Immagazzinamento di idrogeno in materiali 2D e 3D basati su grafene

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National Enterprise for nanoScience and nanoTechnology

NEST

Outline

- Introduction to Hydrogen Storage
- Hydrogen Storage on Graphene by Chemisorption
- Hydrogen Storage on Graphene by Physisorption
- New Materials

Outline

- Introduction to Hydrogen Storage
- Hydro
  Chem
- Hydro
  Physi

It is conventionally accepted that the energetic threshold separating the binding energy of "physisorption" from that of "chemisorption" is about 0.5 eV per adsorbed species.

Source: Wikipedia

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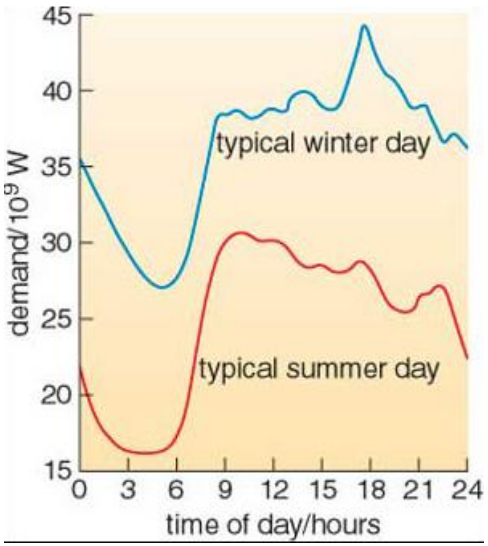
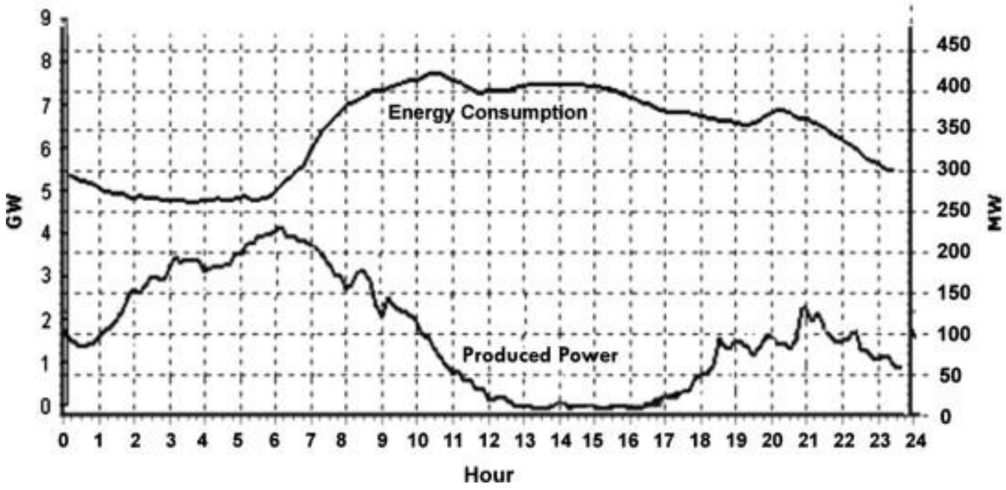
Renewable Energies

Renewable Energies

Renewable energy suffer from intermittency of supply

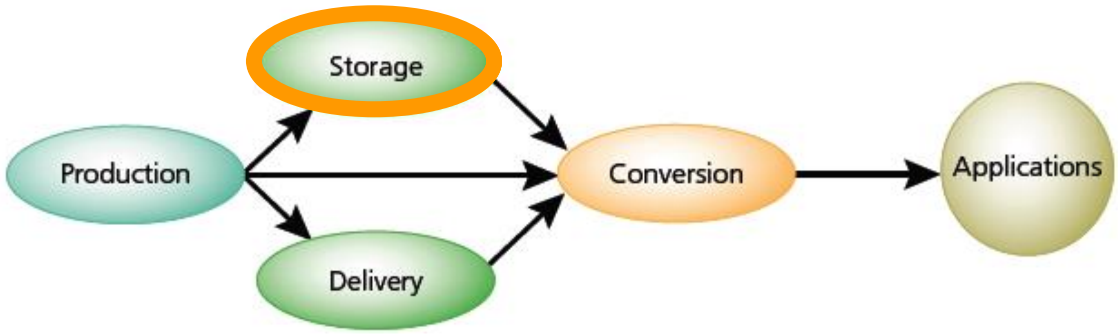
Wind Power does not allow electricity to be produced when it is most needed, i.e. when demand is highest.





Applied Energy (2010), 87(8), 2581–2588.

Renewable Energies



Renewable energy suffers from intermittency of supply

Wind Power does not allow electricity to be produced when it is most needed, i.e. when demand is highest

Energy Storage in a safe and cheap way is **a critical issue**

Energy Storage

- Storage of Potential Energy (Water)

Energy Storage

- Storage of Potential Energy (Water)
- Electrochemical Storage (Batteries)

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Energy Storage

- Storage of Potential Energy (Water)
- Electrochemical Storage (Batteries)
- Electrical Storage (Supercapacitors)

Energy Storage

- Storage of Potential Energ
- Electrochemical Storage (
- Electrical Storage (Superc
- Heat Storage (Water, Salt)

Latentwärmespeicher im Testbetrieb in Carboneras, Spanien (14 t $NaNO_3$, Phasenwechsel bei 305 °C)

Energy Storage

- Storage of Potent
- Electrochemical S
- Electrical Storage
- Heat Storage (Wa

- Chemical Storage (Hydrogen)

Energy Storage

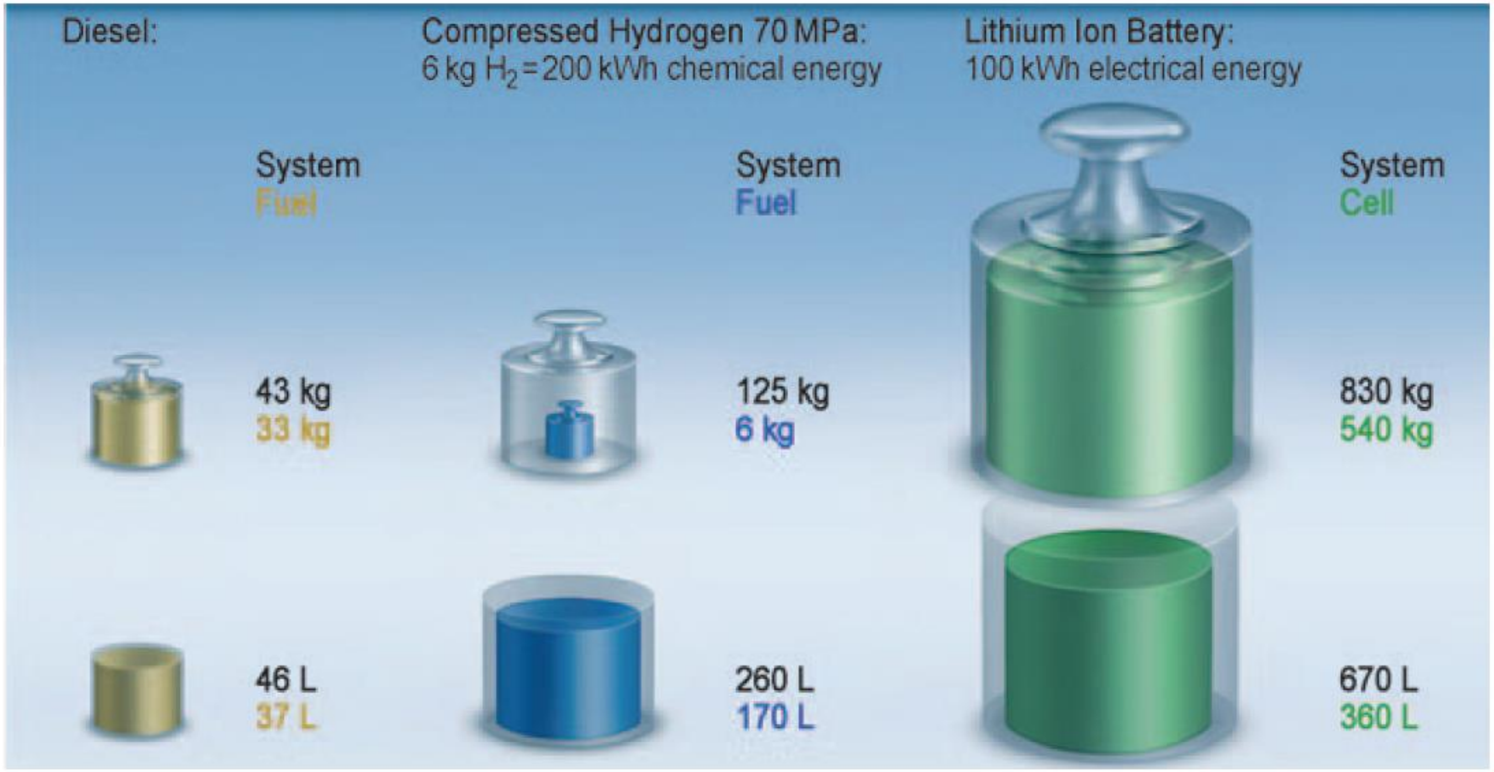

Figure 1. The weight and volume of various fuels and tank systems required for a 500 km range vehicle.

U. Eberle et al., Angew. Chem. Int. Ed. 2009, 48, 6608.

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Why Hydrogen?

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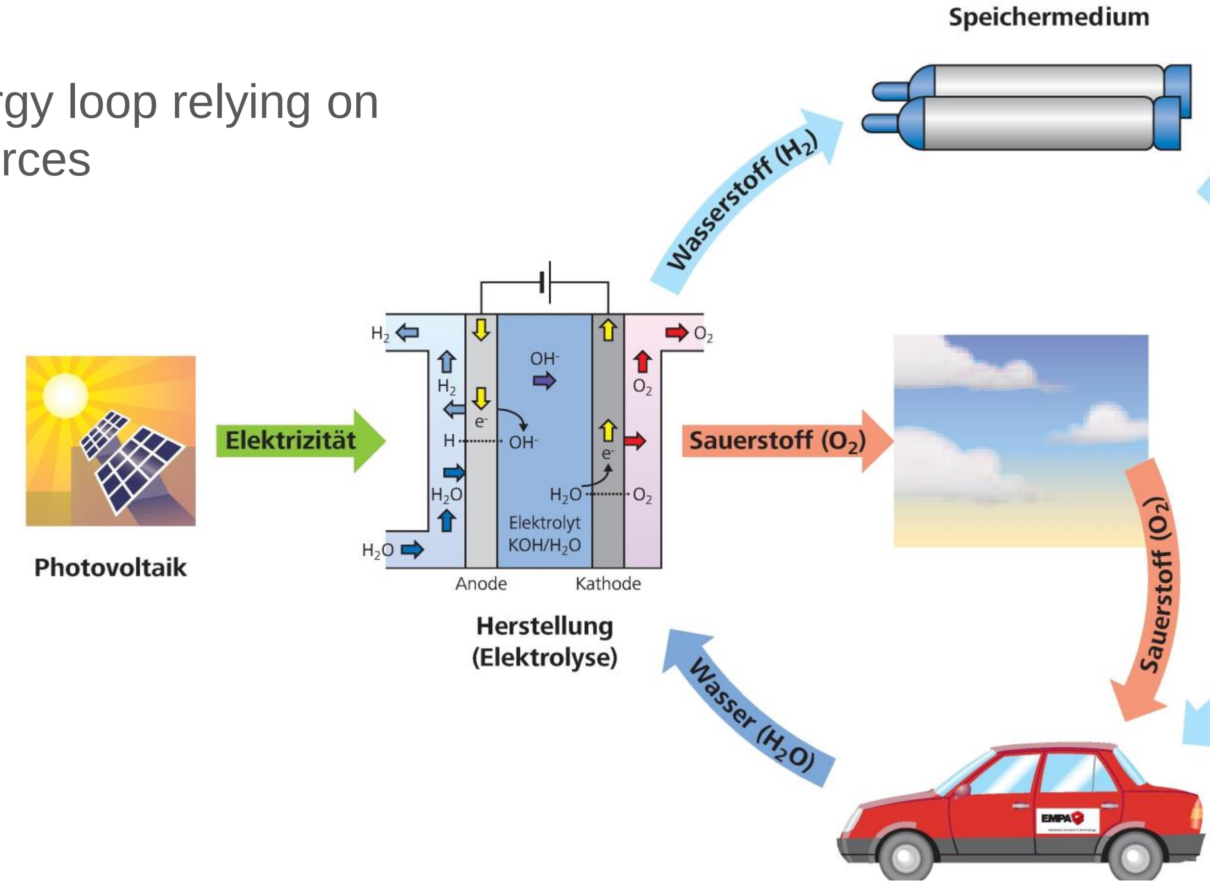
Hydrogen Life Cycle

Complete energy loop relying on renewable sources

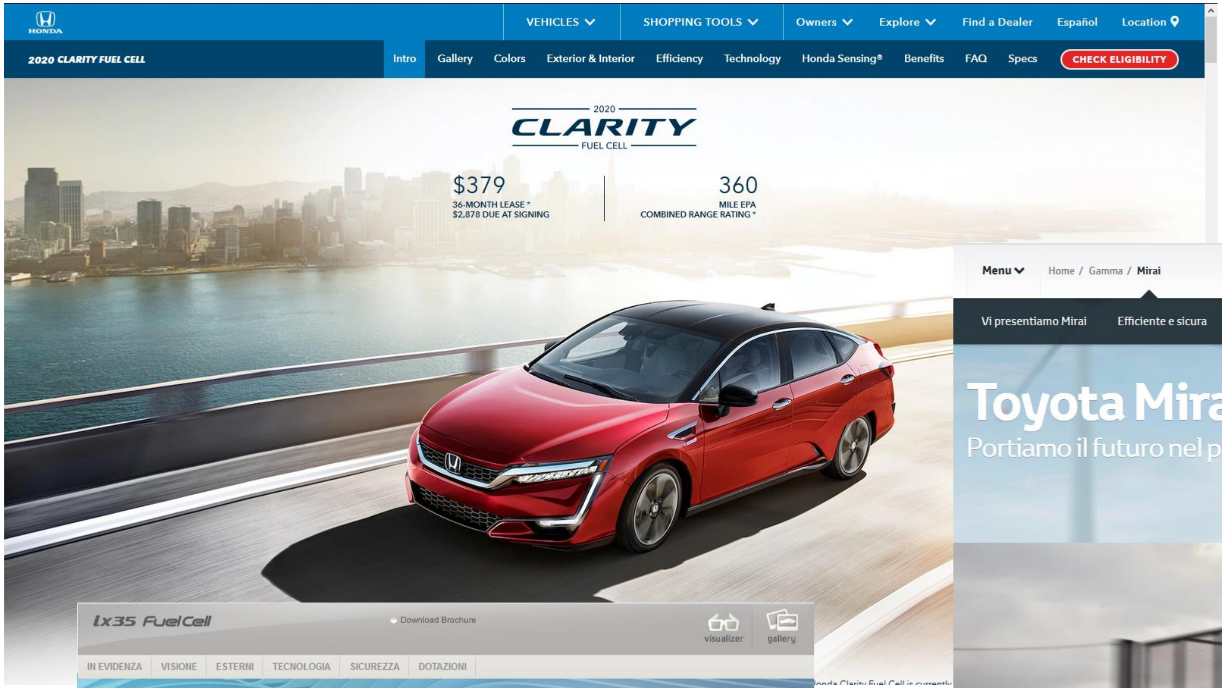


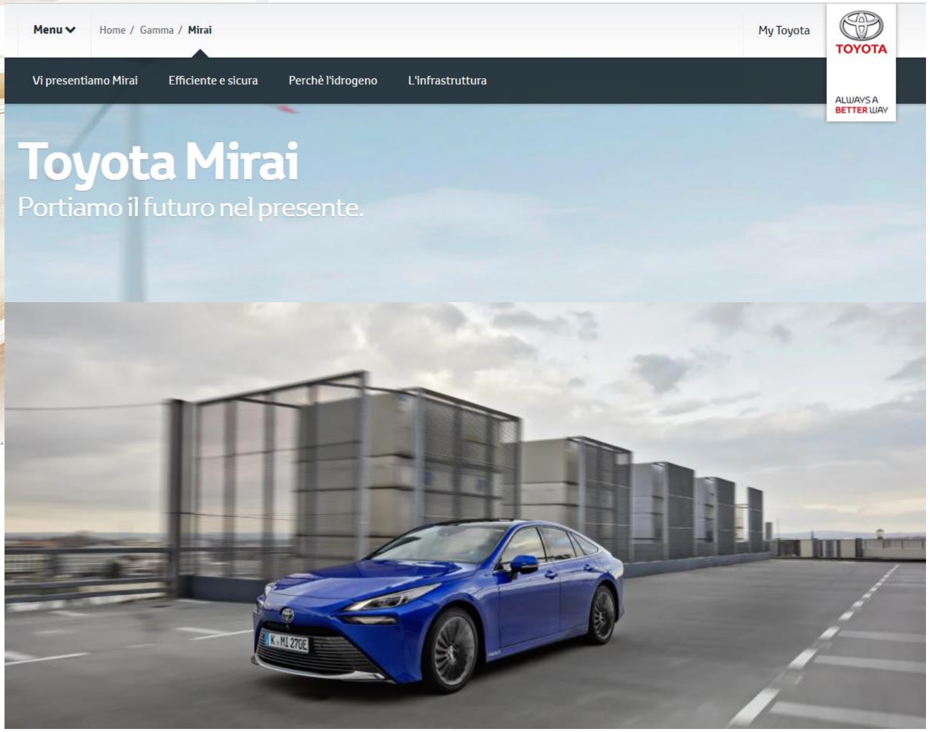
Hydrogen Storage in a safe and cheap way is **a critical issue**

Hydrogen-fuelled vehicles ....

