Prospects for Hydrogen Storage in Graphene

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National Enterprise for nanoScience and nanoTechnology

Outline

- Introduction to Hydrogen Storage
- Hydrogen and Graphene
- Three-dimensional arrangement of epitaxial graphene on porous SiC

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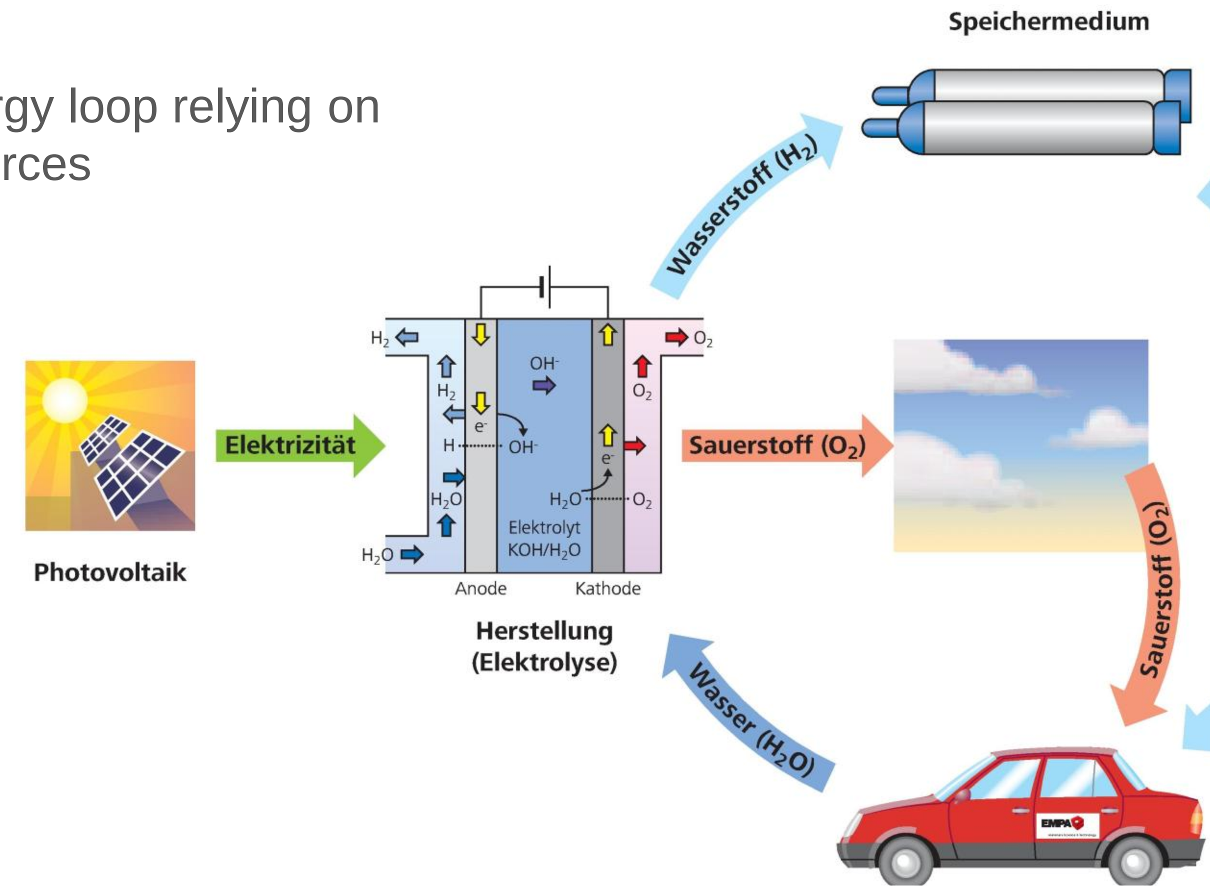
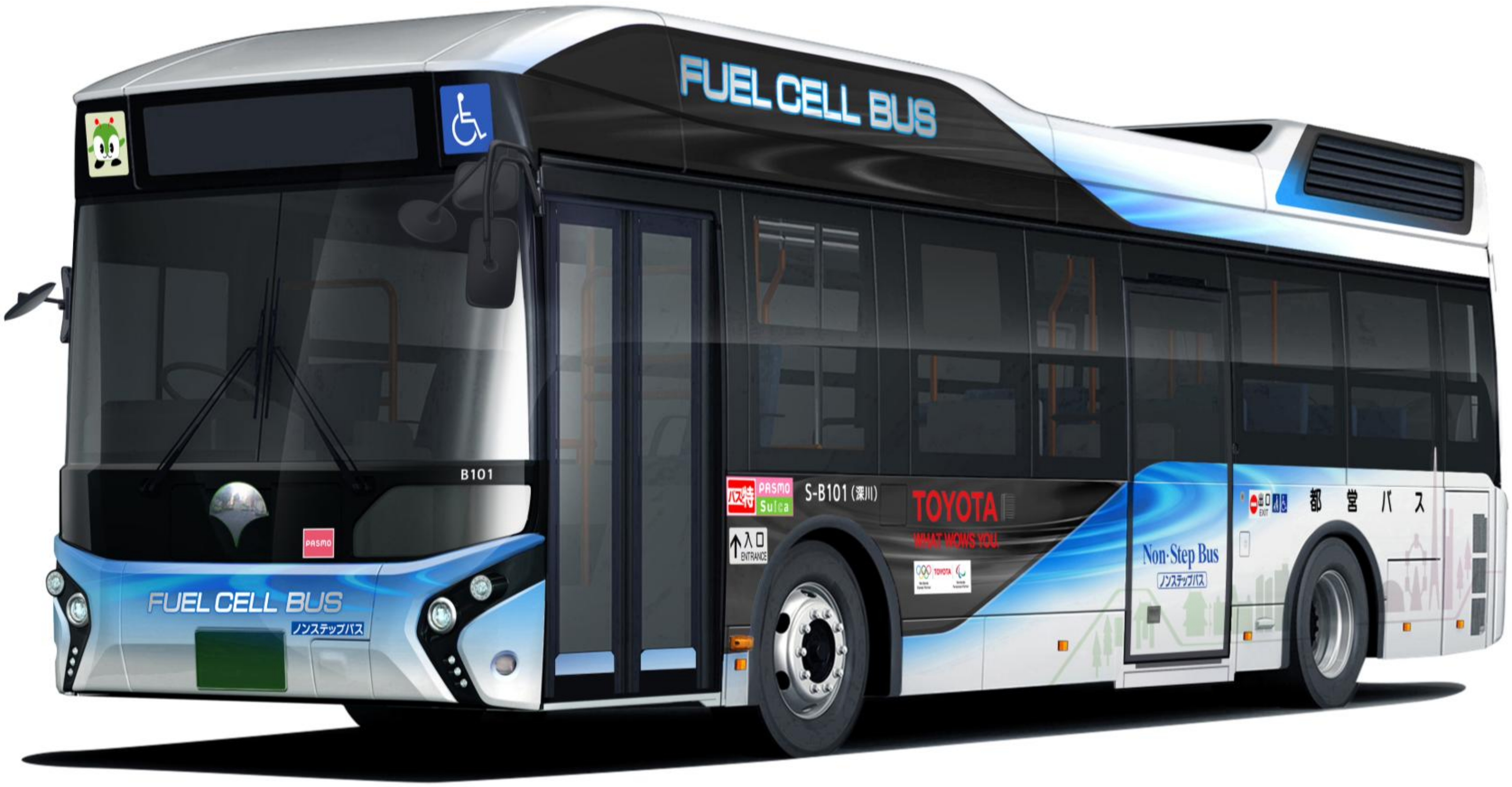
Hydrogen Life Cycle

Complete energy loop relying on renewable sources



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

Hydrogen-fueled vehicles ....



… since the 1970s …

… now for sale

Hydrogen-fueled Train

Coradia iLint regional train

Fahrplan iLint ab 18.03.19

Montag bis Freitag

ab	Bremervörde	08:38	Uhr	an	Bremerhaven Hbf	09:20	Uhr
ab	Bremerhaven Hbf	09:36	Uhr	an	Cuxhaven	10:27	Uhr
ab	Cuxhaven	10:39	Uhr	an	Bremerhaven Hbf	11:23	Uhr
ab	Bremerhaven Hbf	11:36	Uhr	an	Bremervörde	12:20	Uhr
ab	Bremervörde	12:25	Uhr	an	Buxtehude	13:09	Uhr
ab	Buxtehude	13:37	Uhr	an	Bremervörde	14:23	Uhr
ab	Bremervörde	16:38	Uhr	an	Bremerhaven Hbf	17:20	Uhr
ab	Bremerhaven Hbf	17:36	Uhr	an	Bremervörde	18:20	Uhr
ab	Bremervörde	18:38	Uhr	an	Buxtehude	19:26	Uhr
ab	Buxtehude	19:53	Uhr	an	Bremervörde	20:36	Uhr
ab	Bremervörde	20:38	Uhr	an	Bremerhaven Hbf	21:20	Uhr

… but it better be safe

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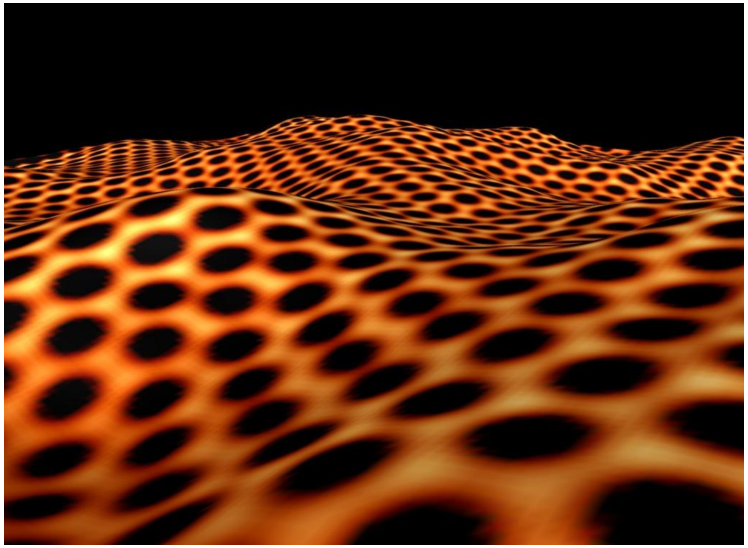
- Introduction to Hydrogen Storage
- Hydrogen and Graphene
- Three-dimensional arrangement of epitaxial graphene on porous SiC

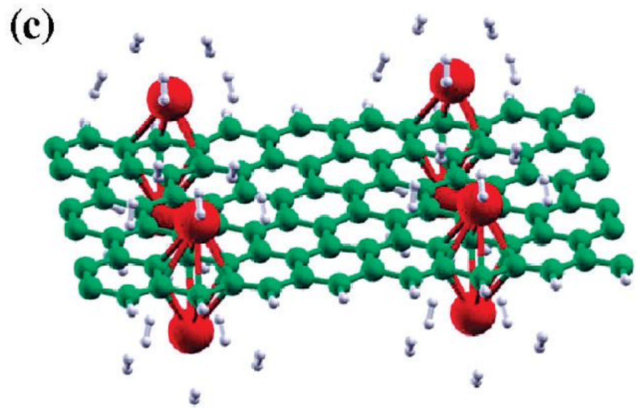
Graphene for hydrogen storage

- Graphene is lightweight, inexpensive, robust, chemically stable
- Large surface area (~ 2600 m^2/g)

