Epitaxial graphene on a 3D porous structure: toward hydrogen storage and sensing applications

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The University of Manchester and National Graphene Institute, December 1st 2023

Outline

1. Introduction to hydrogen storage
   - Hydrogen and Graphene
2. Three-dimensional arrangement of epitaxial graphene (3DG) on porous SiC
   - Graphene on Porous SiC
   - Hydrogen storage
   - Functionalization with metal nanoparticles
3. 3DG for sensing

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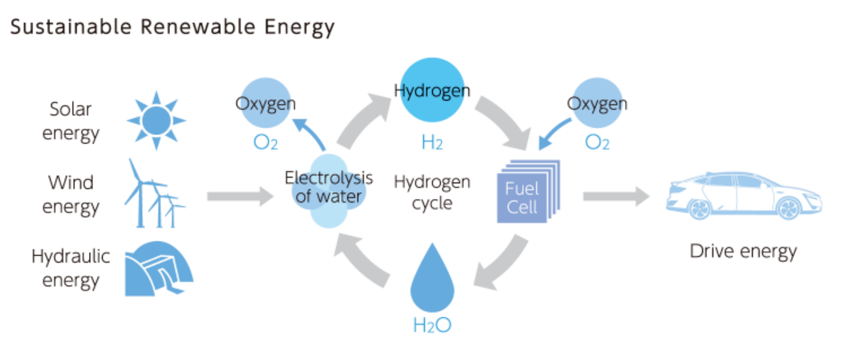
Hydrogen life cycle

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



Hydrogen life cycle

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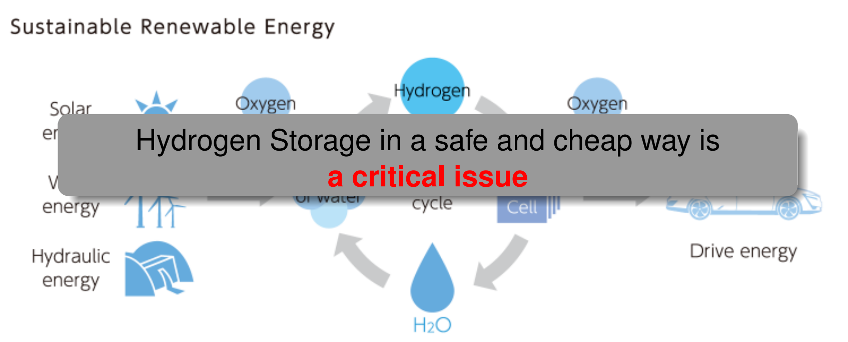


Hydrogen Storage in a safe and cheap way is
a critical issue

Hydrogen-fuelled vehicles

Since the 1970s

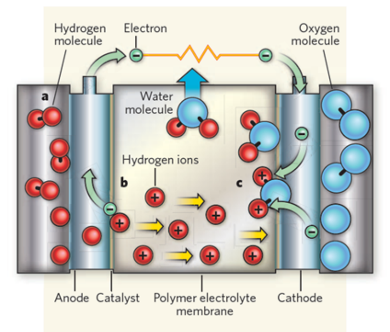
Hydrogen-fuelled vehicles

hydrogen & energy

As a fuel, hydrogen has advantages:

- Highest energy-to-mass ratio
- $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ Δ H = -2.96eV
- Non-toxic and "clean" (by-product = water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency

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.



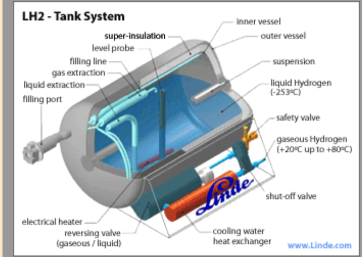
Hydrogen fuel cell

hydrogen storage techniques

High pressure tank

$P \simeq 700$ bar established technology

Liquid H2 tank



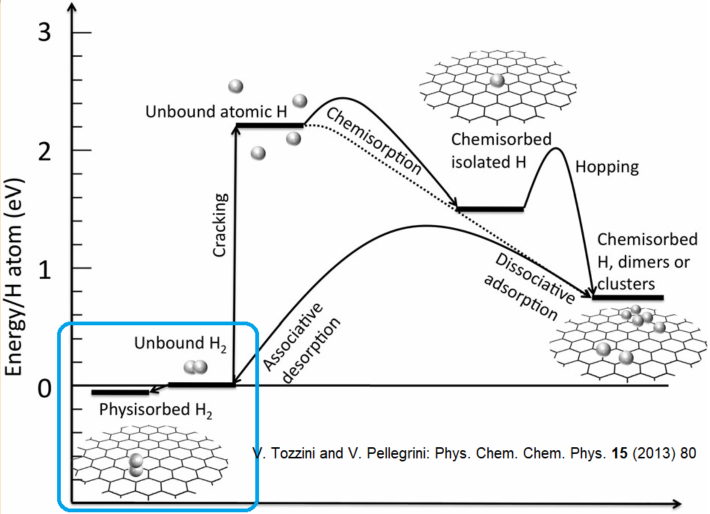
$P \simeq 1$ bar, $T = 21$ K

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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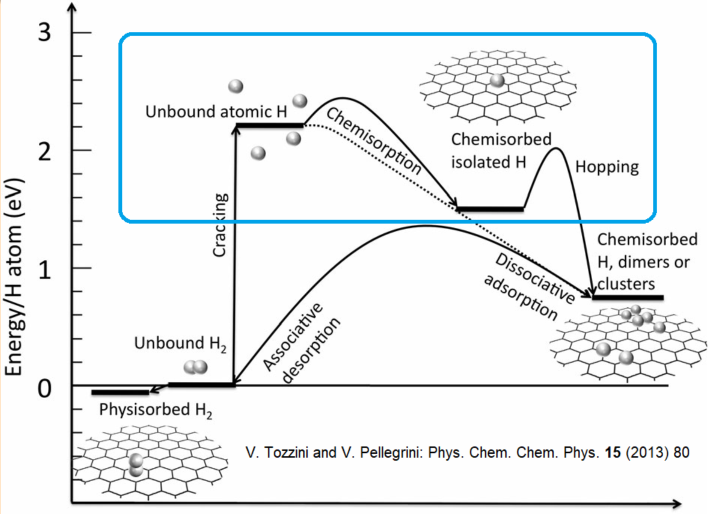

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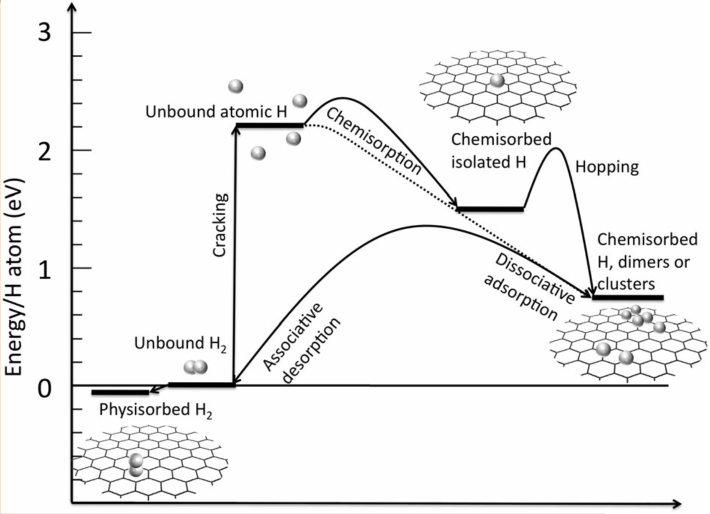
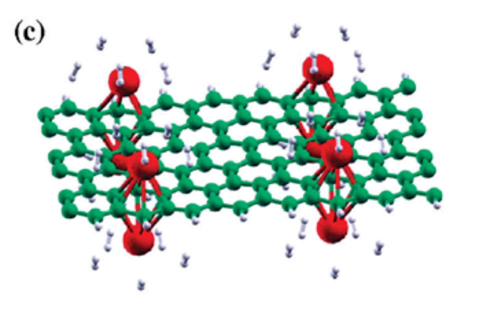


