 125449 (2011).

BL vs. QFMLG



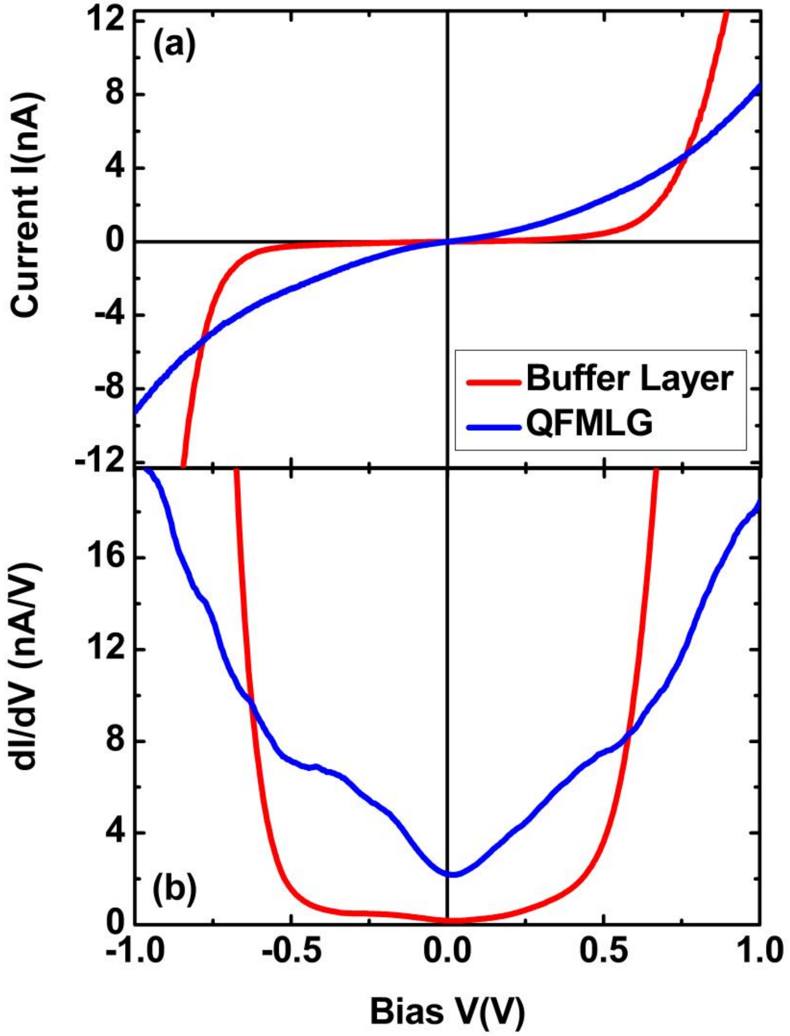
S. Goler *et al.*: Carbon **51**, 249 (2013).

BL vs. QFMLG



S. Goler *et al.*: Carbon **51**, 249 (2013).

BL vs. QFMLG



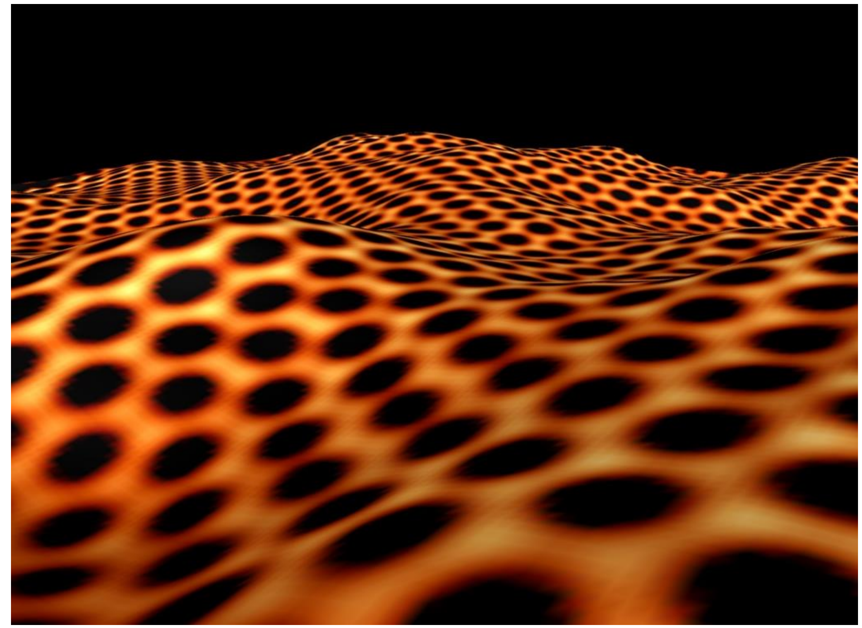
S. Goler *et al.*: Carbon **51**, 249 (2013).