… since the 1970s …

… now for sale





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Trucks and Buses

Hydrogen-fuelled Train

Die Züge werden elektrisch angetrieben. Die elektrische Energie wird an Bord in einer Brennstoffzelle erzeugt und in Batterien zwischengespeichert.

Coradia iLint regional train

Hydrogen-fuelled Airplane

Zero-emission air transport –
first flight of four-seat passenger aircraft HY4

29 September 2016

Airbus


AIRBUS
ZEROe
H2 energy
ZERO emission aircraft
ZEROe AIRBUS
H2 powered
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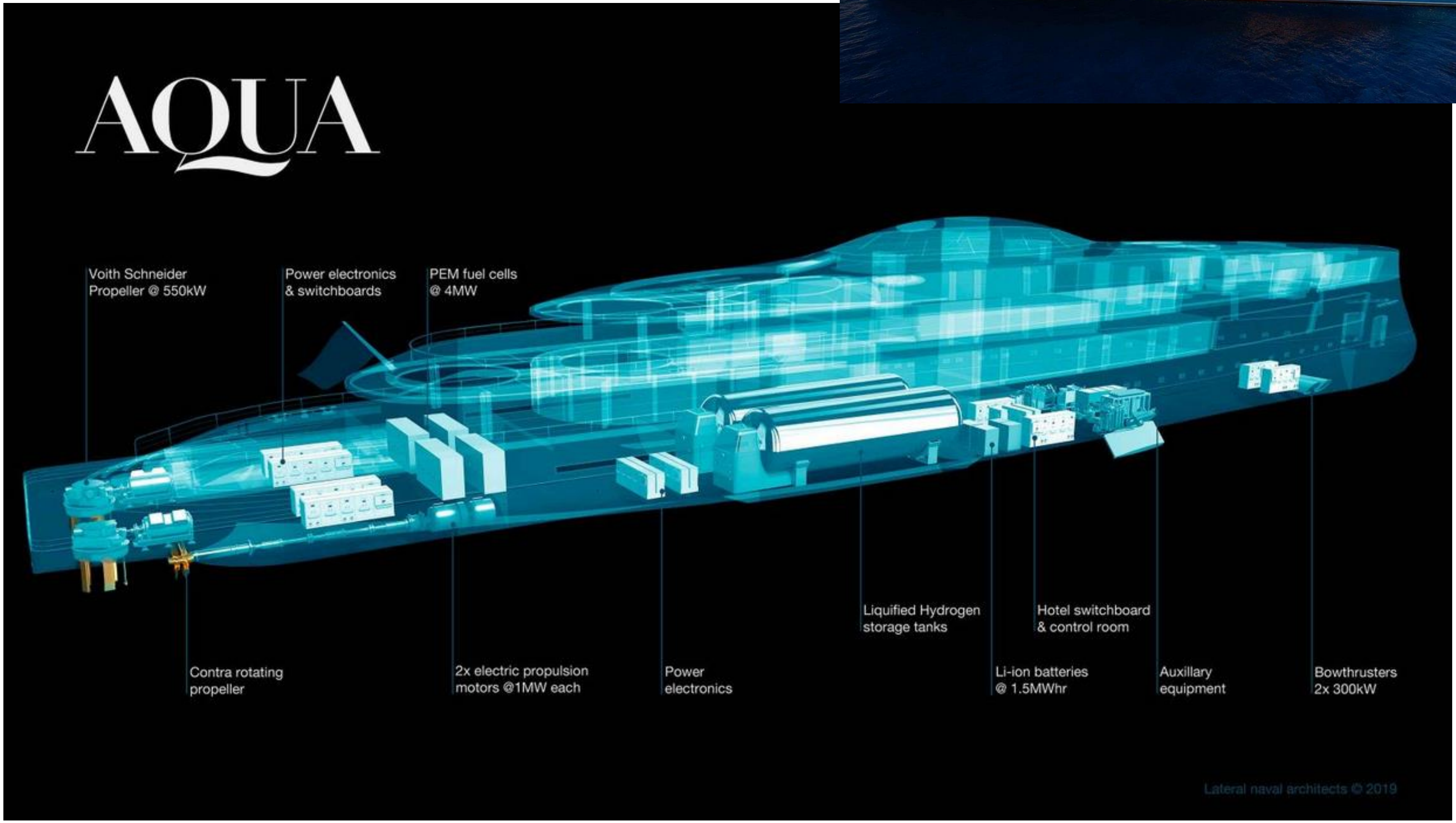
Yacht

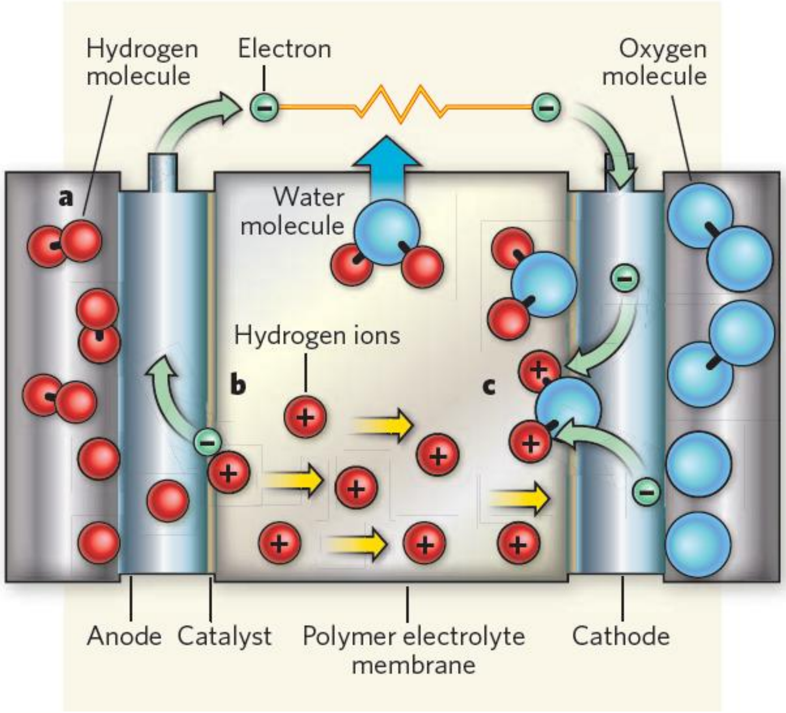


https://sinot.com/

Hydrogen & energy

As a fuel, hydrogen has advantages:

- Highest energy-to-mass ratio
- $H_2 + 1/2\ O_2 \rightarrow H_2O$ $\Delta H = -2.96eV$
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency



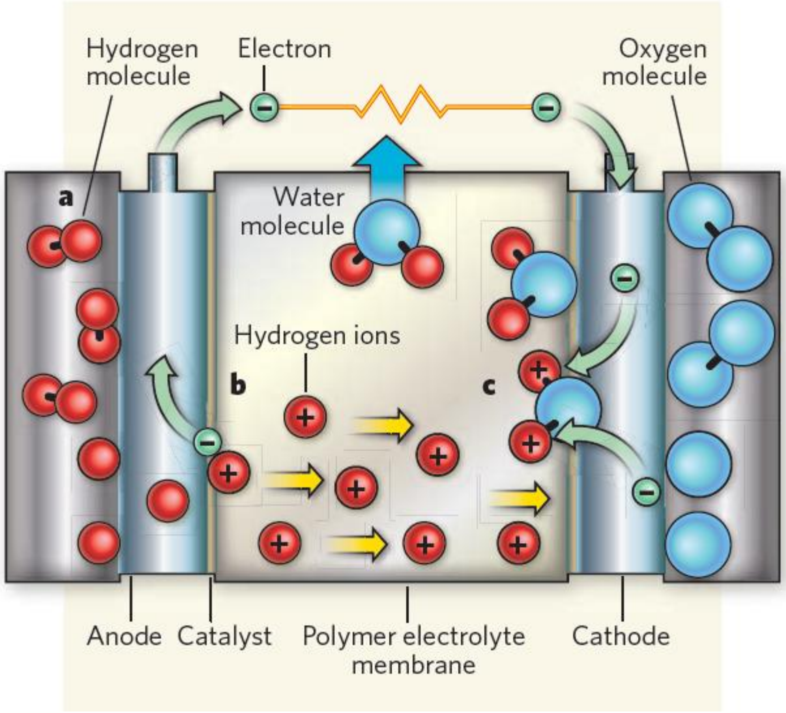
Hydrogen fuel cell

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 & energy

Hydrogen is an energy carrier (such as electricity) and its advantages must be considered with respect to storage and transportation devices

- ❖High energy storage capacity ✓
- ❖Low dispersion (✓)
- ❖Easy and practical use in standard conditions (✓)
- ❖Safety (✓)



Hydrogen fuel cell

Graphene has potentially all of these properties

… but it better be safe

Hindenburg disaster, 1937, New Jersey (USA)

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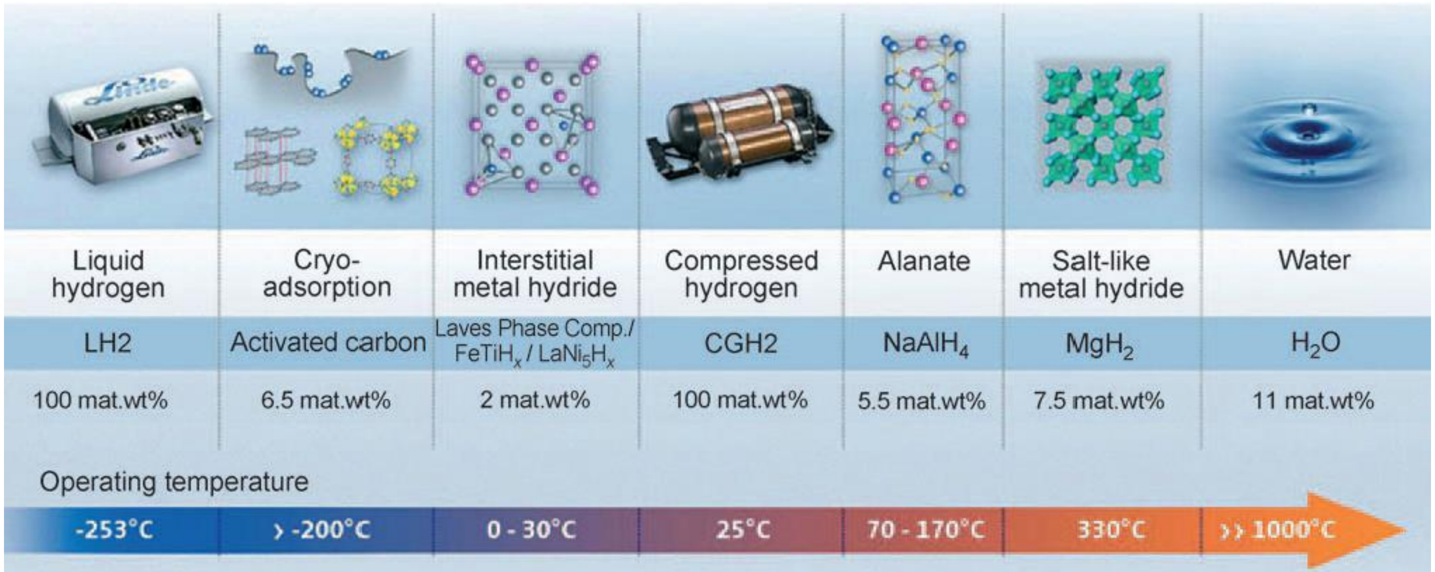
Hydrogen Storage