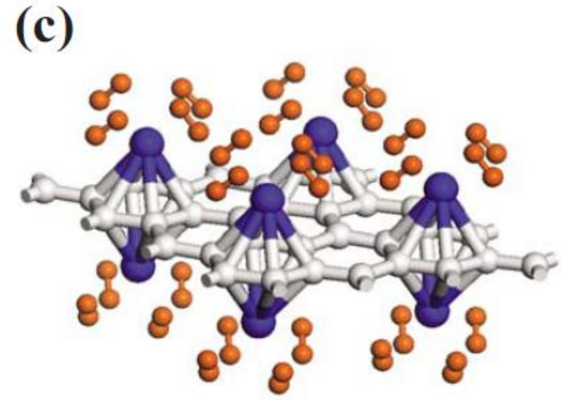


Functionalized Graphene

- 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

Functionalized Graphene

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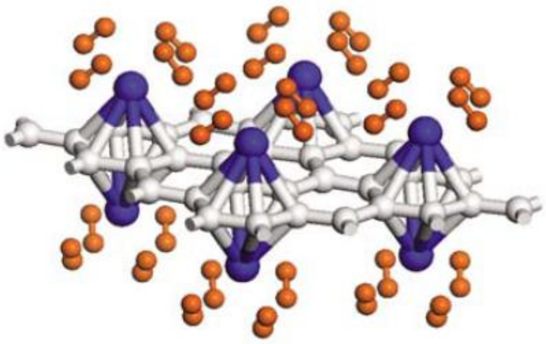
We have so far explored functionalization of epitaxial monolayer graphene with Ti, Li, Rb, Pt, Au, Ni



en et al., PRB 77 (2007) 085405

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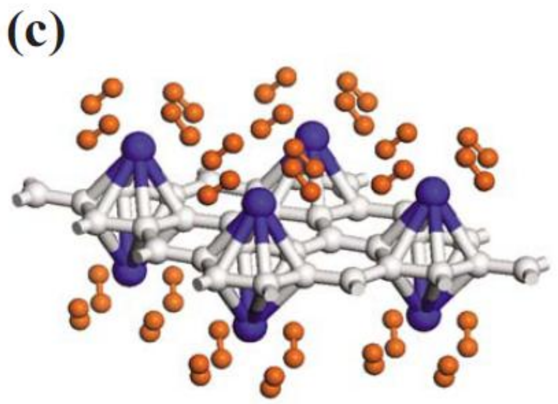
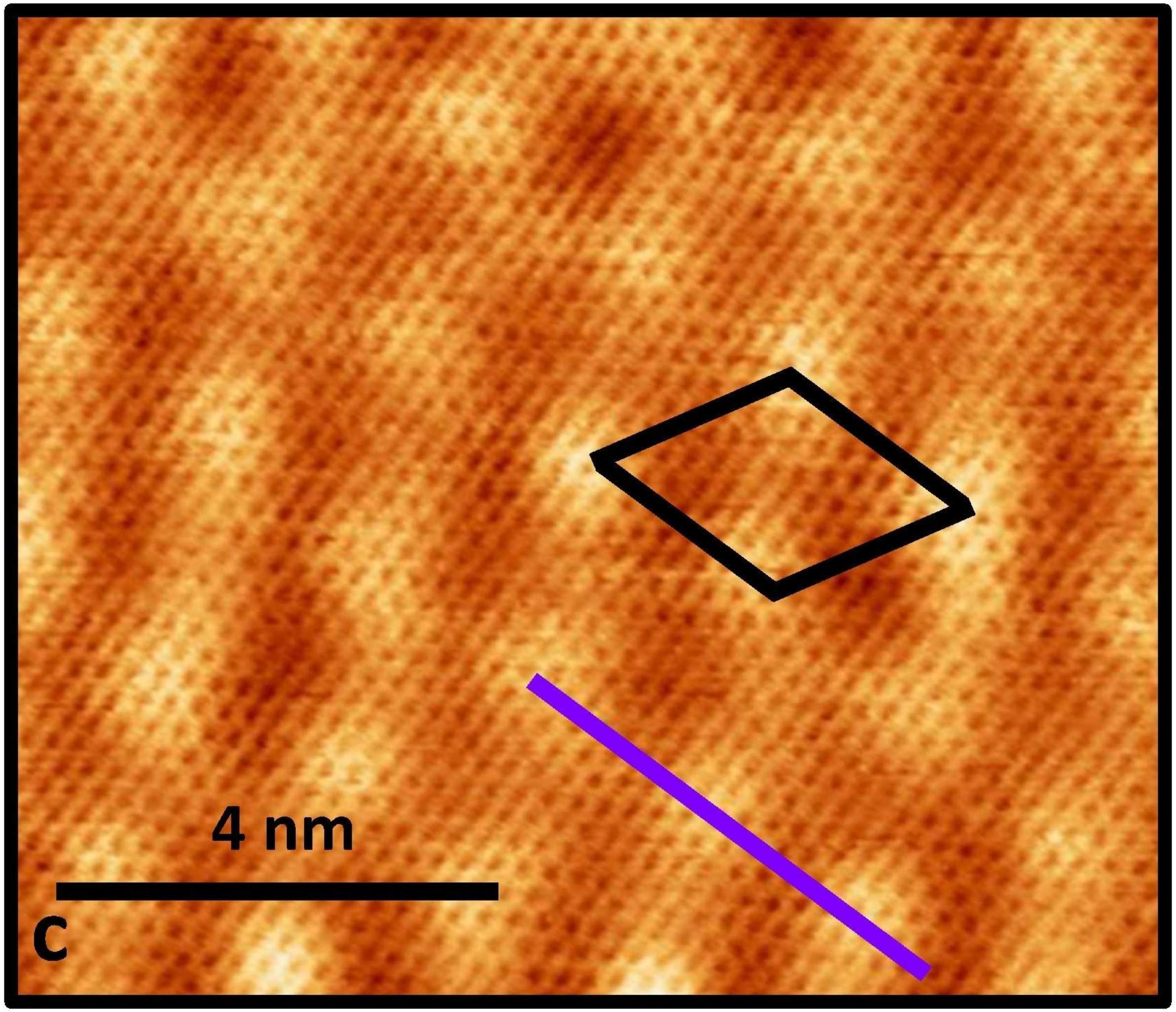
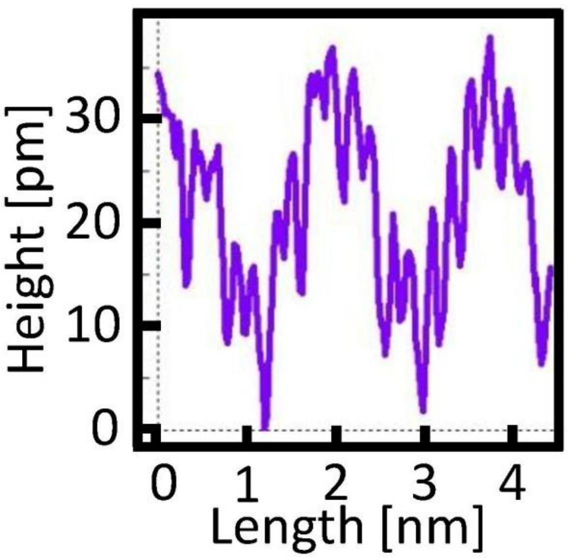


...en et al., PRB 77 (2007) 085405

Monolayer Graphene



STM



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

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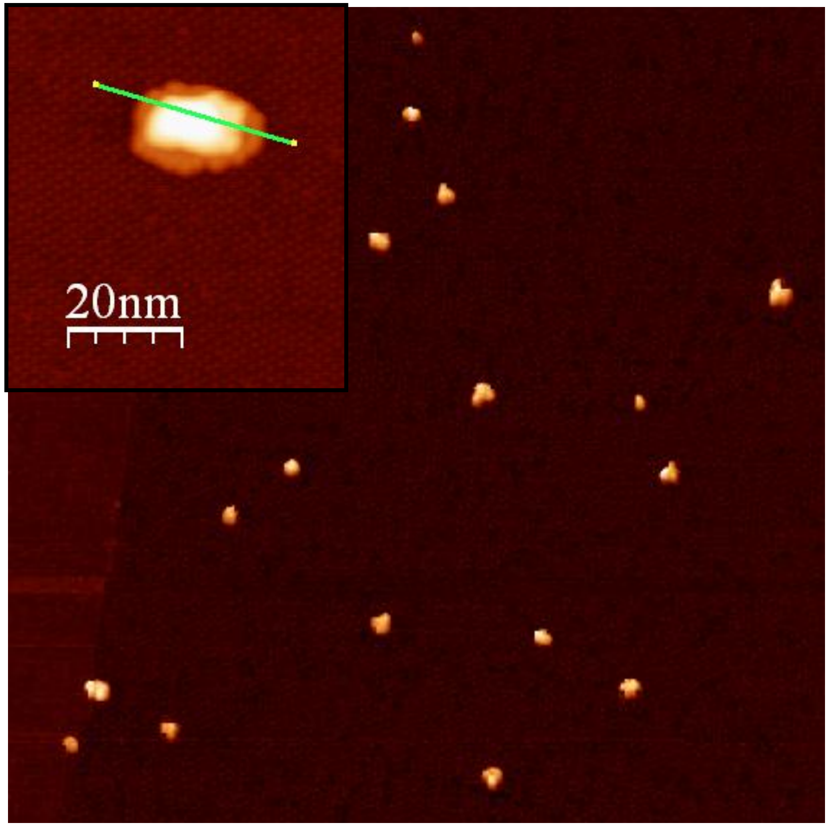
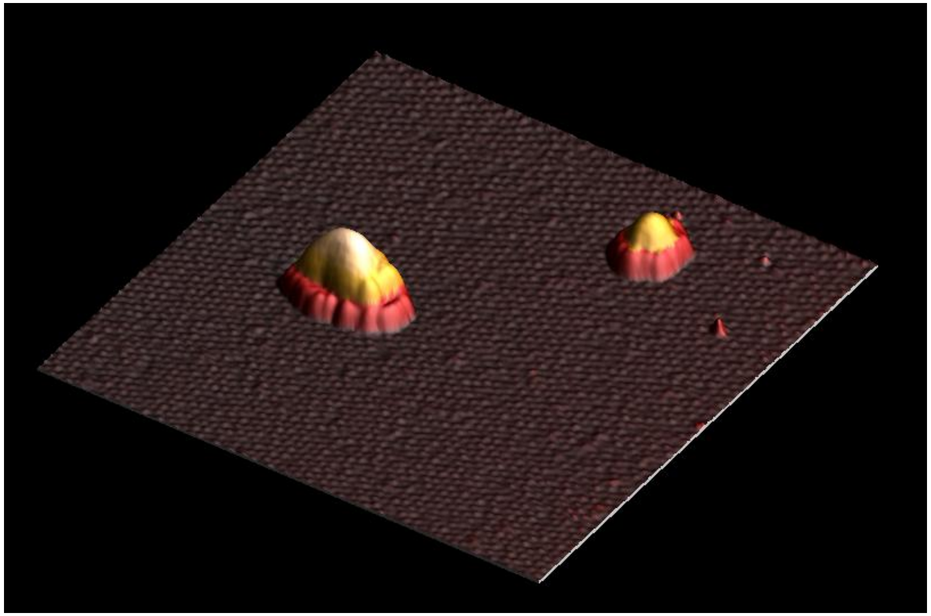
Titanium on graphene



After deposition of Ti at RT



Titanium Islands on Graphene on SiC(0001) ($100x100nm^2$)