Outline

- Presentation of NEST
- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Corrugation
- Hydrogen Storage by Functionalization

Graphene Curvature

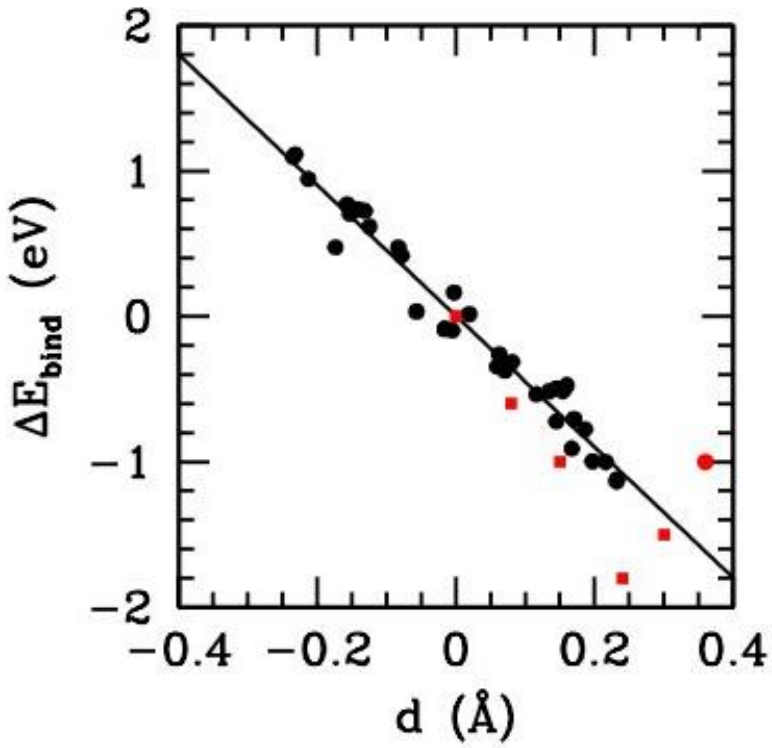
- Exploit graphene curvature for hydrogen storage at room temperature and pressure



V. Tozzini and V. Pellegrini: J. Phys. Chem. C **115**, 25523 (2011).

Graphene Curvature

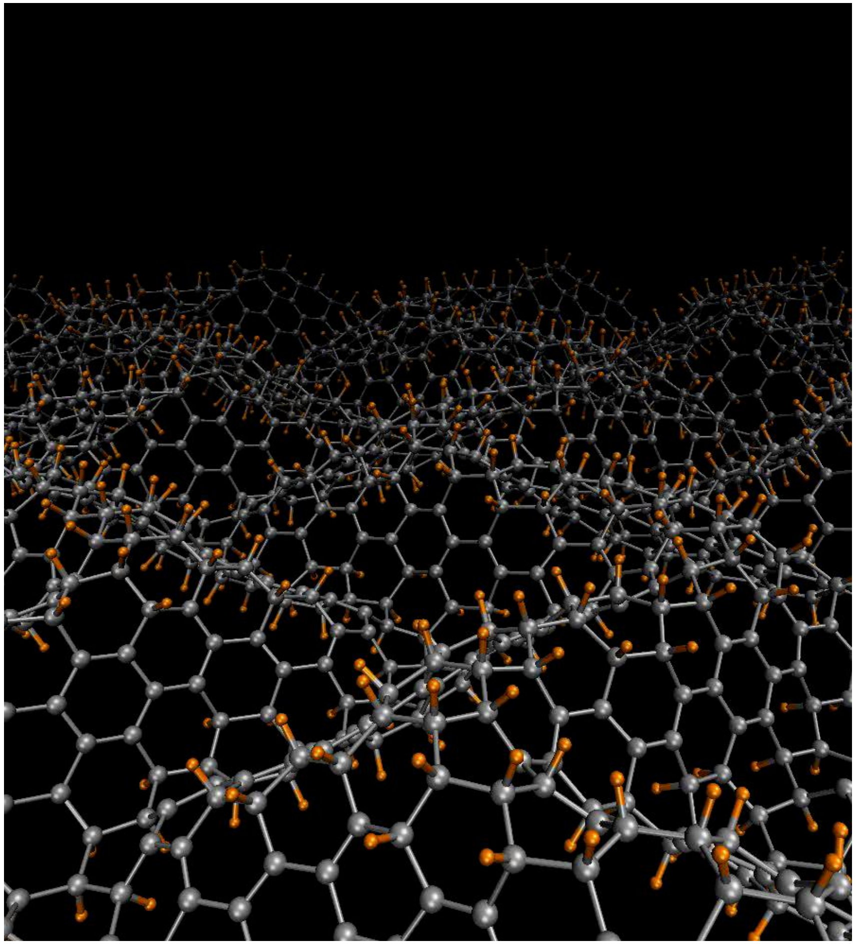
- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts



