The influence of graphene curvature and functionalization on hydrogen adsorption: towards hydrogen storage devices

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National Enterprise for nanoScience and nanoTechnology
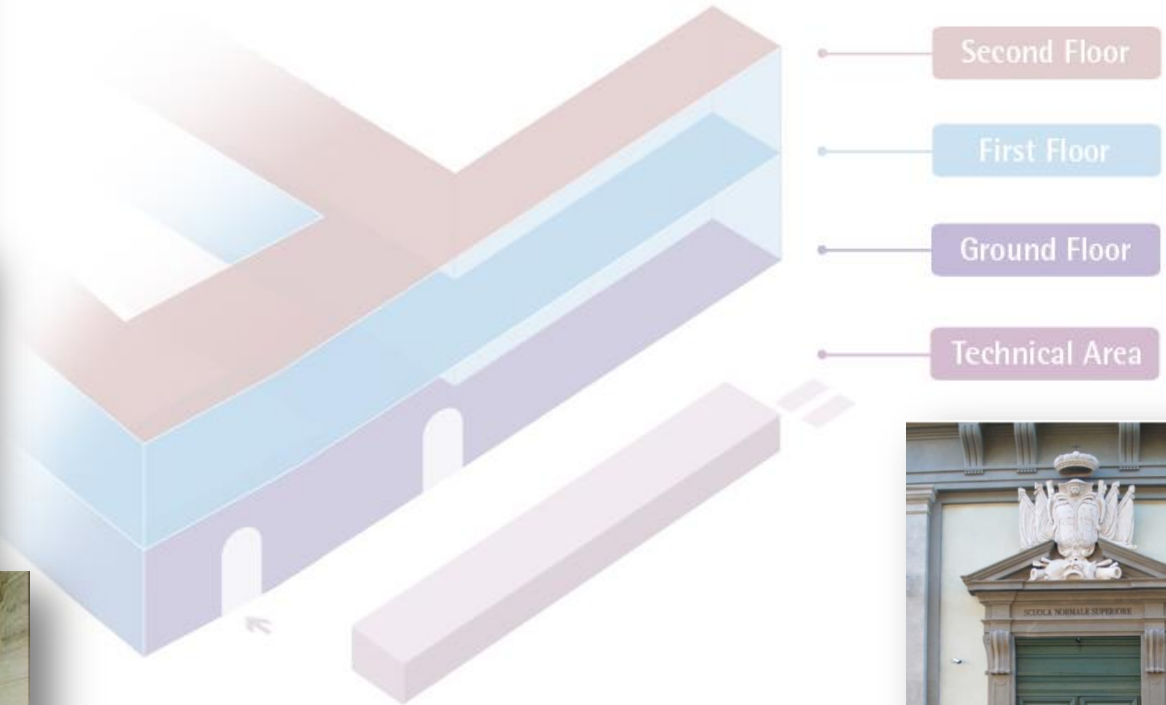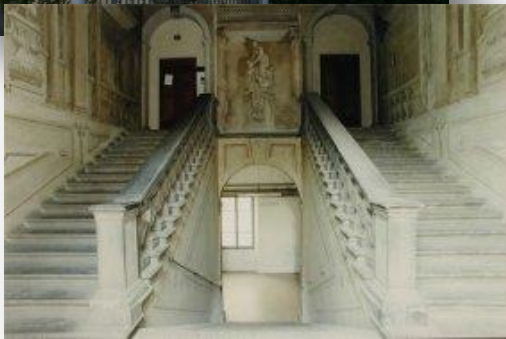
NEST

Outline

- Presentation of NEST

- Introduction to Hydrogen Storage

- Epitaxial Graphene

- Hydrogen Storage by Corrugation

- Hydrogen Storage by Functionalization

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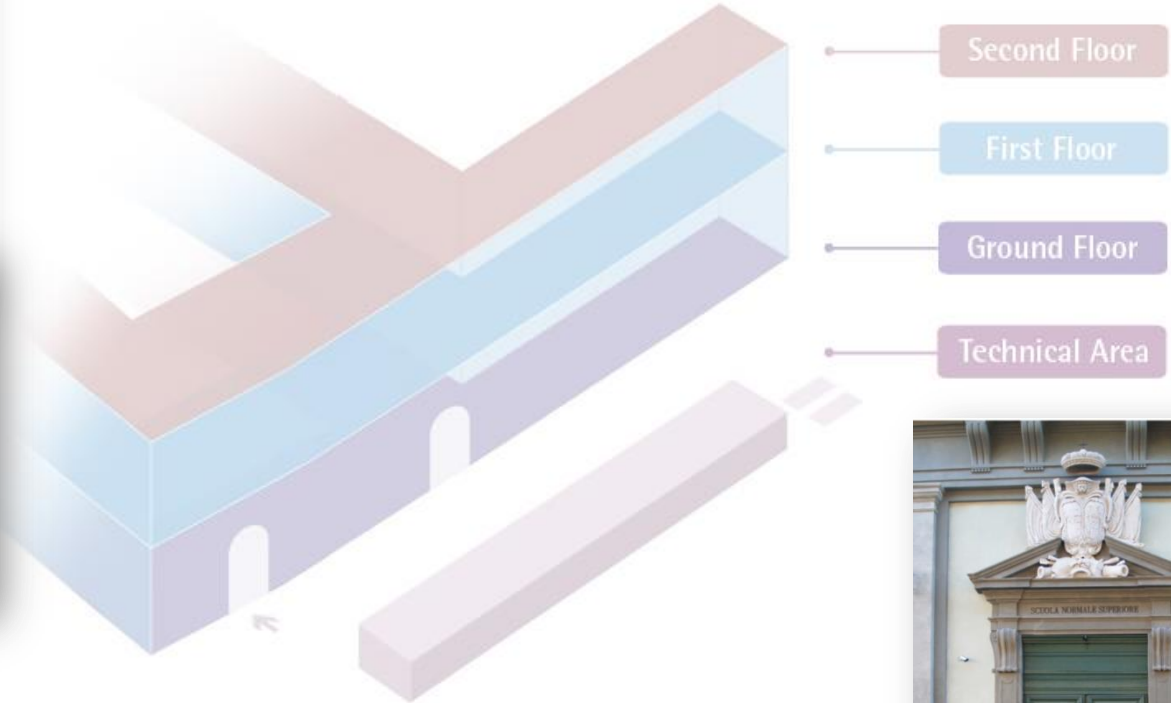
- Hydrogen Storage by Functionalization

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NEST

NEST Pisa

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Second Floor

First Floor

Ground Floor

Technical Area

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ISTITUTO ITALIANO
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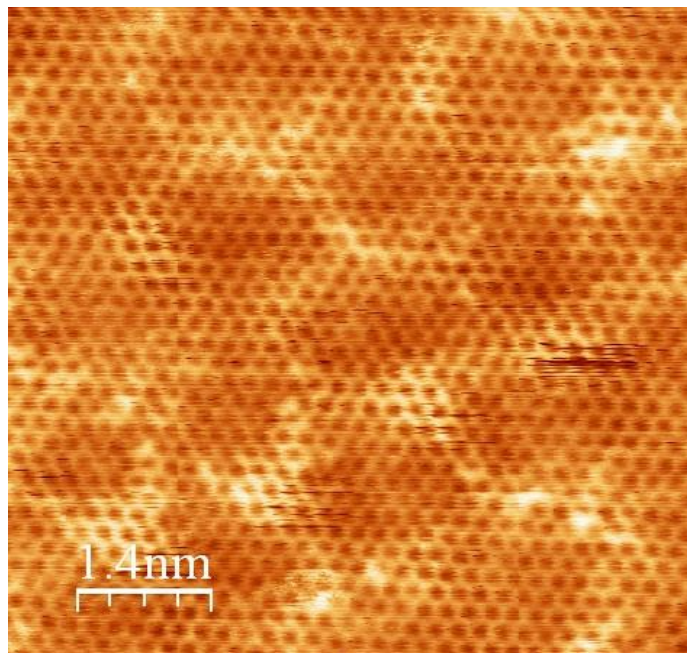National Enterprise for nanoScience and nanoTechnology

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
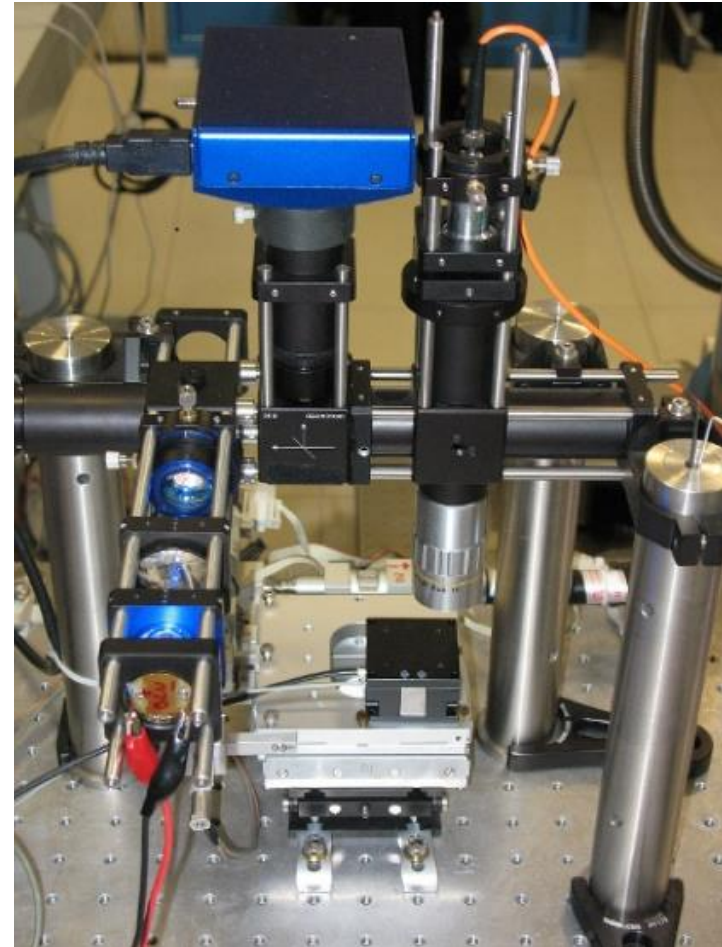
NEST facilities

