Hydrogen absorption in a novel three-dimensional graphene structure: Towards hydrogen storage applications

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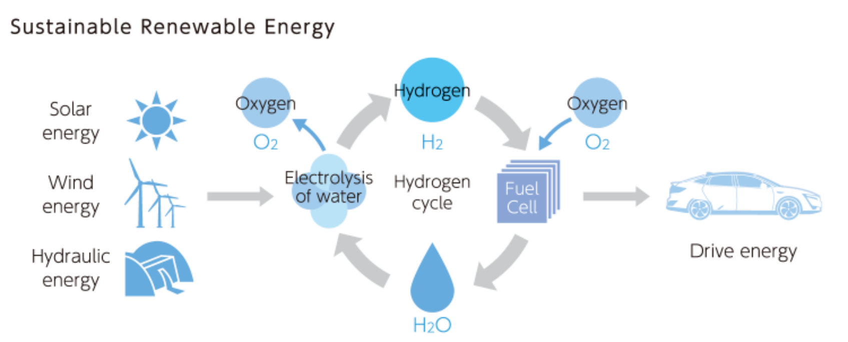
Outline

Hydrogen life cycle

- Fossil fuels ⇒ green house effect
- Renewables are intrinsically intermittent
- Energy storage
- H-Storage



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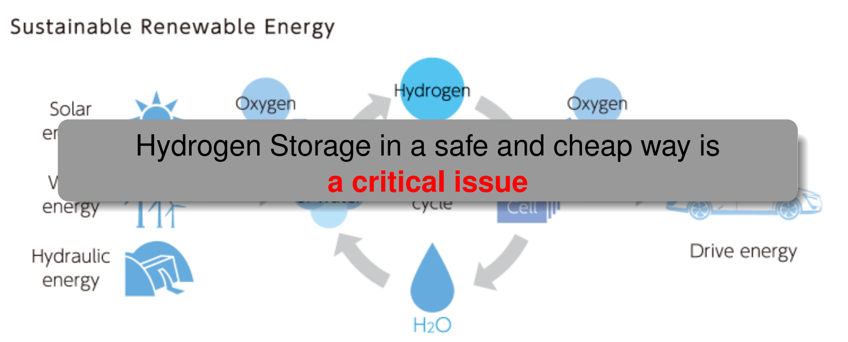


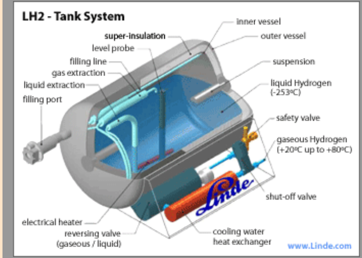
Hydrogen Storage in a safe and cheap way is **a critical issue**

hydrogen storage techniques

High pressure tank

$P \simeq 700$ bar established technology

Liquid H2 tank



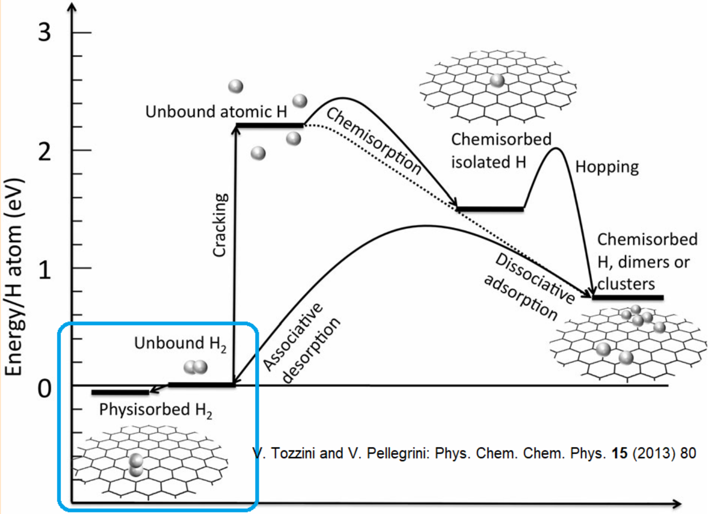
$P \simeq 1$ bar, $T = 21$ K

Solid state storage

$P \simeq 1\text{-}50$ bar, $T = 300$ K

Graphene for hydrogen storage

- Physisorption weakly bounds hydrogen $\Longrightarrow$ acceptable storage densities only at low temperatures and/or high pressure;