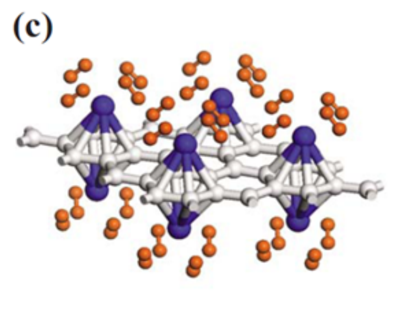
Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate $\sim$ eV) $\Longrightarrow$ chemisorbed H is stable , but catalytic mechanisms are necessary

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)

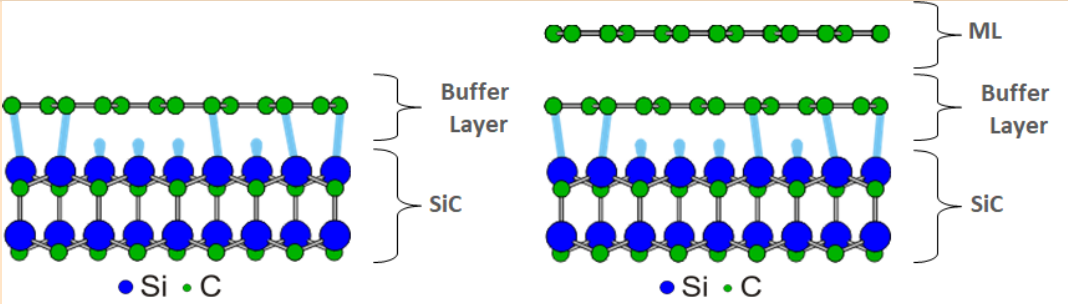


Lee et al., Nano Lett. 10 (2010) 793

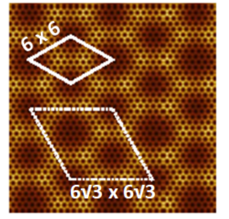


Durgen et al., PRB 77 (2007) 085405

Graphene growth on SiC(0001)



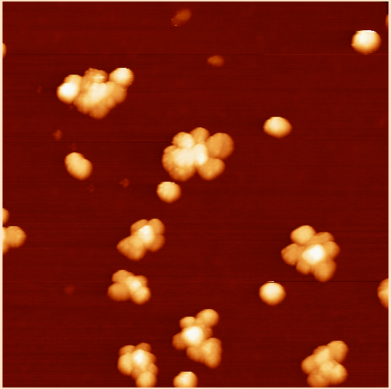
Buffer layer:
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp^3 $C - Si$ bonds.

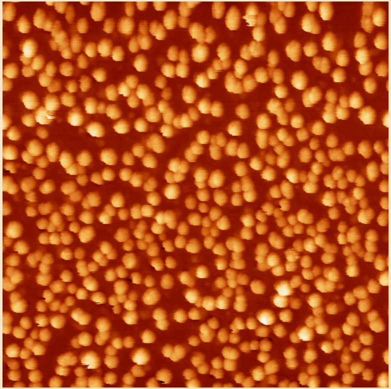


F. Varchon, et al., PRB 77, 235412 (2008)

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

Titanium on Graphene



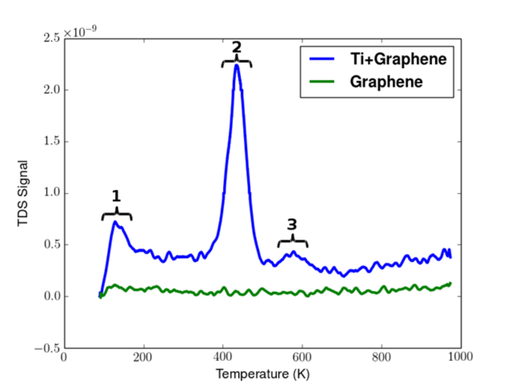


Titanium islands on EMLG Titanium islands after defect engineering

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

Thermal desorption spectroscopy

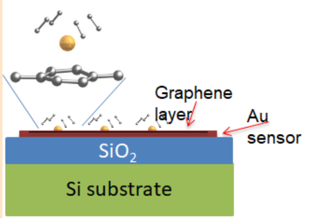
- Deposition of different amounts of metal
- Offering Hydrogen (D_2) 1x10^{-7} mbar for 5 min
- Heating sample with constant rate (4÷10K/s)
- Measuring mass-sensitive desorption with a mass spectrometer

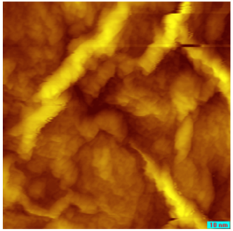


K. Takahashi et al.: J. Phys. Chem. C 120, 12974 (2016)

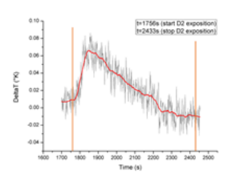
Calorimetry of Ti functionalized SLG

- **Our system:** Single Layer Graphene (SLG) functionalized with Ti
- **Measurement idea:** detect the heat release during deuterium loading with a gold film thermometer
- **Methodology:** tailored Wheatstone bridge with lock-in signal acquisition
- **Sensitivity:** $\Delta T \approx 0.01$ K





STM image of SLG on gold



Thermal signal during Hydrogen loading. Ti coverage 100%, $P(D_2) = 10^{-7}$ mbar

	Ti (ML)	E_d /molecule (eV)	H_r (μJ)	
		TDS	calorimetry	TDS
$G3_{(1)}$	12.4	1.32 ± 0.07	23.4 ± 4.7	21.8 ± 1.3
$G3_{(2)}$	16.6	1.24 ± 0.09	58 ± 12	53.8 ± 4.3

Calorimetric results summary

Is graphene route feasible?

A car need about 1 kg of H_2 for 100 km range. So to allow an useful range of about 400 km we need to store 4 kg of H_2.