Hydrogen Storage



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

$\rho_m > 5.5$ wt%

$\rho_V > 50$ kg H_2 /m^3

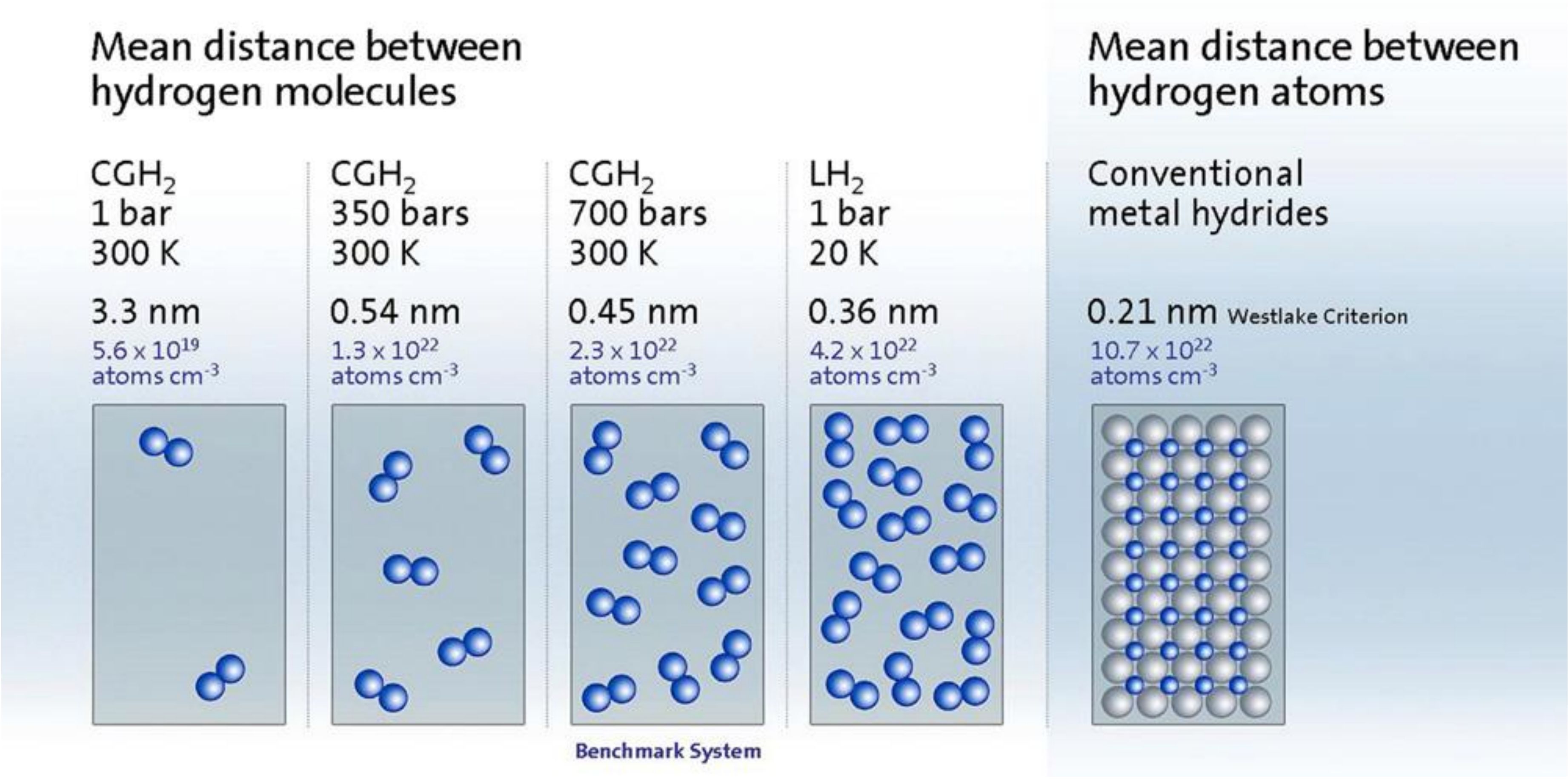
$P_{eq} \approx 1$bar at T< 100°C

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

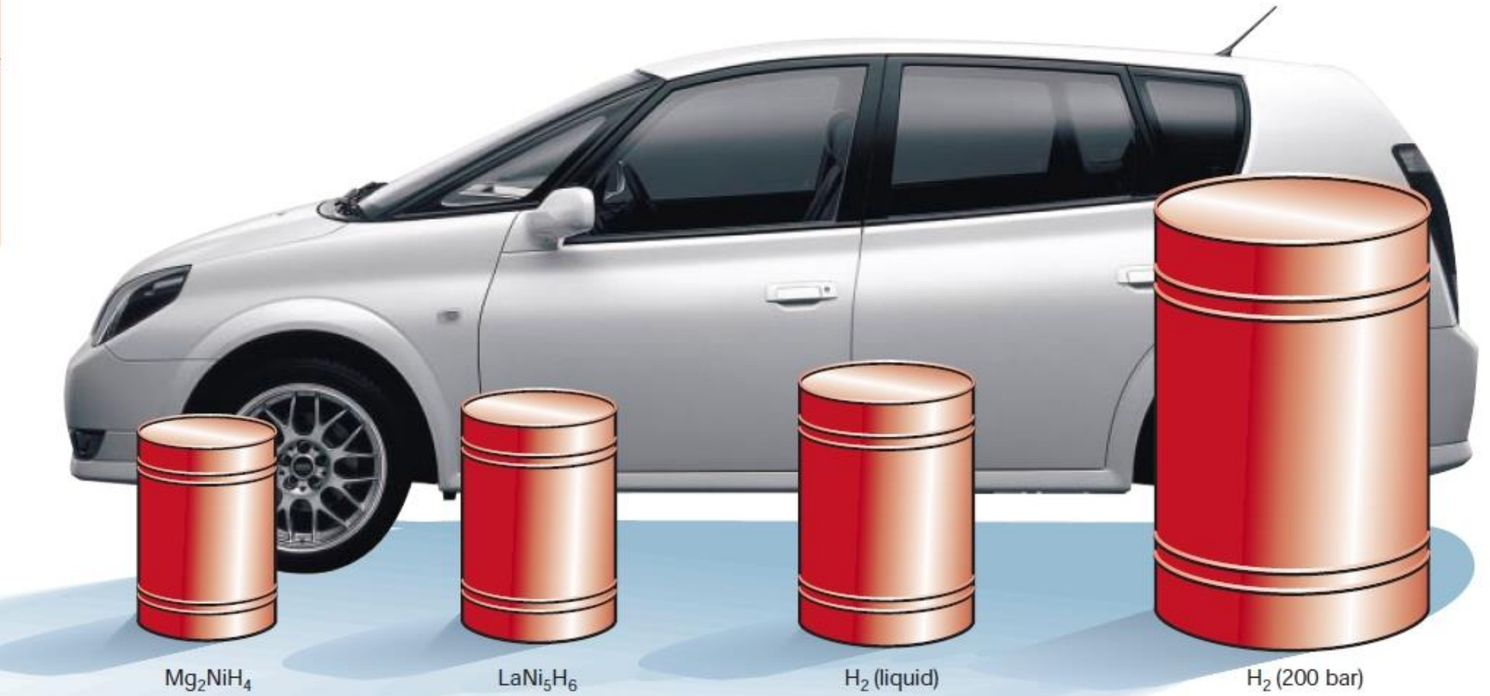
Hydrogen Storage



R. v. Helmolt, U. Eberle: J. Power Sources **165**, 833 (2007).

Hydrogen storage
On-Board a Vehicle

Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)



Storing hydrogen

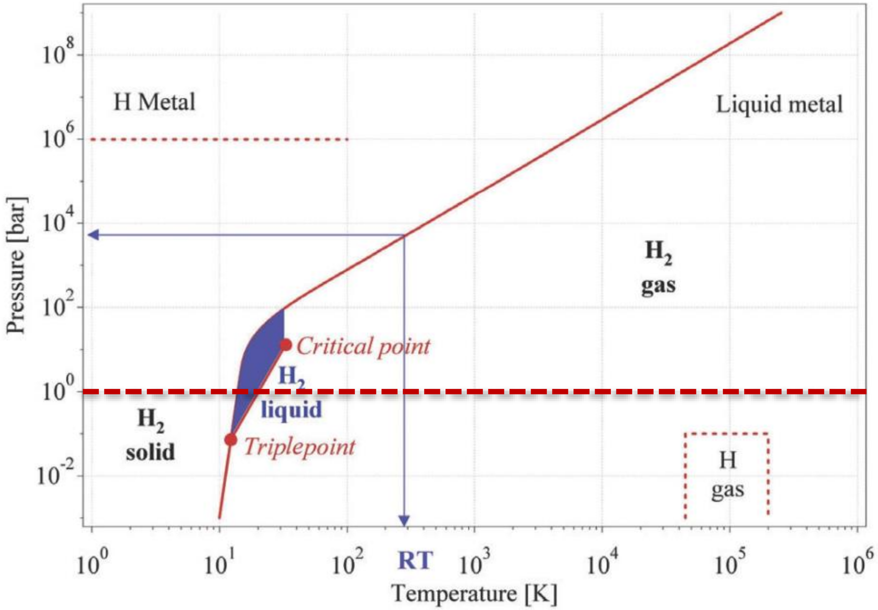


Fig. 1 Primitive phase diagram for hydrogen[46]. Liquid hydrogen only exists between the solidus line and the line from the triple point at 21.2 K and the critical point at 32 K.

A. Zuettel, Materials Today, 09/2003, p. 24

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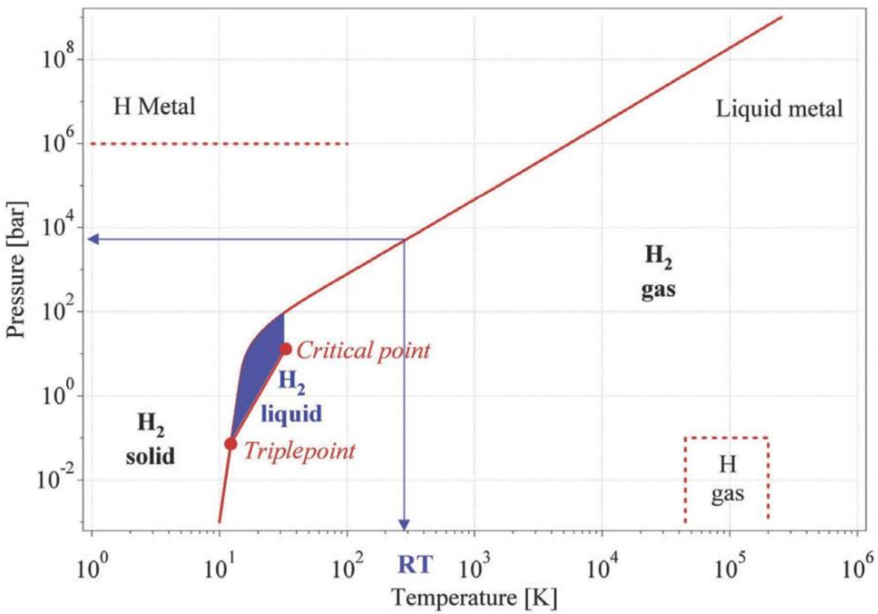
Storing hydrogen as a gas



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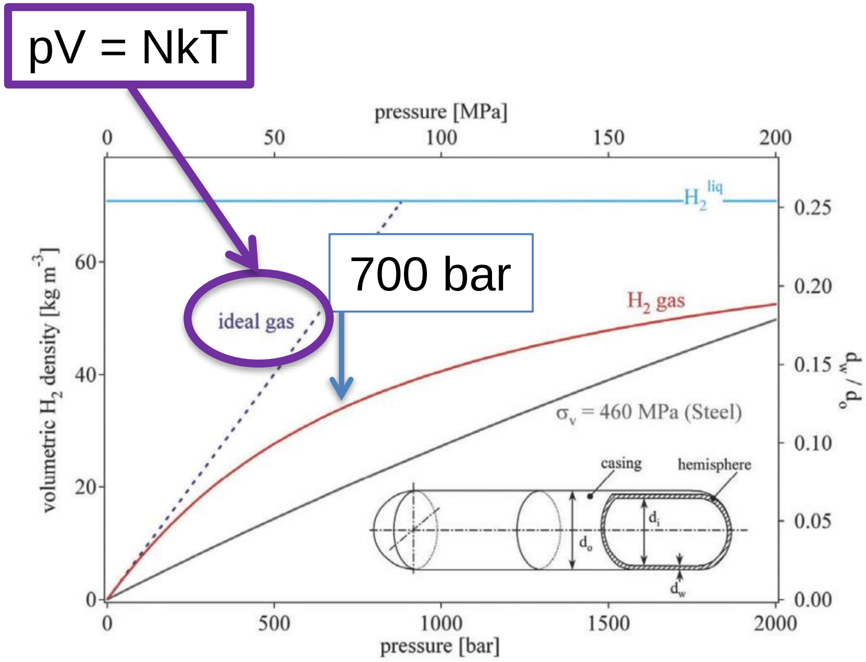

Fig. 2 Volumetric density of compressed hydrogen gas as a function of gas pressure, including the ideal gas and liquid hydrogen. The ratio of the wall thickness to the outer diameter of the pressure cylinder is shown on the right hand side for steel with a tensile strength of 460 MPa. A schematic drawing of the pressure cylinder is shown as an inset.

A. Zuettel, Materials Today, 09/2003, p. 24

Liquid hydrogen storage

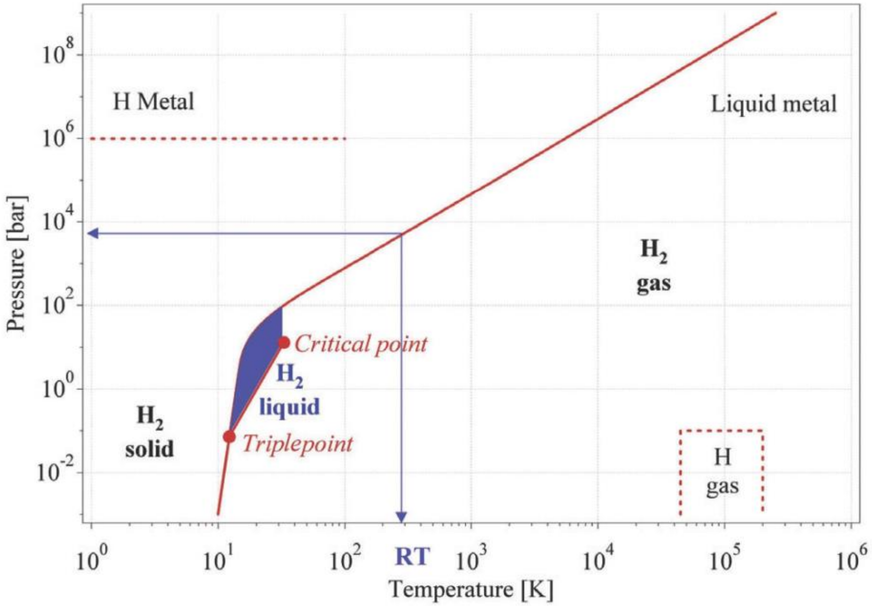

Fig. 1 Primitive phase diagram for hydrogen[46]. Liquid hydrogen only exists between the solidus line and the line from the triple point at 21.2 K and the critical point at 32 K.

- T = 21.2 K
- Ambient pressure
- Energy consumption to liquefy hydrogen:
  - Theo 3.23 kWh/kg
  - Technical 15.2 kWh/kg
  - 50% of hydrogen energy density
- Boil-off < 0.4% per day

A. Zuettel, Materials Today, 09/2003, p. 24

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Physisorption of hydrogen

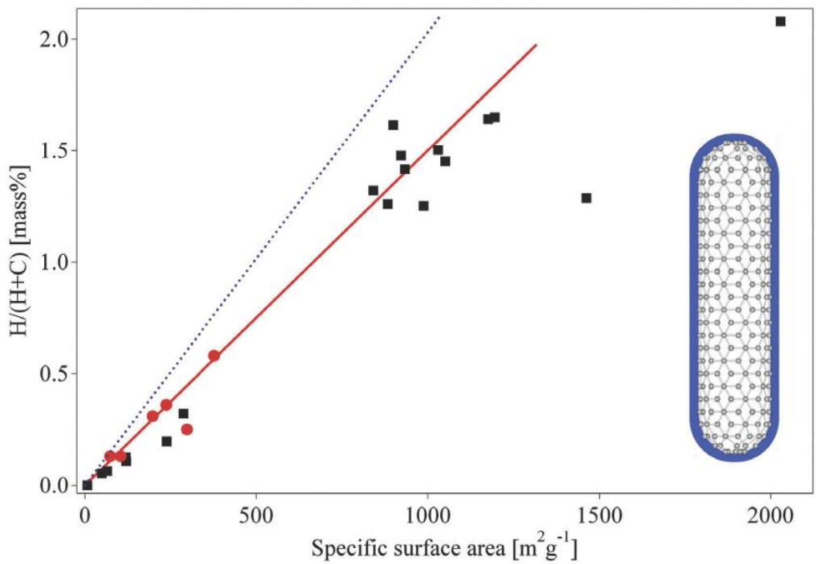

Fig. 3 Reversible amount of hydrogen adsorbed (electrochemical measurement at 298 K) versus the surface area (red circles) of a few CNT samples including two measurements on high surface area graphite (HSAG) samples together with the fitted line. Hydrogen gas adsorption measurements at 77 K from Nijkamp et al.[19] (black squares) are included. The dotted line represents the calculated amount of hydrogen in a monolayer at the surface of the substrate.