- UHV VT STM

1.4nm
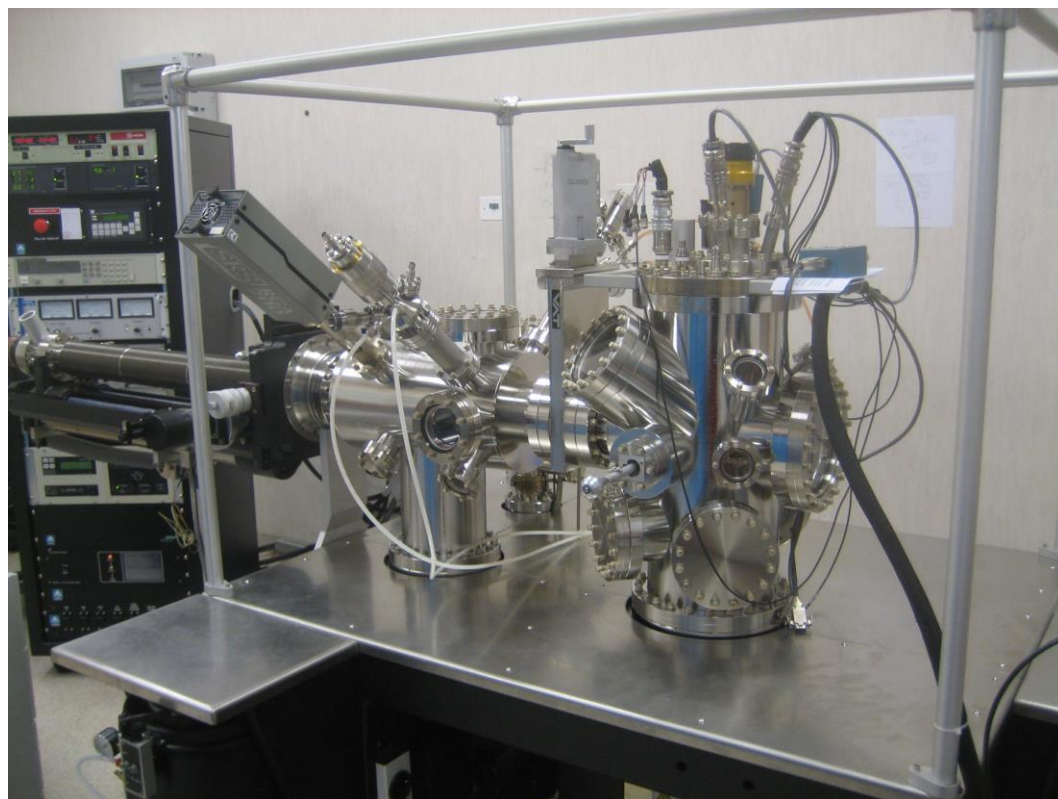
NEST facilities

- UHV VT STM

- Graphene Growth

NEST facilities

- UHV VT STM

- Graphene Growth

- Micro-Raman

NEST facilities

- UHV VT STM

- Graphene Growth

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- AFM

NEST facilities

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- AFM

- SEM

NEST facilities

- UHV VT STM

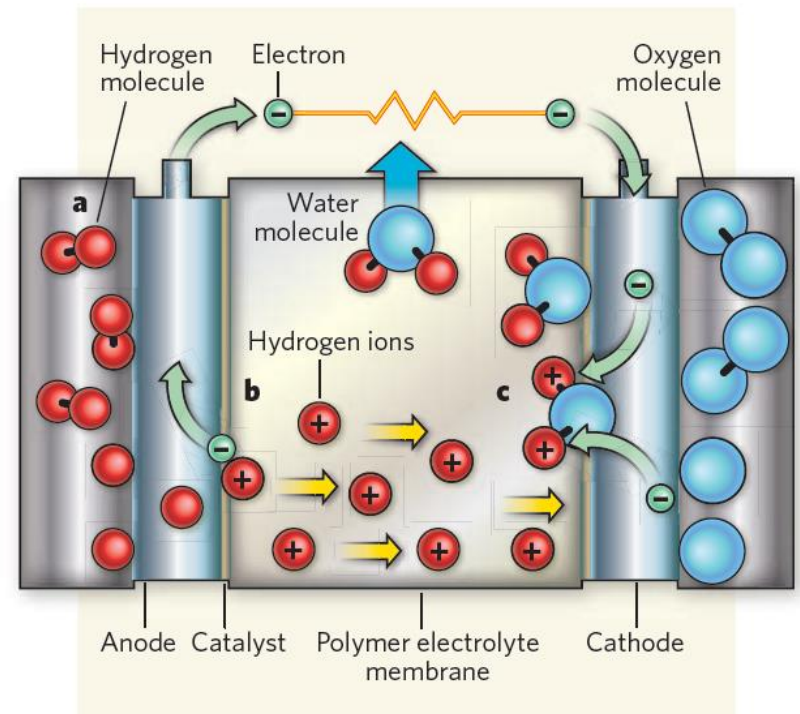- Graphene Growth

- Micro-Raman

- AFM

- SEM

- Theory

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NEST

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Hydrogen & energy

As a fuel, hydrogen has advantages:

- high energy-to-mass ratio

- $H_2 + 1/2\ O_2 \rightarrow H_2O$ $\Delta H = -2.96eV$

- 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.
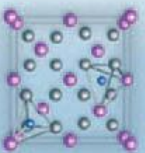

Hydrogen fuel cell

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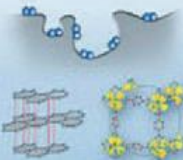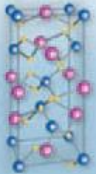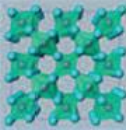
Hydrogen-fuelled vehicles

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Hydrogen Storage

Liquid hydrogen	Cryo-adsorption	Interstitial metal hydride	Compressed hydrogen	Alanate	Salt-like metal hydride	Water
LH2	Activated carbon	Laves Phase Comp./ $FeTiH_x$ / $LaNi_5H_x$	CGH2	$NaAlH_4$	MgH_2	H_2O
100 mat.wt%	6.5 mat.wt%	2 mat.wt%	100 mat.wt%	5.5 mat.wt%	7.5 mat.wt%	11 mat.wt%

Operating temperature

-253°C	> -200°C	0 - 30°C	25°C	70 - 170°C	330°C	>> 1000°C

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

ρ_m > 5.5 wt%

ρ_V > 50 kg H_2 /m³

P_{eq}≈1bar at T< 100°C

Compressed H_2:
High pressure and heavy container to support such pressure
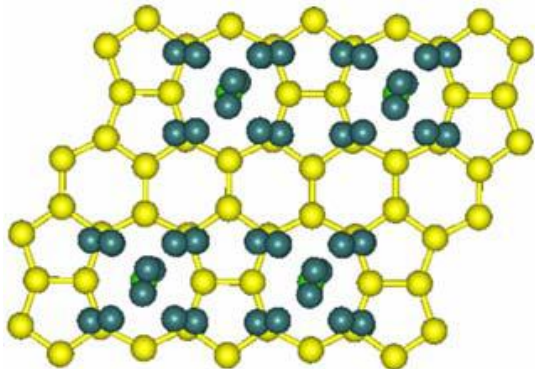
Solid State:
Physisorption
Chemisorption

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

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

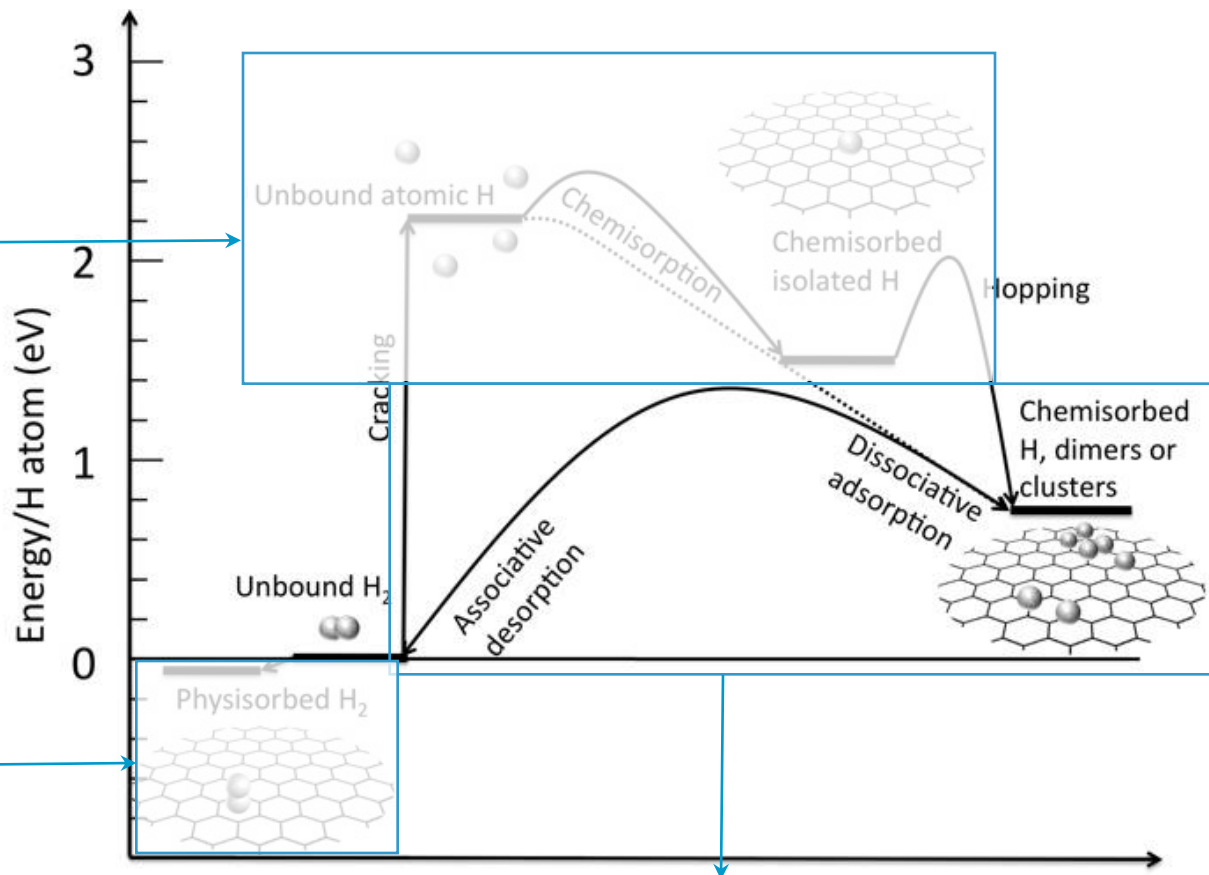Yang et al., PRB 79 (2009) 075431

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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

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What is Graphene?

A SINGLE layer of carbon atoms!

The atoms are arranged in a honeycomb lattice composed of two intertwined equivalent sublattices.

a = 0.246 nm
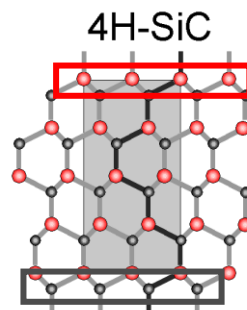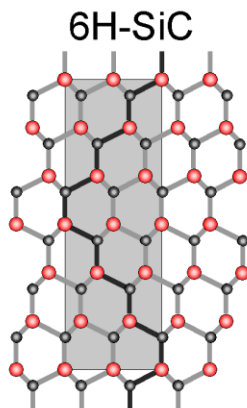
C-C spacing = 0.142 nm