- DOE prescription on H-S capacity $\geq$ 5.5 wt% means a tank weight $\leq$ 75 kg
- Let us consider a GD $\sim$10%
- we need 40 kg of graphene
- graphene has density 2600 m^2/g $\Rightarrow$ about 100 km^2 of graphene
- considering graphene foils of 1 m^2 we need 10^8 foils
- with a distance between two foils of about 1 nm $\Rightarrow$ 10^9 foils/m^3
- Thus, 40 kg of graphene would fit into a 100 liter tank

summarising

- Molecular hydrogen is weakly bound to graphene and it is unstable at room temperature
- offering atomic hydrogen is energetically expensive
- In a real world device 2D material must be arranged in a 3D structure to have a proper surface-to-volume ratio

$$\Downarrow$$

- tailor graphene to achieve the uptake of molecular hydrogen
- tailor graphene to achieve a catalytic hydrogen splitting at the surface
- develop proper 3D structure of graphene

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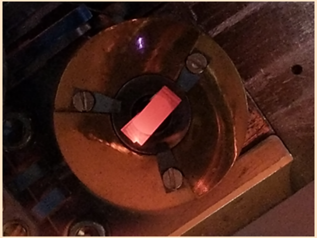
2D vs 3D

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

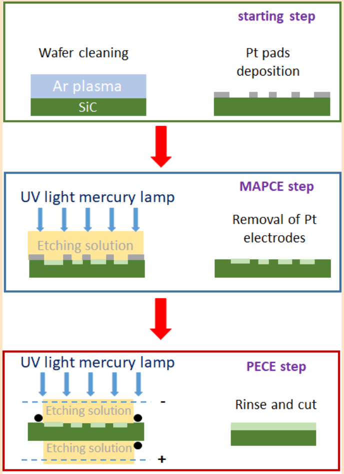
Would strongly benefit from a high surface-to-volume ratio and a **3D** structure: Catalysis , photoassisted water splitting, gas detection and storage, drug delivery, high performance electrodes, supercapacitors, battery cathodes, water treatment and filtration.

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 porous substrate, and preserving an high quality.