V. Tozzini and V. Pellegrini: Phys. Chem. Chem. Phys. **15** (2013) 80

Graphene for hydrogen storage

- Atomic hydrogen chemisorption has a small or negligible chemisorption barrier $\Longrightarrow$ feasible but H_2 must be cracked;
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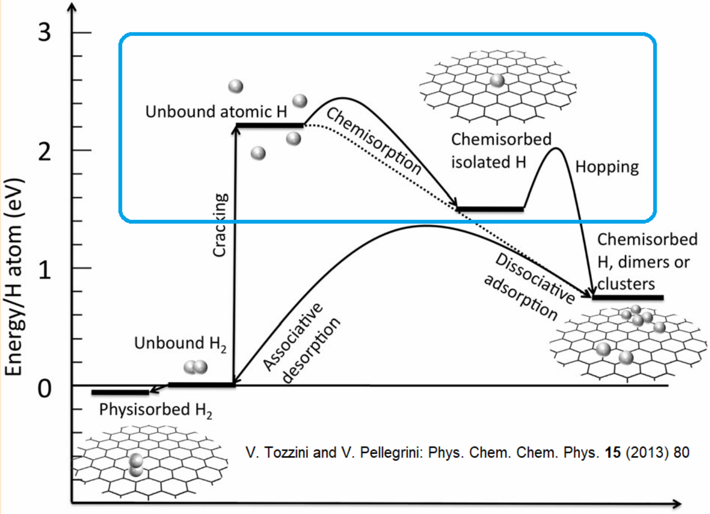

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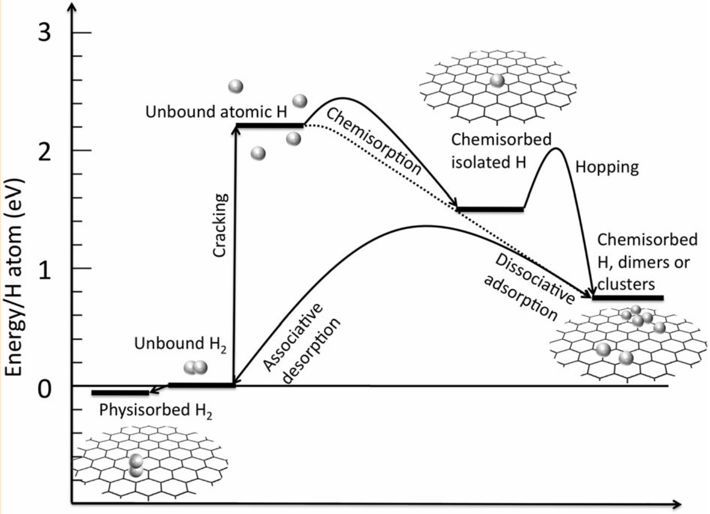


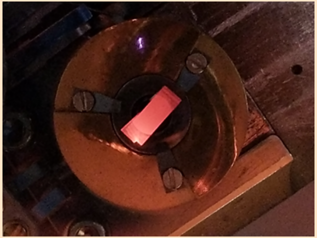
Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate $\sim$ eV) $\Longrightarrow$ chemisorbed H is stable , but catalytic mechanisms are necessary

2D vs 3D

2D materials are excellent model systems for optoelectronic applications, flexible electronics, graphene based sensors, biological applications, ...

Would strongly benefit from a high surface-to-volume ratio and a **3D** structure: Catalysis , photoassisted water splitting, gas detection and storage, drug delivery, high performance electrodes, supercapacitors, battery cathodes, water treatment and filtration.

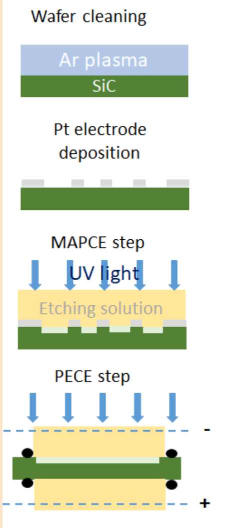
Our choice is the use of porousified 4H-SiC(0001) wafer to grow epitaxial graphene by thermal decomposition in UHV environment around 1370° C, achieving a **3D** arrangement conformal to the substrate, and preserving an high quality.