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

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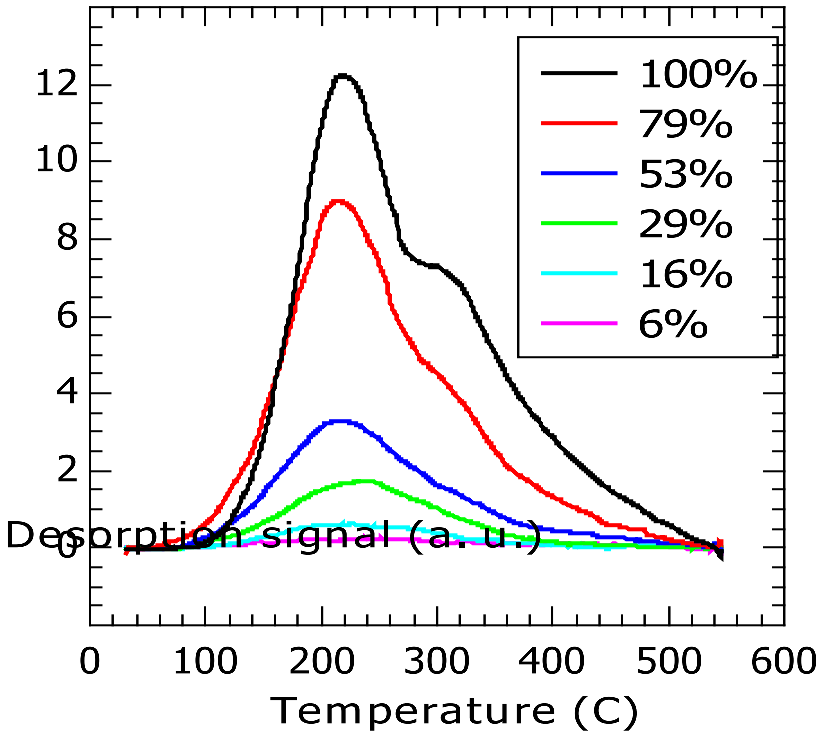
Thermal desorption spectroscopy

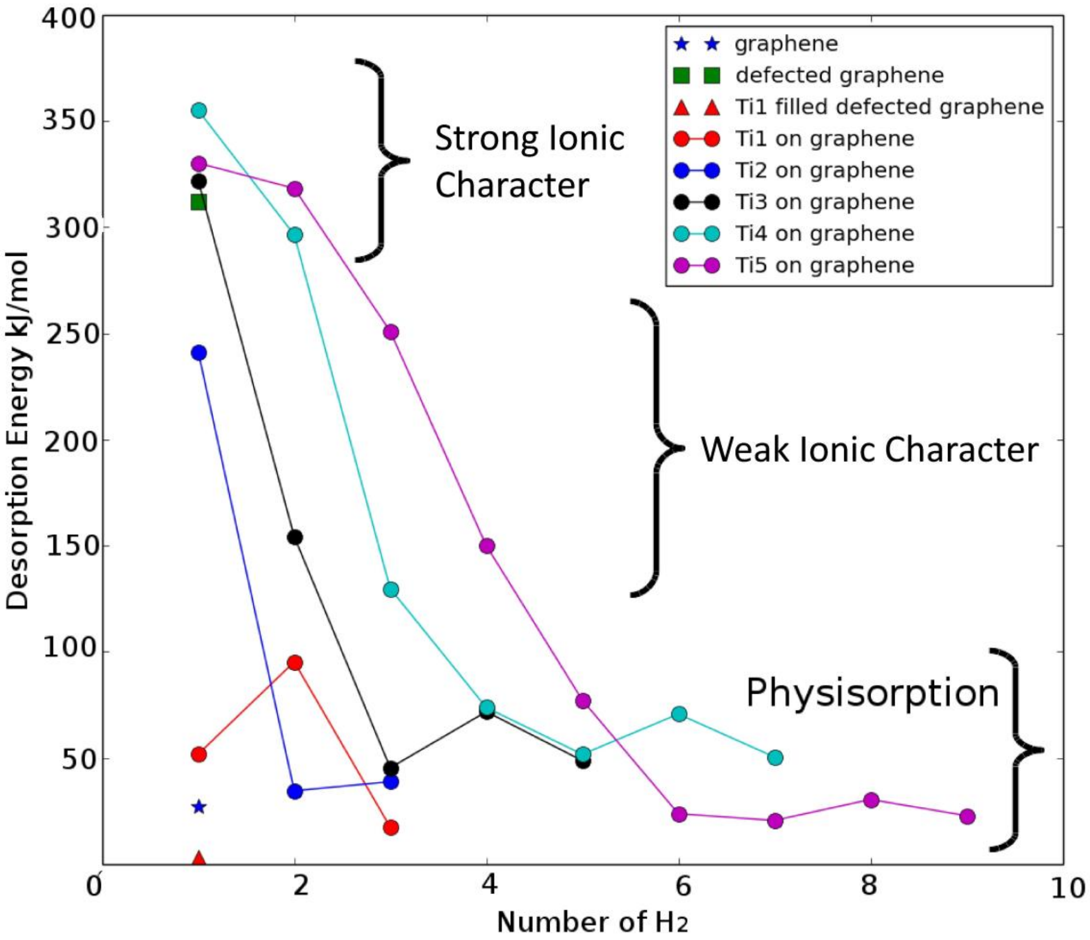
- Deposition of different amounts of Titanium
- Offering Hydrogen (D_2) $1x10^{-7}$ mbar for 5 min
- Heating sample with constant rate (10K/s) up to 550° C
- Measuring mass-sensitive desorption with a mass spectrometer

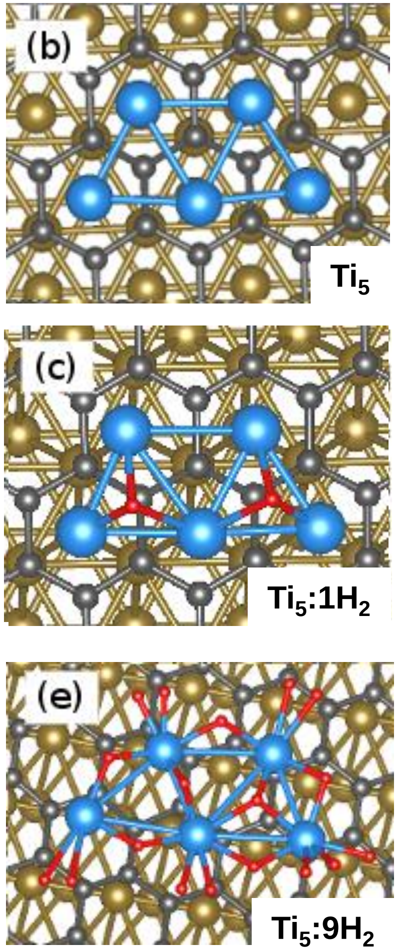
Spectra for different Ti-coverages



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

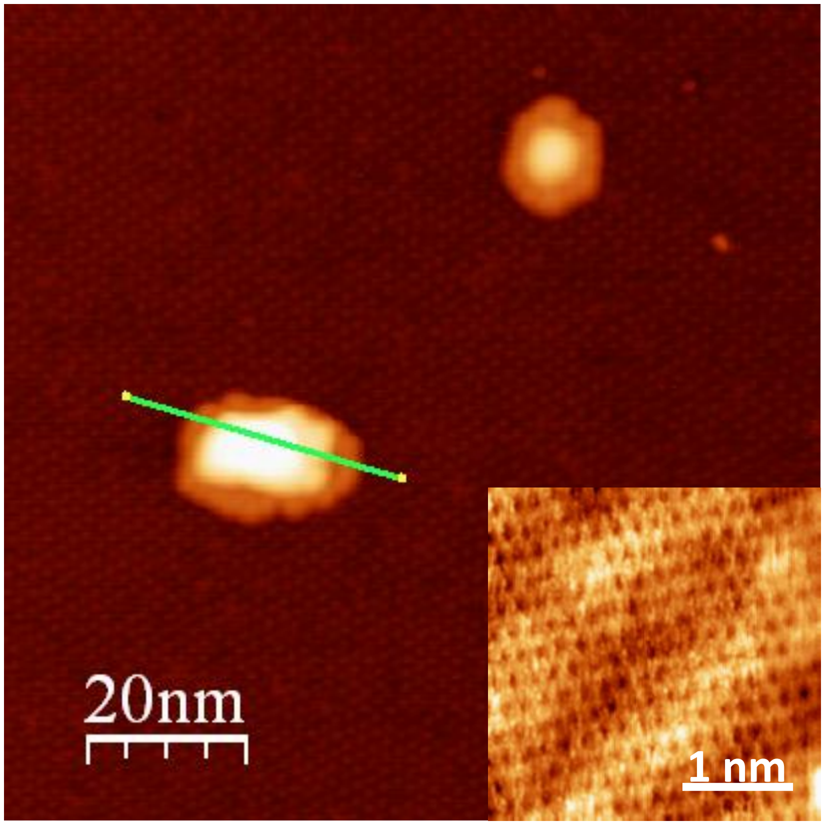
Different bonding types



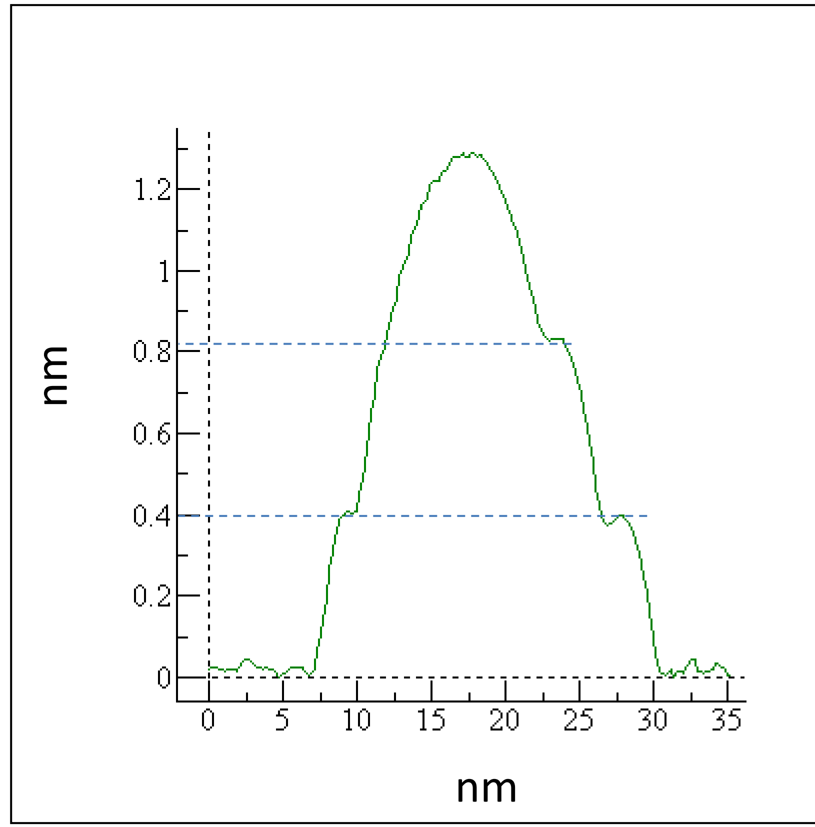


K. Takahashi *et al.*: J. Phys. Chem. C 120, 12974 (2016).

Forming of Islands



100 nm, 1 V, 82 pA



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

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PHYSICAL REVIEW B **87**, 014102 (2013)