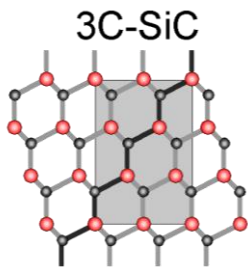National Enterprise for nanoScience and nanoTechnology
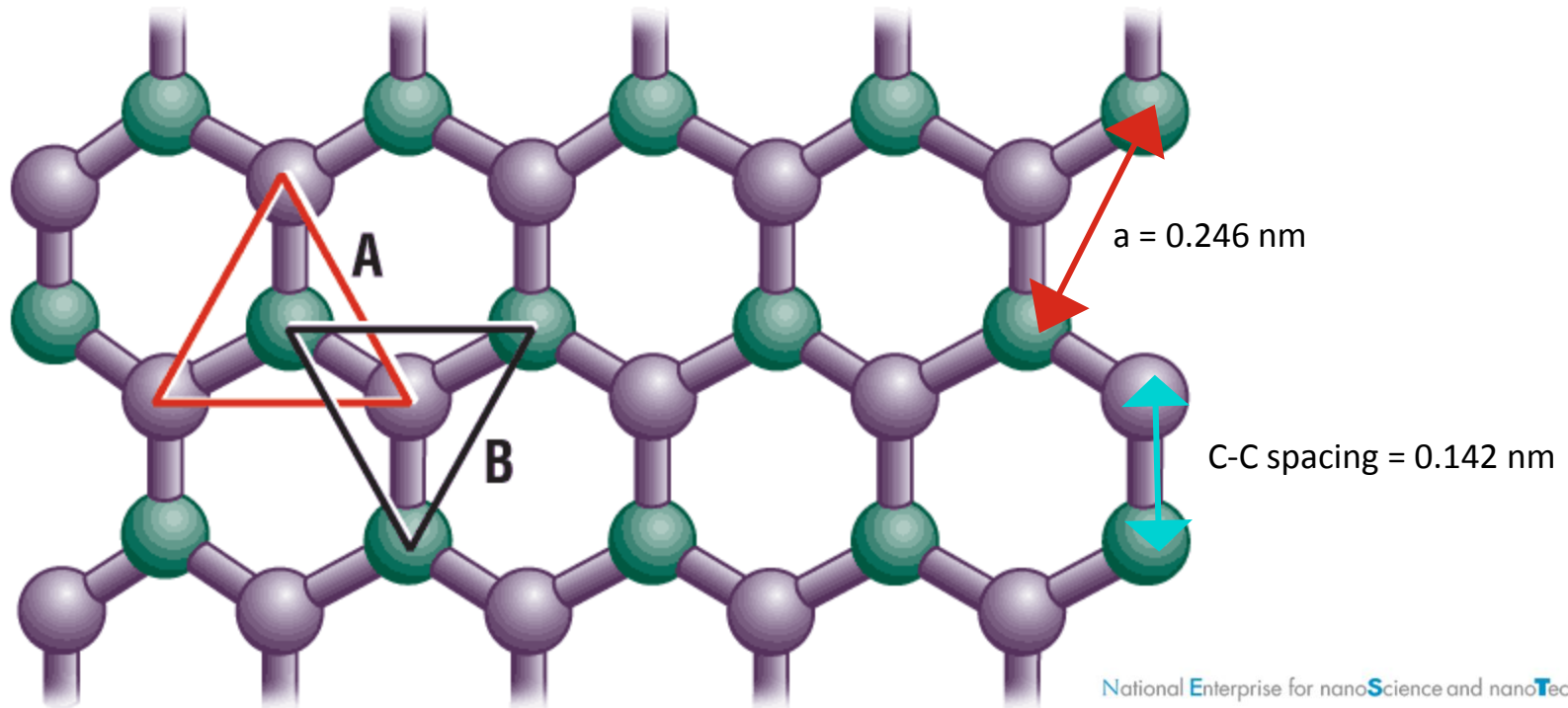
Graphene growth on SiC

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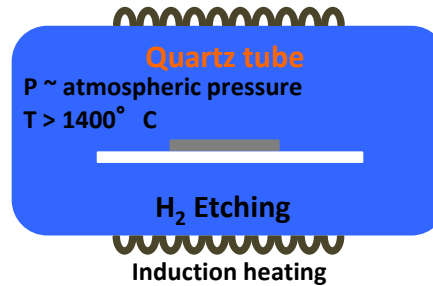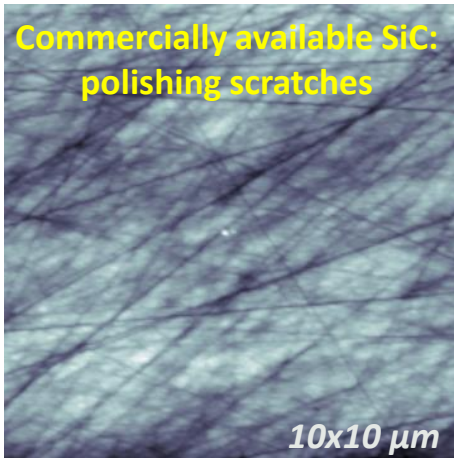

SiC
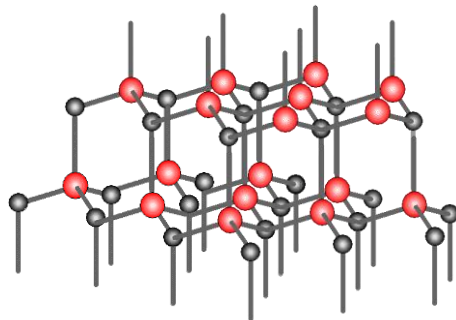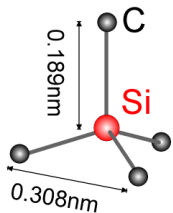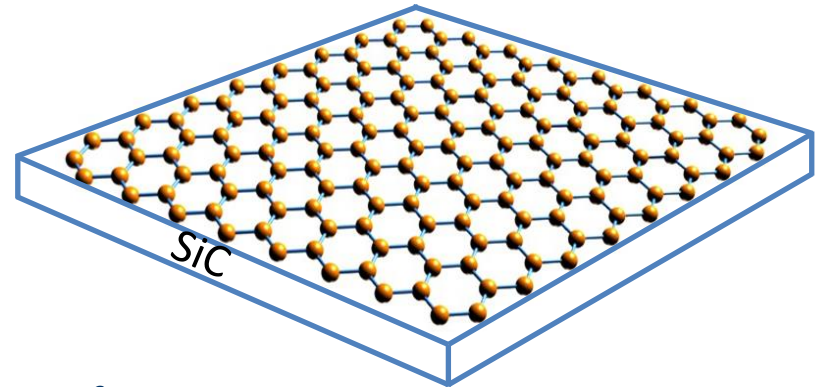
Bilayer of Si-C tetrahedra

C

0.189nm

Si

0.308nm

3C-SiC   6H-SiC   4H-SiC

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

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

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Graphene growth on SiC(0001)

Commercially available SiC: polishing scratches

10x10 µm

Quartz tube
P ~ atmospheric pressure
T > 1400° C

H₂ Etching

Induction heating

C. Coletti et al., *Appl. Phys. Lett.* 91, 061914 (2007)

Atomically flat SiC

5x5 µm

6H-SiC

Quartz tube
P ~ atmospheric pressure
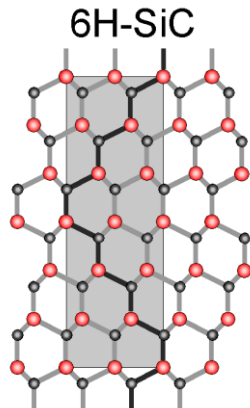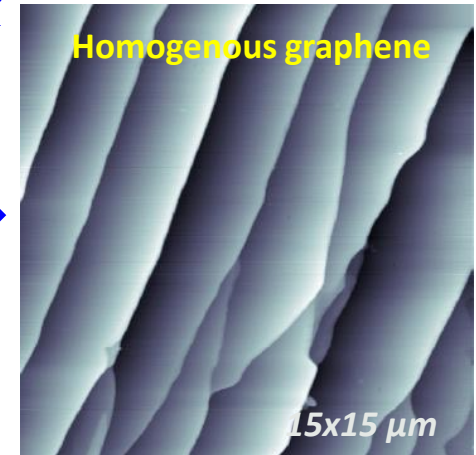T ~ 1400° C (ZL) ~ 1480° C (ML)

Ar-Annealing

Induction heating
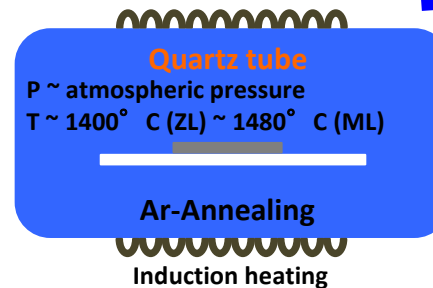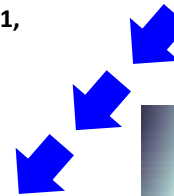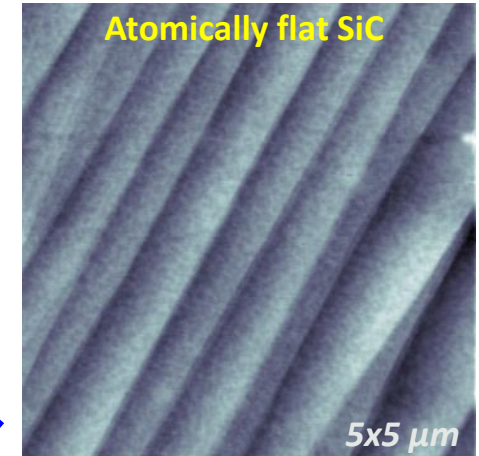
K.Emtsev et al., Nature Mater. 8, 203 (2009)

Homogenous graphene

15x15 µm

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NEST

Graphene growth on SiC(0001)

ML

Buffer Layer
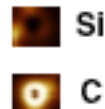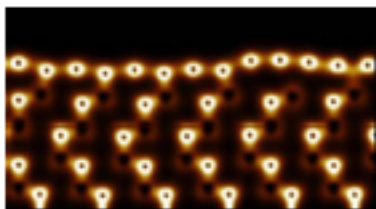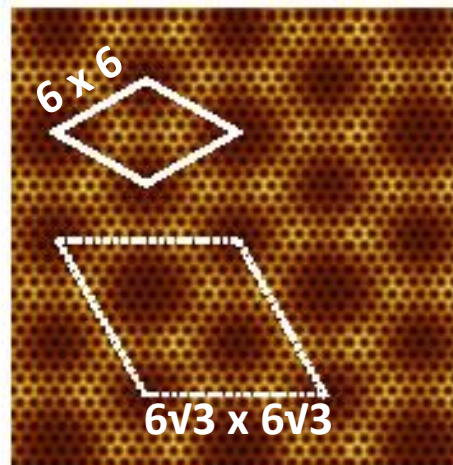
SiC

● Si ● C
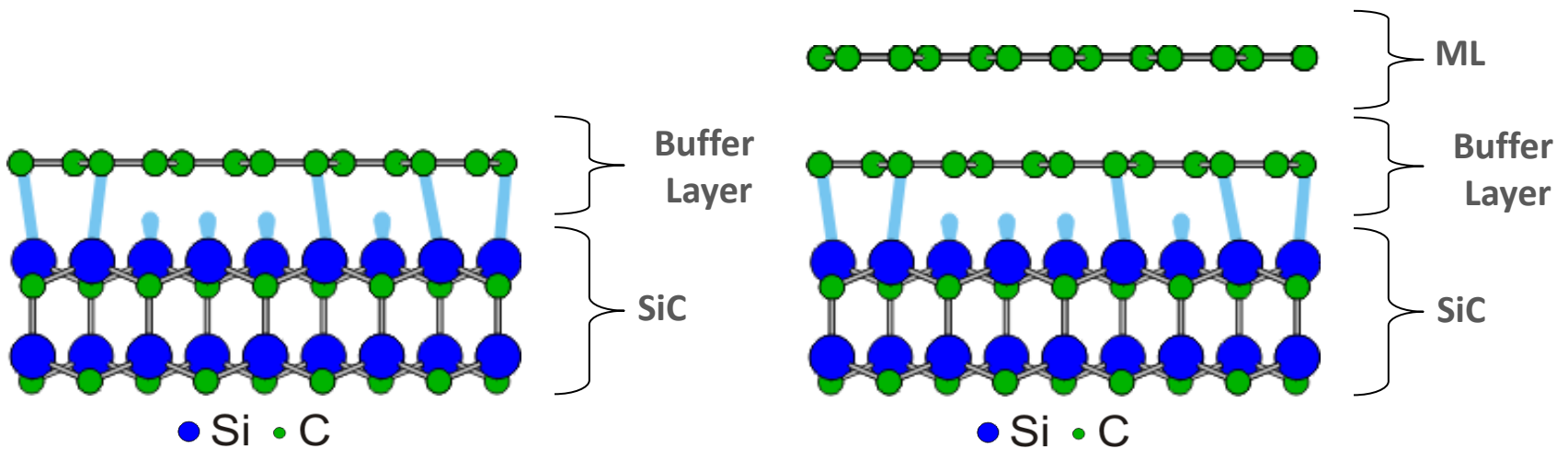
Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp³ C-Si bonds.