V. Tozzini and V. Pellegrini: J. Phys. Chem. C **115**, 25523 (2011).

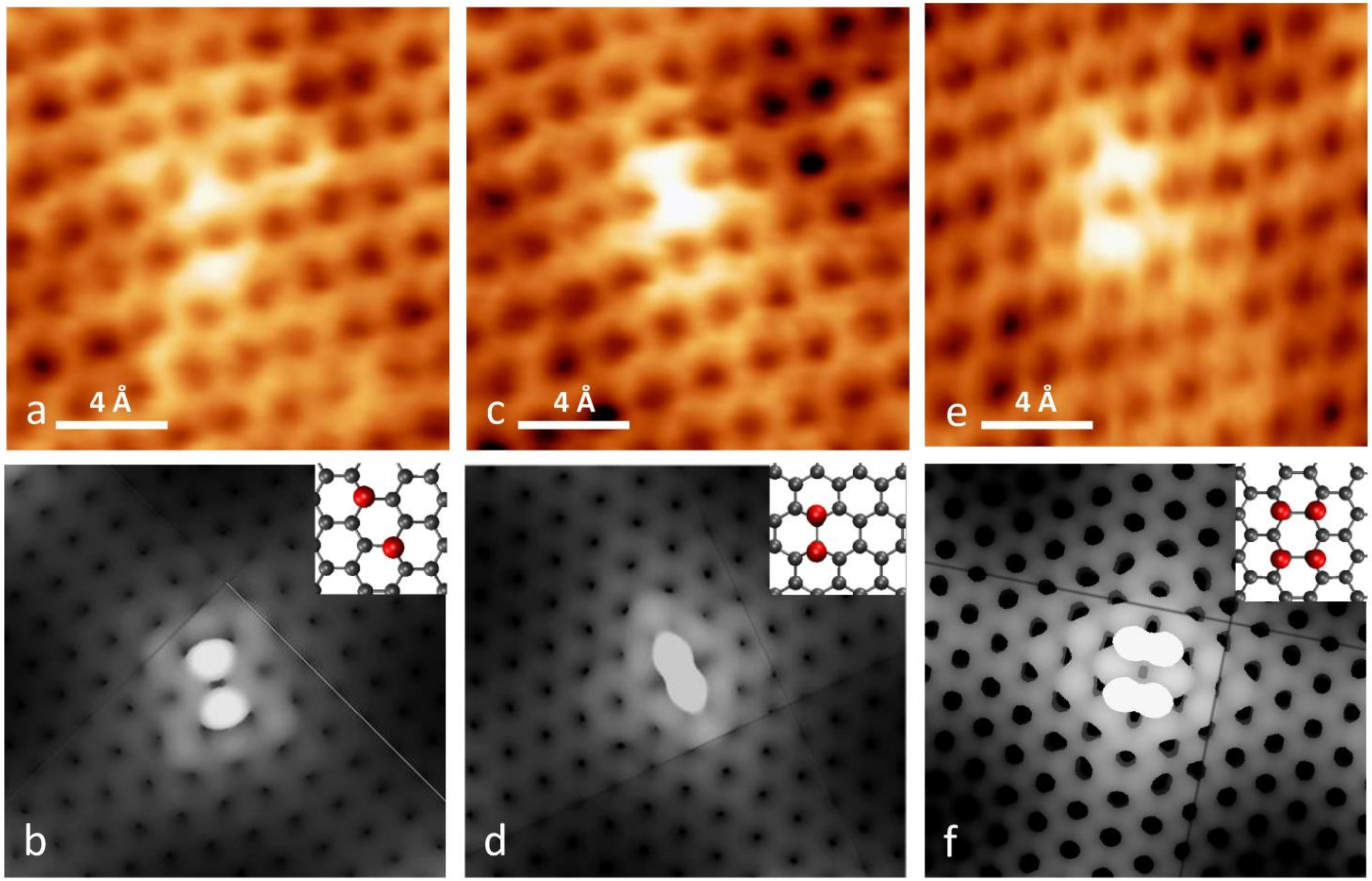
Graphene Curvature

- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts
- Atomic hydrogen spontaneously sticks on convex parts; inverting curvature H is expelled