Hydrogen adsorption capacity of adatoms on double carbon vacancies of graphene: A trend study from first principles

K. M. Fair,[1,2] X. Y. Cui,[3,4,*] L. Li,[1] C. C. Shieh,[1] R. K. Zheng,[1,3] Z. W. Liu,[3,5] B. Delley,[6] M. J. Ford,[2] S. P. Ringer,[3,4] and C. Stampfl[1,7]

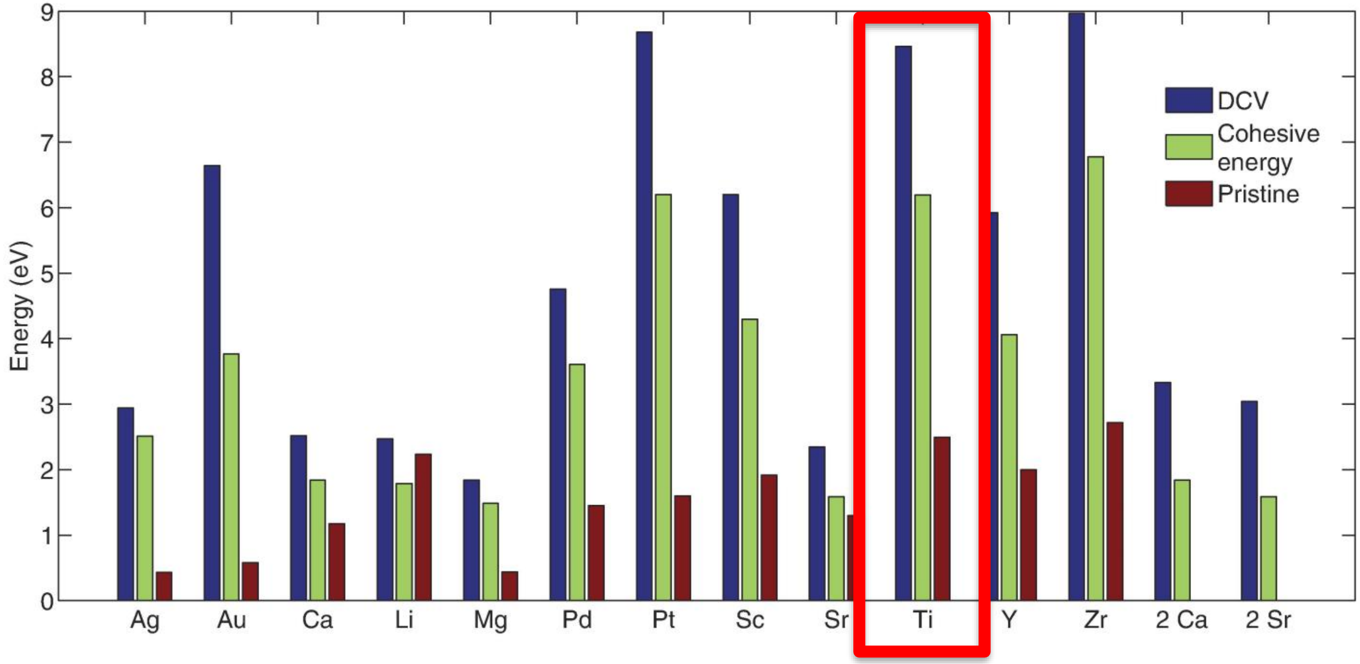
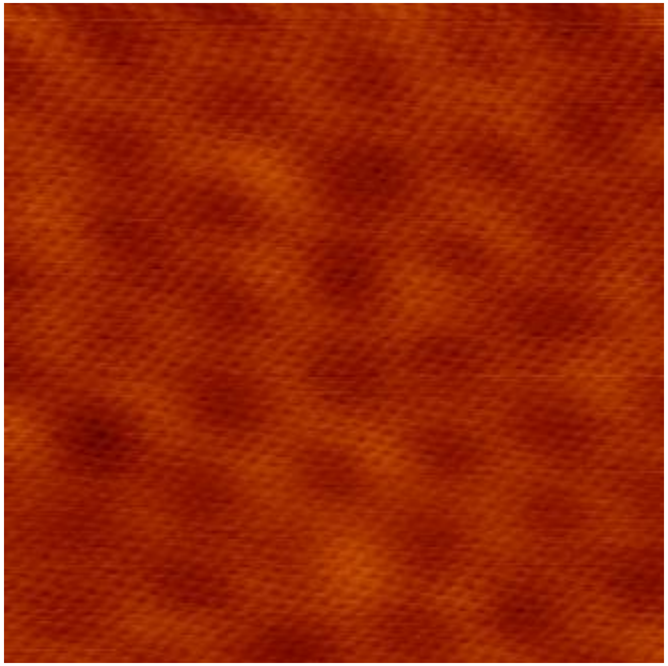


FIG. 1. (Color online) The binding energy of adatoms to graphene DCVs (blue), and pristine graphene (red), as well as the cohesive energy of the respective metal (green). Also included are the binding energies per adatom of two Ca and Sr ("2Ca" and "2Sr") adatoms with one on either side of the DCV.

DCV = Double Carbon Vacancy

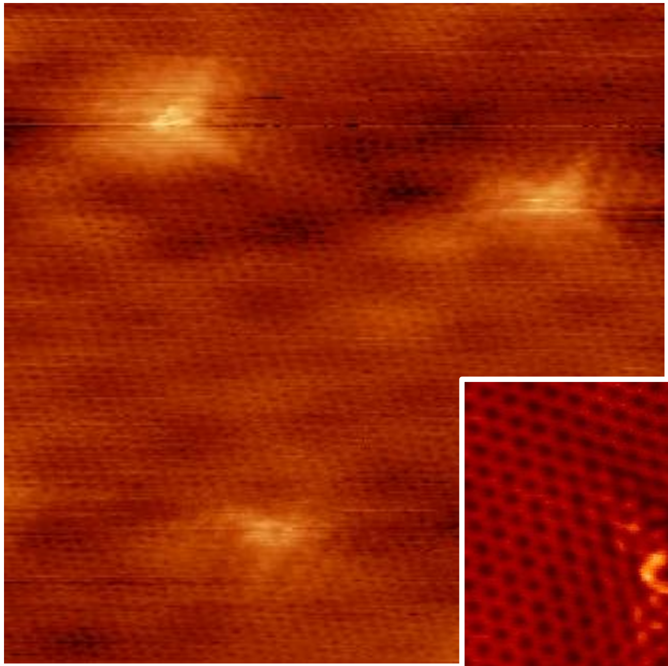
N_2 - sputtering of the graphene surface

Clean graphene surface



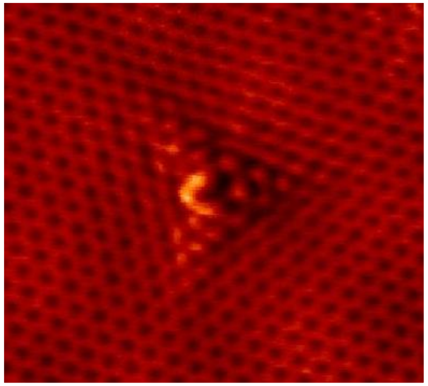
$10x10\ nm^2$, 1V, 0.8nA

Sputtered 150s @100eV



$10x10\ nm^2$, 1V, 0.8nA

200mV
200pA



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. **106**, 083901 (2015).

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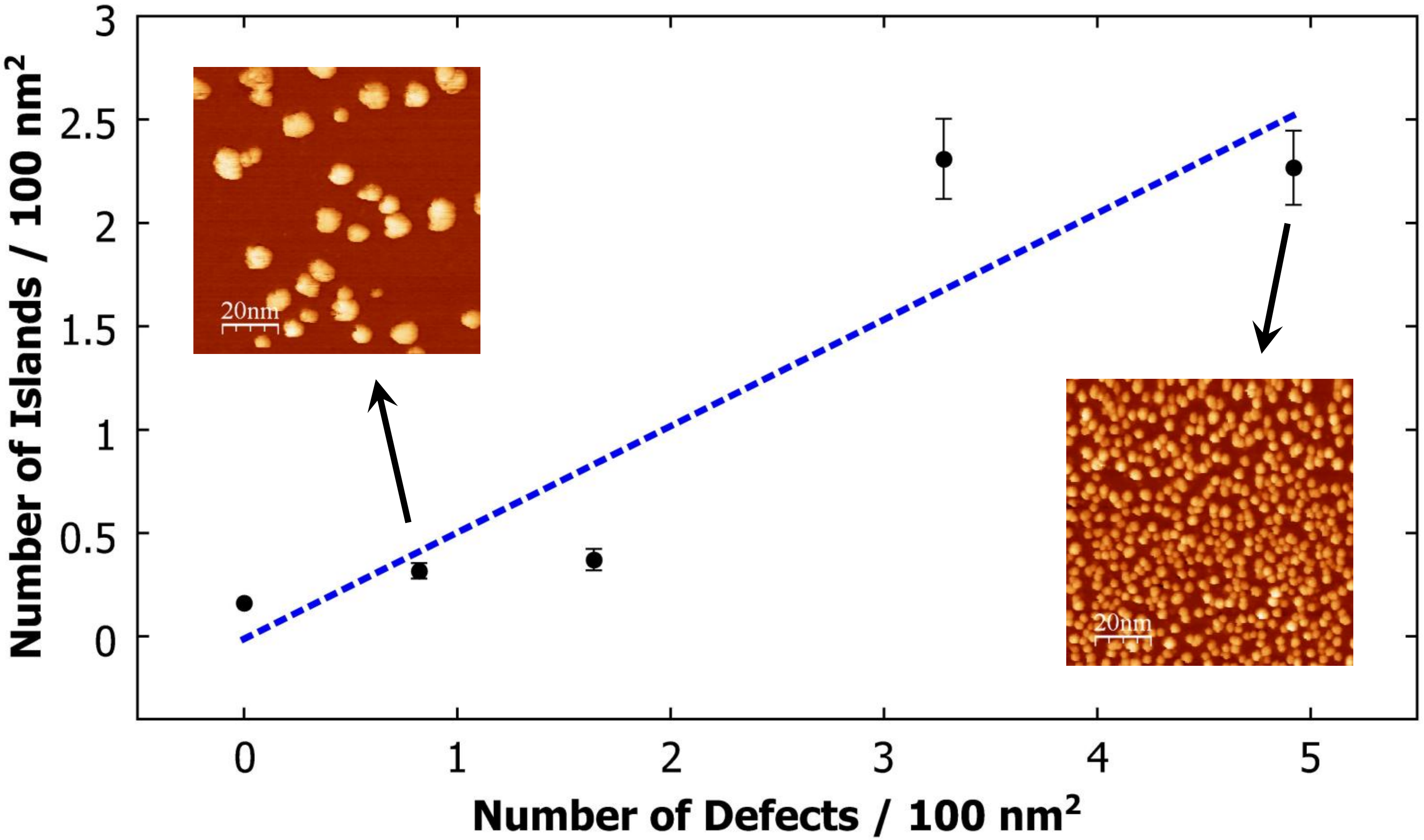
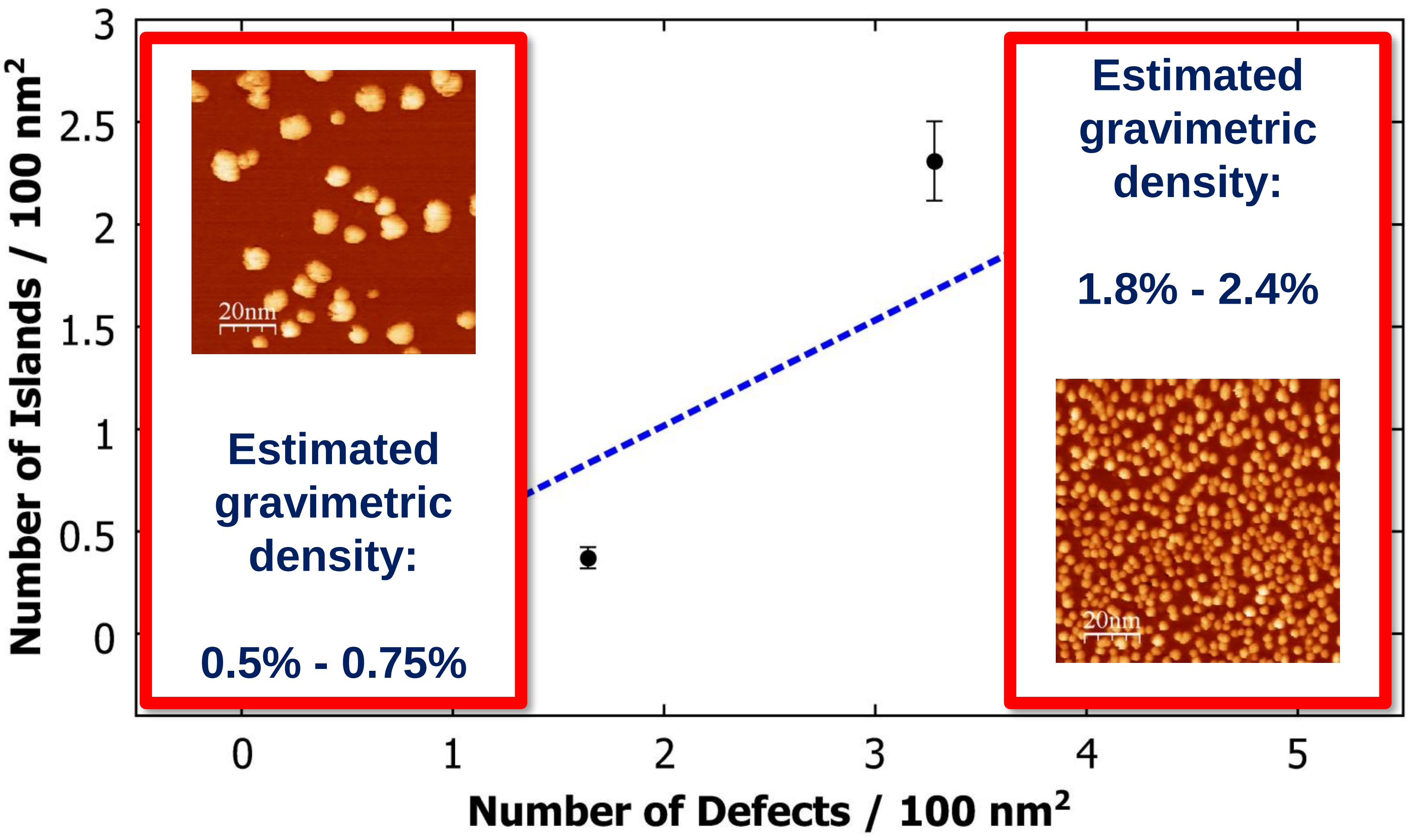
Average Number of Islands per 100 nm^2