- Carbon nanomaterials
- Nanoporous materials (zeolites)
- Metal-organic frameworks
- Amount of adsorbed hydrogen proportional to specific surface area
- Low pressure, low cost, simple design
- Low temperatures (77K) required
- Low gravimetric and volumetric density

A. Zuettel, Materials Today, 09/2003, p. 24

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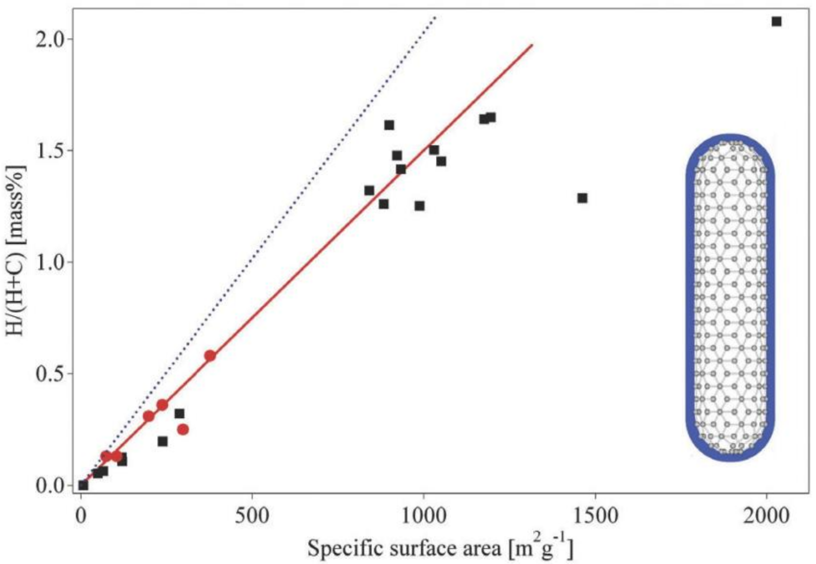
Physisorption of hydrogen



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- For storage at 77K:
- Heat of adsorption is ~2 MJ per kg of H_2.
- Store 5 kg of H_2: heat of 10 MJ is produced.
- Needs ~70 kg of LN_2 for cooling.

U. Eberle et al., Angew. Chem. Int. Ed. 2009, 48, 6608.

Graphene for Hydrogen Storage

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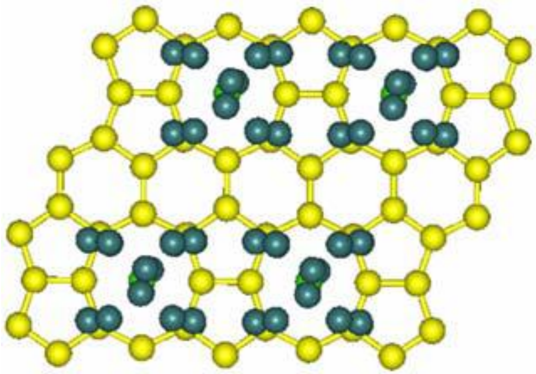
Graphene for hydrogen storage

- 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

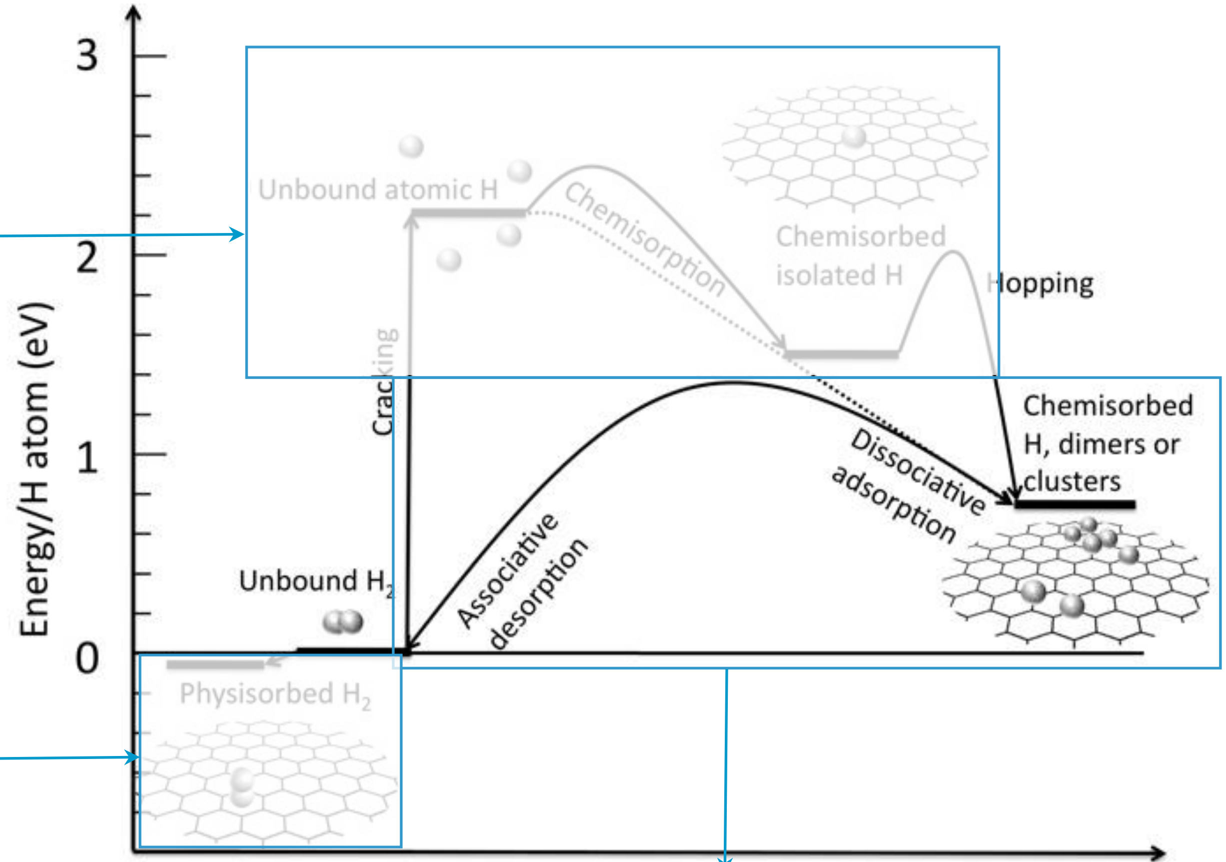
Graphene for hydrogen storage

- To store 4 kg of H_2, assuming ρ_m = 10 wt%, we need 40 kg of graphene.
- Graphene surface area: ~ 2600 m^2/g.
- 40 kg of graphene cover ~10^8 m^2 or 10 km x 10 km.
- Assuming a layer distance of 1 nm, we can put 10^9 graphene layers in a stack of 1 m height.
- Then in 1 m^3 we have 10^9 m^2 graphene.
- Thus, 40 kg of graphene would fit into a 100 liter tank.

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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- Hydrogen Storage on Graphene by Physisorption
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Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane

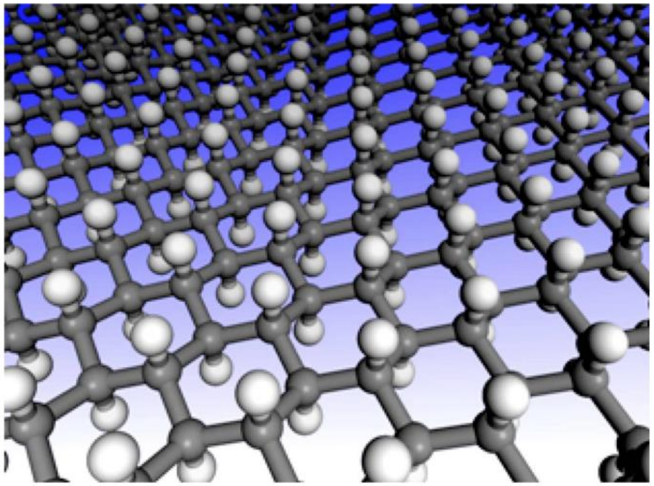
D. C. Elias,[1]* R. R. Nair,[1]* T. M. G. Mohiuddin,[1] S. V. Morozov,[2] P. Blake,[3] M. P. Halsall,[1] A. C. Ferrari,[4] D. W. Boukhvalov,[5] M. I. Katsnelson,[5] A. K. Geim,[1,3] K. S. Novoselov[1]†

Science **323** (2009) 610

PHYSICAL REVIEW B **75**, 153401 (2007)

Graphane: A two-dimensional hydrocarbon

Jorge O. Sofo,[1,2] Ajay S. Chaudhari,[1,2,*] and Greg D. Barber[2]
[1]*Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[2]*Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*
(Received 25 January 2007; published 10 April 2007)



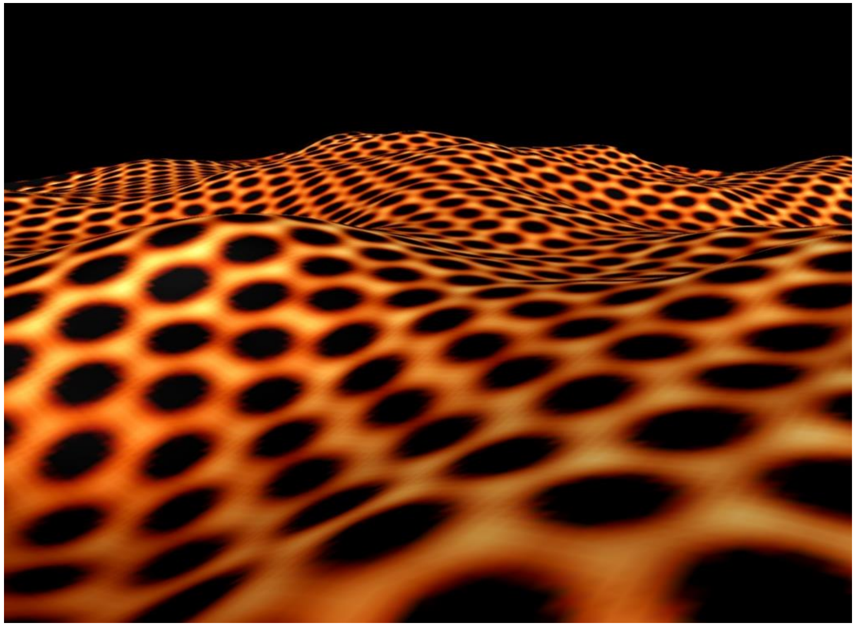
Theoretical (max.) hydrogen storage capacity:

1 H atom per 1 C atom

= 1 / (12+1) = 7.7 wt%

Graphene Curvature

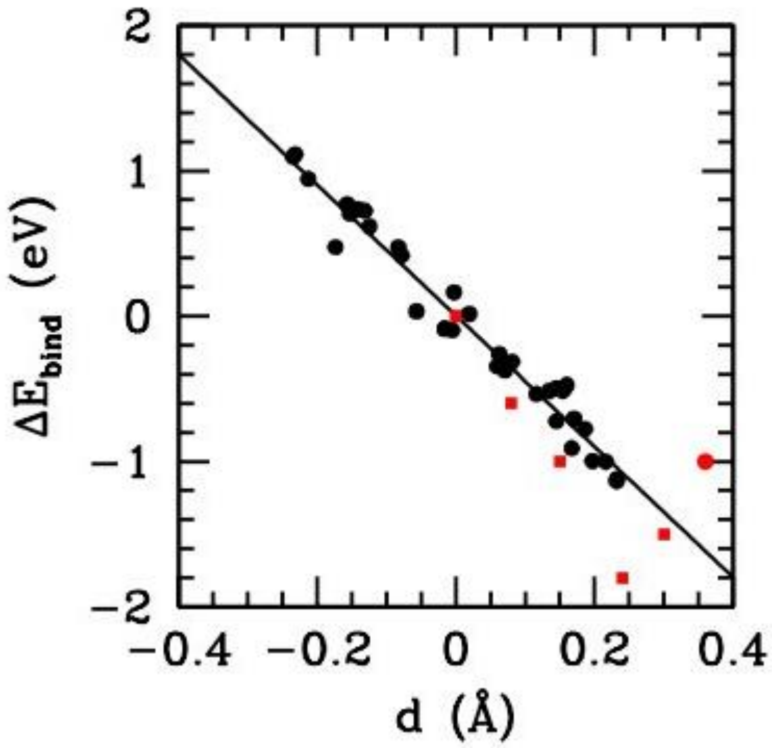
- Exploit graphene curvature for hydrogen storage at room temperature and pressure



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

Graphene Curvature

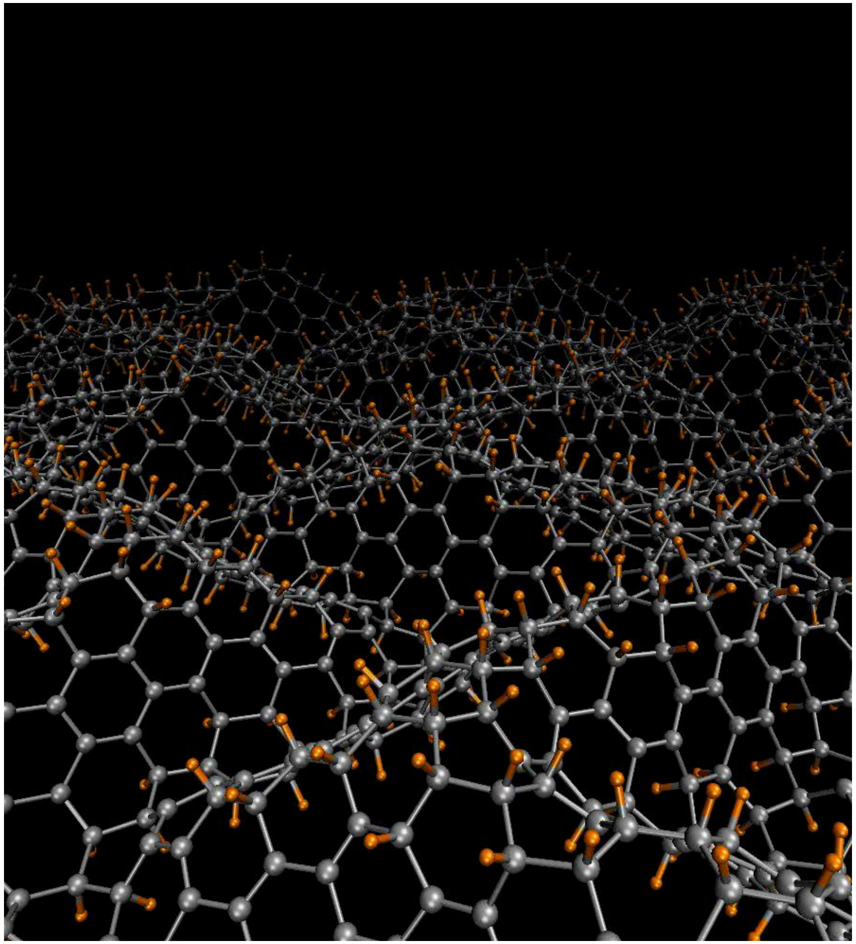
- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts



