ECOSS36

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Platinum-covered graphene as hydrogen storage medium

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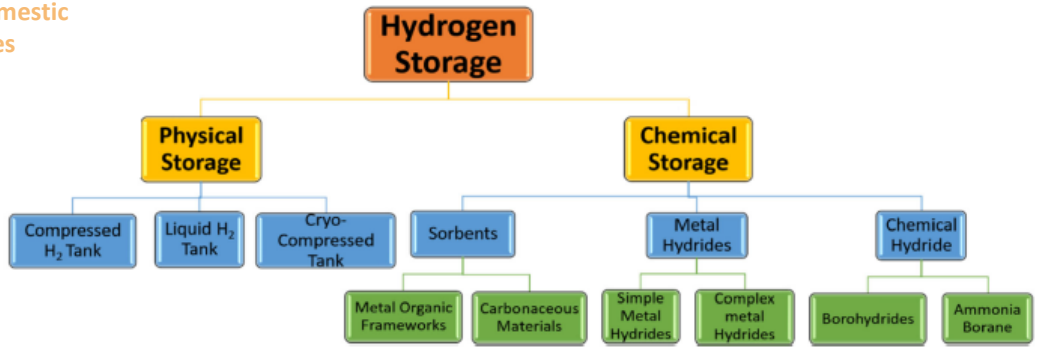
letizia.ferbel@sns.it

Motivation

V. Jain et al., *J. Mater Sci.* **55**, 1865-1903 (2020)

Motivation



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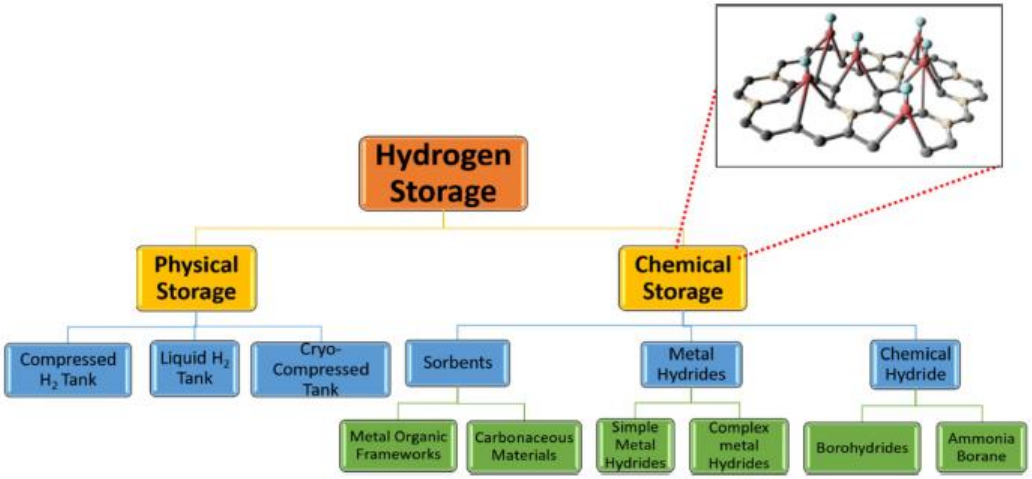
Why Graphene

Graphene is lightweight, inexpensive, robust, chemically stable

Large surface area (~2600 m^2/g)



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Why Graphene

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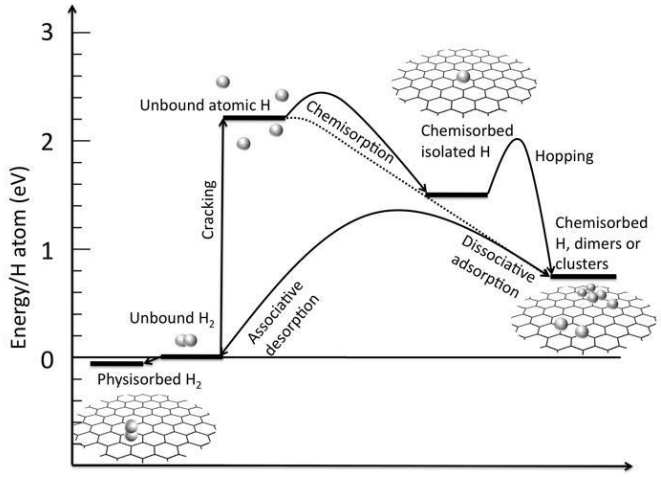
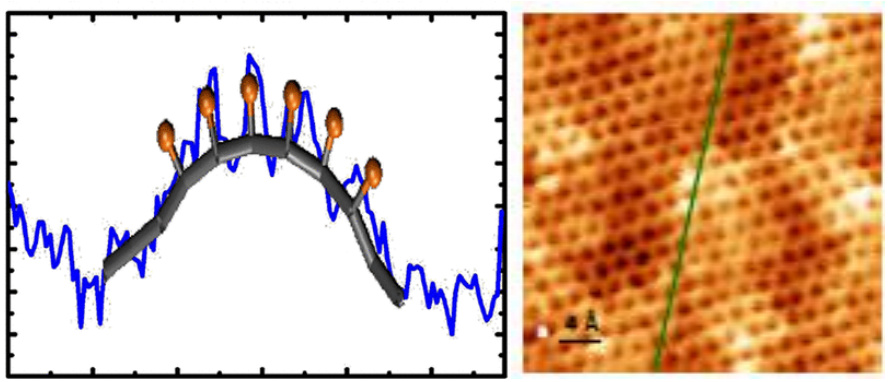
Hydrogen storage possible by chemisorption and physisorption

- *Chemisorption* feasible but H_2 must be cracked
- *Physisorption* of H_2 requires low temperatures and/or high pressure