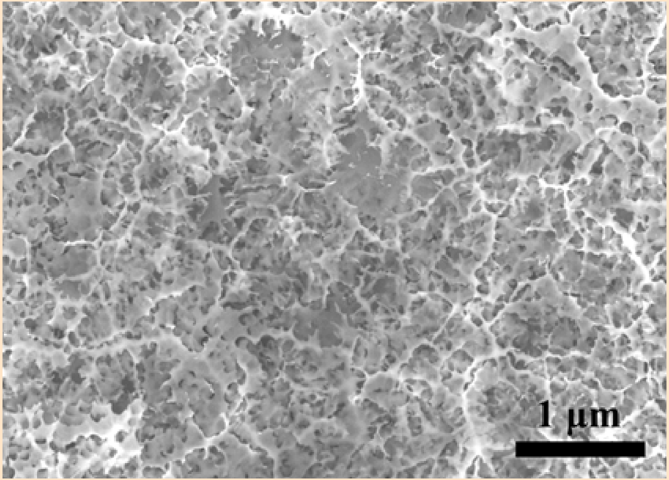
Porous SiC

- 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

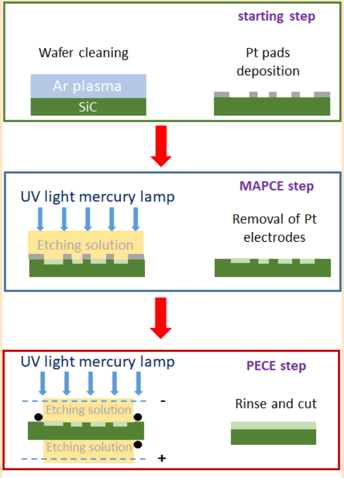


M. Leitgeb et al., J. Phys. D 50 (2017) 435301

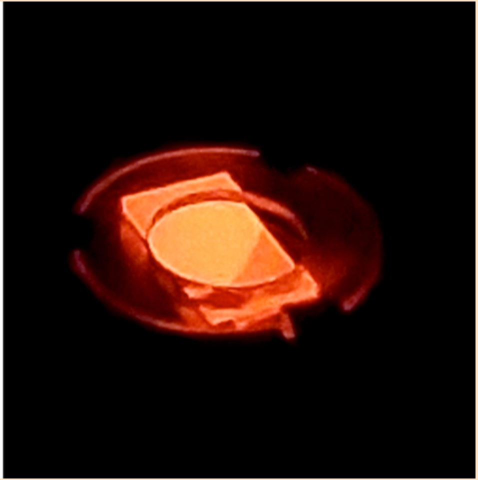
Porous SiC



Top-view SEM of porous Si-face sample
S. Veronesi et al., Carbon 189 (2022) 210



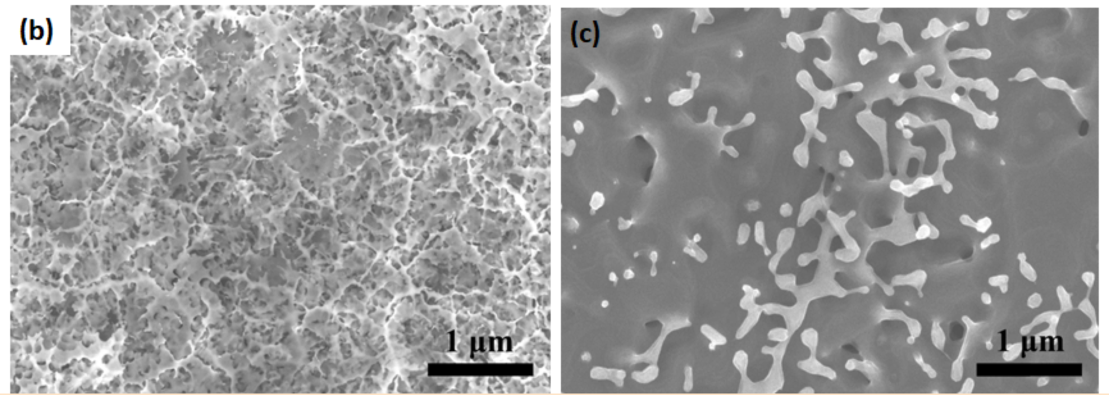
Graphene growth



- Annealing in UHV
- 2 min @ 1370 °C

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

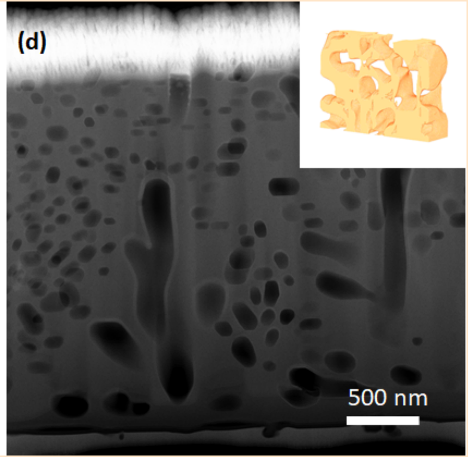
Graphene growth



Before growth | After growth

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

TEM after Graphene growth



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

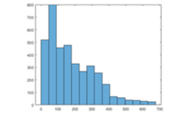
University of Antwerp

Sara Bals

Etching depth 20 μm

Overall graphene area is 200x the surface area

	Volume
Material	67 %
Pores	33 %

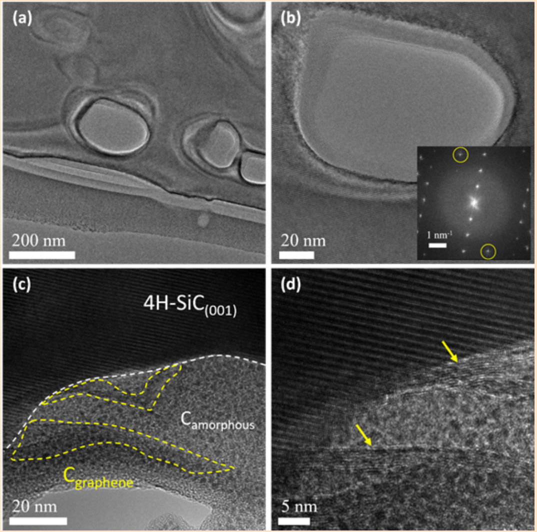


Average pore diameter: 182nm

TEM after Graphene growth

300 keV

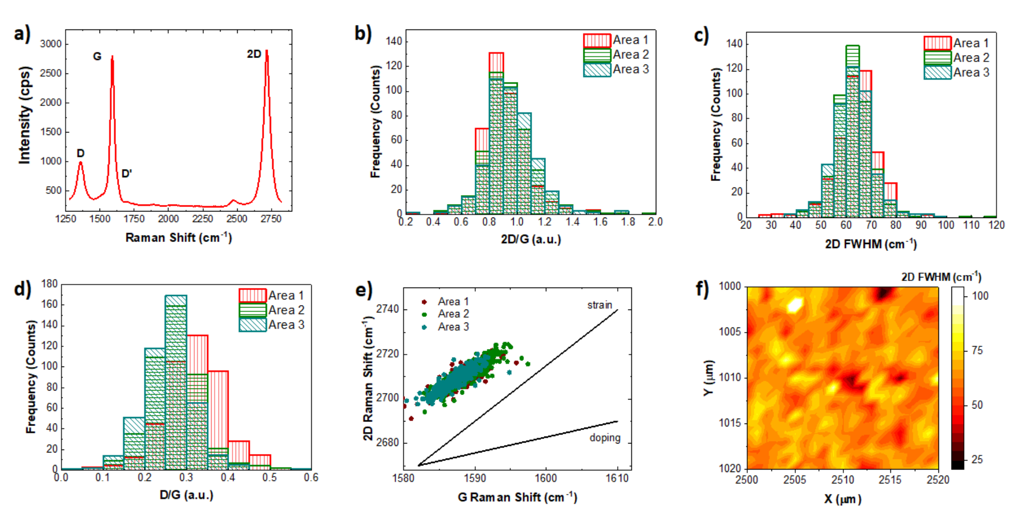
80 keV



◯: interplanar distance 0.34nm (graphene)