Theoretical Calculations

6 x 6

6√3 x 6√3

Si

C

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

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

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

Buffer Layer

Bias: +1.7V
Current: 0.3nA

$6\sqrt{3} \times 6\sqrt{3}$

quasi-(6x6)
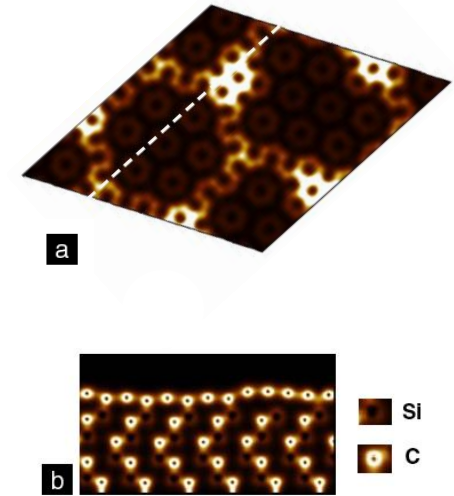
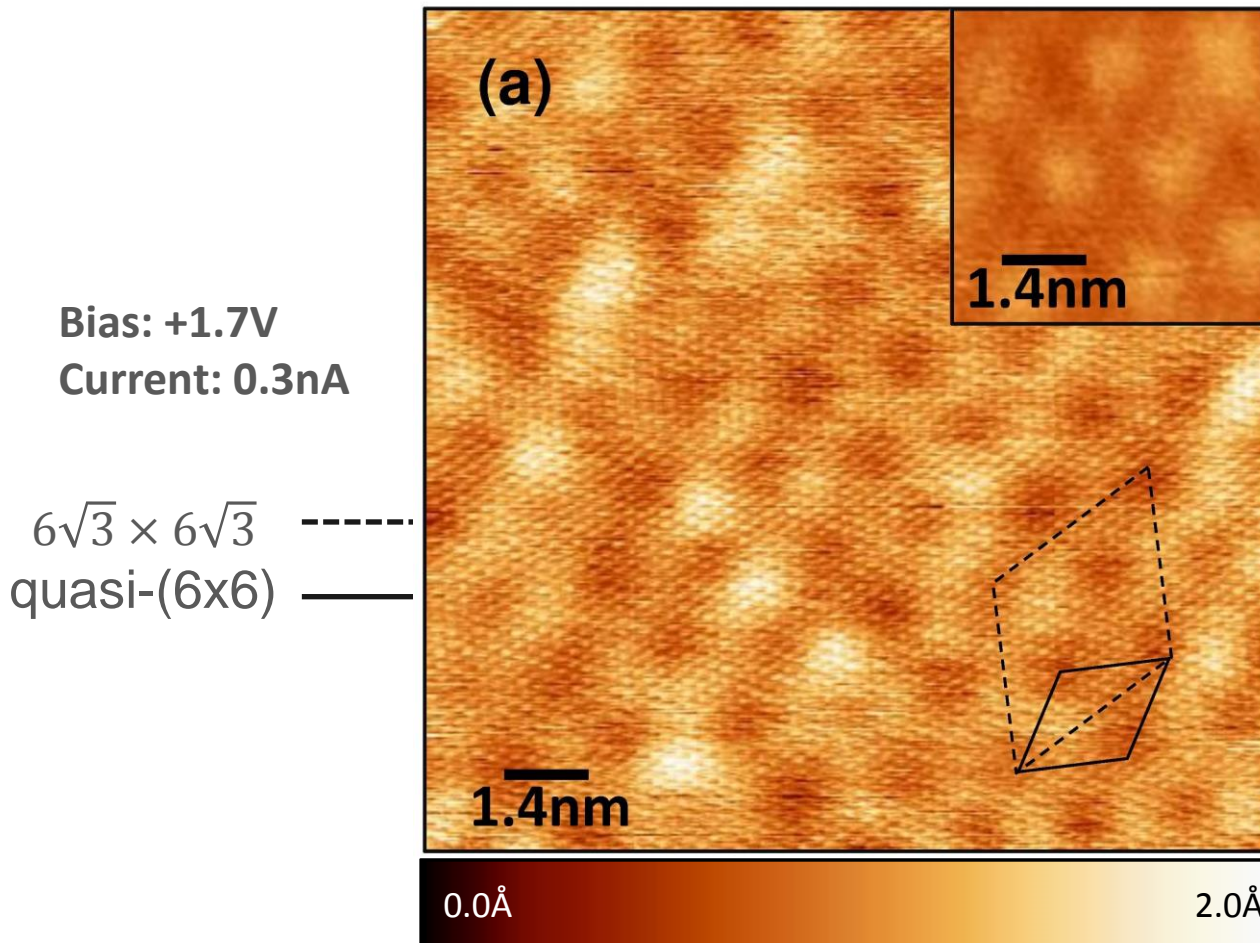(a)

1.4nm

1.4nm

0.0Å   2.0Å

a

b

Si
C

FIG. 2. (Color online) Total charge density of the buffer layer on SiC(001). (a) total charge density in the 6R3-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).
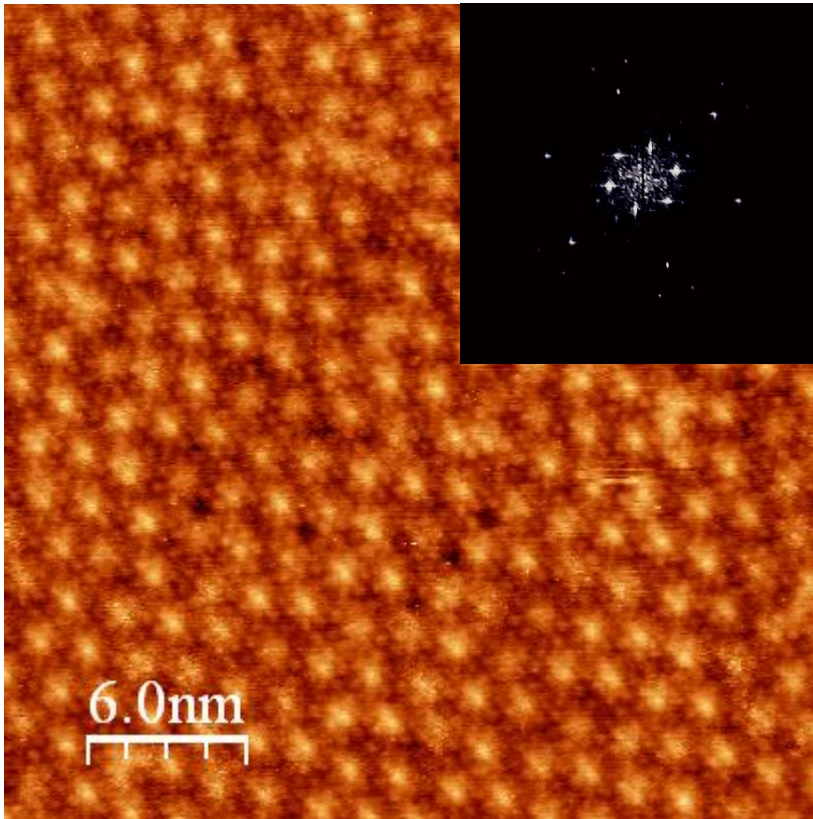
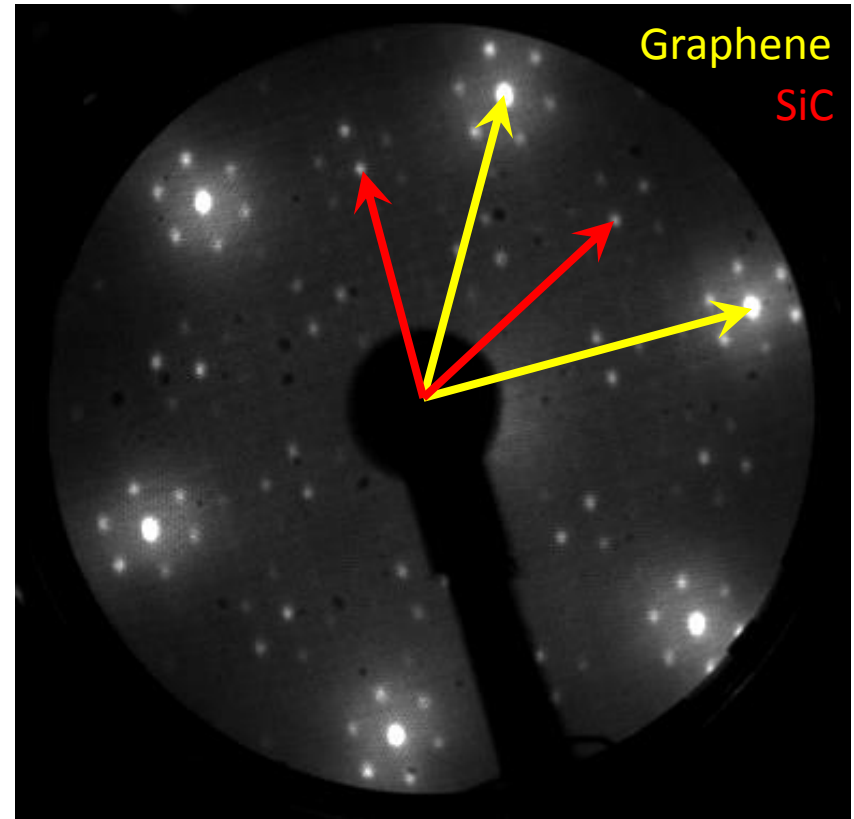**F. Varchon, et al., PRB 77, 235412 (2008).**