V. Tozzini et al., *Phys. Chem. Chem. Phys.* **15**, 80 (2013)

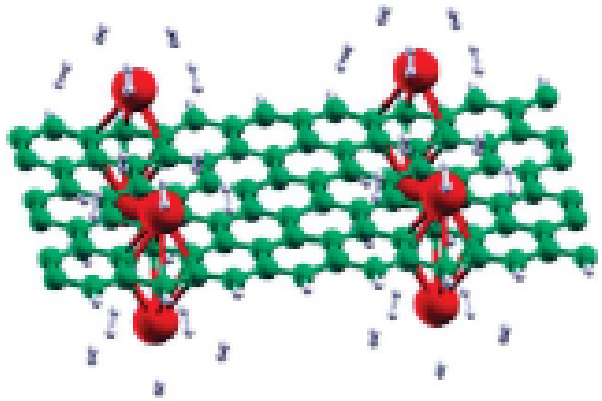


S. Goler et al., *J. Phys. Chem. C* **117**, 11506 (2013)

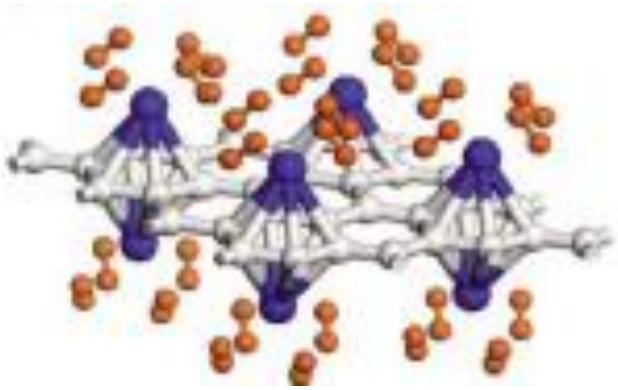
Functionalized graphene

Modify graphene with various chemical species, such as alkaline earth metals (e.g. Ca) or transition metals (e.g. Pt)

- *Functionalized graphene predicted to absorb up to 9 wt% of hydrogen*
- *H_2-storage at nearly ambient conditions*



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

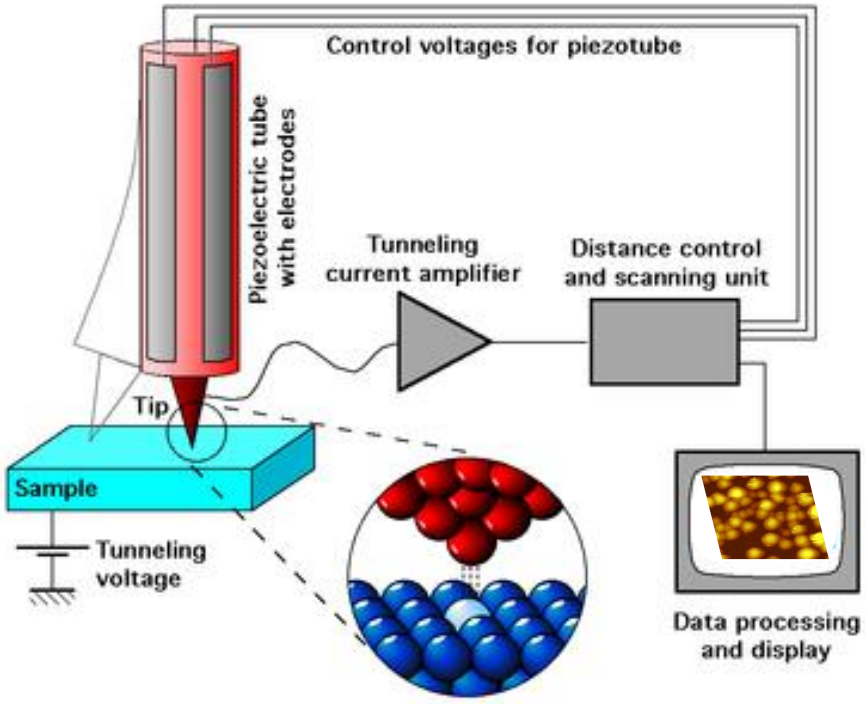


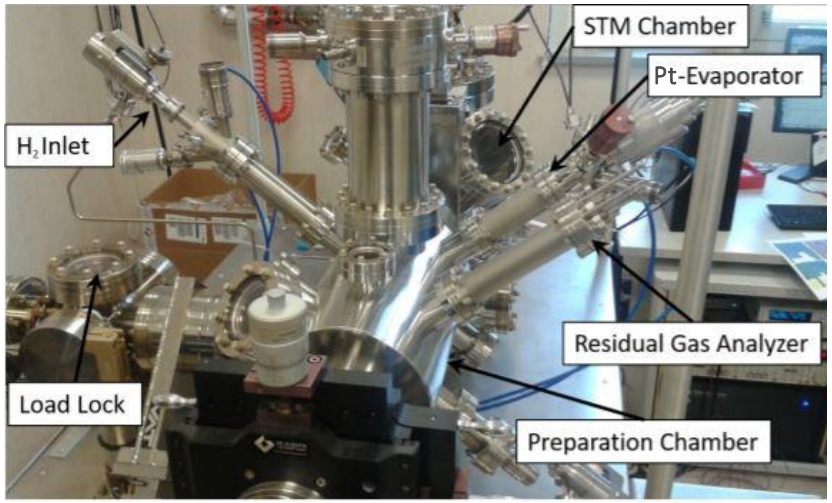
Durgen et al., *Phys. Rev. B* **77**, 085405 (2007)