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

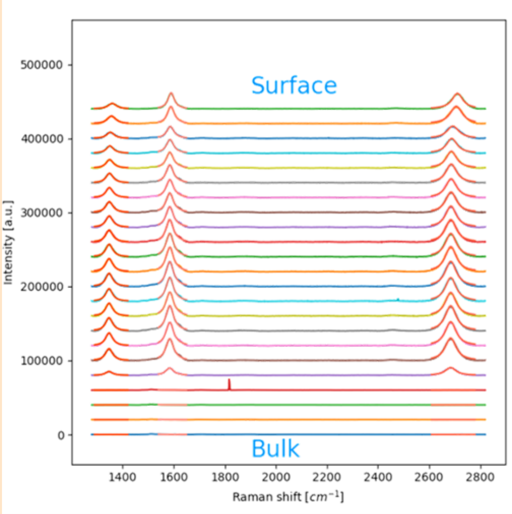
Raman analysis

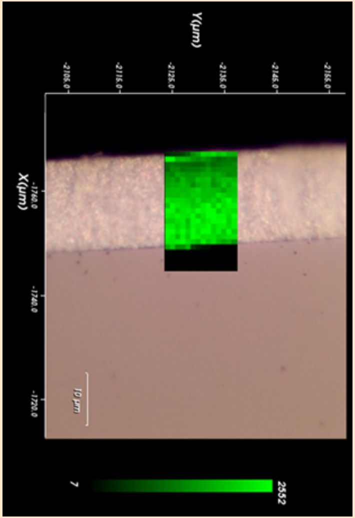


S. Veronesi et al., Carbon 189 (2022) 210

Average grain size of graphene: 70 to 100 nm

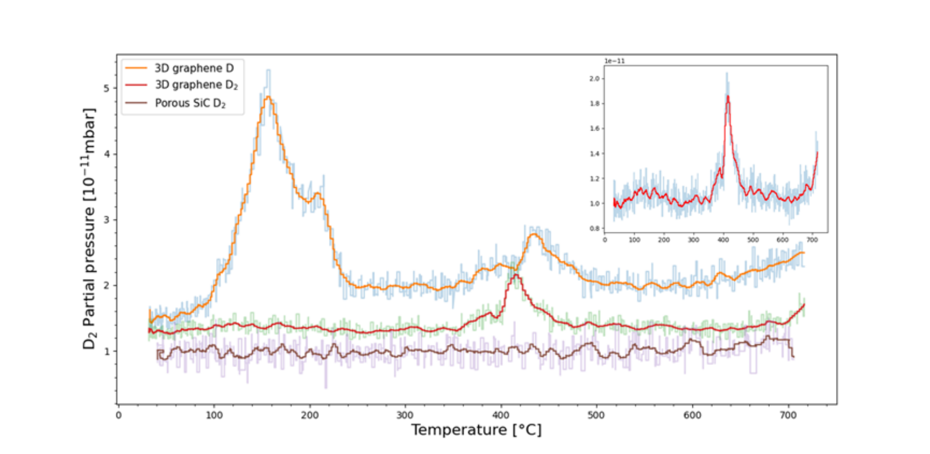
Raman analysis





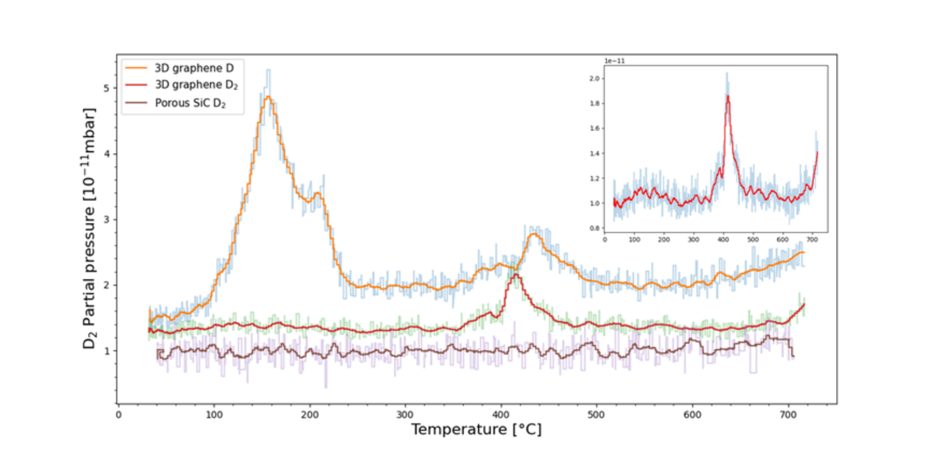
Y. Vlamidis, unpublished

RT hydrogen uptake



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

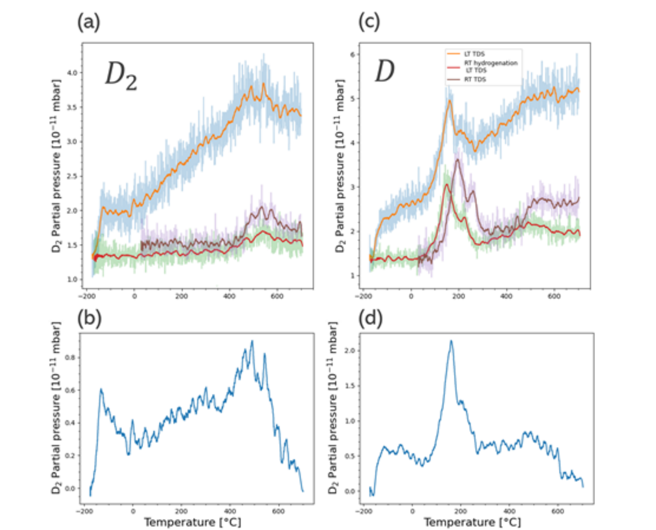
RT hydrogen uptake



Chemisorption $\Longrightarrow$ chemical bond $\Longrightarrow$ catalytic hydrogen-splitting

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

Low Temperature hydrogen uptake



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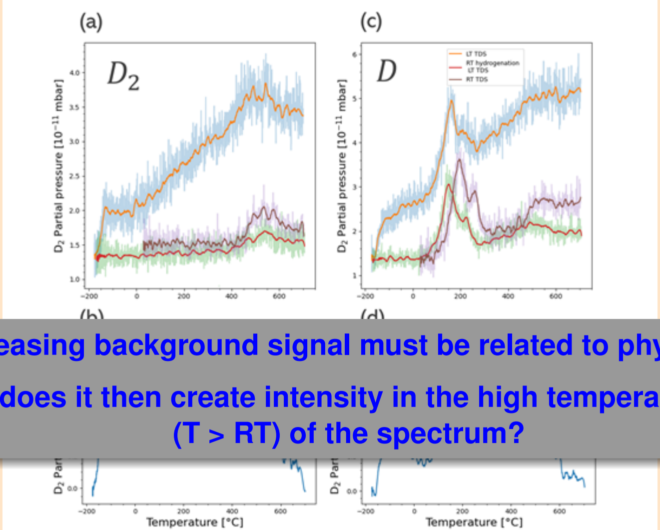
Low Temperature hydrogen uptake

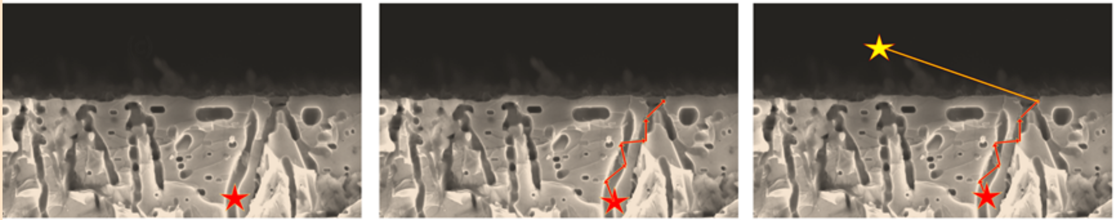


The increasing background signal must be related to physisorption.

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

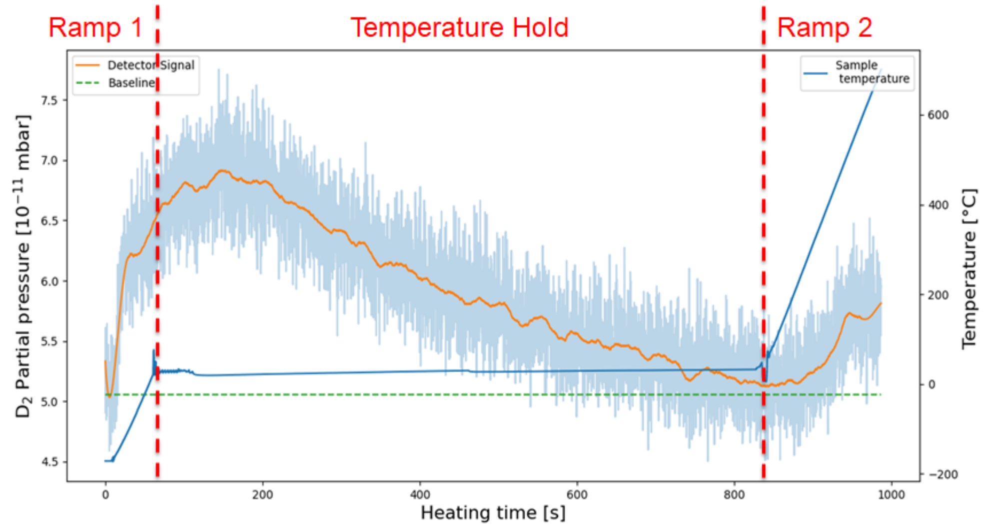
$$\tau = \tau_0 + \tau_d$$
$$T = T_p + \beta\tau_d$$

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



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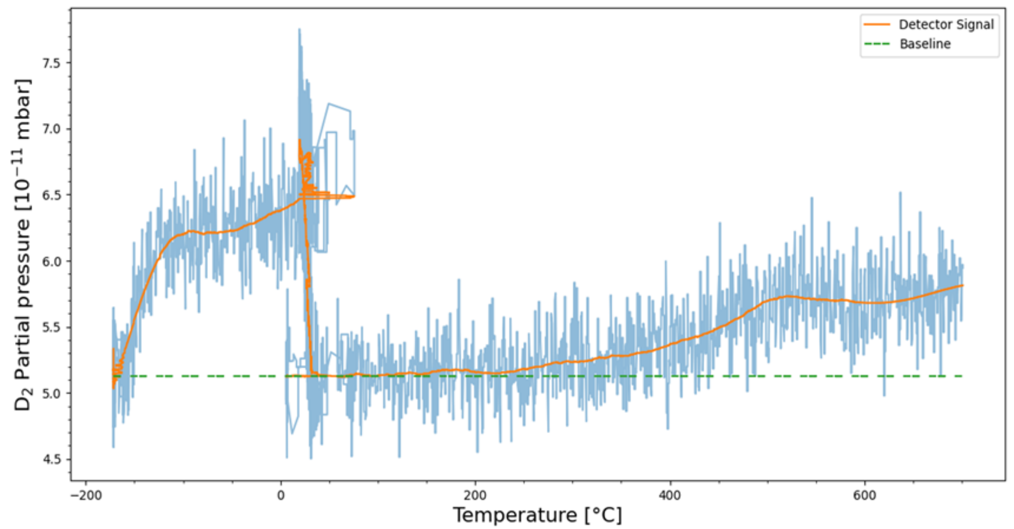