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

Monolayer Graphene

STM

S. Goler *et al.*
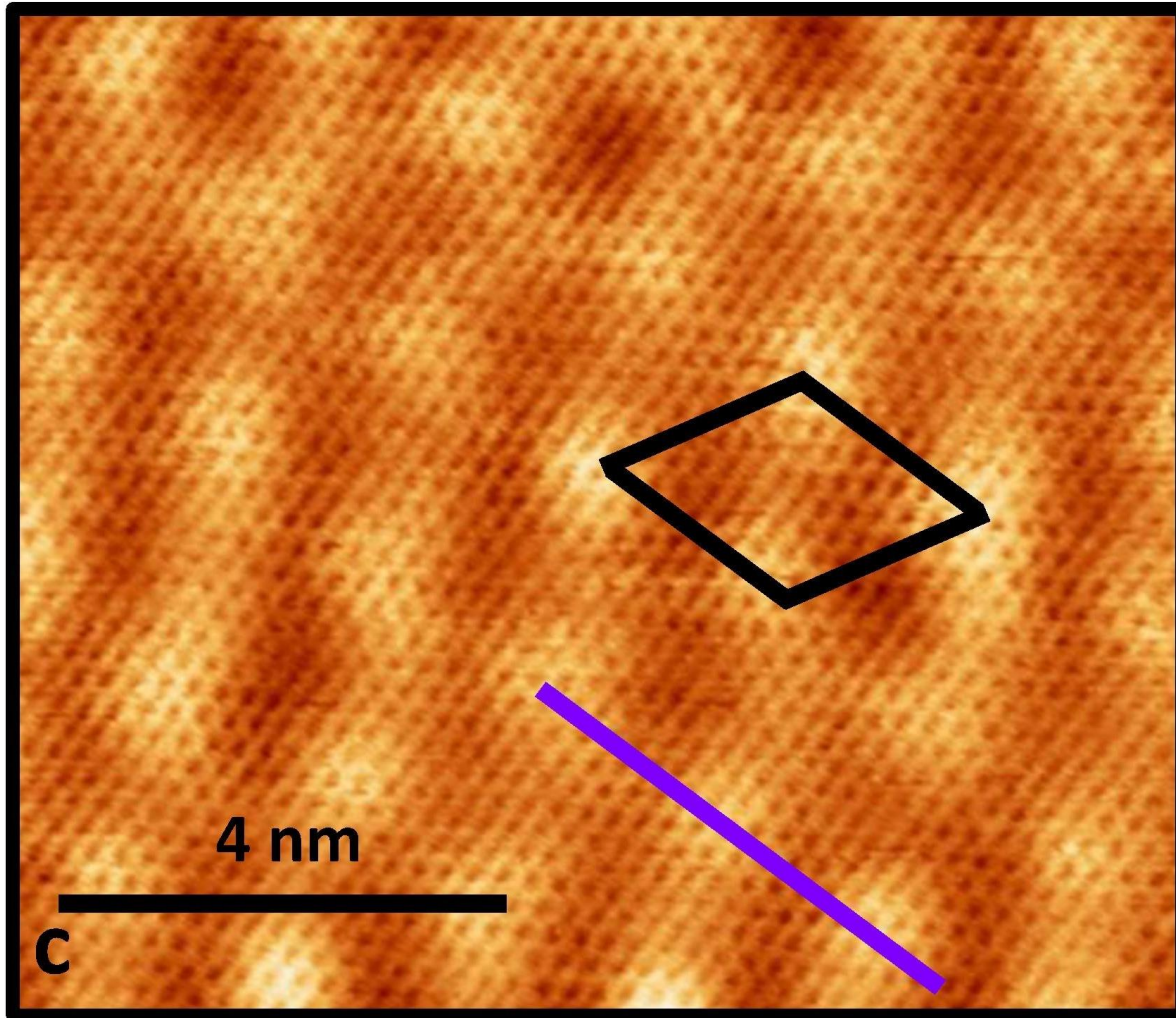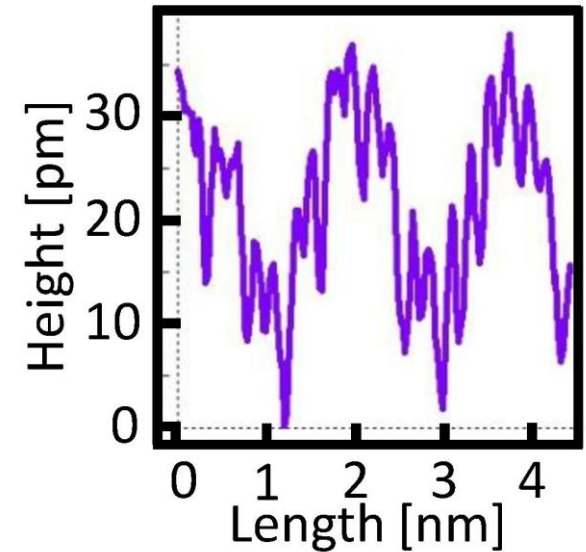
6√3x6√3-Superstructure

30 nm, 1V, 100 pA

Graphene
SiC

E= 75 eV

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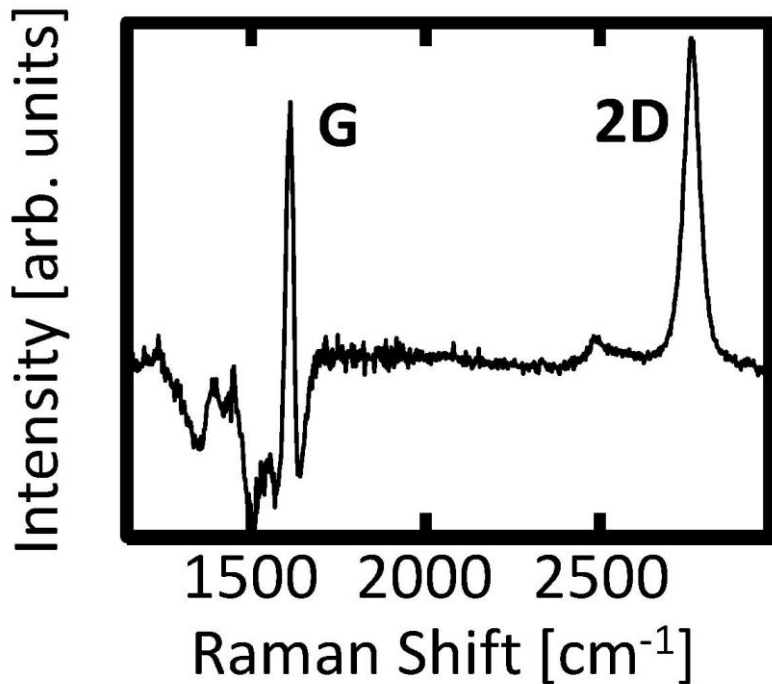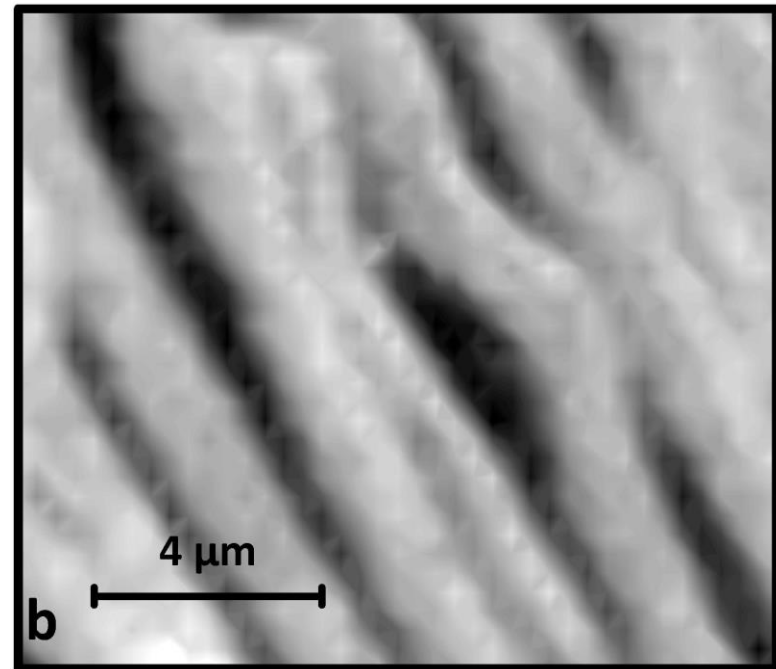
ML: Micro-Raman

Spectrum from 12um x 12um area
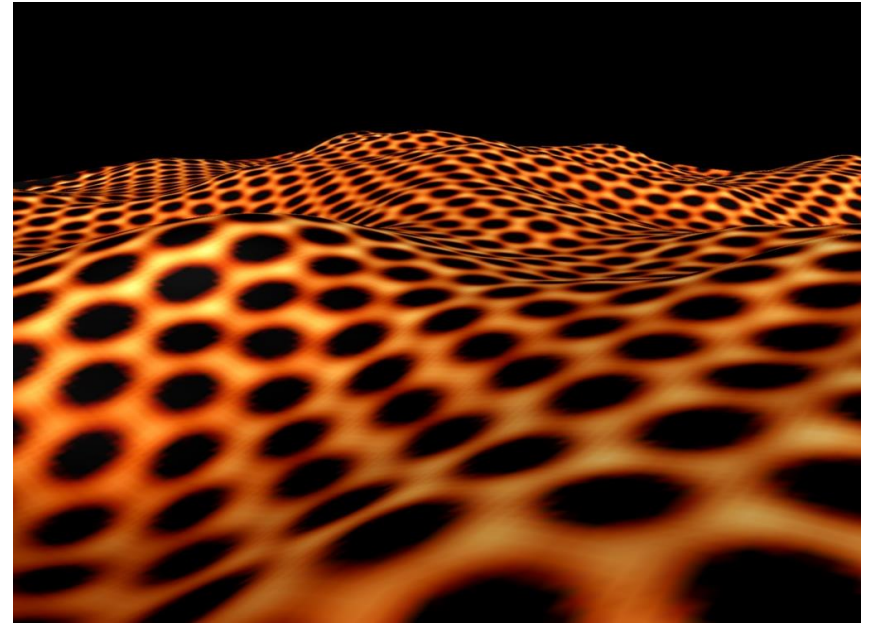SiC background subtracted

Integrated intensity of 2D peak
Bright = ML graphene

S. Goler *et al.*

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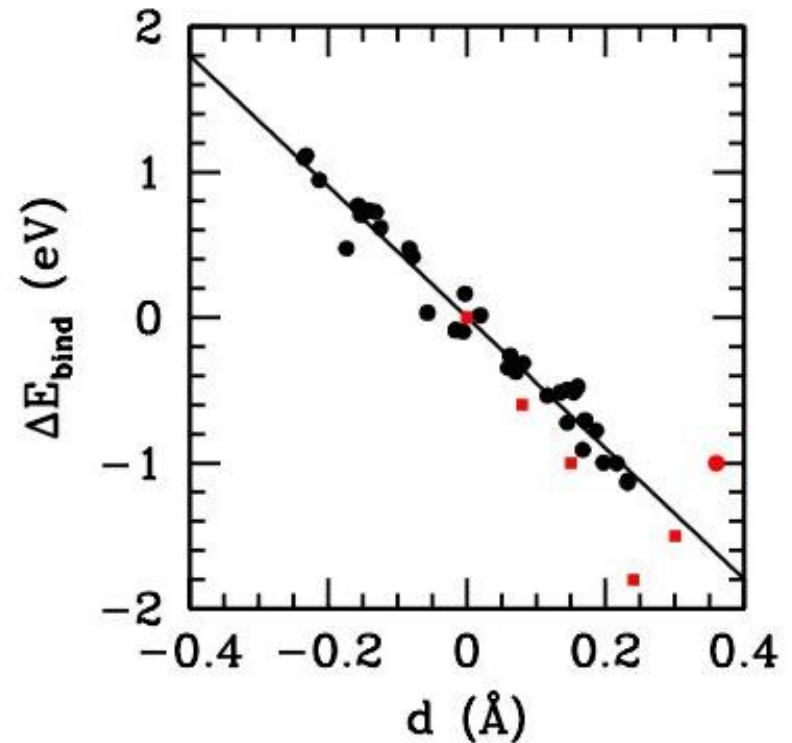
- Hydrogen Storage by Functionalization

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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).