V. Tozzini and V. Pellegrini: J. Phys. Chem. C **115**, 25523 (2011).

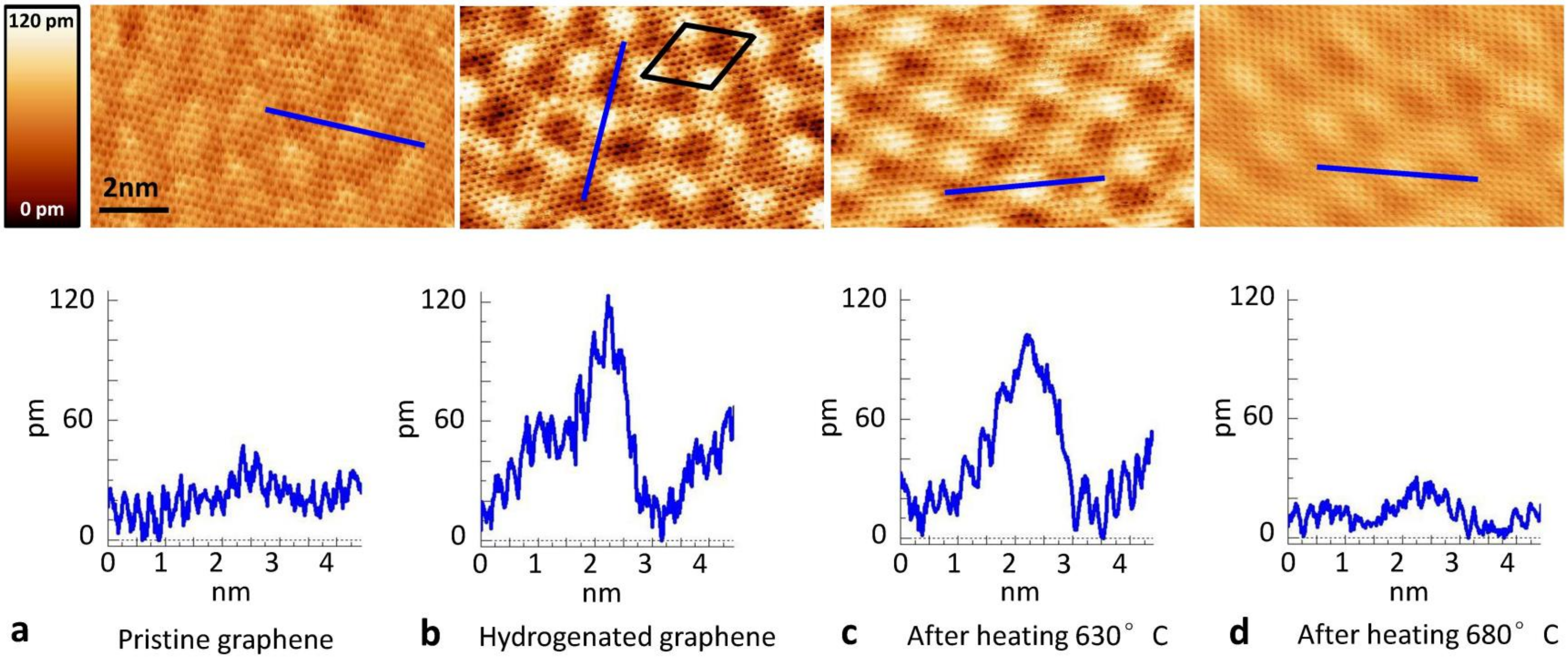
H-dimers and tetramers



Para-dimer Ortho-dimer Tetramer

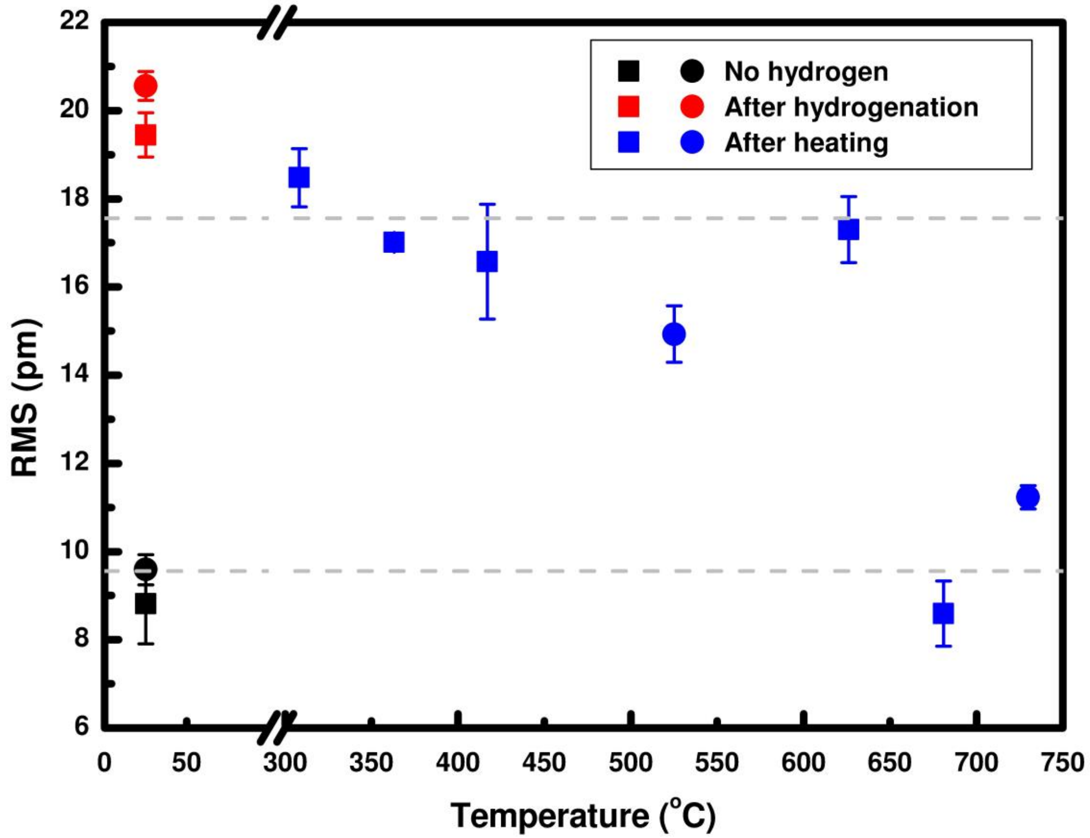
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