Experimental Setup

Pt deposition with e-beam evaporator at constant evaporation flux

Probing the surface morphology with a scanning tunneling microscope





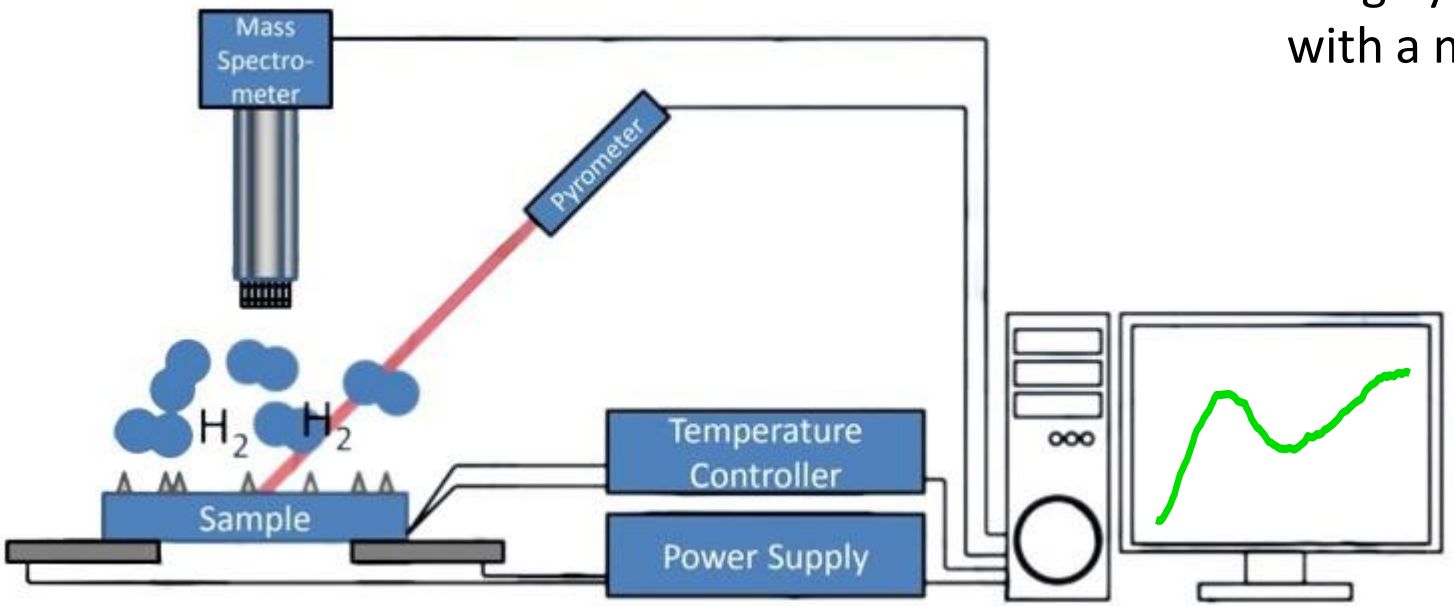
*All the experiments were conducted in-situ under UHV conditions

Experimental Setup

Pt deposition with e-beam evaporator at constant evaporation flux

Sample exposure at Hydrogen (D_2) at $1 \cdot 10^{-7}$ mbar for 5 min

Measuring hydrogen desorption with a mass spectrometer



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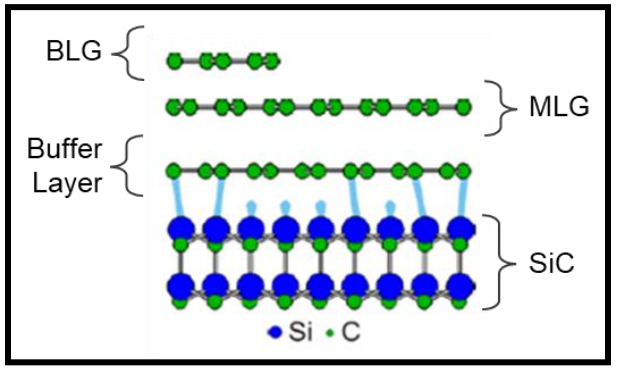
Epitaxial Graphene on SiC(0001)



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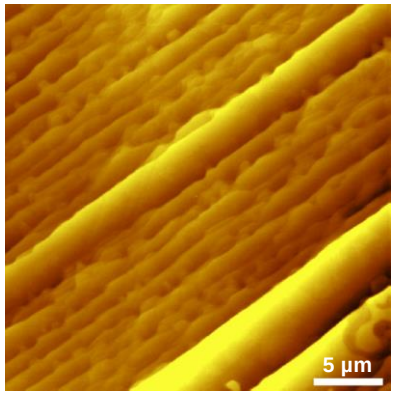

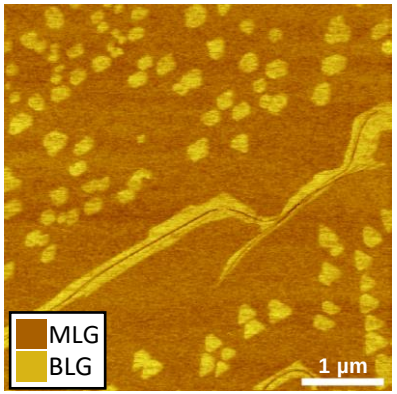

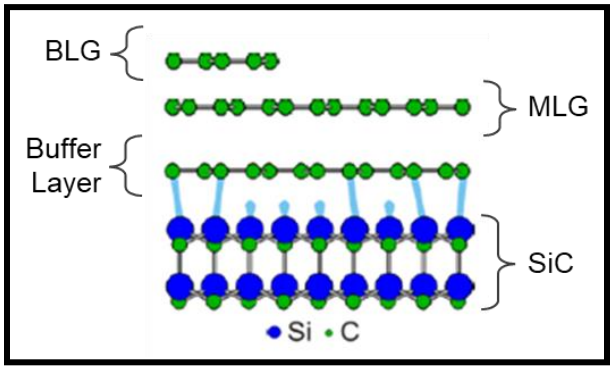

AFM

*ex-situ

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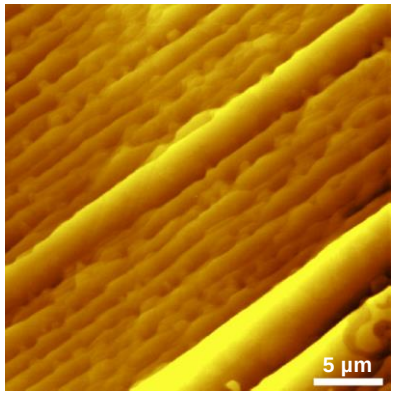