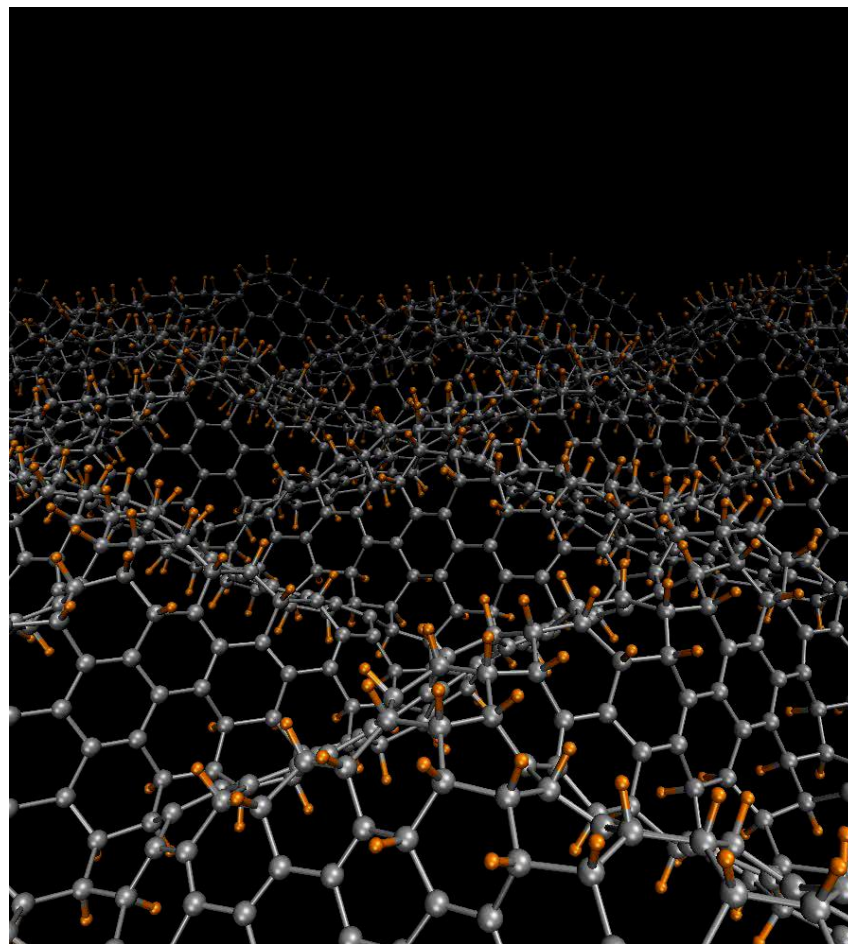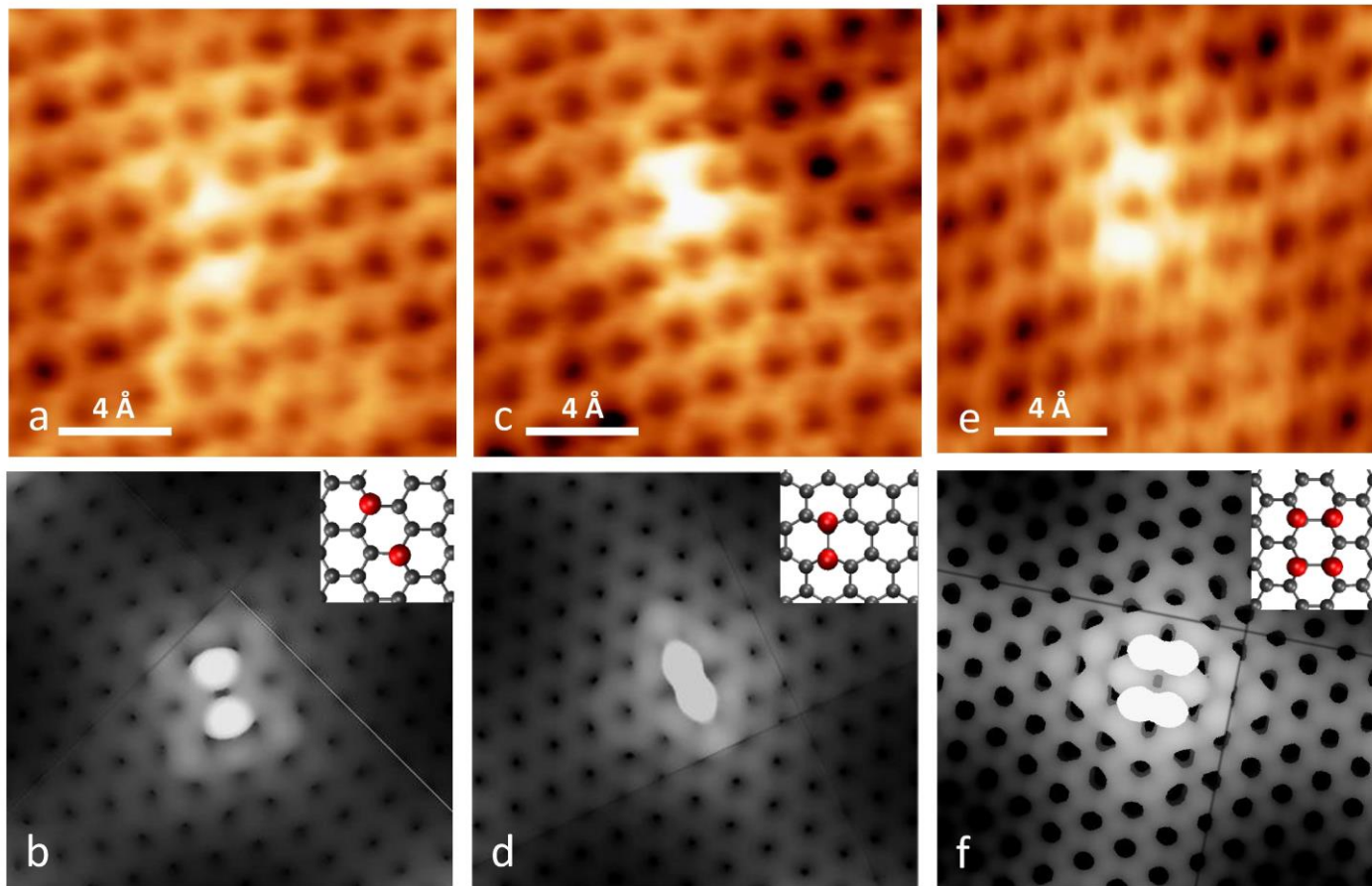National Enterprise for nanoScience and nanoTechnology

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).

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Graphene Curvature

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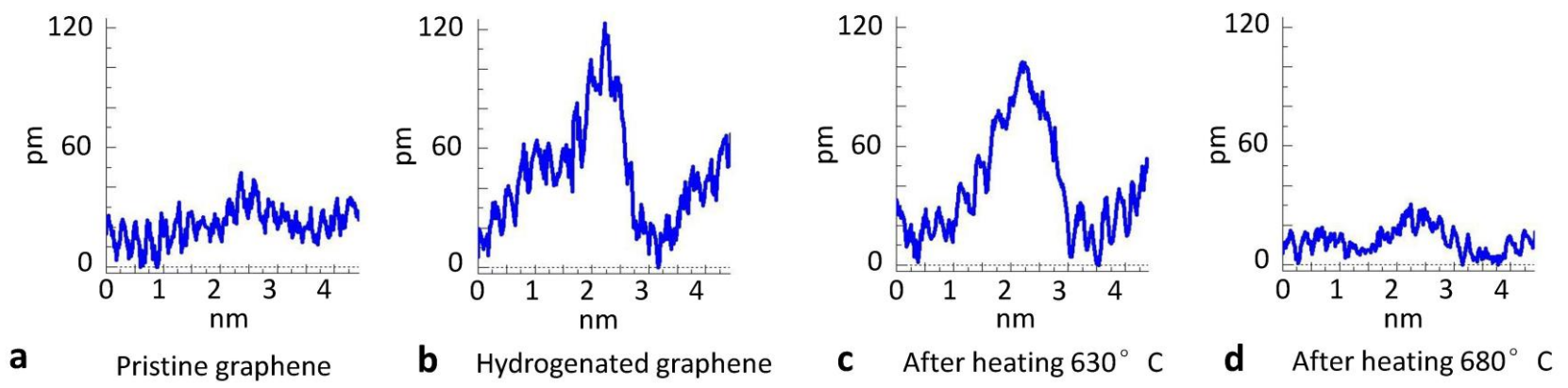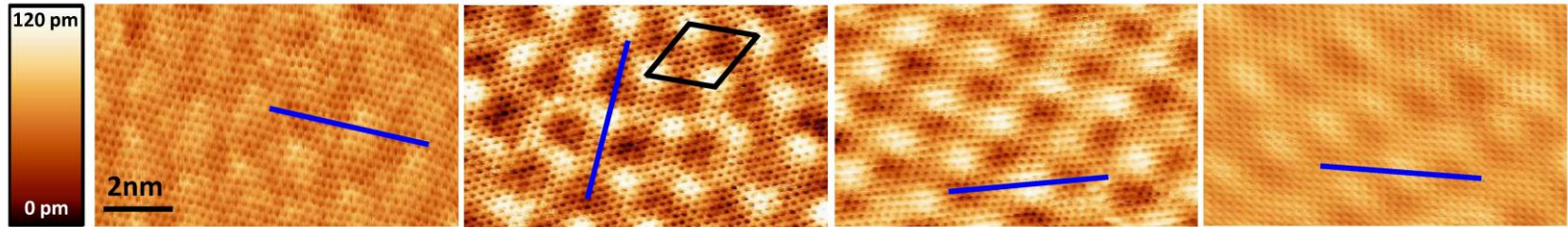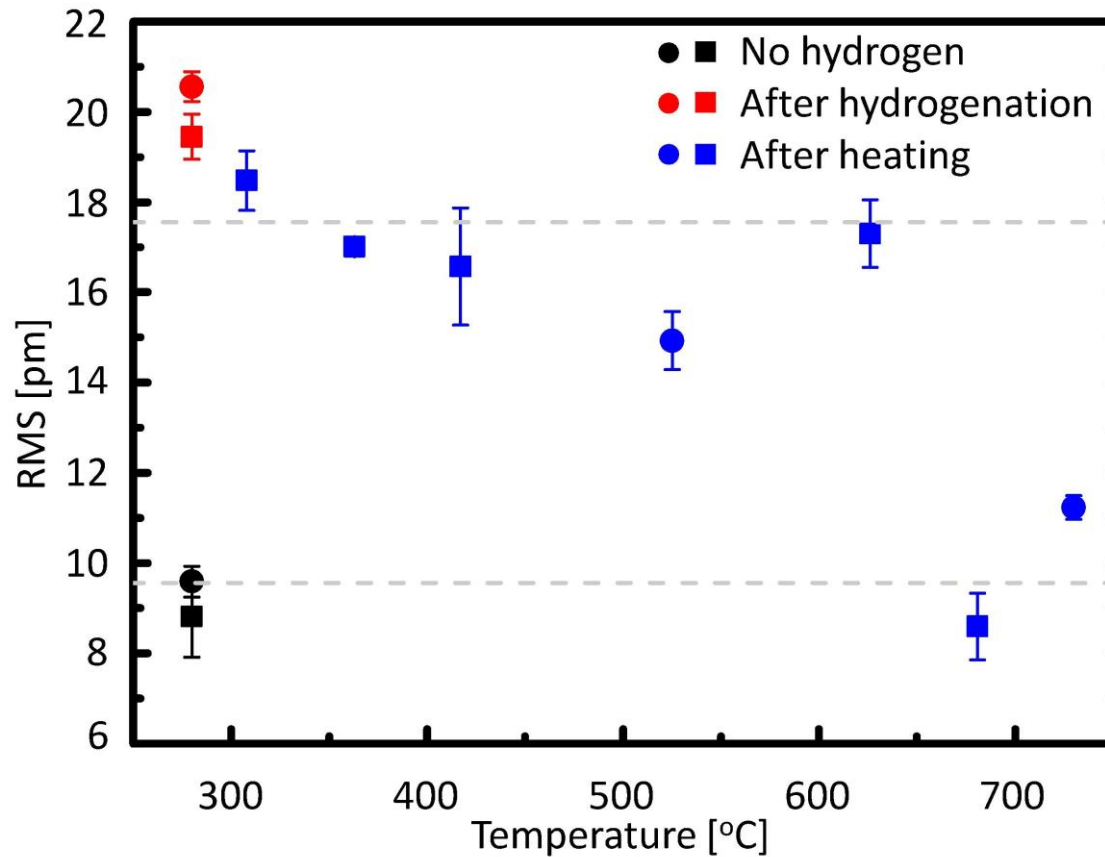- Atomic hydrogen spontaneously sticks on convex parts; inverting curvature H is expelled