H adsorption and desorption



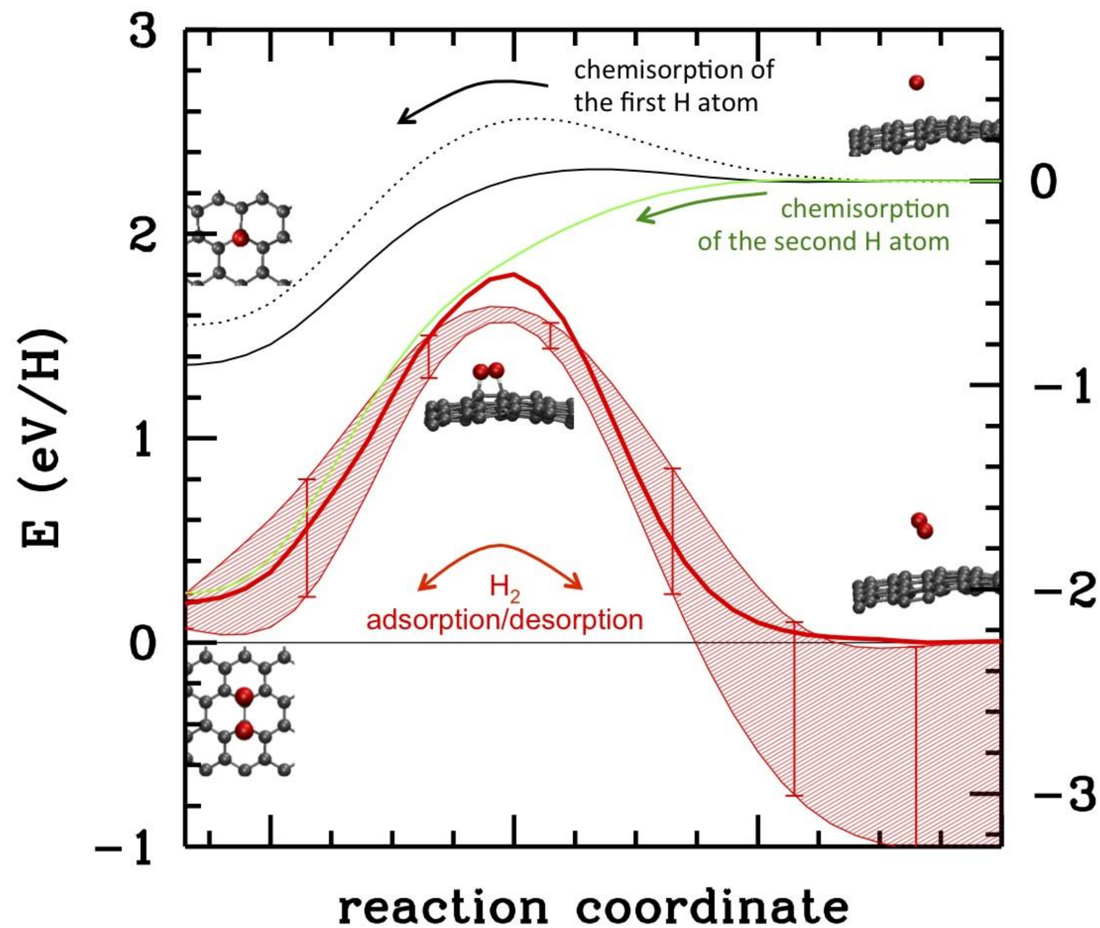
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