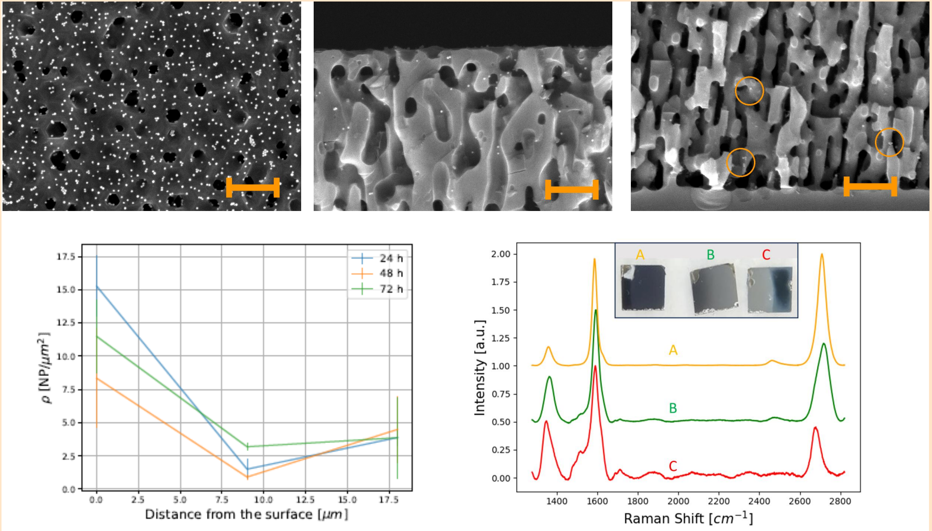
A. Macili et al., Appl. Surf. Sci. 615 (2023) 156375

Metal nanoparticles

In the functionalization experiments two different types of nanoparticles were utilized Gold and Palladium Nanoparticles.

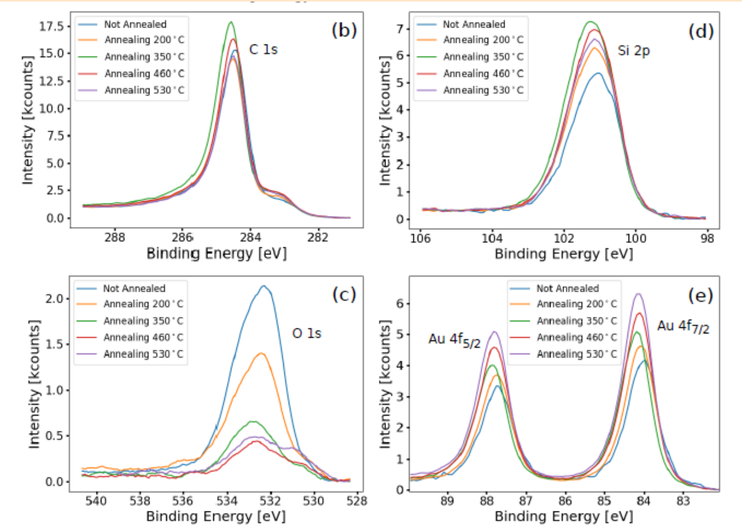
- Gold nanoparticles: commercially available, water suspended, spherical gold nanoparticles with nominal diameter of 20 nm (purchased from BBI Solutions, Au content 0.01% w/v).
- Palladium nanoparicles: synthesized in house, following two different procedures. a) Synthesized from an aqueous solution of palladium(II) acetate (Pd(OAc)2, 98% pure), and sodium dodecyl sulphate (SDS, >99% pure). b) synthesized following the polyol method in which an alcohol is used for the reduction of the metal precursor, Poly(N-vinyl-2-pyrrolidone) (PVP) has been chosen as capping agent.

Gold nanoparticles



E. Pompei et al., arXiv:2310.16797, submitted

Gold nanoparticles: XPS characterization



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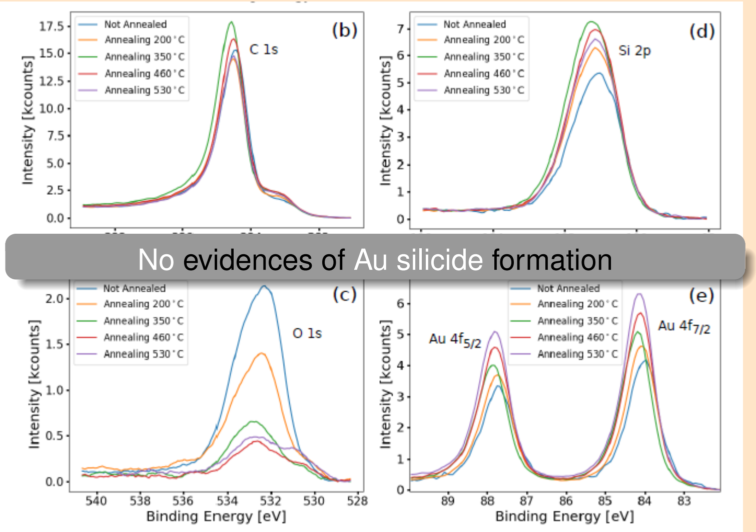