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

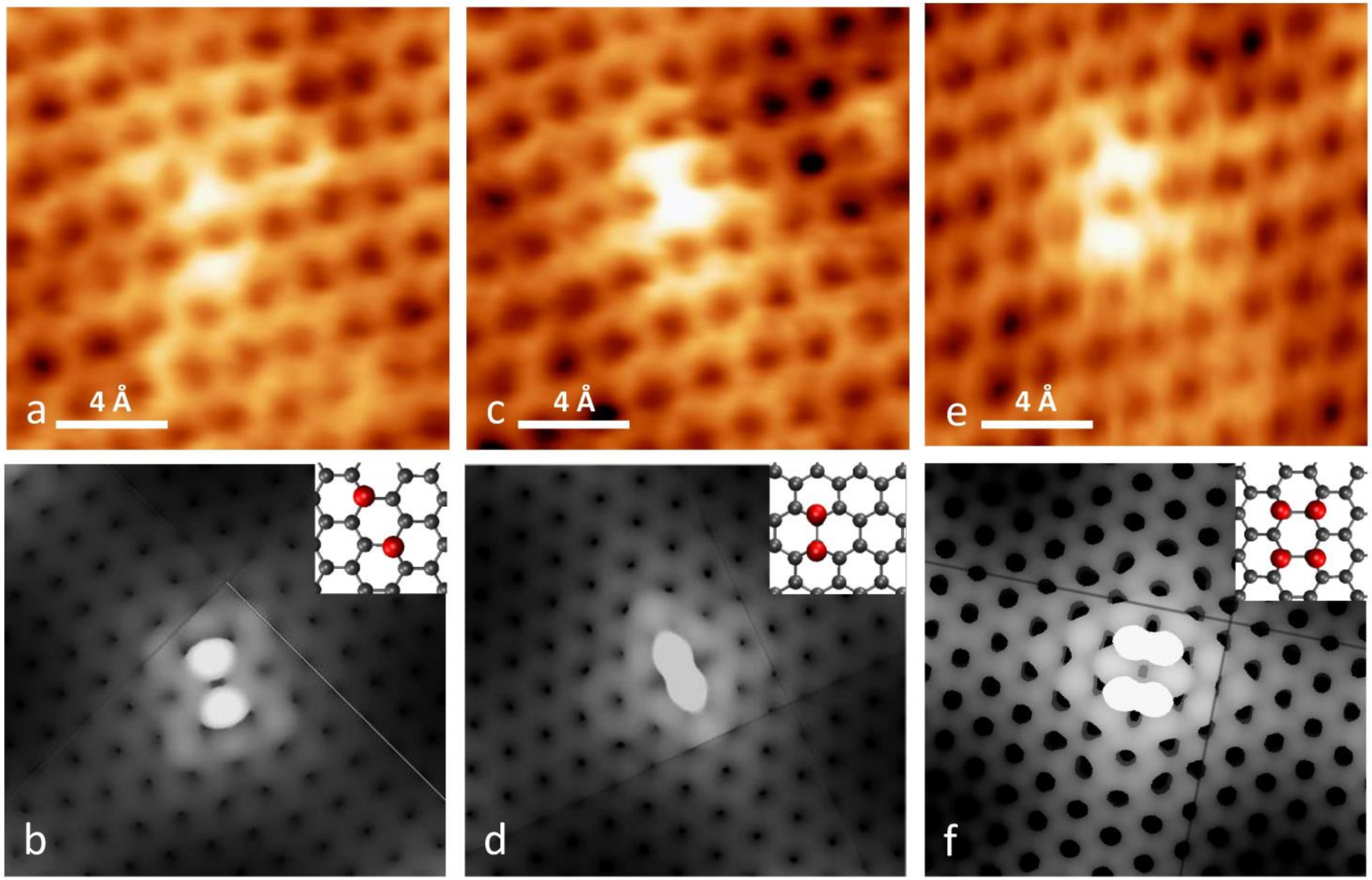


V. Tozzini and V. Pellegrini: J. Phys. Chem. C **115**, 25523 (2011).

Experimental Demonstration

Part I: Site-selective adsorption of hydrogen on convex regions

H-dimers and tetramers



Para-dimer Ortho-dimer Tetramer

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

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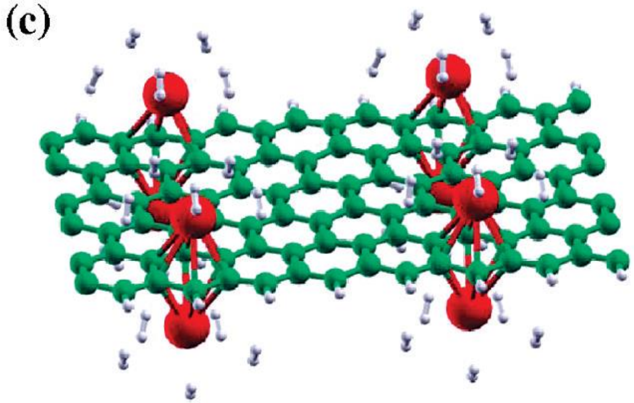
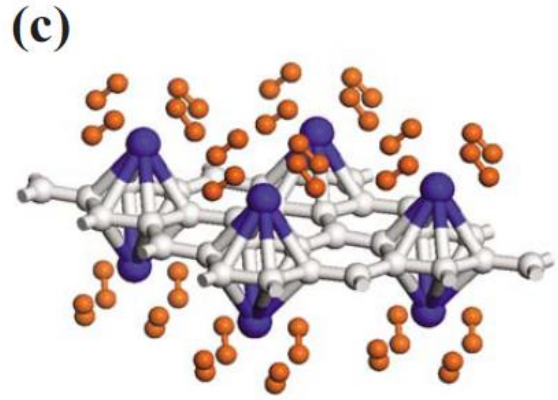
Functionalized Graphene

- 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

THE JOURNAL OF PHYSICAL CHEMISTRY C
ARTICLE
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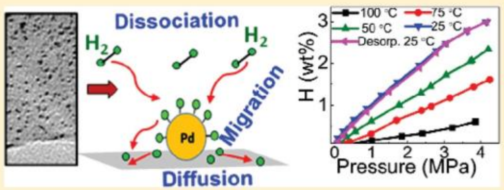
Investigation of Spillover Mechanism in Palladium Decorated Hydrogen Exfoliated Functionalized Graphene

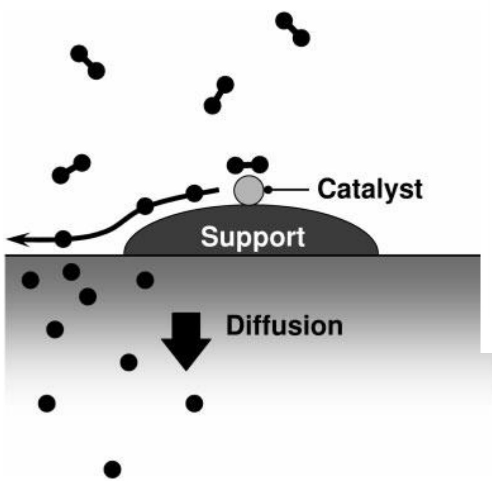
Vinayan Bhagavathi Parambhath,[†,‡] Rupali Nagar,[†] K. Sethupathi,[‡] and S. Ramaprabhu[†,*]

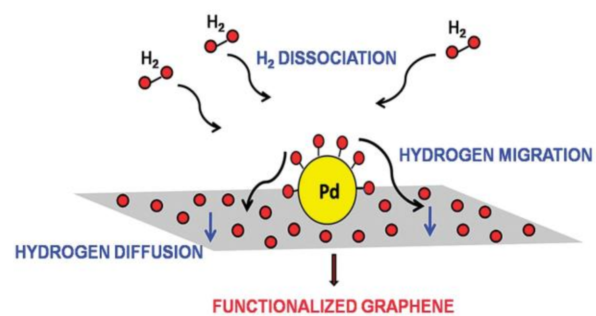
[†]Alternative Energy and Nanotechnology Laboratory (AENL), [1]Nano Functional Materials Technology Centre (NFMTC)
[‡]Low Temperature Physics Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu, 600036, India

S *Supporting Information*

ABSTRACT: Porous activated carbon or nanostructured carbon materials have a promising future as hydrogen storage media. The hydrogen storage capacity of nanostructured carbon materials can be further enhanced by spillover of atomic hydrogen from a supported catalyst. In the present work, both of these factors have been put to test to study the hydrogen storage capacity of palladium (Pd) nanoparticles dispersed over the surface of functionalized hydrogen-exfoliated-graphene (Pd/*f*-HEG). The high-pressure hydrogen storage measurements of HEG and Pd/*f*-HEG show a hydrogen storage capacity of 0.5 and 1.76 wt % respectively at 25 °C and 2 MPa pressure. Functionalization of graphene facilitates uniform dispersion of Pd nanoparticles, which result in an increased hydrogen storage capacity of graphene by 69%. Heats of adsorption have been calculated for HEG and Pd/*f*-HEG that are consistent with the theoretical calculations from literature and provide an experimental evidence for the spillover effect.



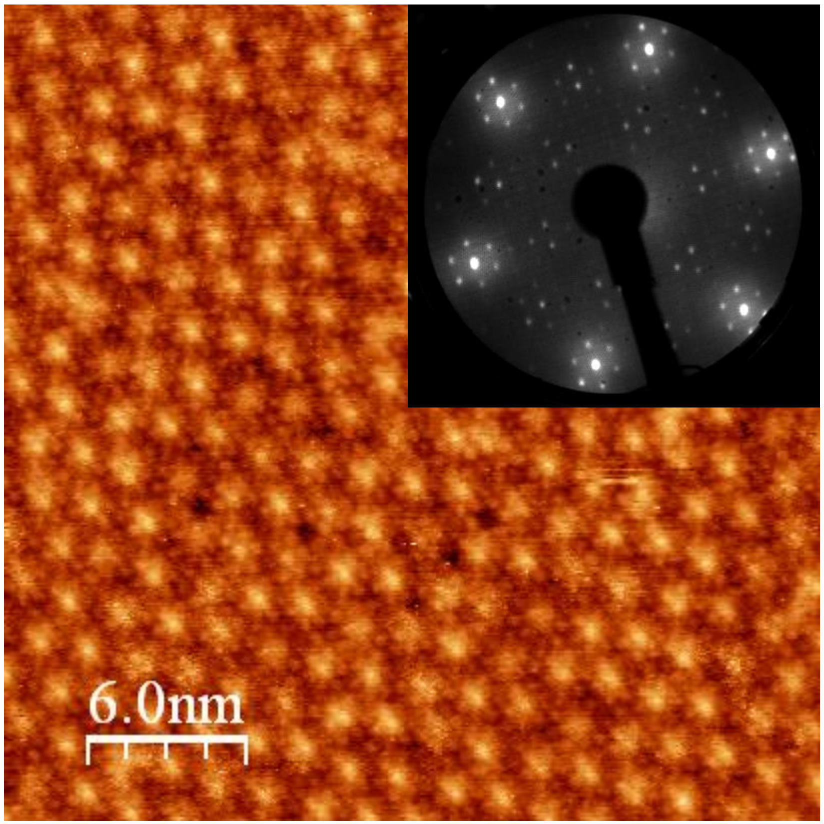




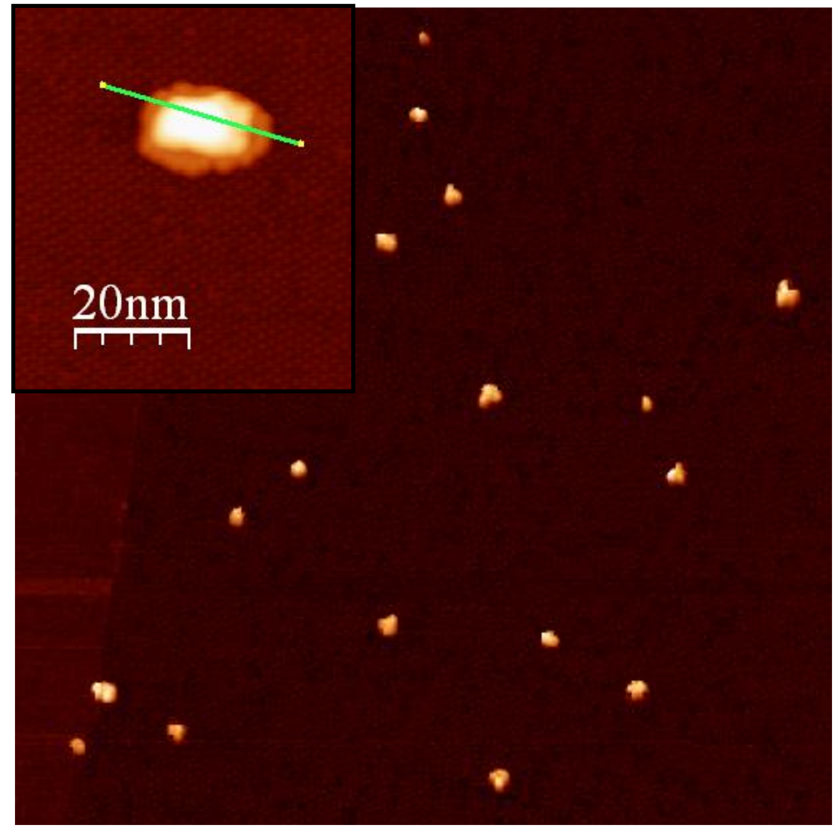
Experiment: V. B. Parambhath et al., J. Phys. Chem C **115** (2011) 15679.
Hydrogen *spill-over* effect

Experiments

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)

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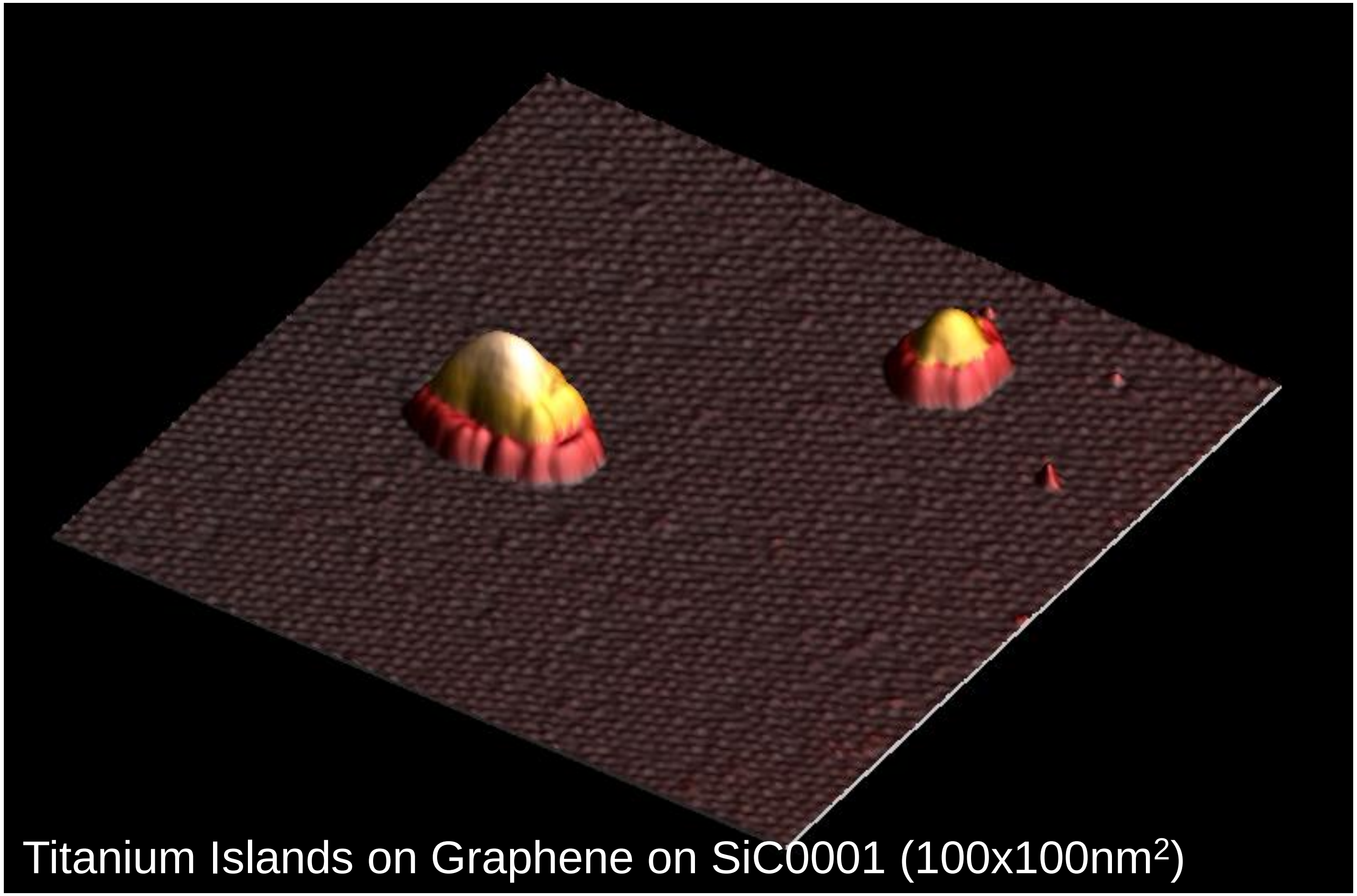
Titanium on graphene