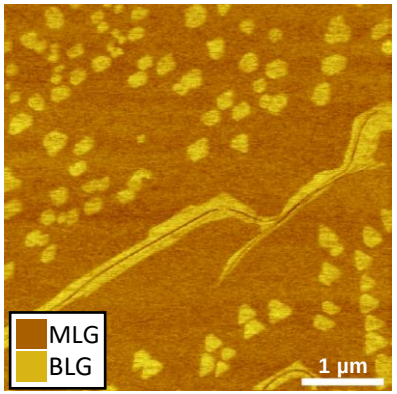

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Samples composition:

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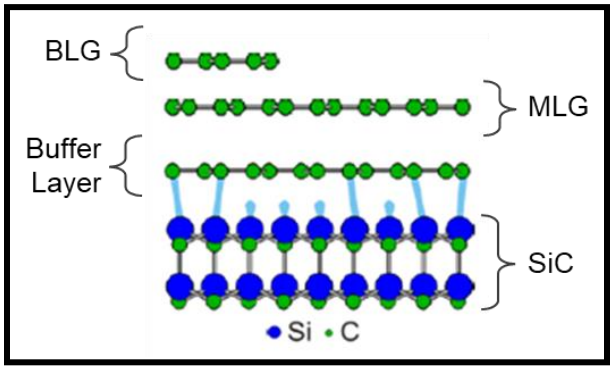
- < 30 % BLG



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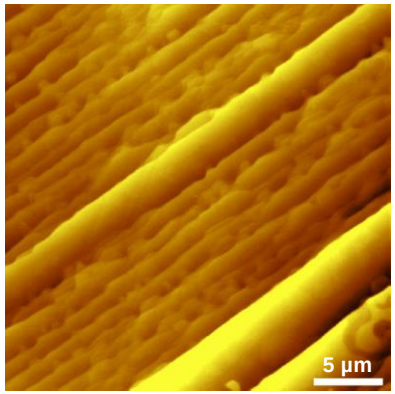

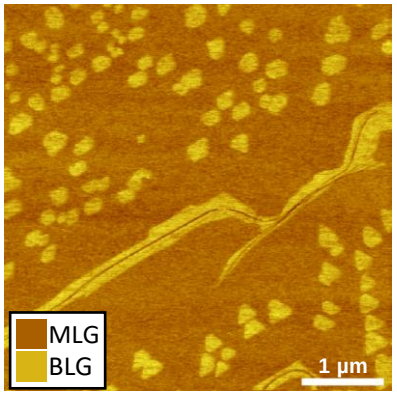

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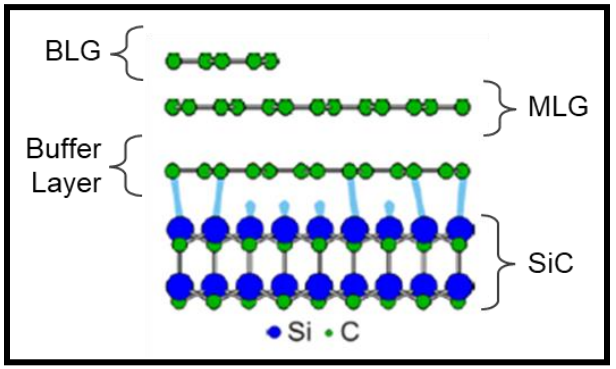

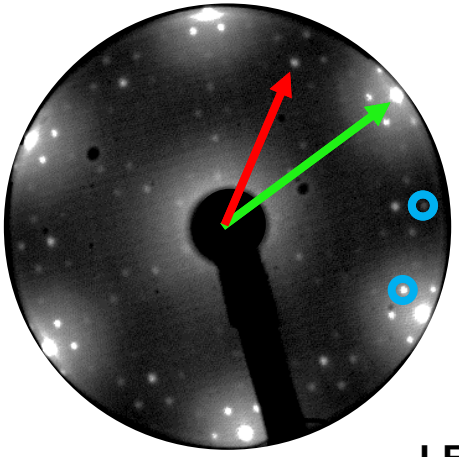

Graphene
SiC
Moirè $(6\sqrt{3})$

LEED

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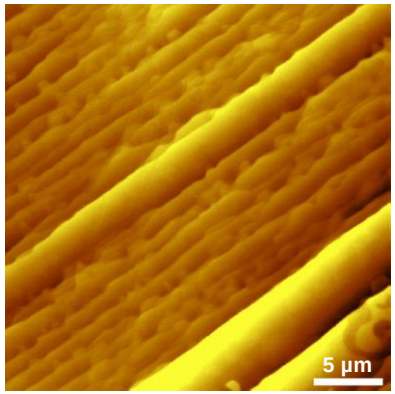

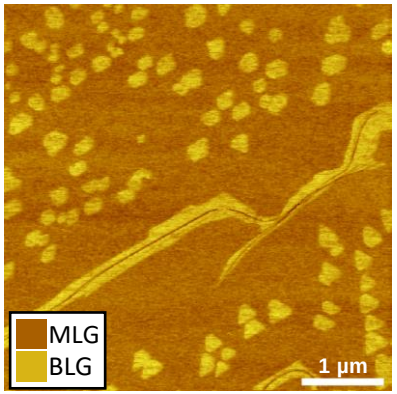

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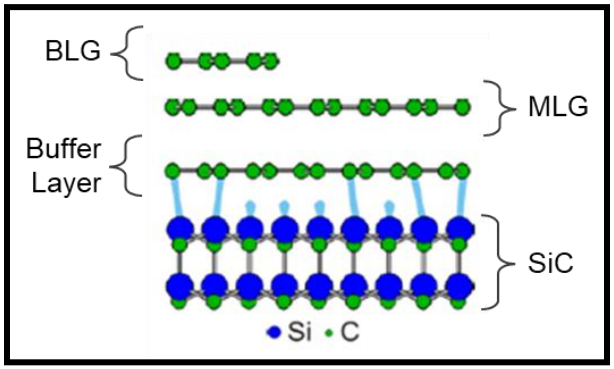