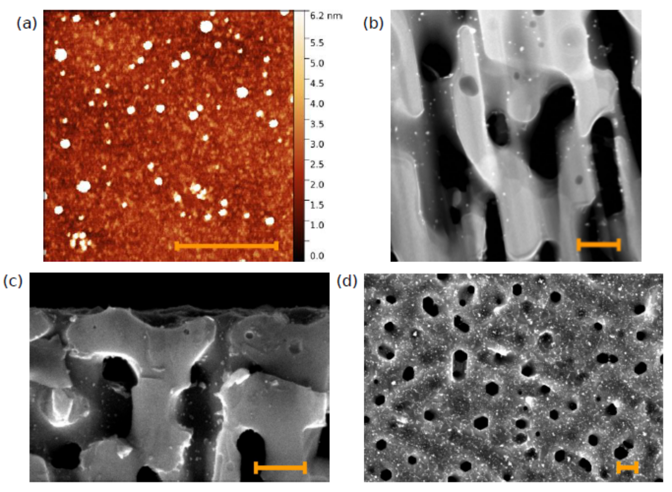
No evidences of Au silicide formation

E. Pompei et al., arXiv:2310.16797, submitted

PVP-Pd nanoparticles

AFM

TEM



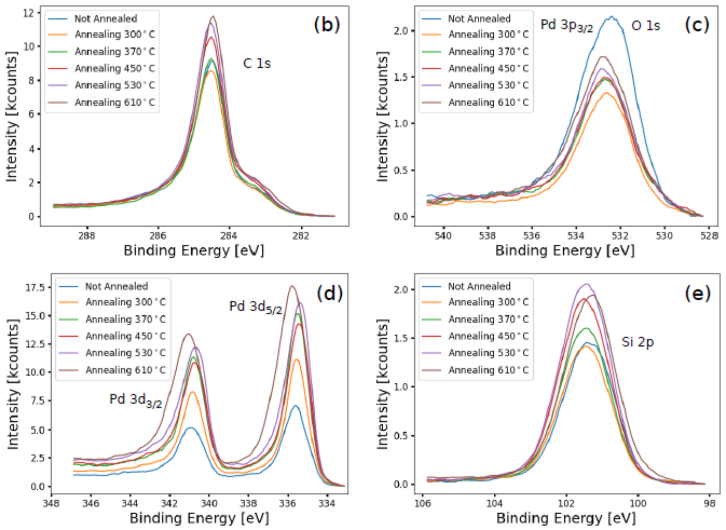
SEM

SEM

scale bars indicate 200 nm

E. Pompei et al., arXiv:2310.16797, submitted

PVP-Pd nanoparticles: XPS characterization



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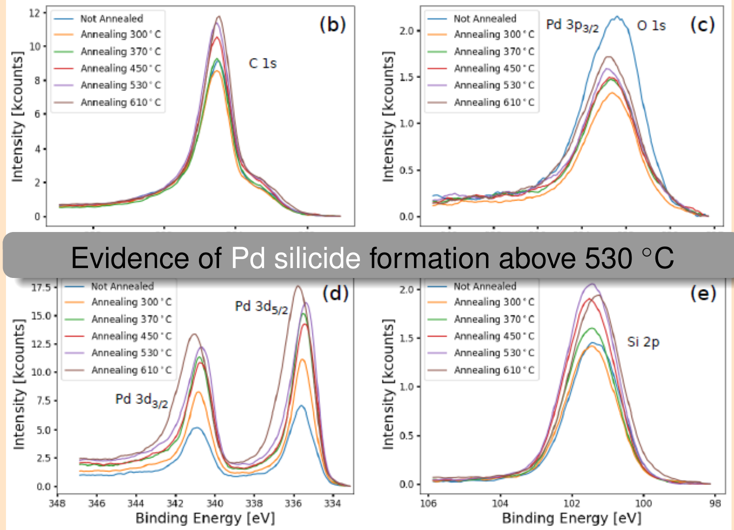
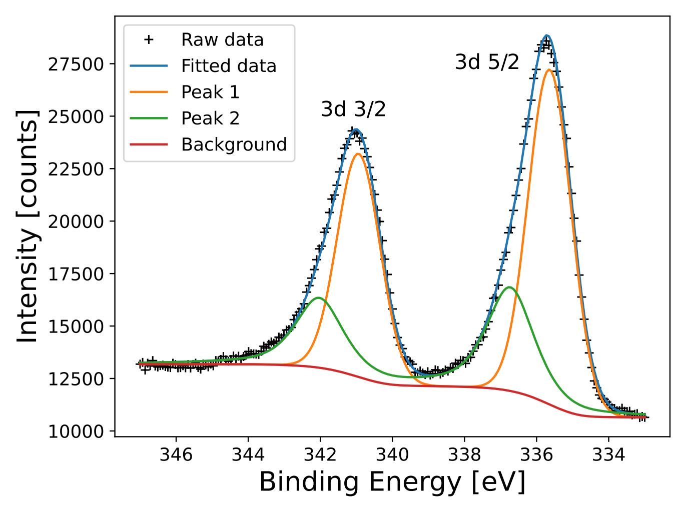


Evidence of Pd silicide formation above 530 °C

E. Pompei et al., arXiv:2310.16797, submitted

PVP-Pd nanoparticles: XPS characterization



Fit of Pd 3d spectrum after annealing at 610 °C. Spin orbit splitting fixed at 5.26 eV. Peak 1 is attributed to Pd metal. Peak 2 has the 5/2 component centered around 336.7 eV and is attributed to Pd_2Si (B. Krause et al. ACS Applied Materials and Interfaces 11,39315 (2019)).

E. Pompei et al., arXiv:2310.16797, submitted

Nanoparticles summary

The functionalization of 3DG with gold and palladium nanoparticles was successfully achieved. In particular, by immersing in the NPs solution, we

- Au-NPs nominal diameter 20 nm
- Au-NPs $(220 \pm 25)\ NPs/\mu m^2$ on the top surface, decreasing to $(3,7 \pm 1.0)\ NPs/\mu m^2$ at the bottom of the porous layer
- No formation of Au silicide
- PVP-Pd NPs diameter $(7.2 \pm 3.0)\ nm$
- PVP-Pd NPs $(3500 \pm 740)\ NPs/\mu m^2$ on the top surface, decreasing to $(170 \pm 60)\ NPs/\mu m^2$ in the first μm
- XPS measurements detected the formation of Pd Silicide, above 530°C

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3 3DG for sensing

Food sensors

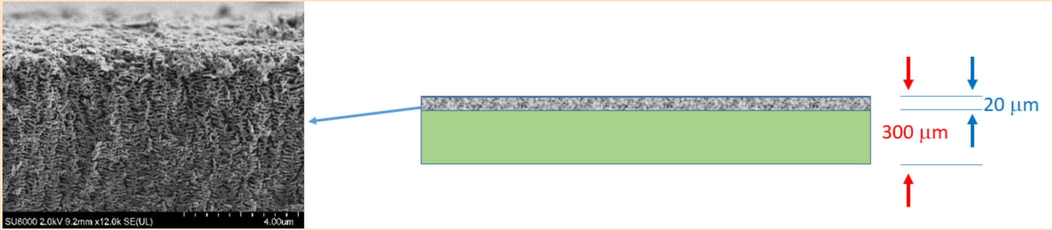
Food sensors are known for their pervasive use in the food chain, to ensure the best preservation conditions of the food and the safety of consumers. Sensors detect the presence or concentration of an analyte or a physical parameter:

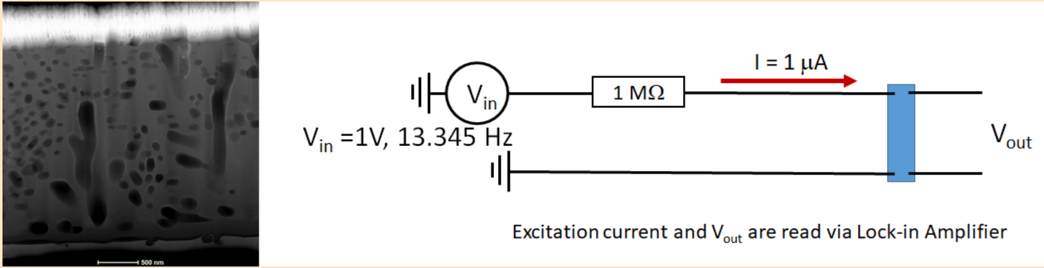
- Biological (allergens, toxins, pathogens, ...)
- Chemical (heavy metals, pesticides, ...)
- Physical (temperature, humidity, ...)

Selectivity is a key parameter.

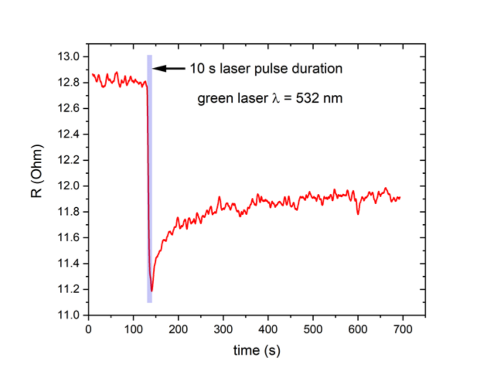
Research on new materials and techniques boosting the sensor performance is ongoing.