RMS roughness



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

DFT calculations



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

National Enterprise for nanoScience and nanoTechnology

Outline

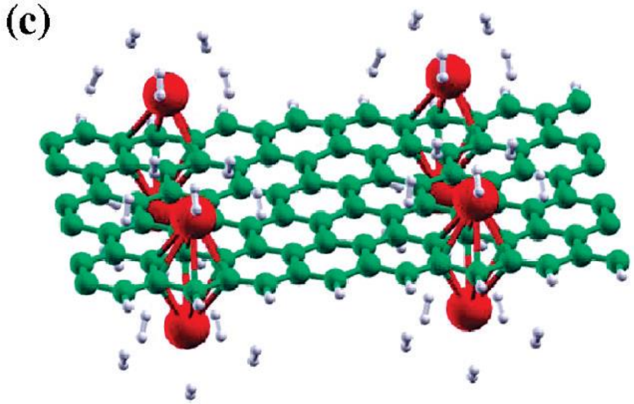
- Presentation of NEST
- Introduction to Hydrogen Storage
- Hydrogen Storage by Corrugation
- Hydrogen Storage by Functionalization

In collaboration with M. Takamura, S. Tanabe, H. Hibino

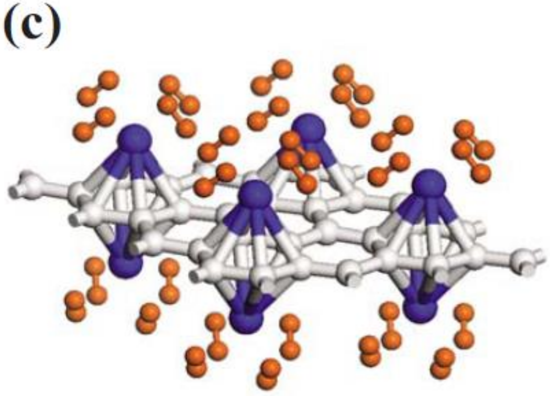
NTT Basic Research Laboratories, Atsugi, Japan

Functionalized Graphene

- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen
- Modify graphene with various chemical species, such as calcium or transition metals (Titanium)