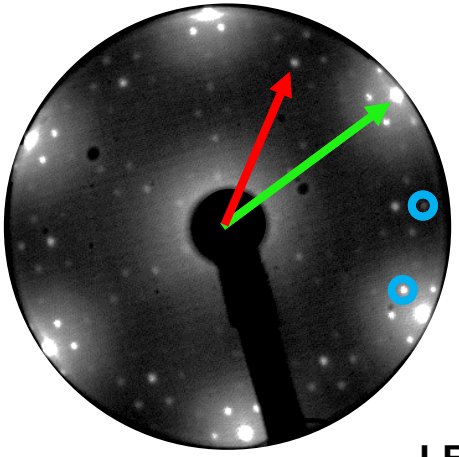

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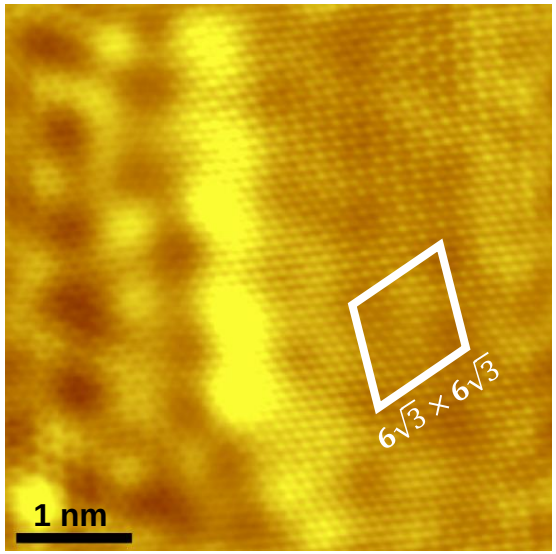

STM

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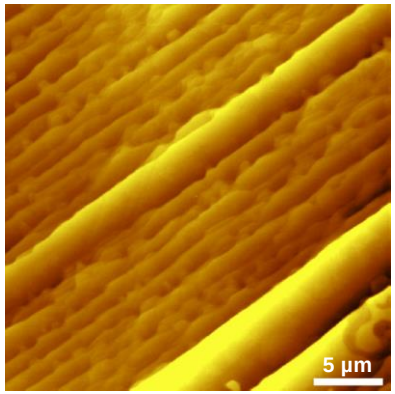

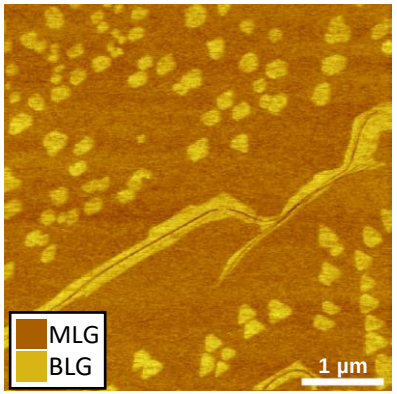

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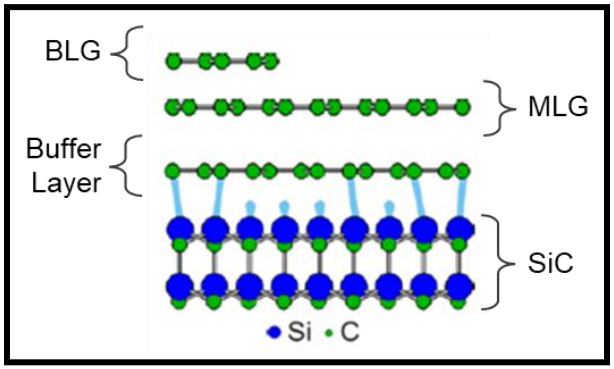

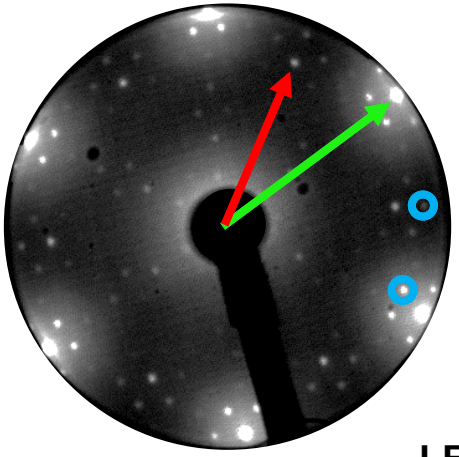

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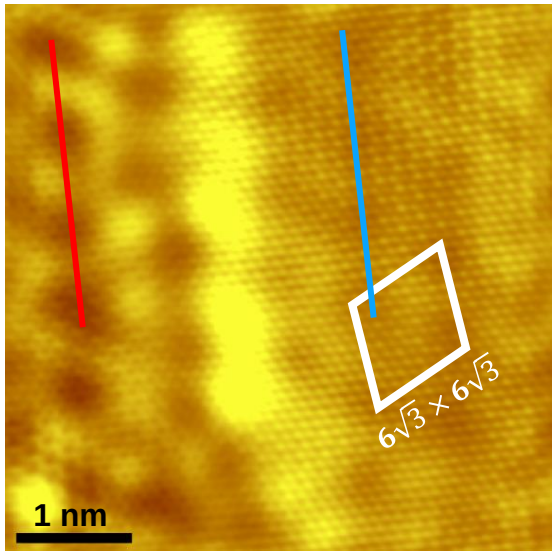
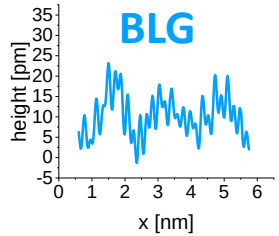
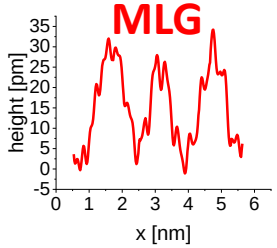