Sputtered 150 s and Deposition of 0.5 ML Titanium

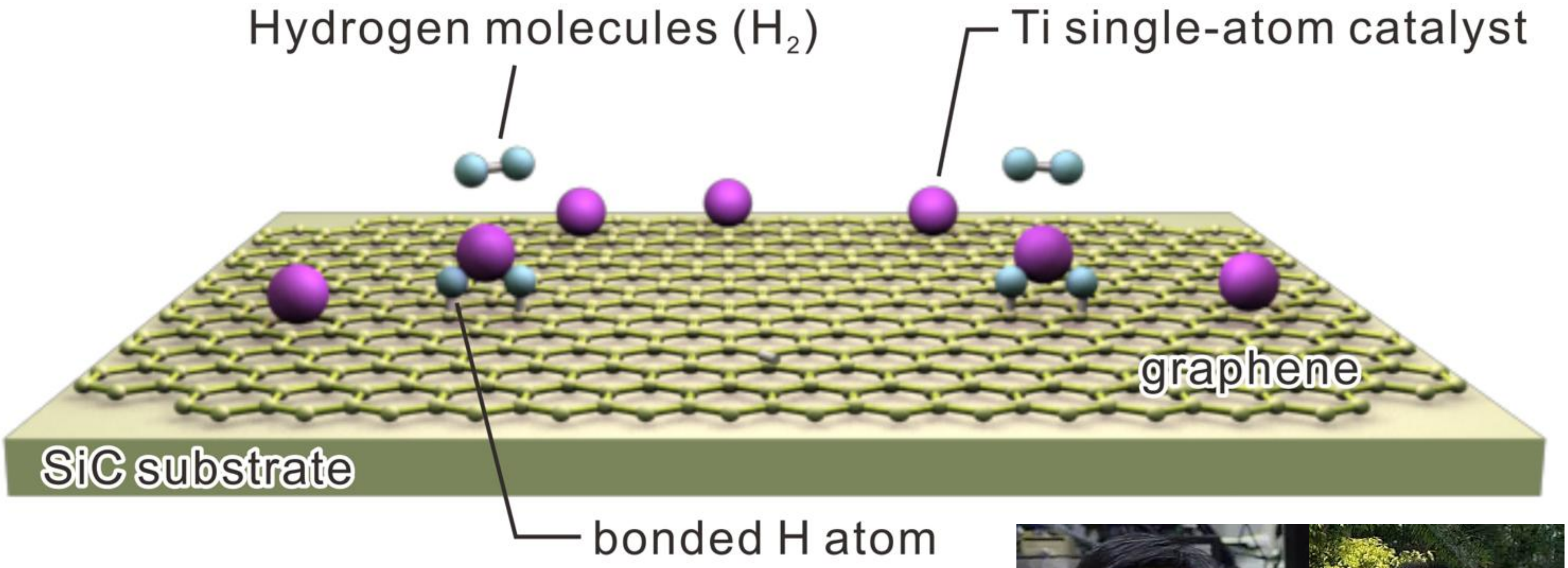
T. Mashoff *et al.*: Appl. Phys. Lett. **106**, 083901 (2015).

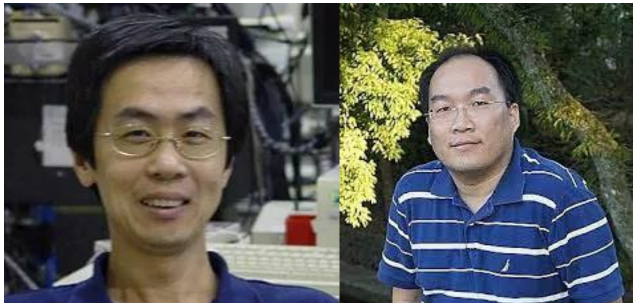
Higher number of defects leads to smaller Ti islands



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

Hydrogen Spillover

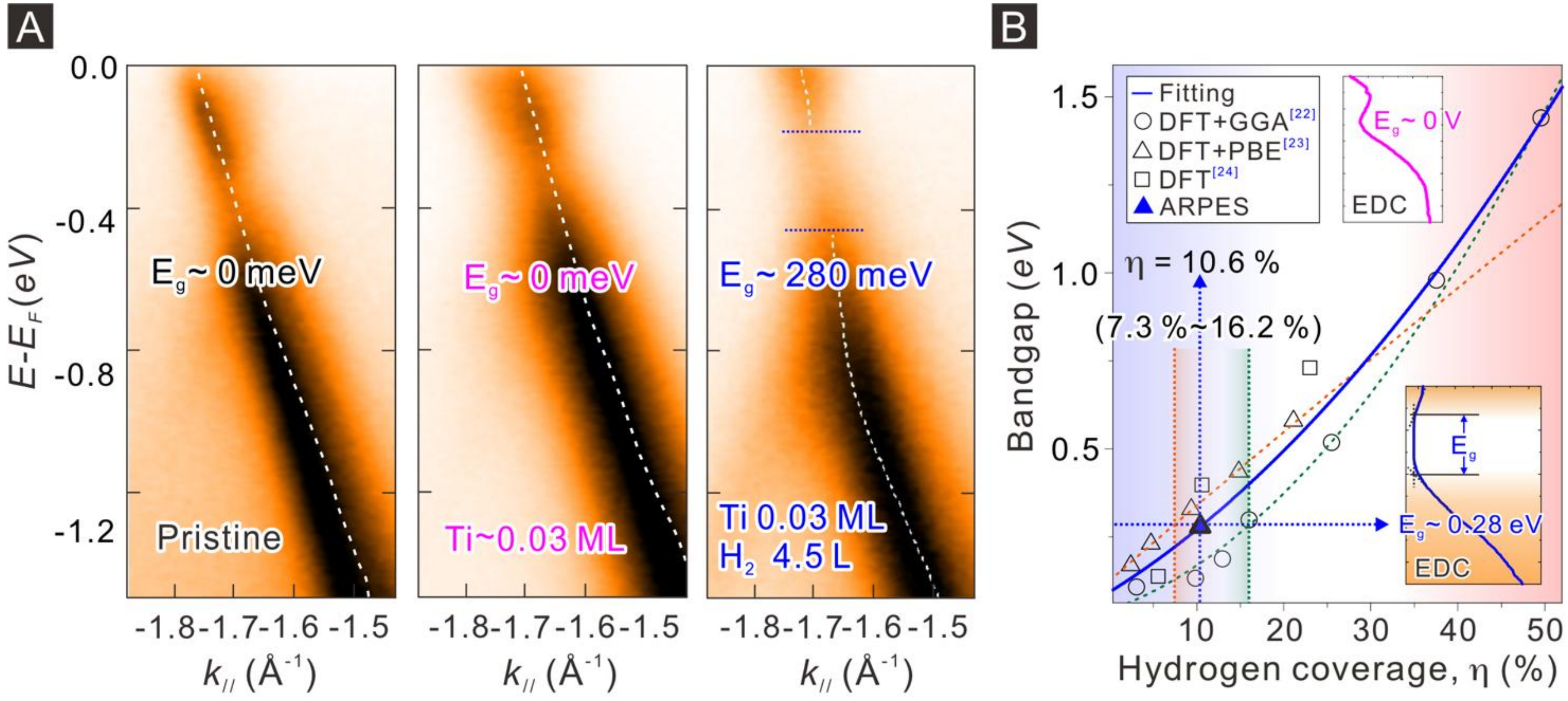




Chia-Hao Chen   Chung-Lin Wu

J.-W. Chen *et al.*, ACS Energy Lett. 7 (2022) 2297.

Band Gap Opening



J.-W. Chen *et al.*, ACS Energy Lett. 7 (2022) 2297.

Is the Graphene Route feasible?

- 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.

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- Three-dimensional arrangement of epitaxial graphene on porous SiC

Porous SiC

Ulrich Schmid
TU Wien

- 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.