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

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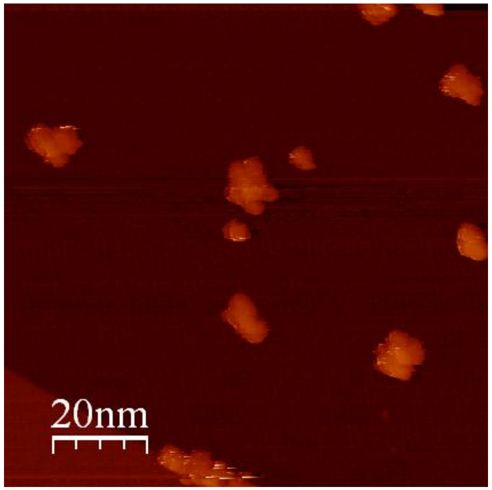
Titanium island growth



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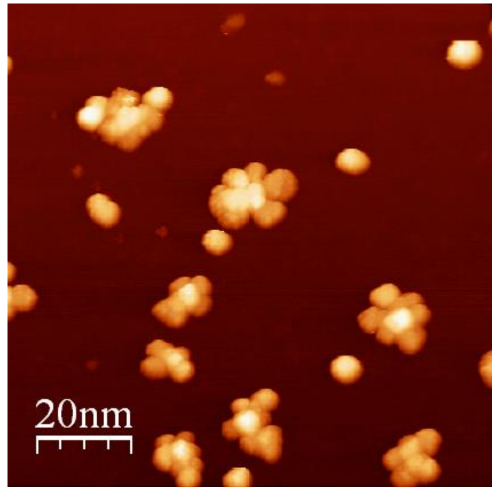

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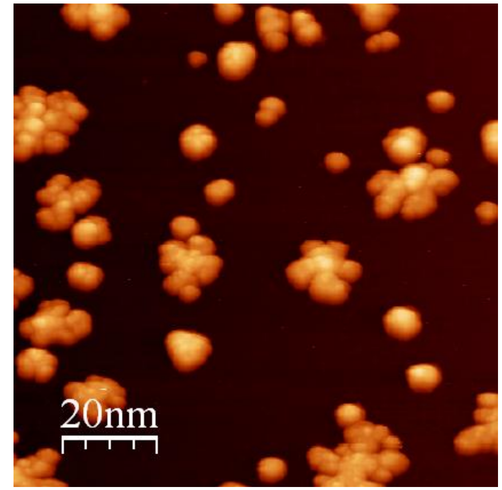

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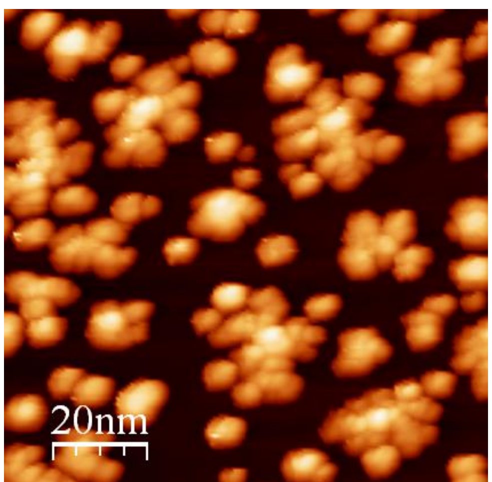
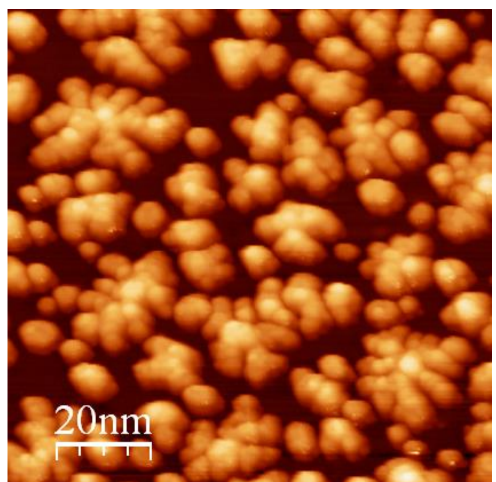


53% Coverage



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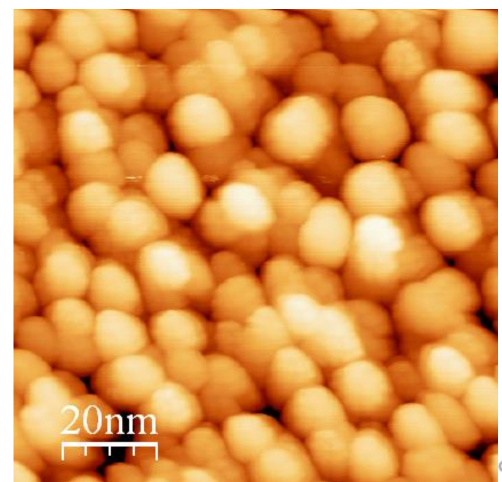
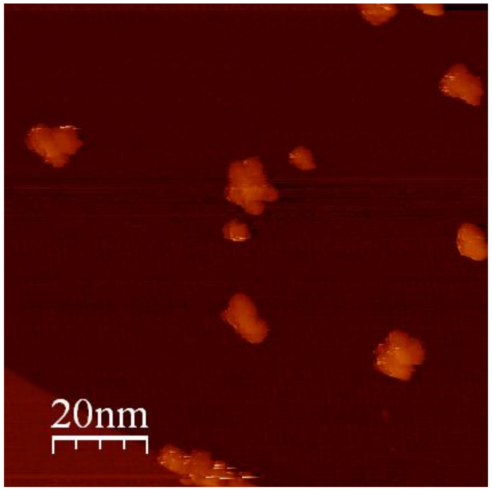
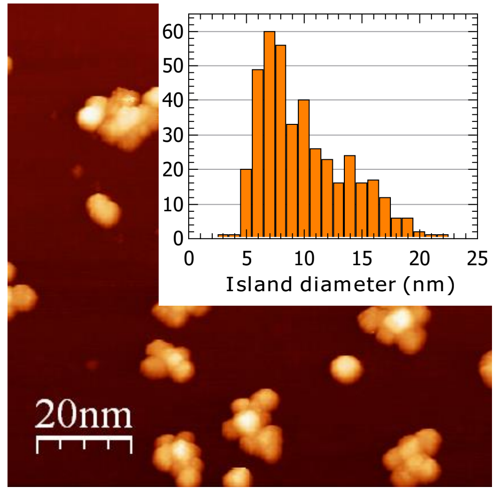


100% Coverage

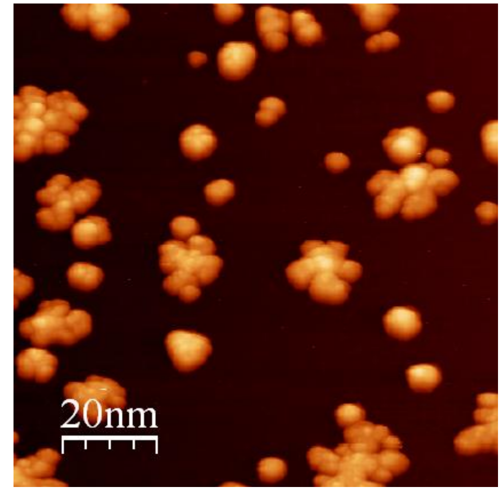
Titanium island growth



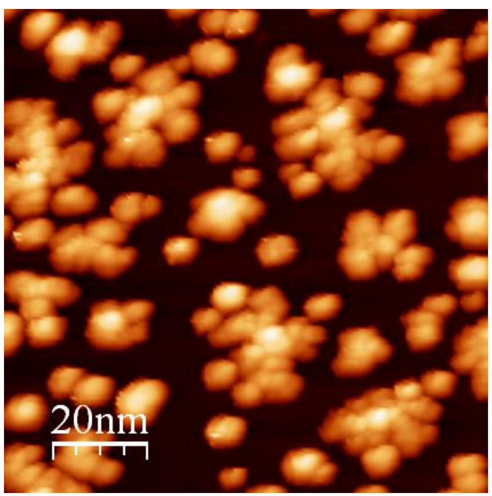
6% Coverage



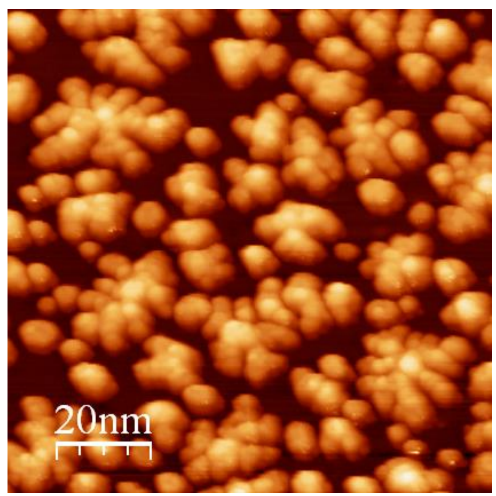
16% Coverage



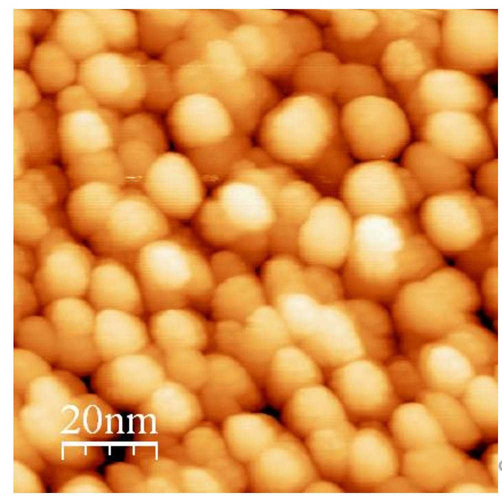
29% Coverage



53% Coverage



79% Coverage

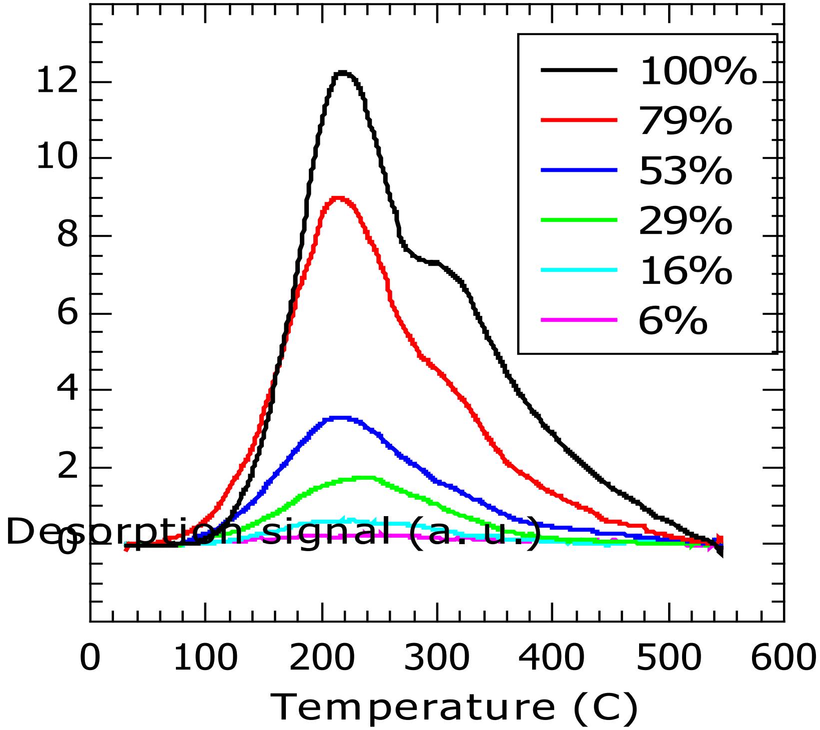


100% Coverage

Thermal desorption spectroscopy

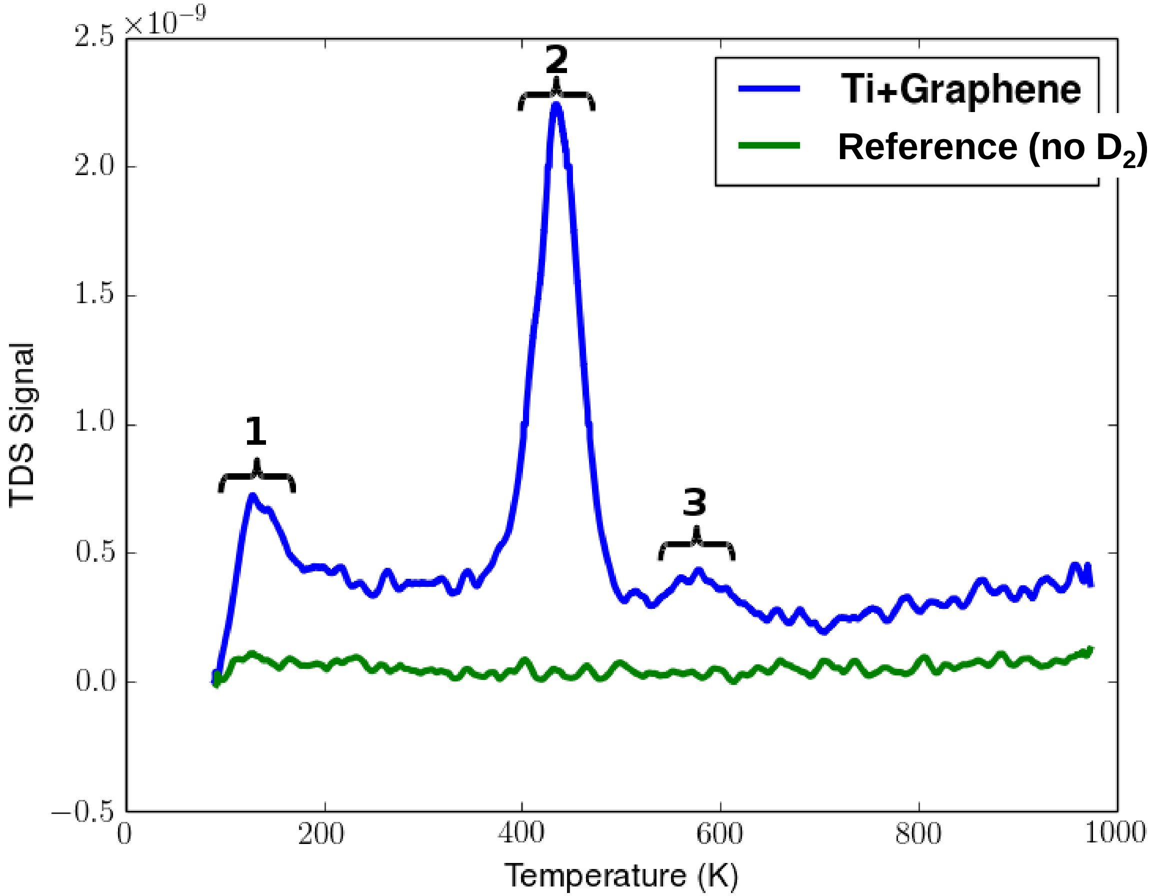
- Deposition of different amounts of Titanium
- Offering Hydrogen (D_2)
- ($1x10^{-7}$ mbar for 5 min)
- Heating sample with constant rate (10K/s) up to 550° C
- Measuring mass-sensitive desorption with a mass spectrometer