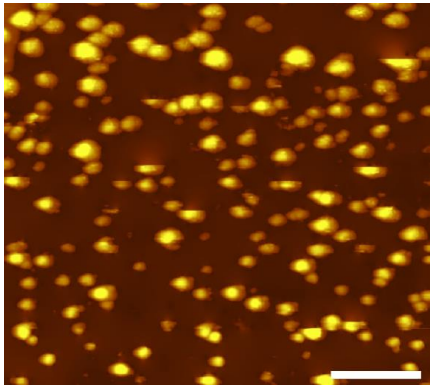




STM

Platinum growth

Pt deposition time: 4 min
Pt covered area: 17 ± 4 %



Pt deposition time: 8 min
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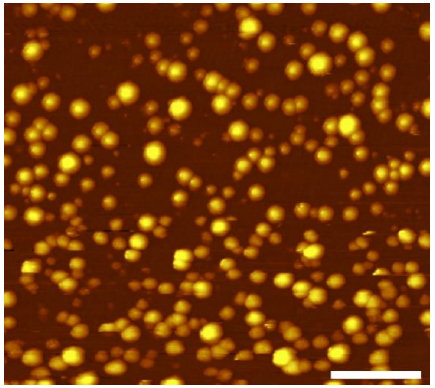

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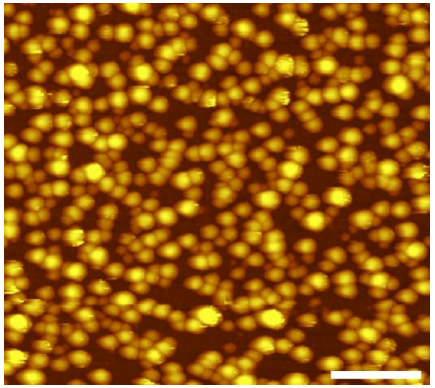

Pt deposition time: 24 min
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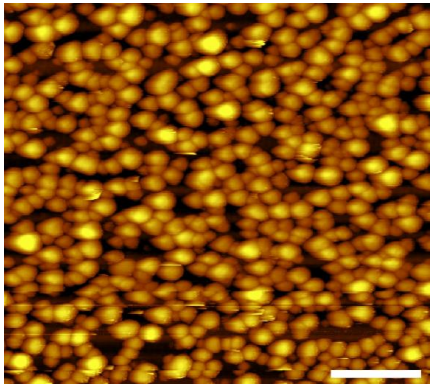
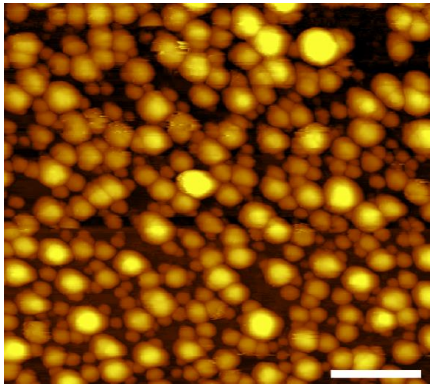


Pt deposition time: 28 min
Pt covered area: 85 ± 9 %



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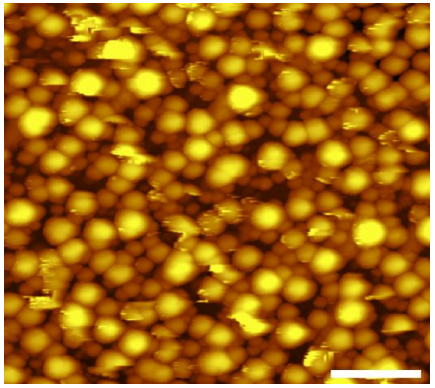

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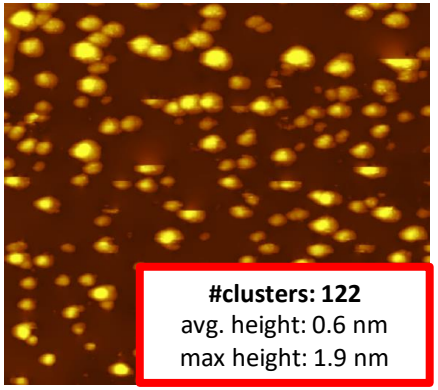

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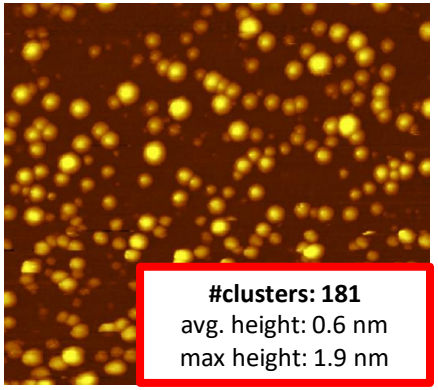

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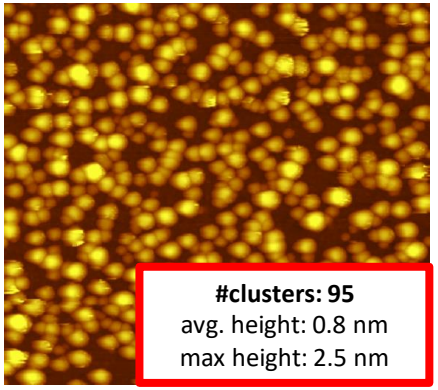