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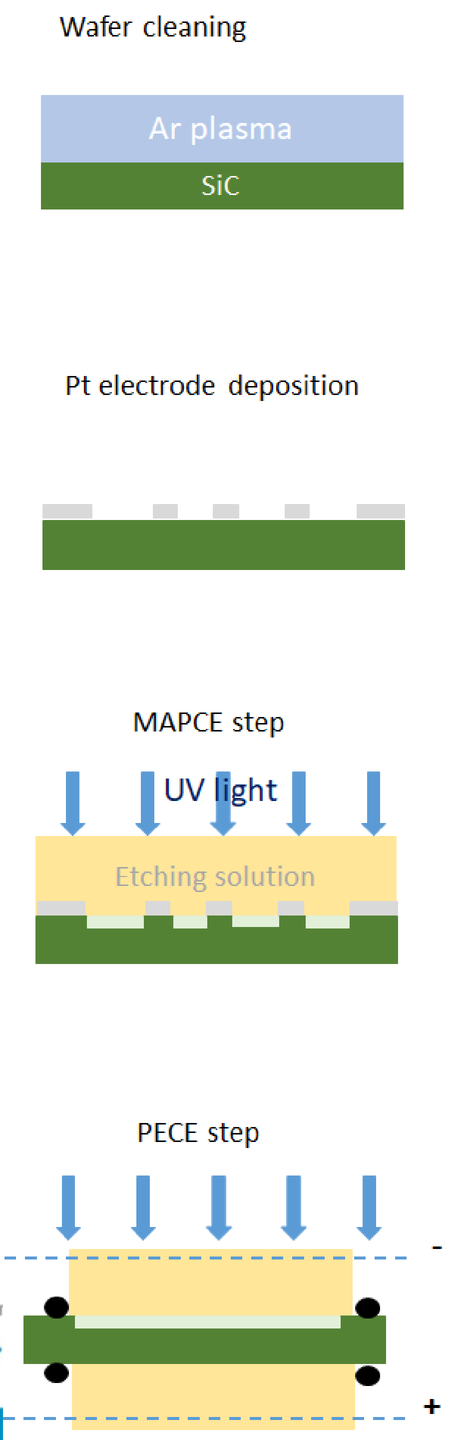
MAPCE = metal-assisted photochemical etching
PECE = photo-electrochemical etching



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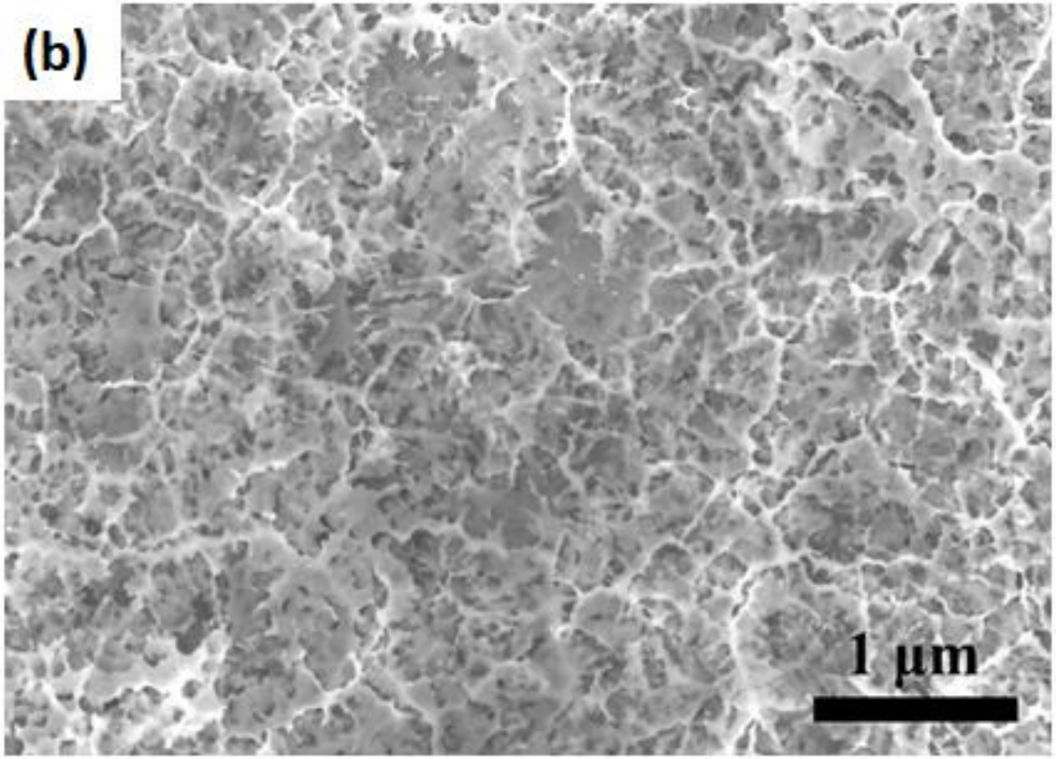
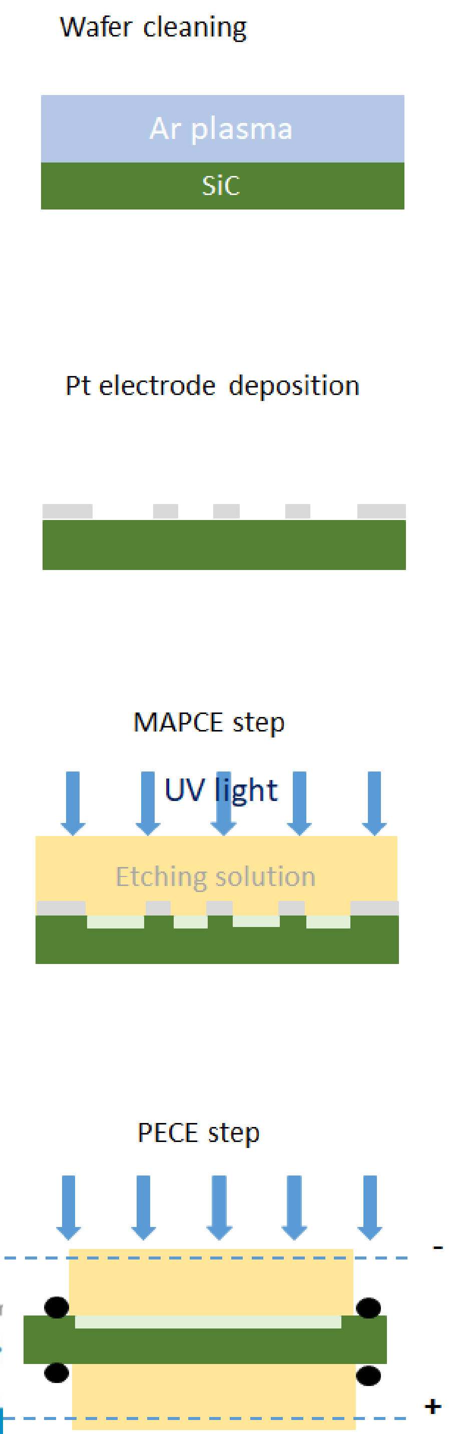
Porous SiC

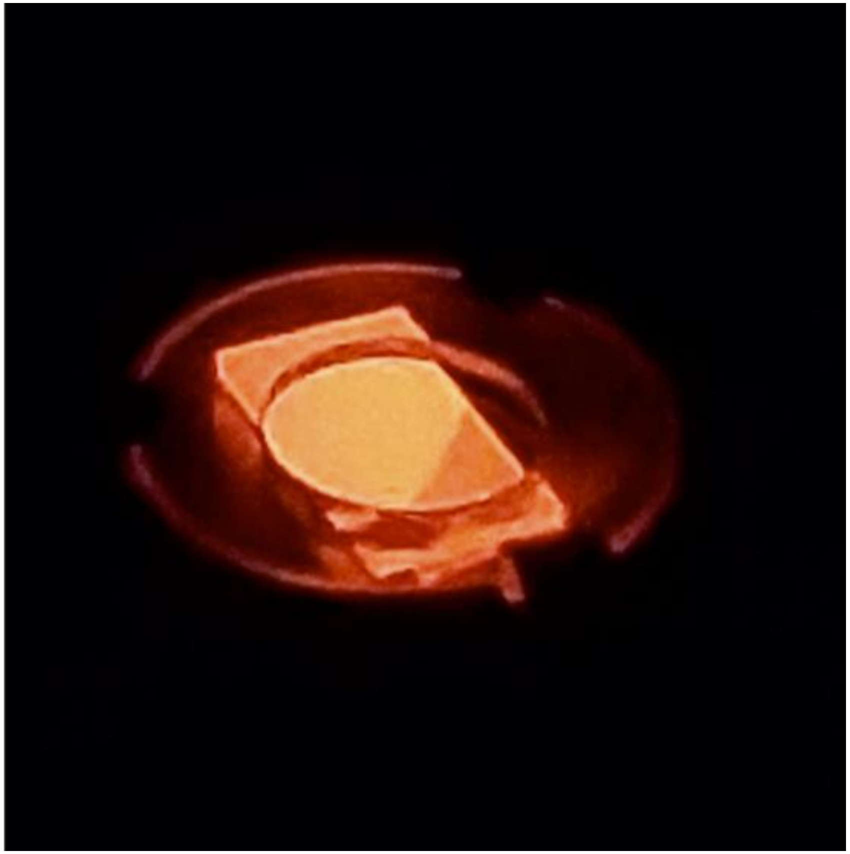


Top-view SEM of porous Si-face sample



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.

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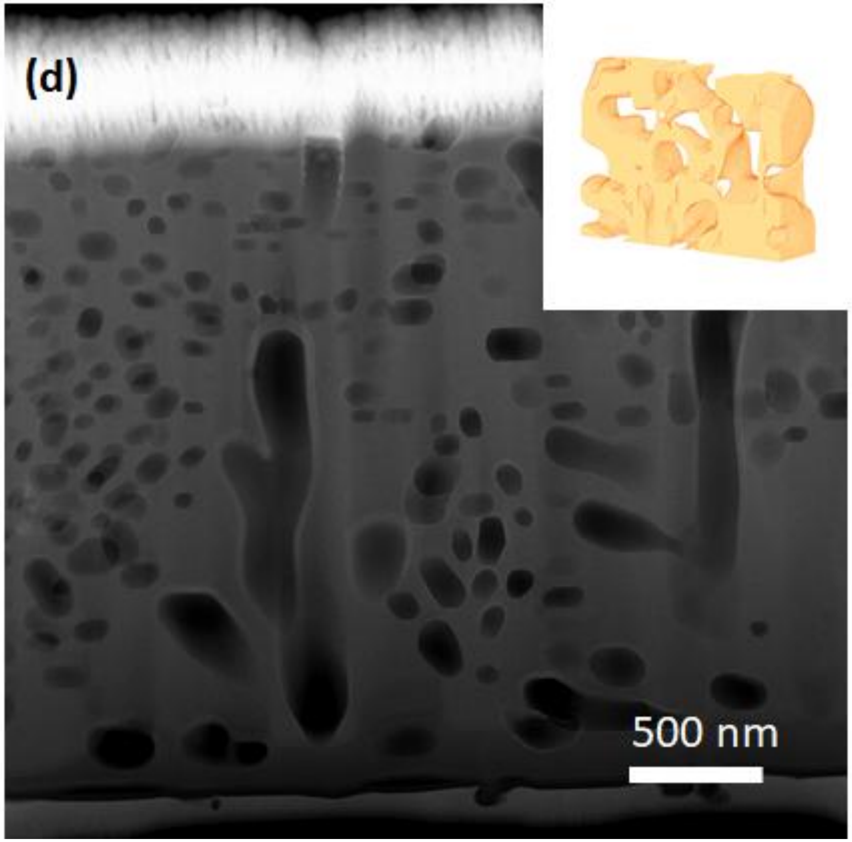
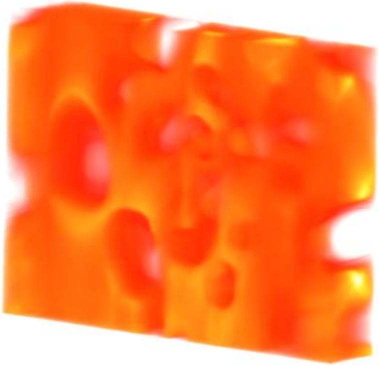
TEM after Graphene Growth