Spectra for different Ti-coverages



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

Thermal desorption spectroscopy



K. Takahashi *et al.*: J. Phys. Chem. C 120, 12974 (2016).

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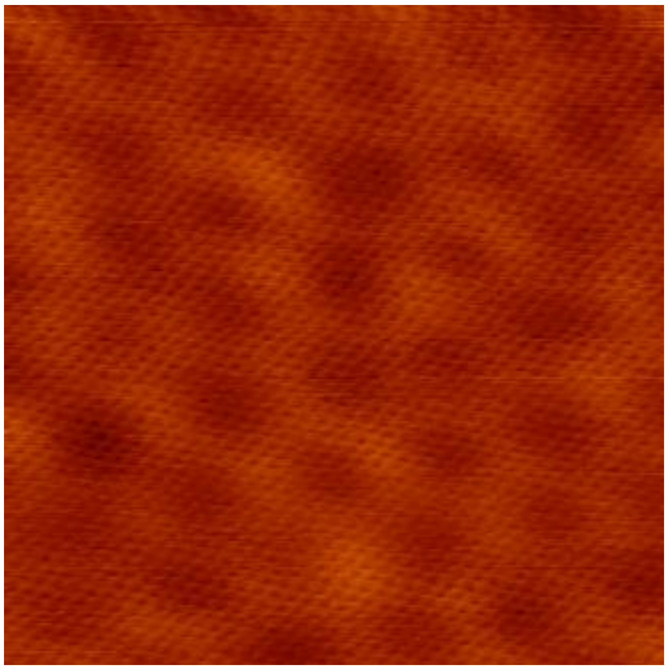
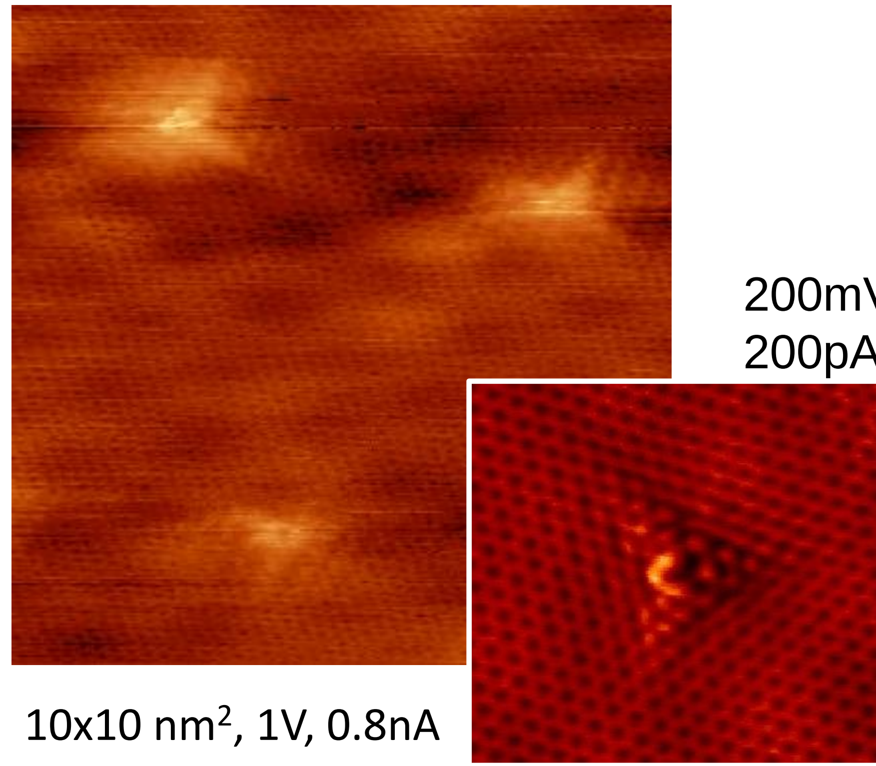
N_2 - sputtering of the graphene surface

Clean graphene surface



10x10 nm^2, 1V, 0.8nA

Sputtered 150s @100eV



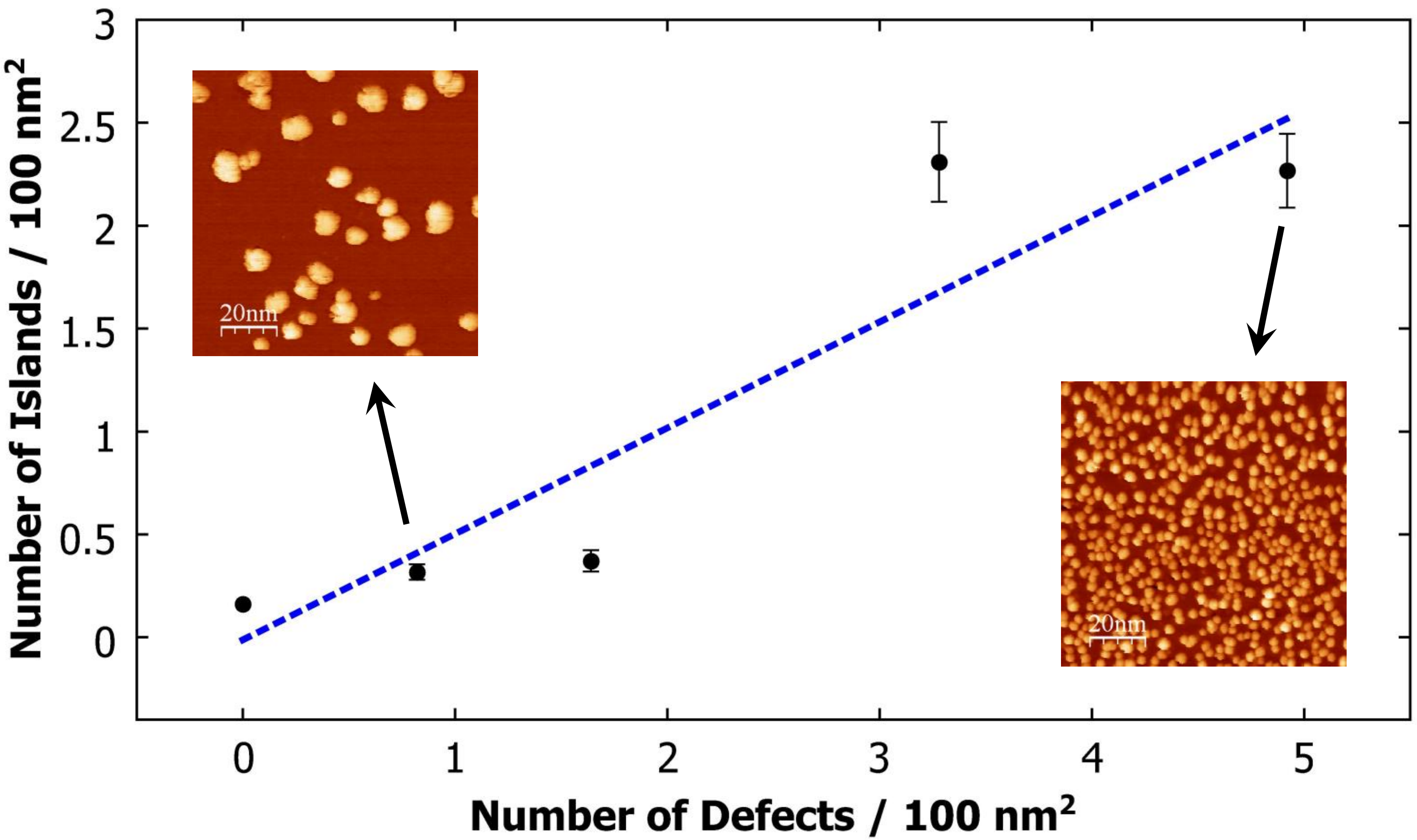
200mV
200pA

10x10 nm^2, 1V, 0.8nA

Defects in the graphene film are expected to reduce the mobility of Ti-atoms and to lead to a larger number of smaller islands.

T. Mashoff *et al.*: Appl. Phys. Lett. **105**, 083901 (2015).

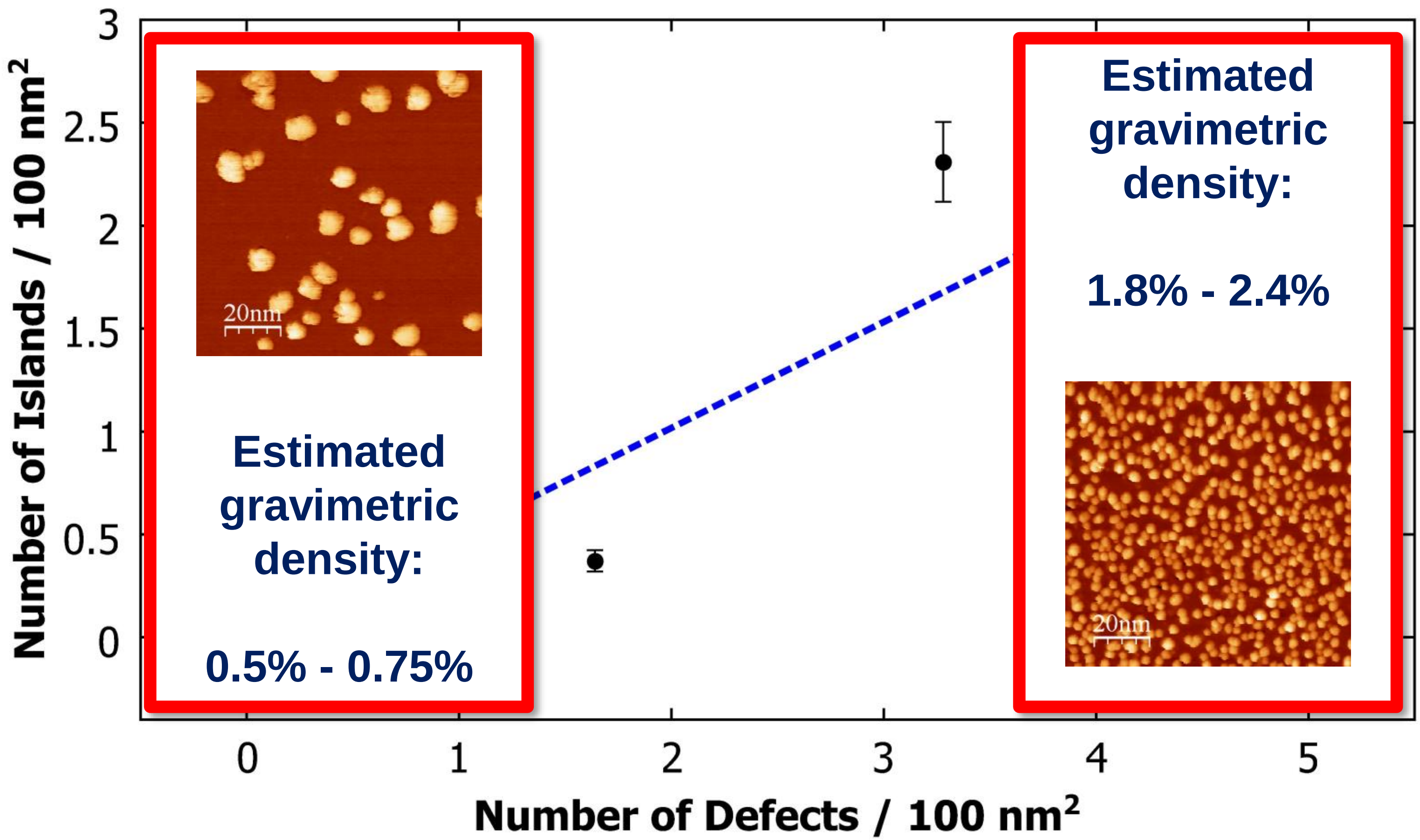
Average Number of Islands per 100 nm^2



T. Mashoff *et al.*: Appl. Phys. Lett. **106**, 083901 (2015).

Sputtered 150 s and
Deposition of 0.5 ML Titanium

Higher number of defects leads to smaller Ti islands



Sputtered 150 s and Deposition of 0.5 ML Titanium

T. Mashoff *et al.*: Appl. Phys. Lett. **106**, 083901 (2015).

Outline

- Introduction to Hydrogen Storage
- Hydrogen Storage on Graphene by Chemisorption
- Hydrogen Storage on Graphene by Physisorption
- New Materials

Beyond 2D

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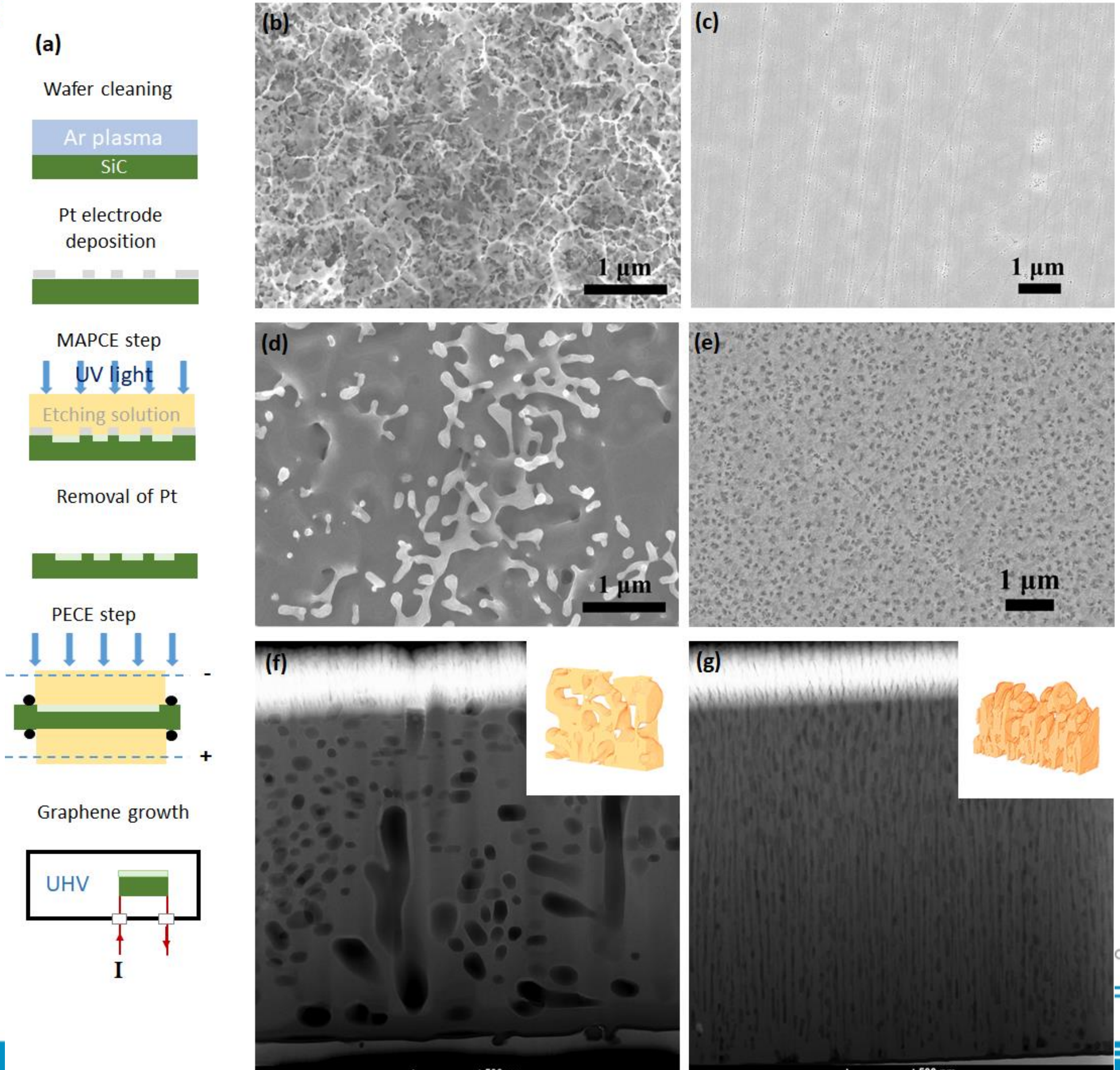
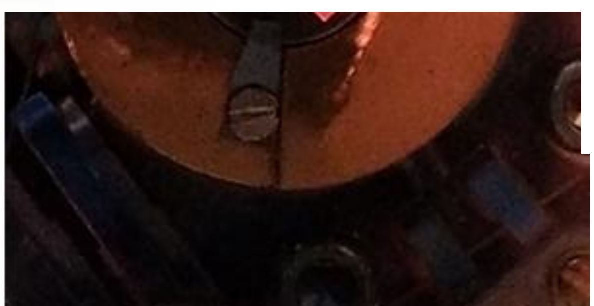
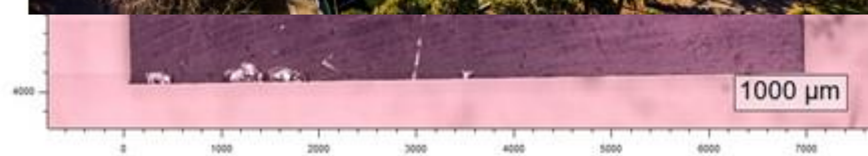
NEST