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

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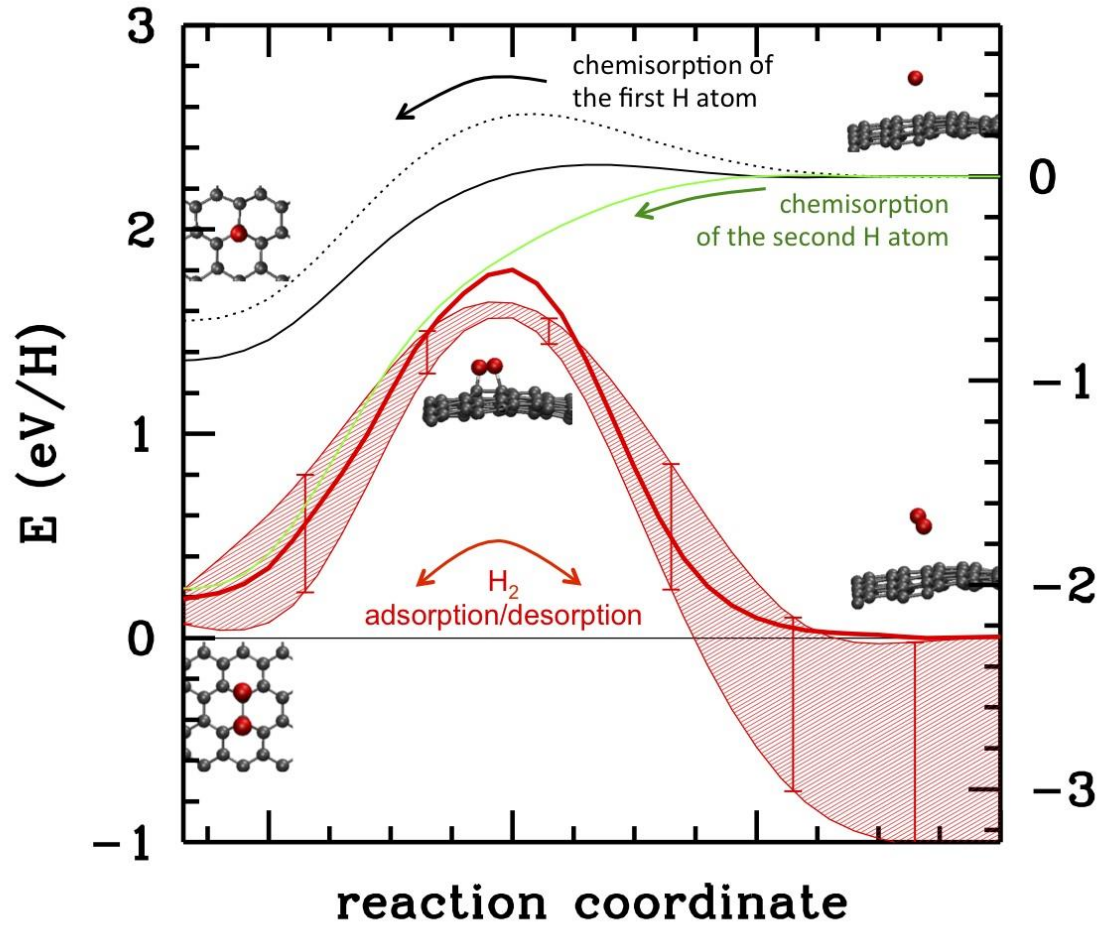
H-dimers and tetramers

Para-dimer   Ortho-dimer   Tetramer

S. Goler *et al.*

H adsorption and desorption

a   Pristine graphene
b   Hydrogenated graphene
c   After heating 630°C
d   After heating 680°C

S. Goler *et al.*

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RMS roughness

S. Goler *et al.*

DFT calculations

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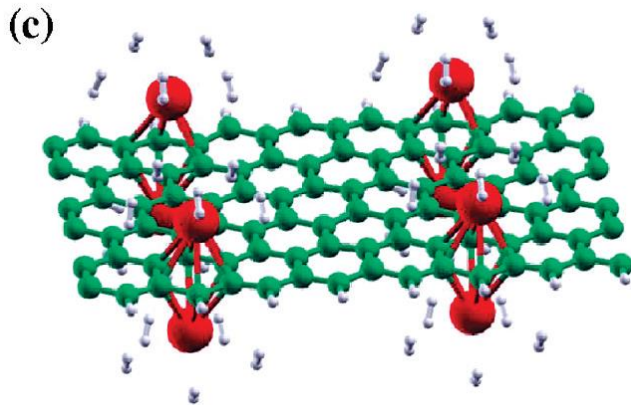
- **Hydrogen Storage by Functionalization**

  In collaboration with M. Takamura, S. Tanabe, H. Hibino
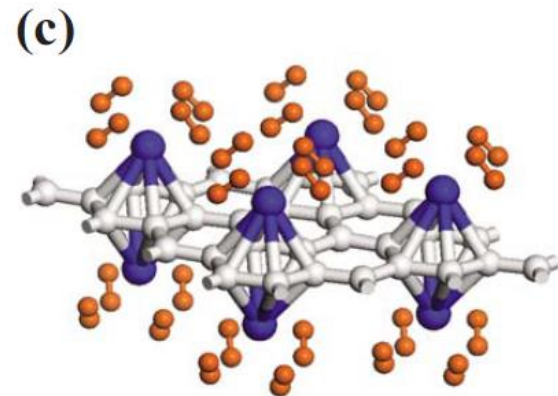 **NTT** Basic Research Laboratories, Atsugi, Japan

Functionalized Graphene

- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen

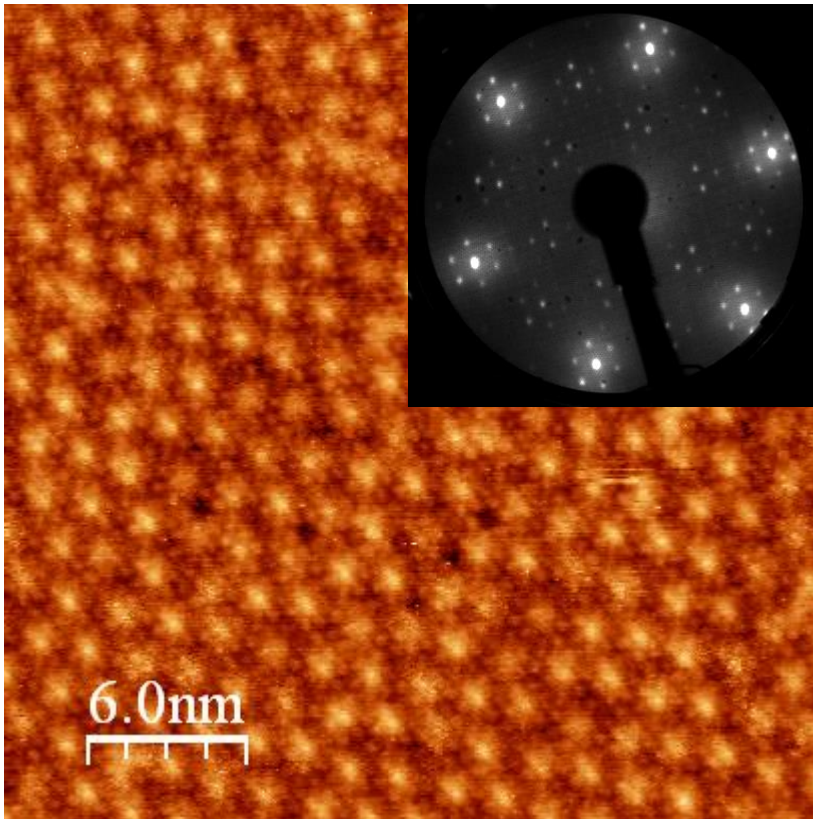- Modify graphene with various chemical species, such as calcium or transition metals (Titanium)

(c)

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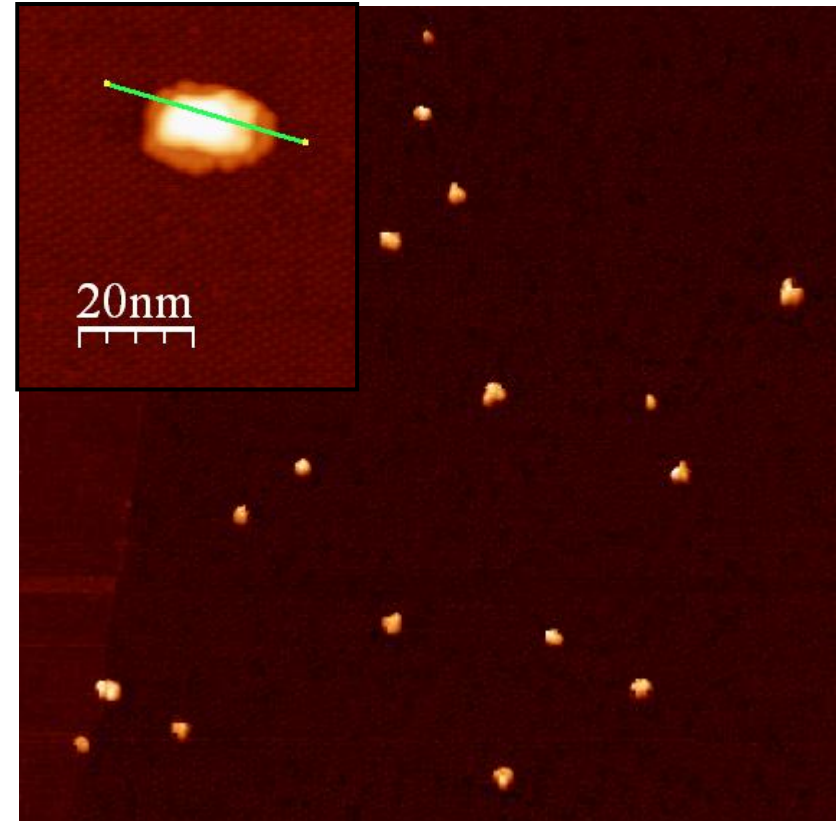