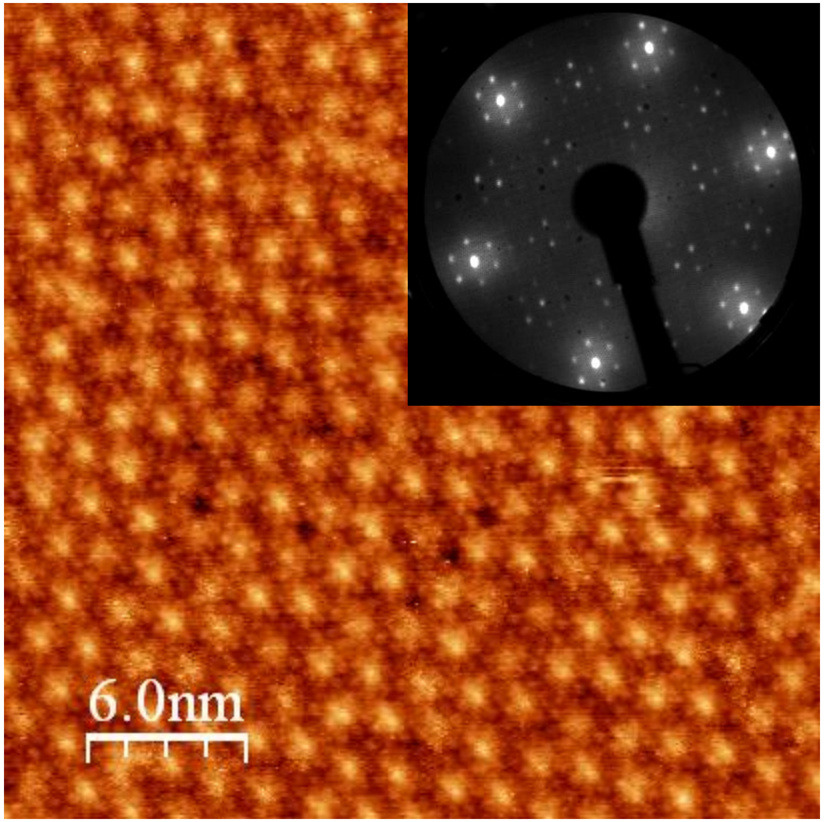


Lee et al., Nano Lett. 10 (2010) 793

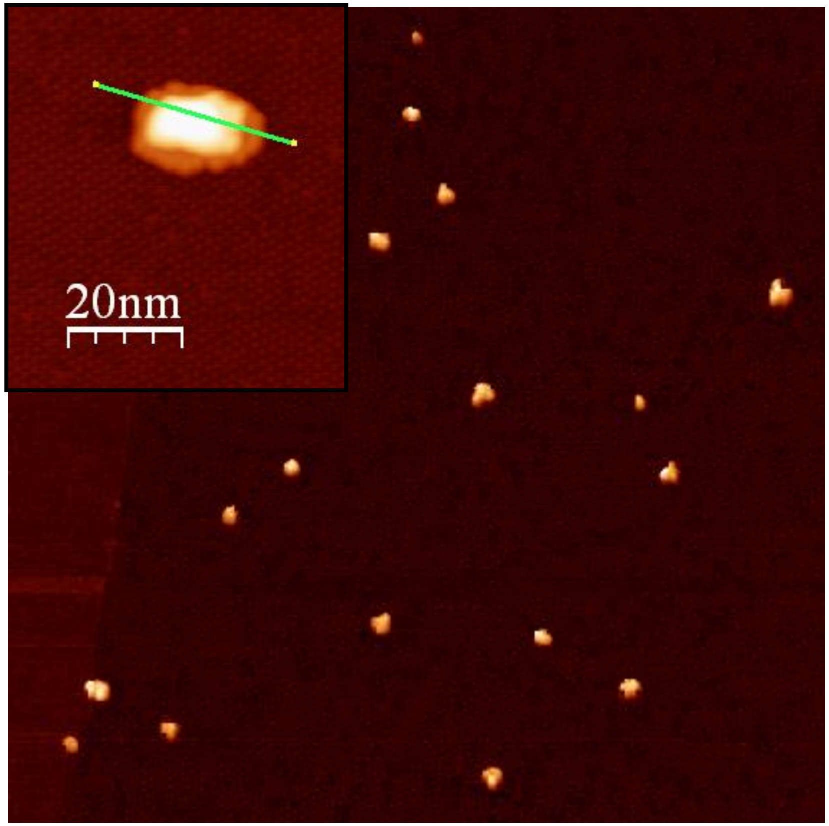


Durgen et al., PRB 77 (2007) 085405

Titanium on graphene



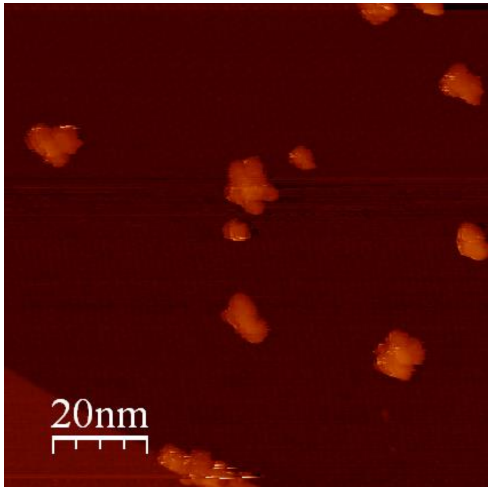
ML graphene on SiC(0001)
with reconstruction