Silicon Carbide (SiC) porosification

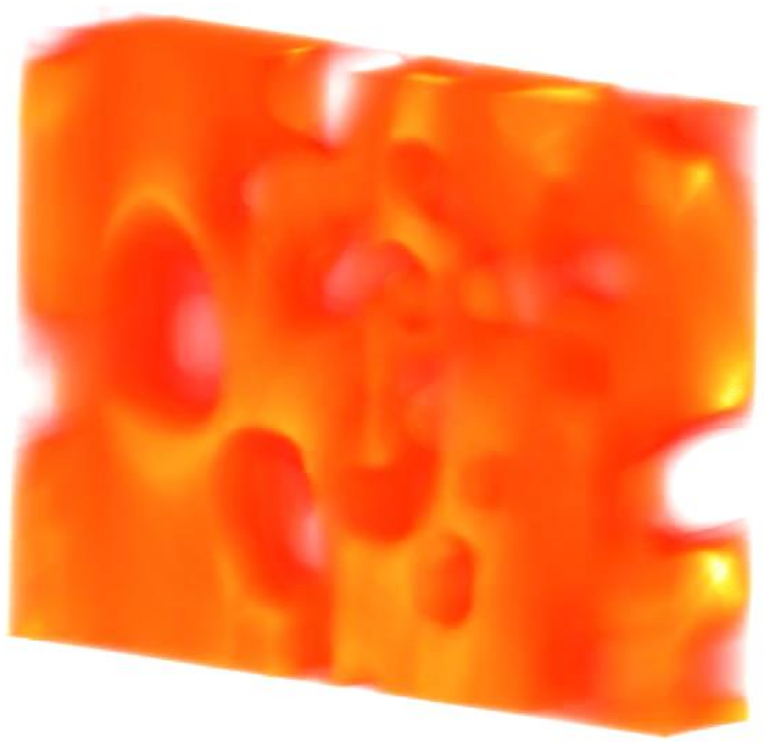


Epitaxial Graphene growth on porous SiC



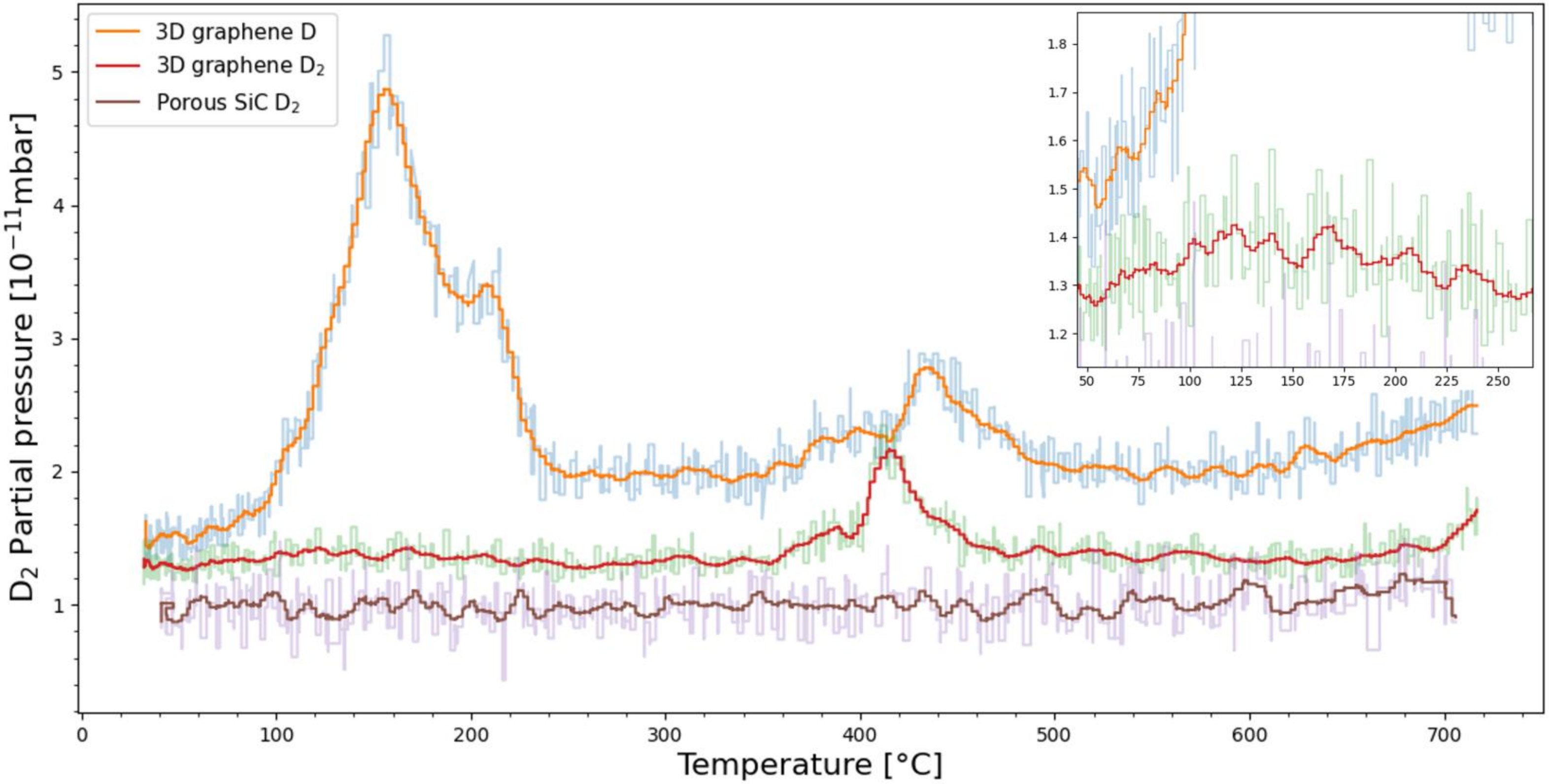


Pores analysis by electron tomography

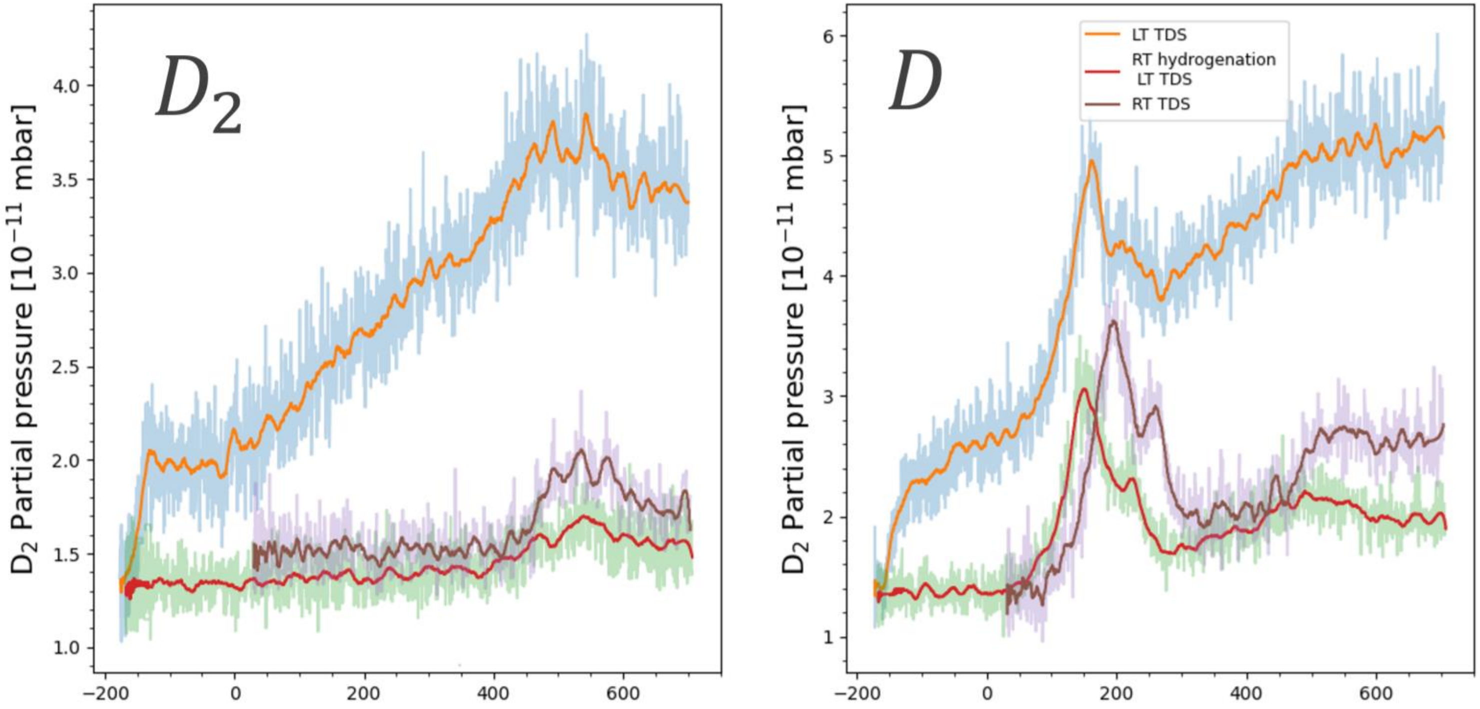


S. Veronesi *et al.*: Carbon **189**, 210 (2022).

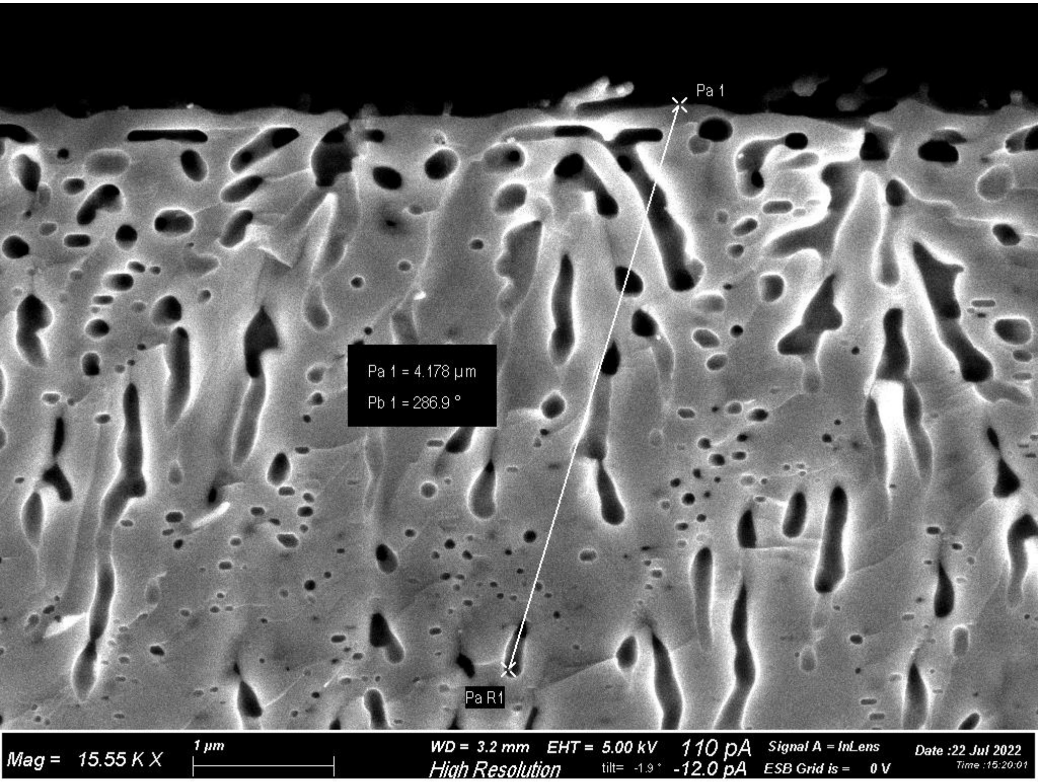
H-storage in 3D graphene arrangement

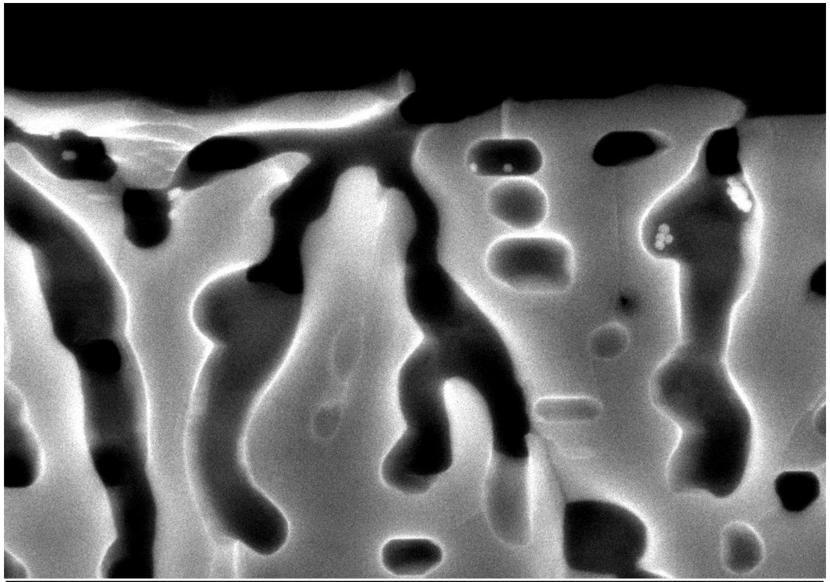


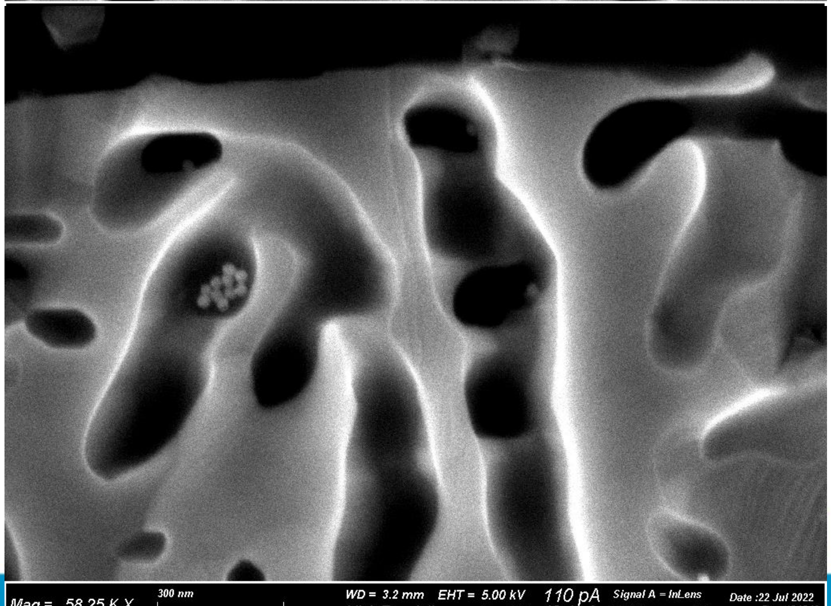
Physisorption in 3D graphene arrangement



Functionalization of 3D graphene with gold nanoparticles







People