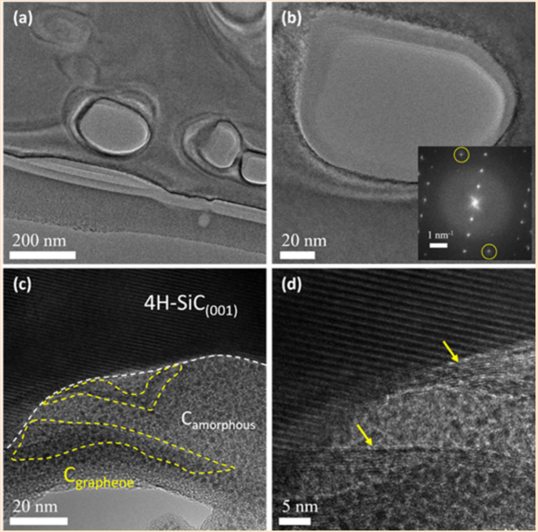
SiC porousification

- Porous SiC from U. Schmid's group (TU Wien)
- Established wafer-scale technology
- Works on Si- and C-face of 4H-SiC(000 ± 1)
- Control of local definition of pores and degree of porosity with depth
- Stacked layers of different porosity can be made
- Porous layer can be detached from wafer

M. Leitgeb et al., J. Phys. D 50 (2017) 435301



TEM after Graphene growth



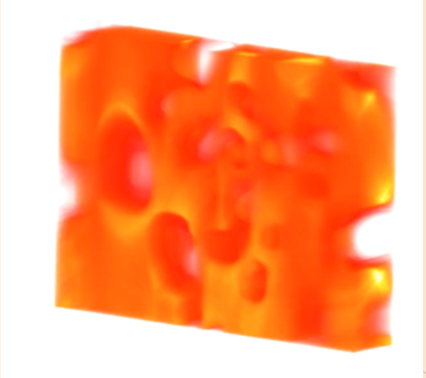
S. Veronesi et al., Carbon 189 (2022) 210