(c)

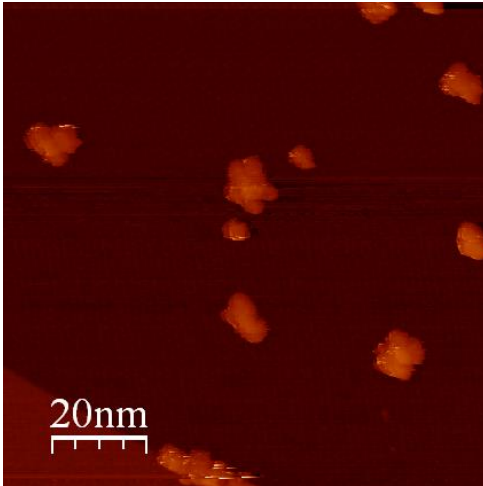Durgen et al., PRB 77 (2007) 085405

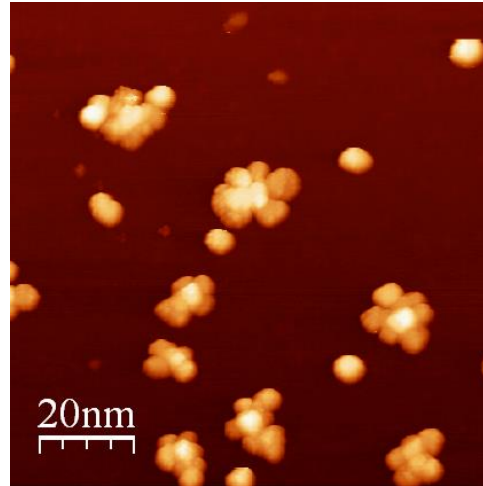# Titanium on graphene

ML graphene on SiC(0001)
with reconstruction

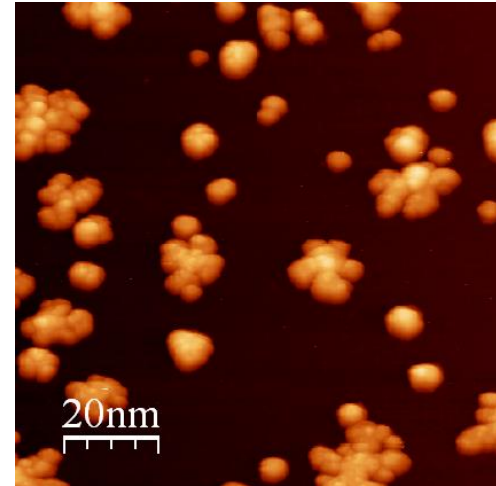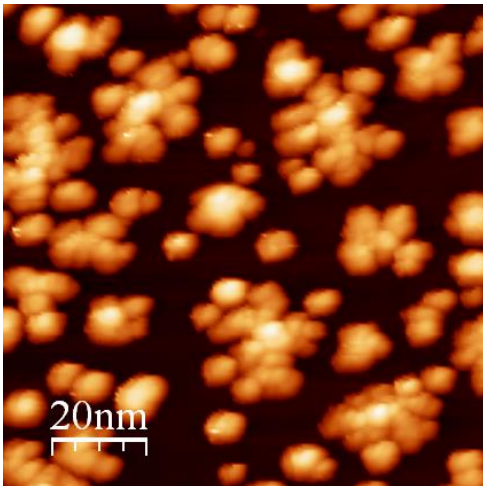After deposition of Ti at RT

T. Mashoff *et al.*

Titanium island growth
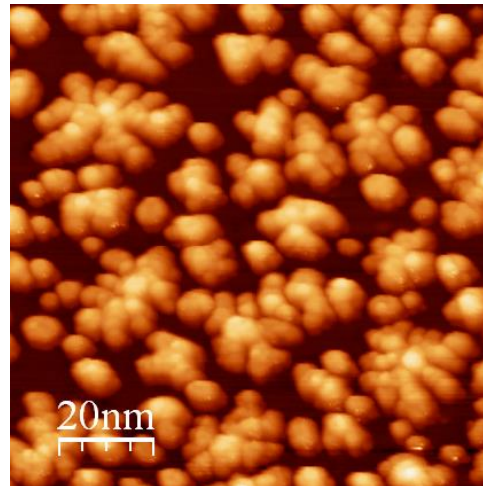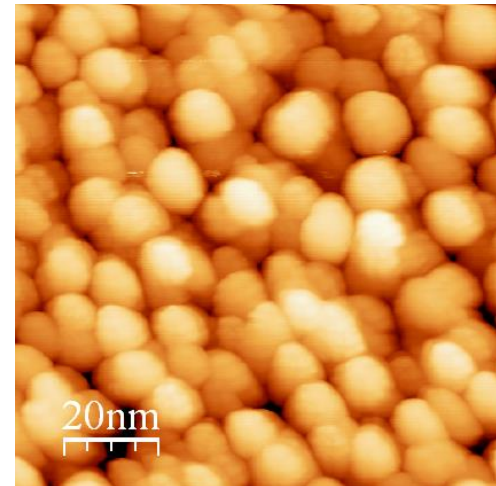

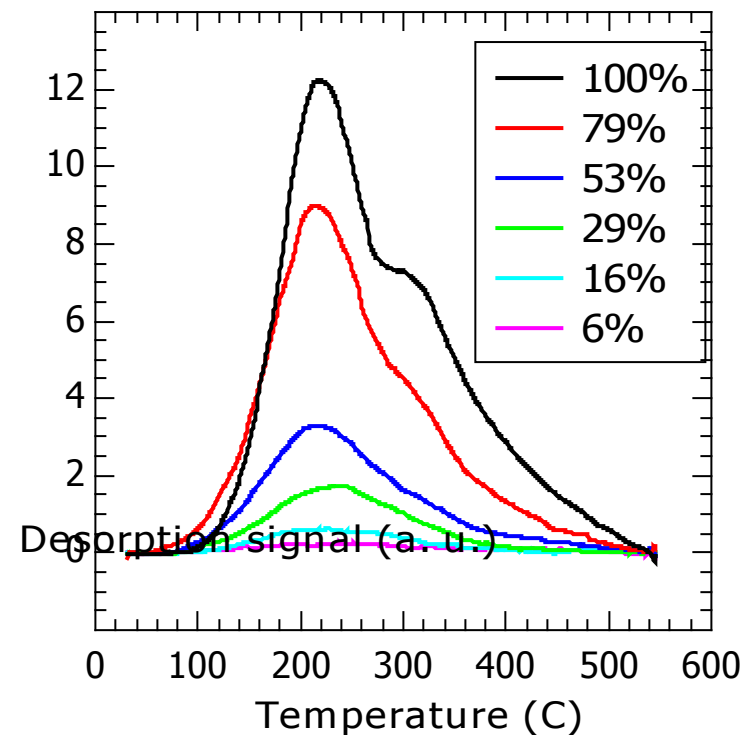6% Coverage

16% Coverage

29% Coverage

53% Coverage

79% Coverage

100% Coverage

Thermal desorption spectroscopy

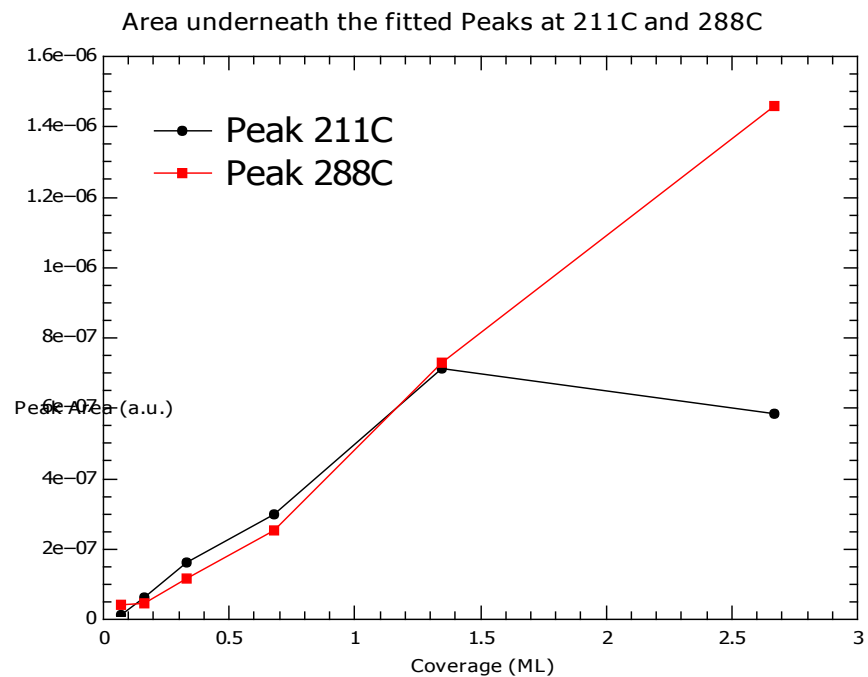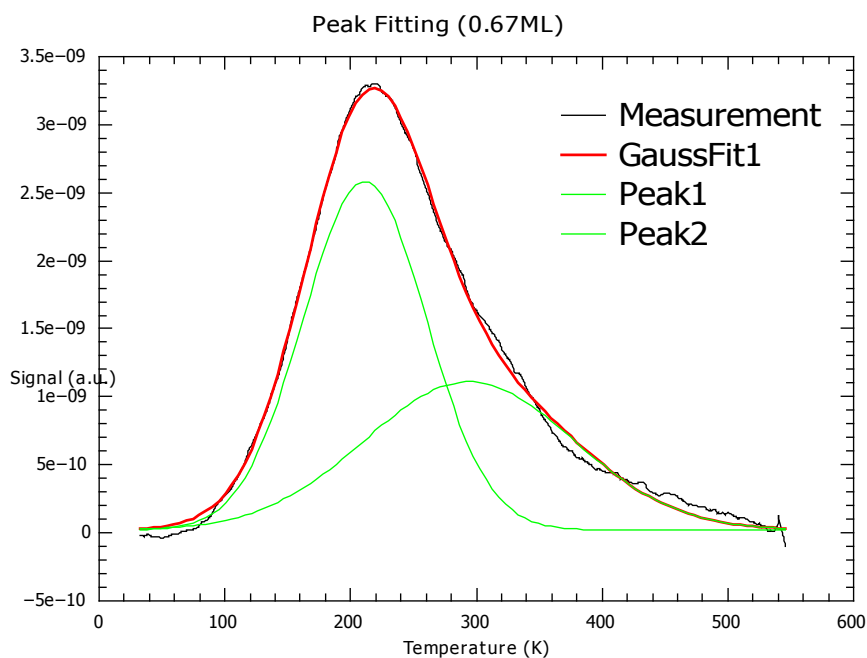- Deposition of different amounts of Titanium
- Offering Hydrogen (D_2)
- (1×10^{-7} mbar for 5 min)
- Heating sample with constant rate (10K/s) up to 550° C
- Measuring mass-sensitive desorption with a mass spectrometer

Spectra for different Ti-coverages

Desorption signal (a. u.)

Temperature (C)

Legend:
- 100%
- 79%
- 53%
- 29%
- 16%
- 6%

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TDS peak intensity

Peak fitting

Peak Fitting (0.67ML)

Area underneath the fitted Peaks at 211C and 288C

All curves could be fitted nicely
with 2 peaks at 211C and 288 C

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

National Enterprise for nanoScience and nanoTechnology