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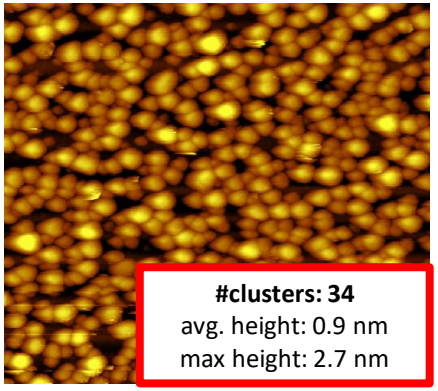

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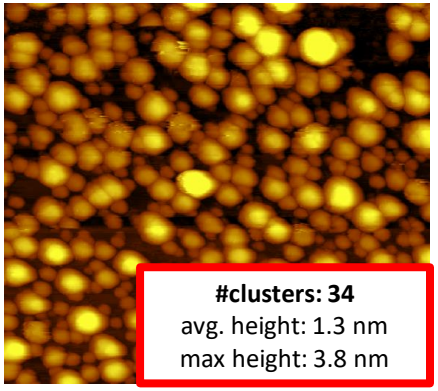

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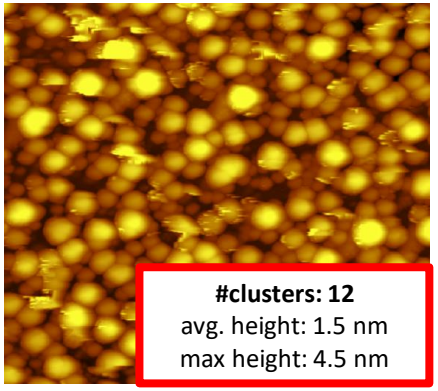

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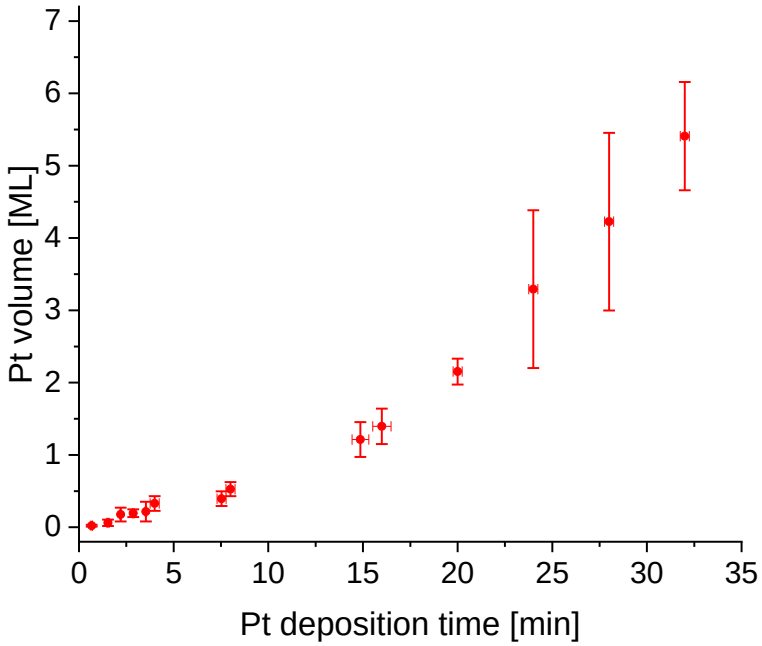
Platinum growth

With constant sticking coefficient, one would expect a linear relationship between the Pt deposition time and the total islands volume



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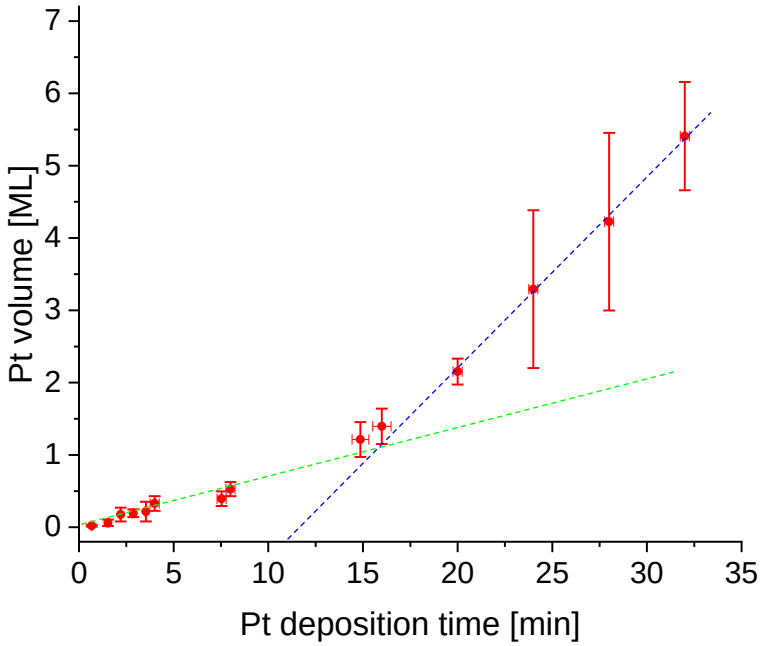
… But a single linear fit does not work