University of Antwerp

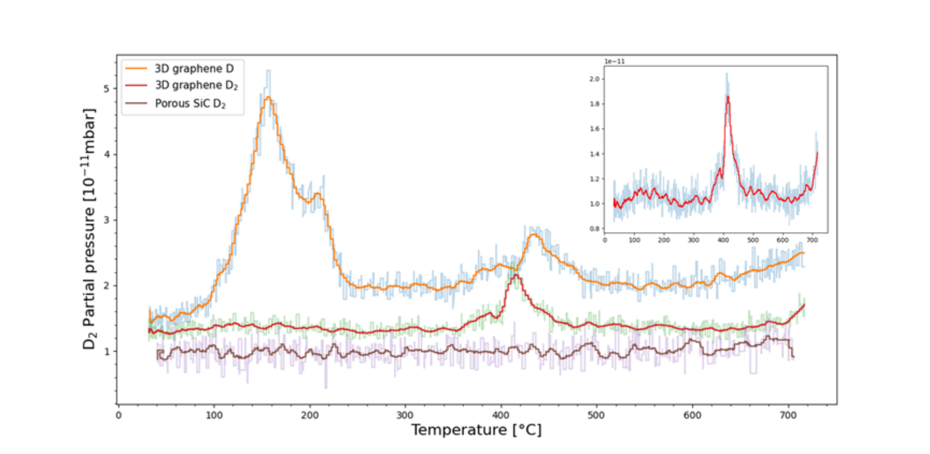
Sara Bals

300 keV

80 keV

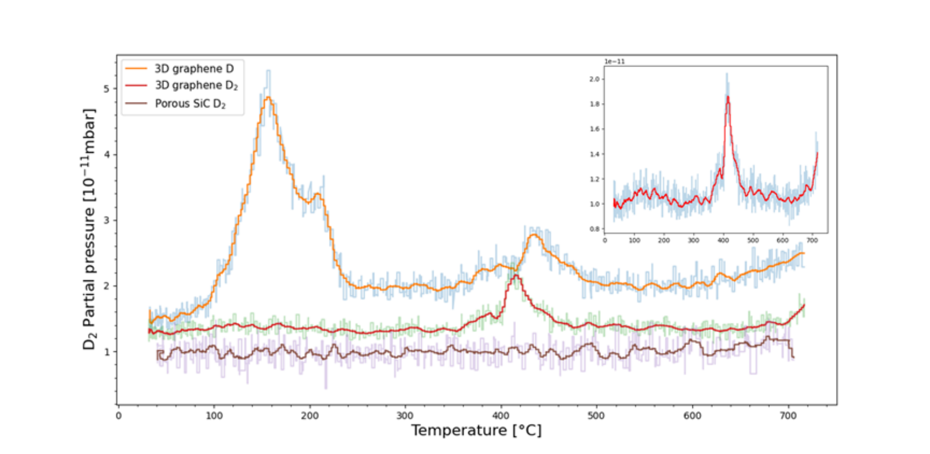


RT hydrogen uptake



A. Macili et al., Appl. Surf. Sci. 615 (2023) 156375

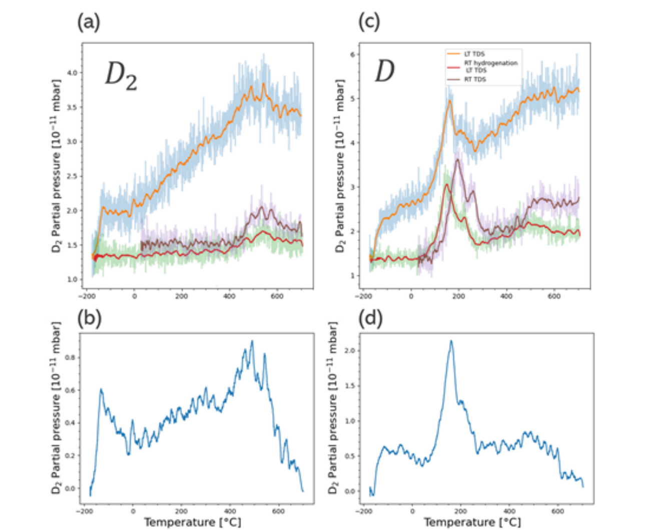
RT hydrogen uptake



Chemisorption ⟹ chemical bond ⟹ catalytic hydrogen-splitting

A. Macili et al., Appl. Surf. Sci. 615 (2023) 156375

Low Temperature hydrogen uptake



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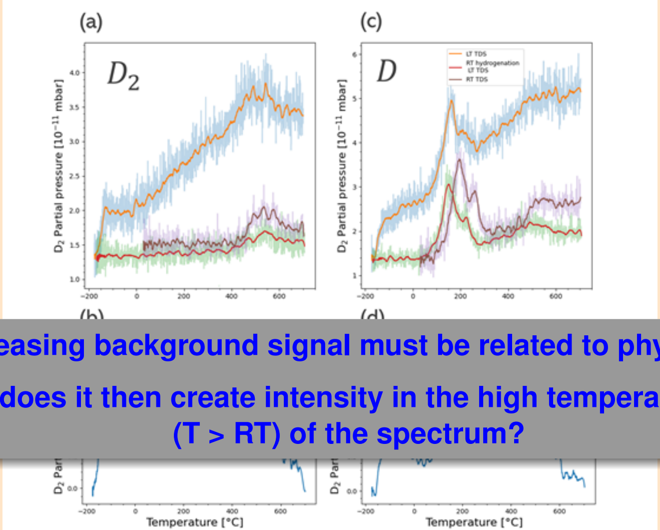
Low Temperature hydrogen uptake

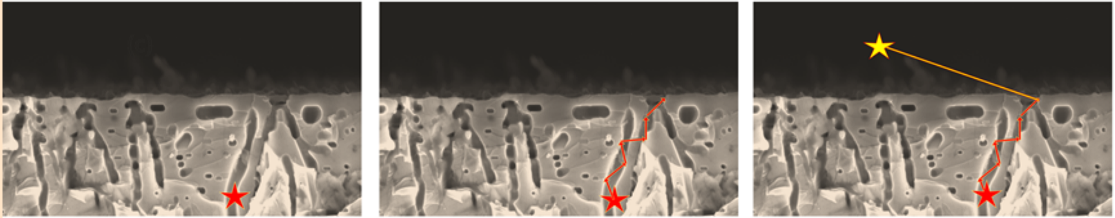


The increasing background signal must be related to physisorption.

But why does it then create intensity in the high temperature branch (T > RT) of the spectrum?