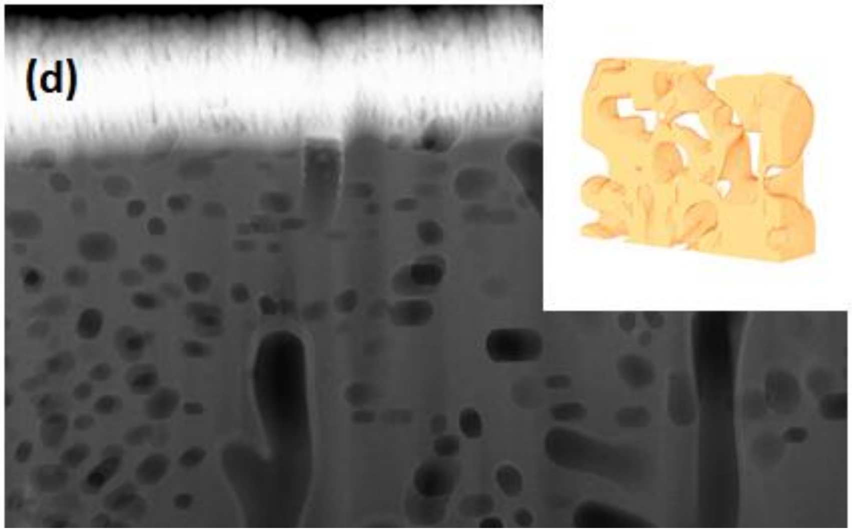
Sara Bals
U Antwerp





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

TEM after Graphene Growth

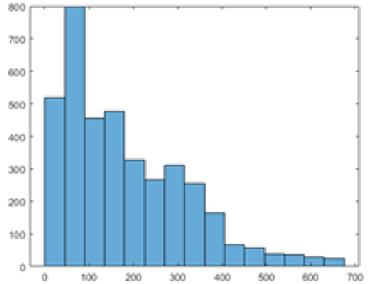


Sara Bals
U Antwerp

Etching depth 20 µm

Overall graphene area is 200x the surface area

	Volume
Material	67 %
Pores	33 %



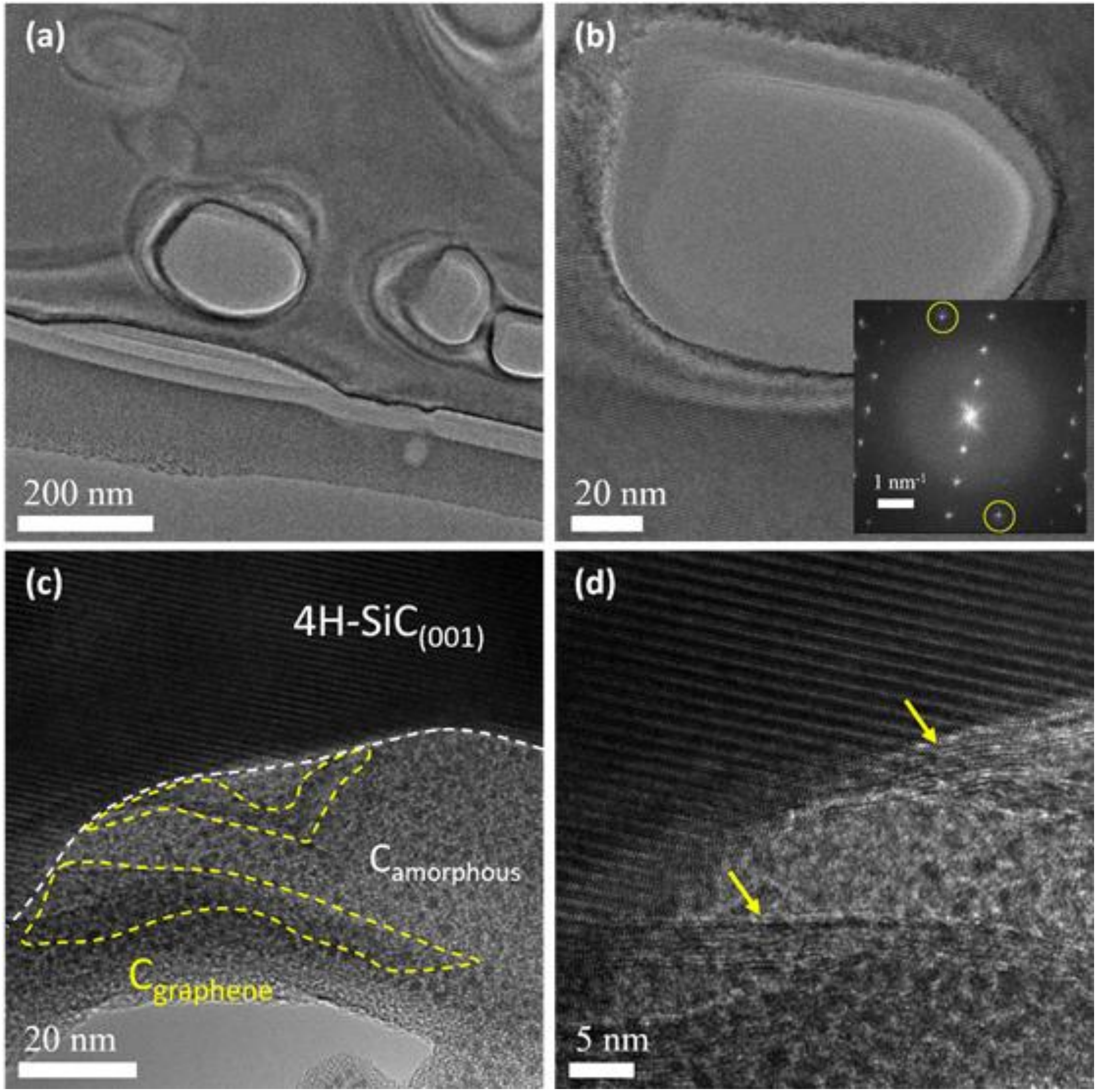
Average pore diameter: 182nm

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

TEM after Graphene Growth

300 kV

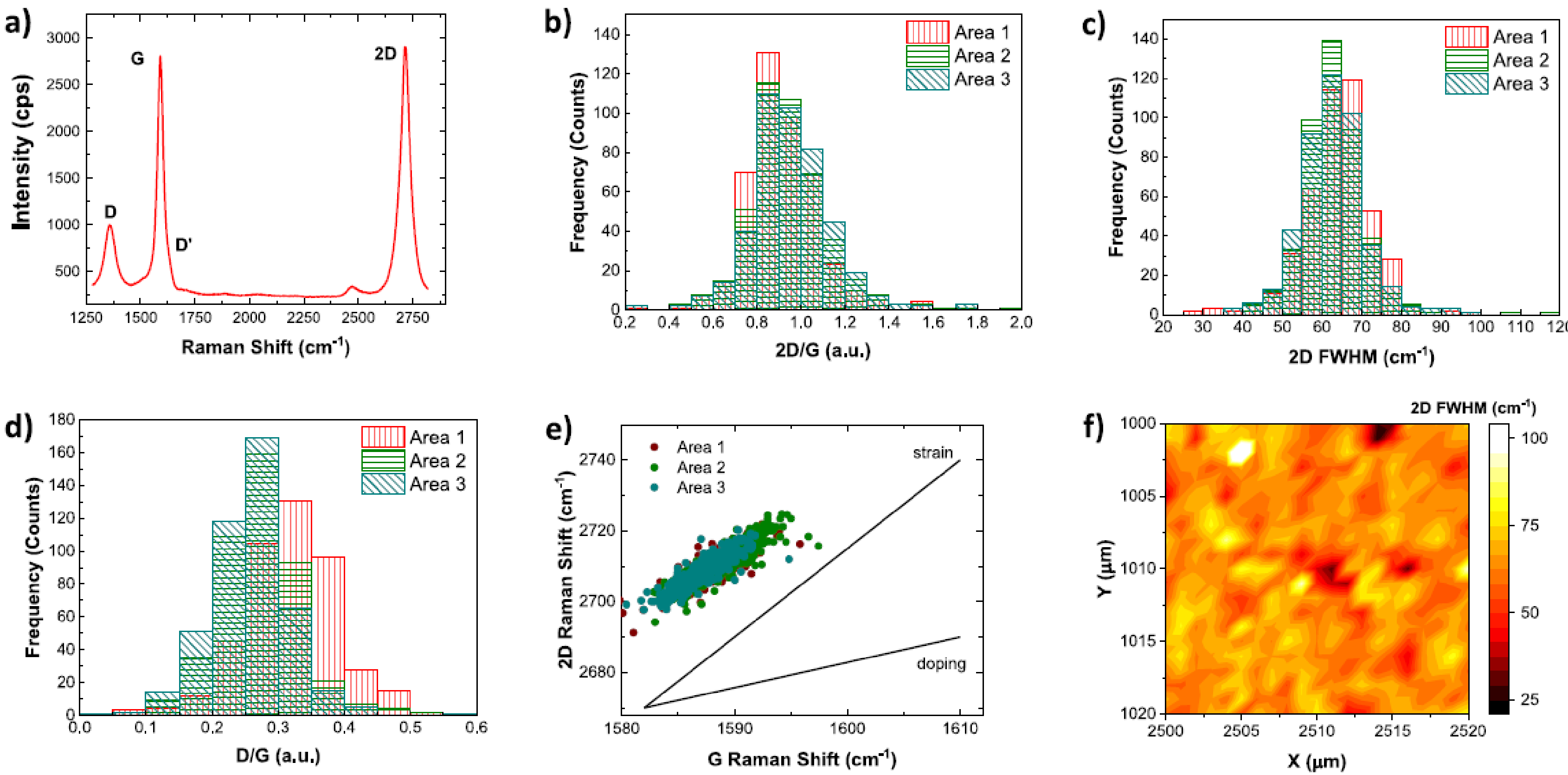
80 kV



O: interplanar distance 0.34nm (graphene)