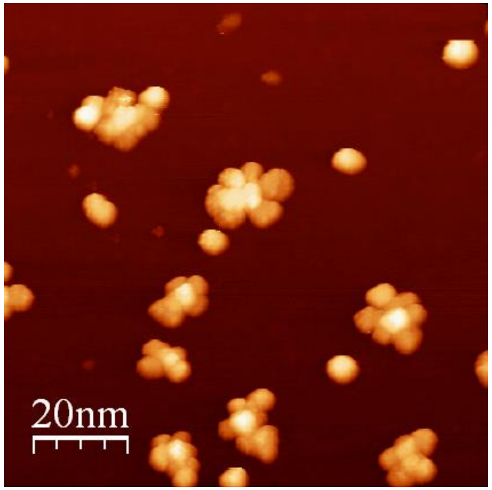
After deposition of Ti at RT

T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

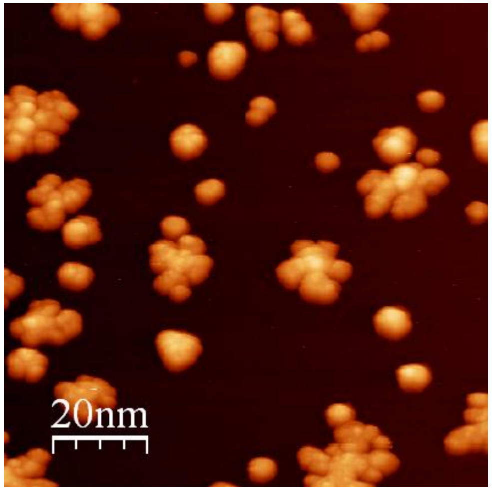
Titanium island growth



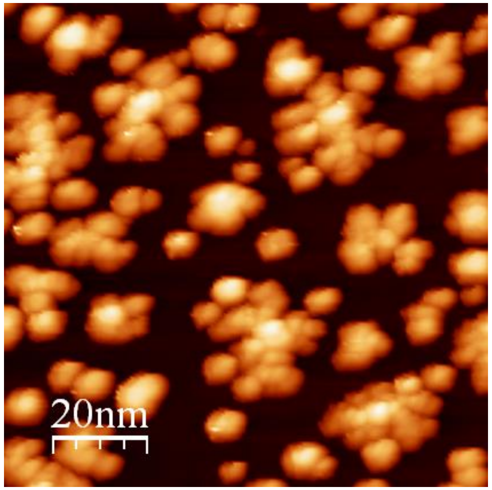
6% Coverage



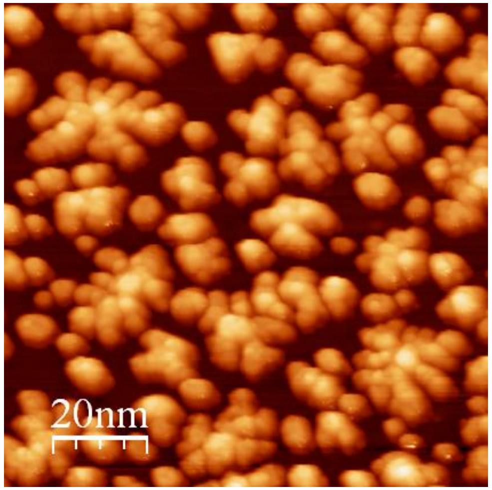
16% Coverage



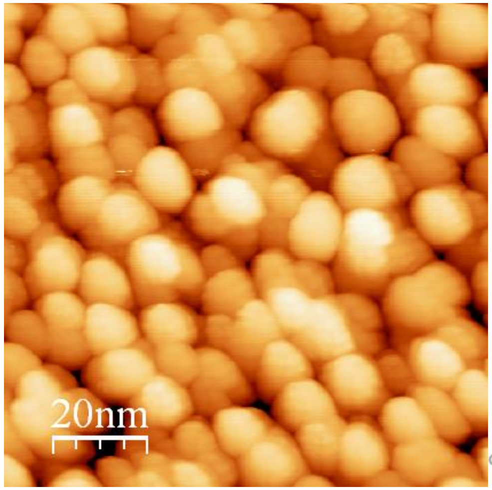
29% Coverage



53% Coverage



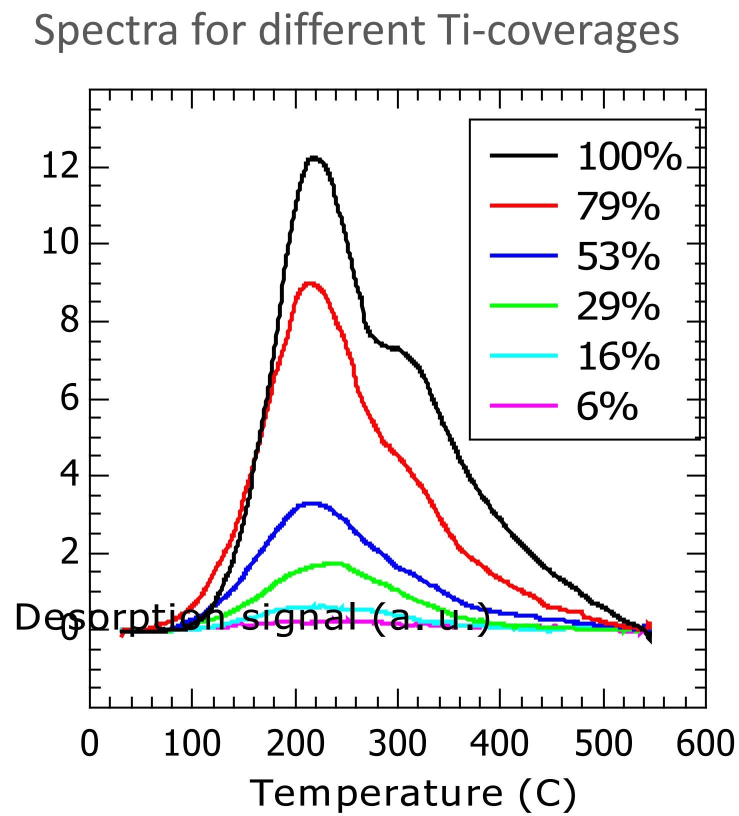
79% Coverage



100% Coverage

Thermal desorption spectroscopy

- Deposition of different amounts of Titanium
- Offering Hydrogen (D_2)
- ($1x10^{-7}$ mbar for 5 min)
- Heating sample with constant rate (10K/s) up to 550° C
- Measuring mass-sensitive desorption with a mass spectrometer



T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

National Enterprise for nanoScience and nanoTechnology

Conclusions

- Graphene is a promising material for hydrogen storage
- Curvature-dependent adsorption and desorption of hydrogen
  - reusable hydrogen storage devices that do not depend on temperature or pressure changes.
- Graphene functionalized by Ti:
  - Stability of hydrogen binding at room temperature
  - Hydrogen desorbes at moderate temperatures