A. Macili et al., Appl. Surf. Sci. 615 (2023) 156375

Delayed emission model



Desorption

$$\tau = \tau_0$$
$$T = T_p$$

Diffusion

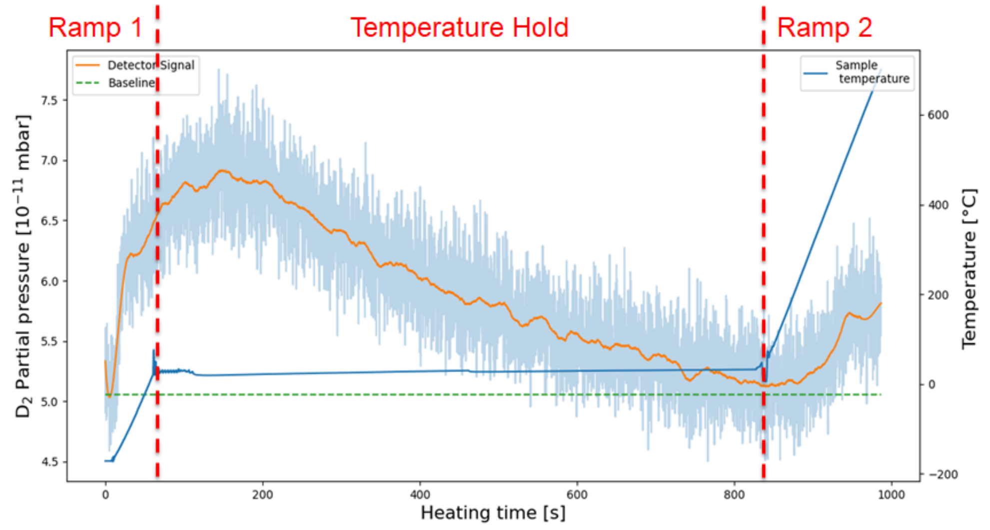
$$\tau = \tau_0 + \tau_d$$
$$T = T_p + \beta\tau_d$$

Detection

$$\tau = \tau_0 + \tau_d + \tau_{ex}$$
$$T = T_p + \beta(\tau_d + \tau_{ex})$$

A. Macili et al., Appl. Surf. Sci. 615 (2023) 156375

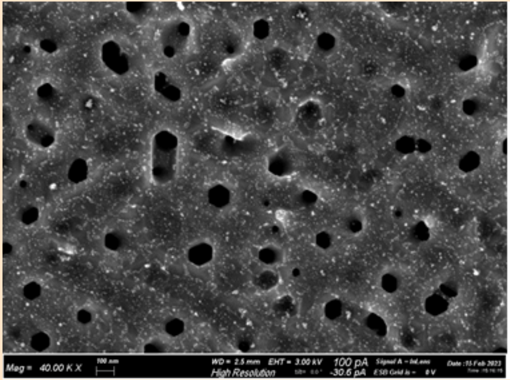
Delayed emission model

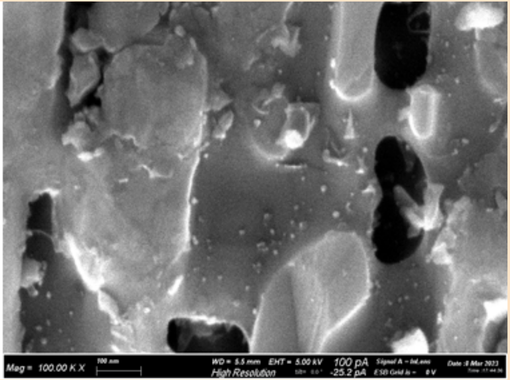


A. Macili et al., Appl. Surf. Sci. 615 (2023) 156375

Outlook: metal nanoparticles

- Pd nanoparticles made using PolyVinylPyrrolidone and ethylene glycol, then dispersed in ethanol
- Dimension in the range 3 to 12 nm (AFM)





E. Pompei unpublished

Conclusions

- Graphene is a promising material for hydrogen storage
- 3D arrangement of graphene in porous SiC
  - ⇒ Uniform high-quality graphene growth in the pores
  - ⇒ 200 times increase in active surface area
  - ⇒ Chemisorption after exposure to molecular hydrogen
  - ⇒ Enhancement of hydrogen storage performance by metal functionalization ?

People


A. Macili
Y. Vlamidis
E. Pompei
S. Heun
S. Bals
U. Schmid
M. Leitgeb
G. Pfusterschmied

thanks

Thank you for your attention

Thursday 07 at 16:00, GS-22 room 26.1.5

Deterministic organic functionalization of exfoliated monolayer graphene via high-resolution surface engineering