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

Raman Analysis



Average grain size of graphene: 70 to 100 nm

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

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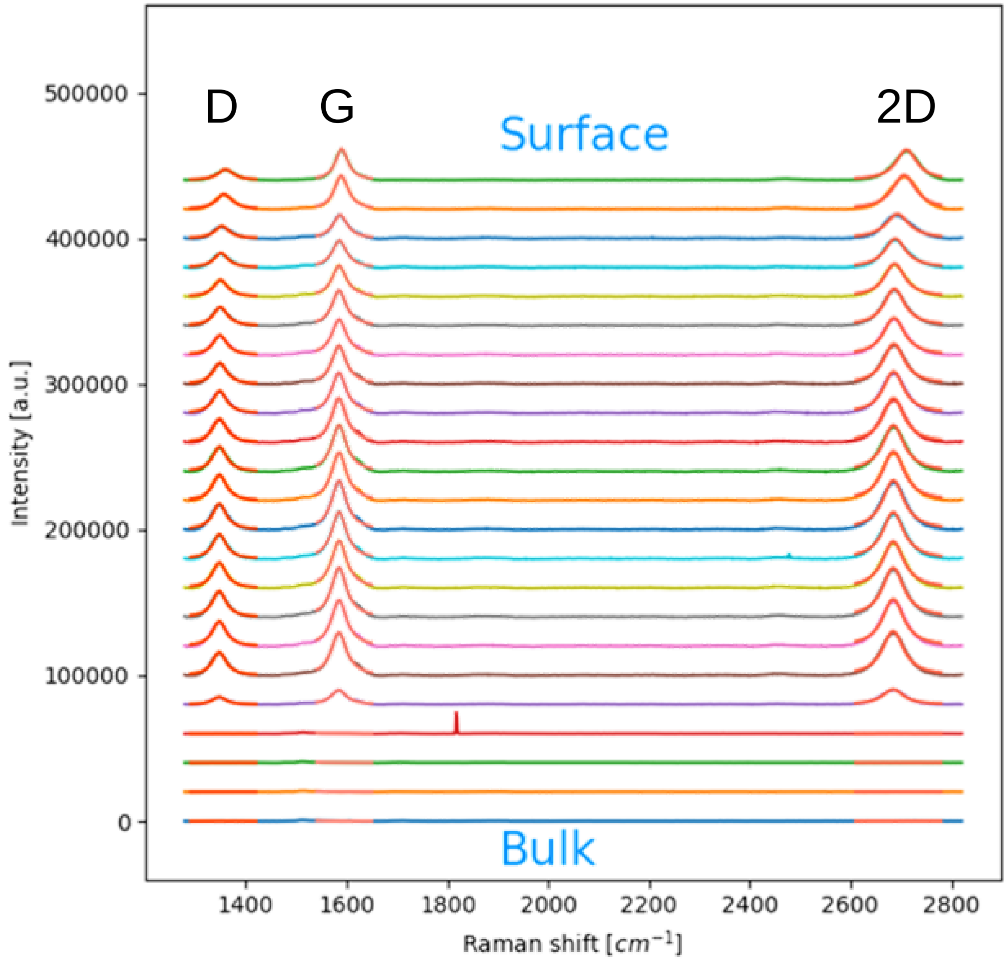
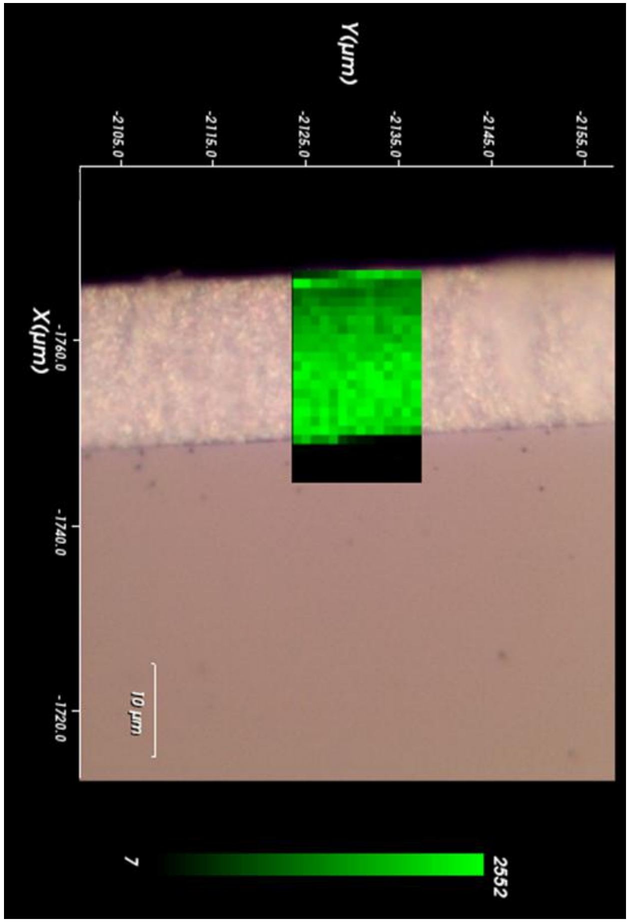
Cross-sectional Raman



G band intensity



Y. Vlamidis, unpublished.

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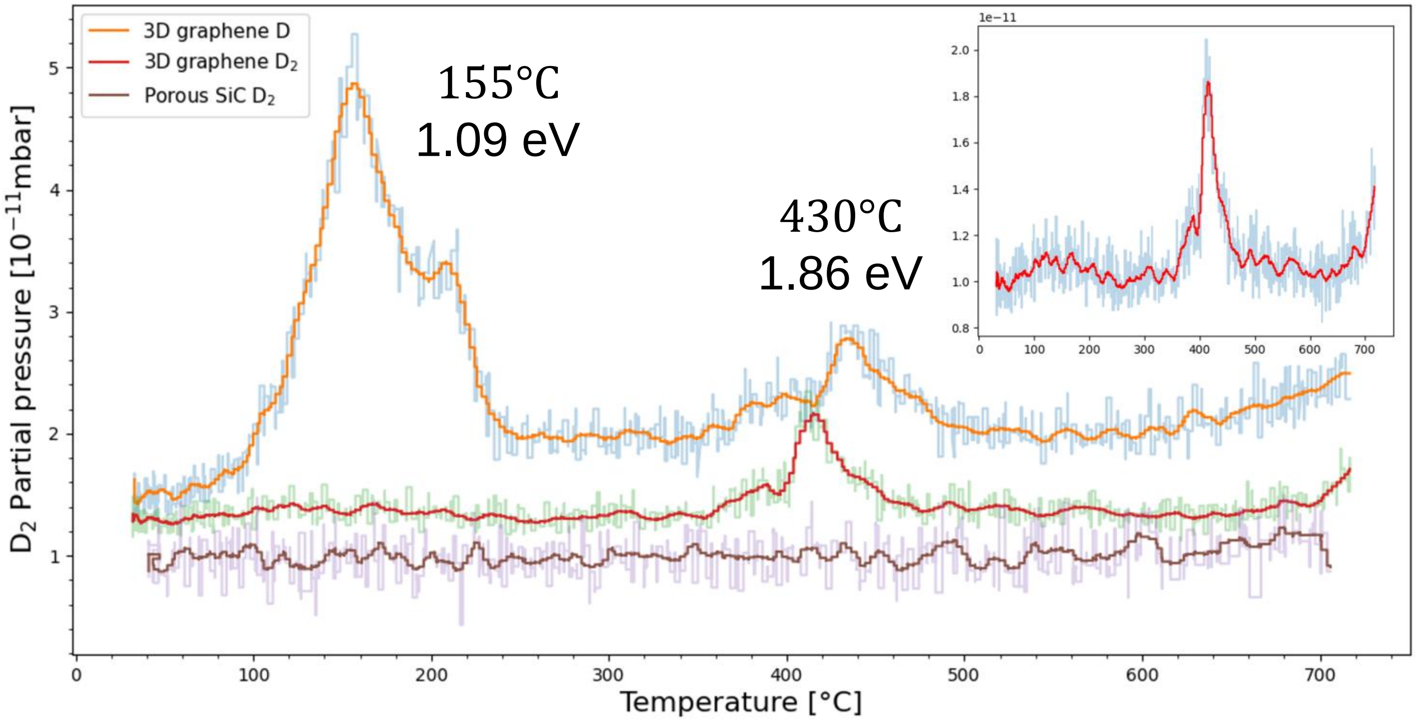
RT - TDS



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

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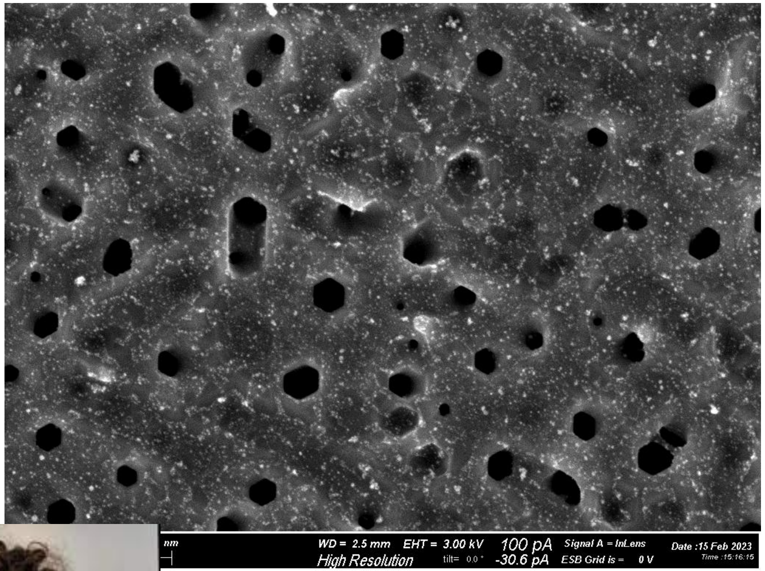
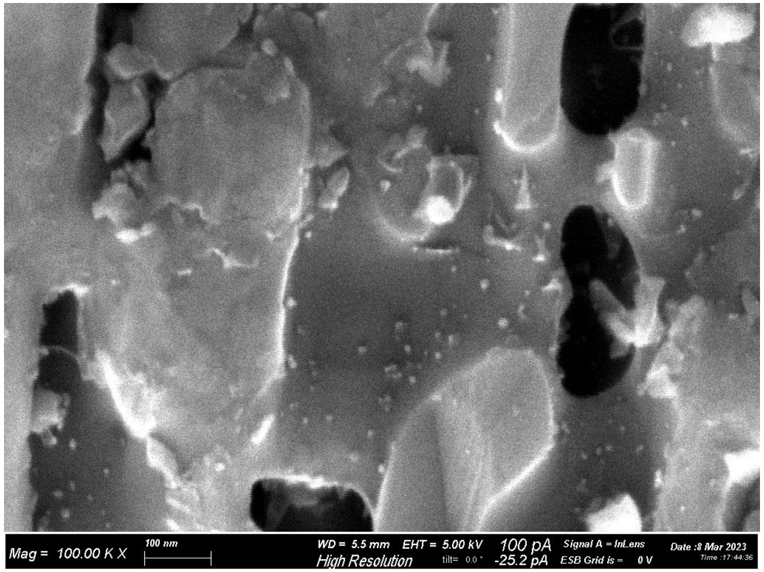
Functionalization with metal nanoparticles

- On 3D Graphene, we have so far explored functionalization with metal nanoparticles of Au, Pd, Ni





E. Pompei, Nanoscale, 2024, 16, 16107.

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Conclusions

- Graphene is a promising material for hydrogen storage
- Graphene functionalized by Ti:
  - Stability of hydrogen binding at room temperature
  - Hydrogen desorbs at moderate temperatures
  - Defect engineering allows to control the size and distribution of Ti islands
  - Evidence for hydrogen spillover
- 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 ?

The Pisa Team

T. Mashoff

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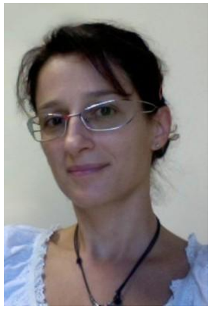
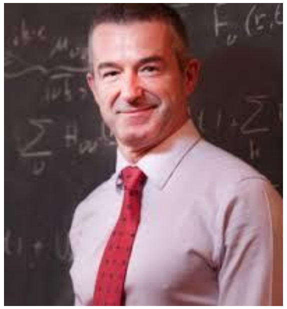
A. Macili

O. Arif



V. Tozzini



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D. Convertino

V. Miseikis

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Sara Bals

Thank you for your attention!

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