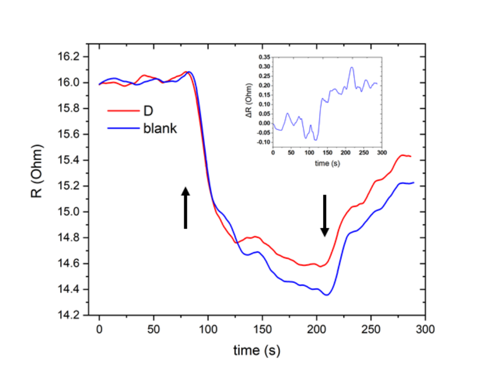
Preliminary tests on 3DG sensing perspectives





Sensing light and hydrogen





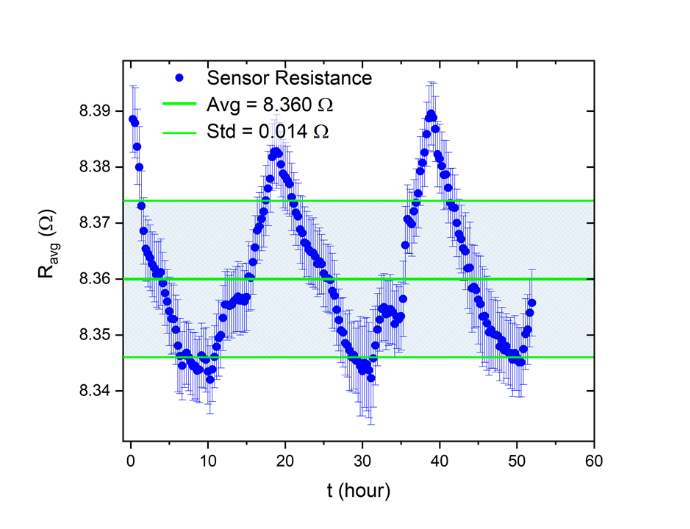
Black arrow points at laser off

Black arrows point at hydrogen flux on and off

S. Veronesi et al. J. Sci. Food Agric. http://doi.org/10.1002/jsfa.13118 (2023)

The effect of Circadian temperature cycle

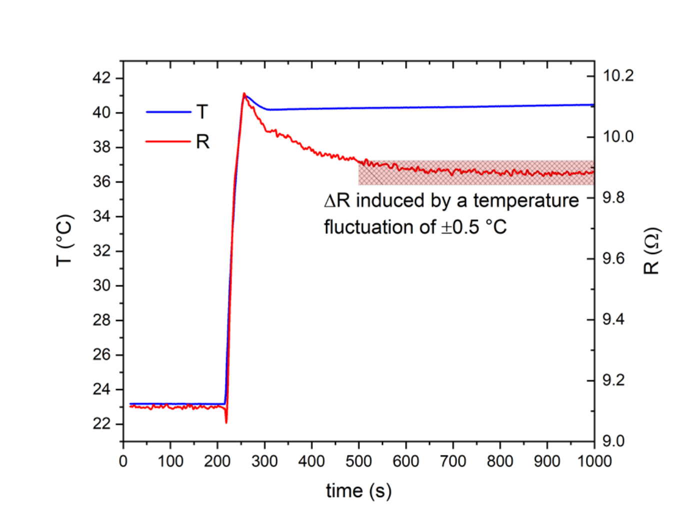
Sensor resistance variation during a two day long acquisition. The main oscillation is due to the residual circadian temperature oscillation of the air-conditioned laboratory.



S. Veronesi et al. J. Sci. Food Agric. http://doi.org/10.1002/jsfa.13118 (2023)

Active temperature control

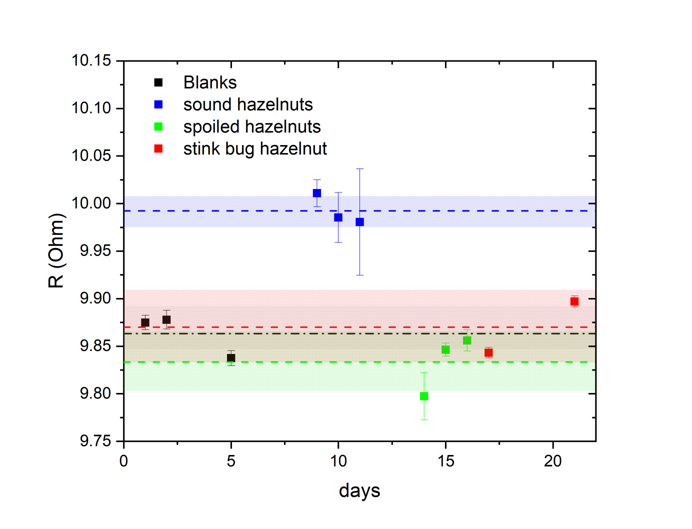
Variation in sensor temperature and resistance during 15 minutes, including the switch on of the temperature stabilization. The reddish area visualizes the effect of a $\pm 0.5\,^{\circ}C$ temperature fluctuation on the resistance readout.



S. Veronesi et al. J. Sci. Food Agric. http://doi.org/10.1002/jsfa.13118 (2023)

Constant temperature operation

The temperature stabilization of the sensor reduces dramatically data fluctuation, allowing to clearly discriminate between healthy and harmed fruits.



S. Veronesi et al. J. Sci. Food Agric. http://doi.org/10.1002/jsfa.13118 (2023)

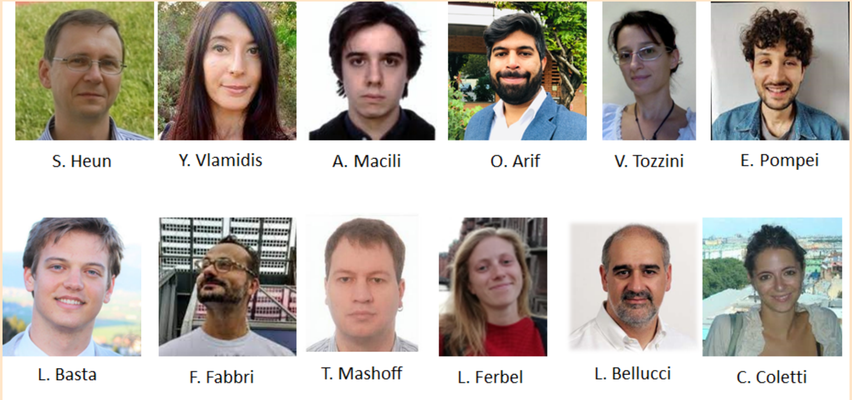
Outlook

- Asses the hydrogen storage efficiency of 3DG functionalized with PVP-Pd nanoparicles
- 3DG functionalization with differrent metals (Pt, Ni, ...)
- Perform hydrogenations at higher pressure, closer to the conditions in a real world utilization
- extend the exploration of 3DG-based sensors

Conclusions

- 3D arrangement of graphene in porous SiC (3DG)
  - ⇒ Uniform high-quality graphene growth in the pores
  - ⇒ 200 times increase in active surface area
  - ⇒ Chemisorption after exposure to molecular hydrogen
- 3DG is a promising material for hydrogen storage
- 3DG functionalization with Au and Pd nanoparticles
  - ⇒ Au-NPs nominal diameter 20 nm, $(220 \pm 25)\ NPs/\mu m^2$ on the top surface
  - ⇒ No formation of Au silicide
  - ⇒ PVP-Pd NPs diameter $(7.2 \pm 3.0)\ nm$, $(3500 \pm 740)\ NPs/\mu m^2$ on the top surface
  - ⇒ XPS measurements detected the formation of Pd Silicide, above 530°C
  - ⇒ Enhancement of hydrogen storage performance by metal functionalization ?
- 3DG-based sensor able to discriminate between healthy and harmed hazelnuts

The Pisa team



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thanks

Thank you for your attention