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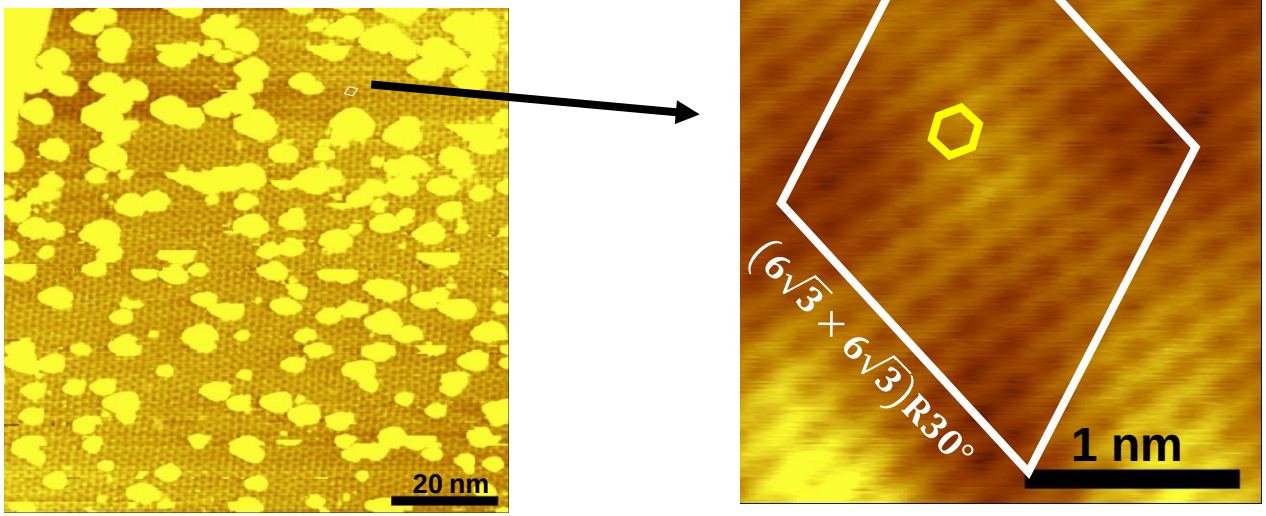
Platinum growth

Loss of material at low coverages is due to a sticking coefficient of Pt on graphene <1

No Pt intercalation at RT was observed

Coverage: 17 ± 4 % - 0.33 ± 0.10 ML



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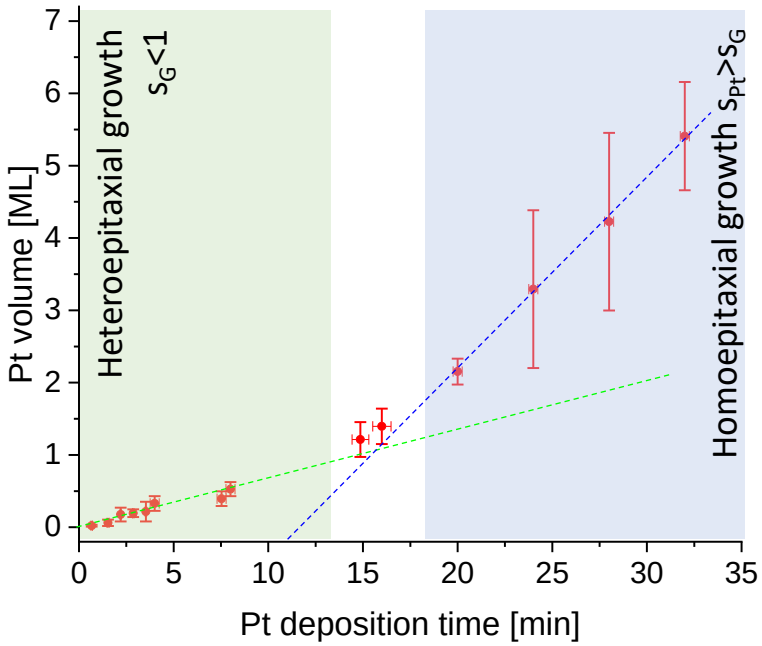
Platinum growth

Two growth mechanisms that have different sticking coefficients



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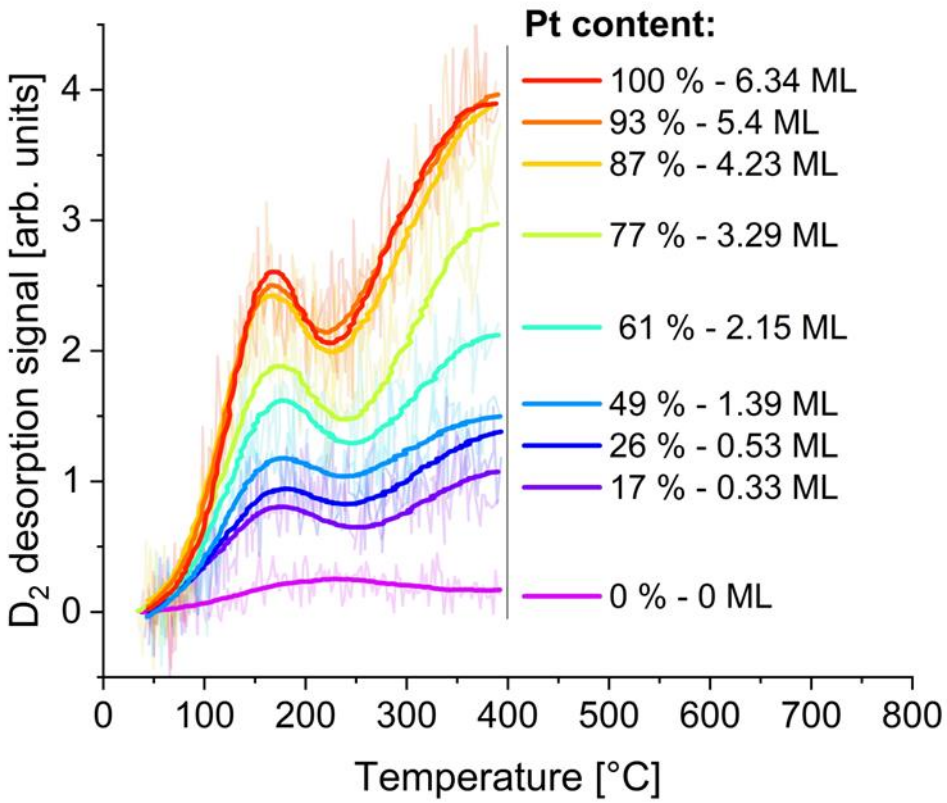
TDS of D_2 for different Pt coverage



Pt islands on graphene can store Hydrogen.

* Successive Pt evaporation onto the same sample

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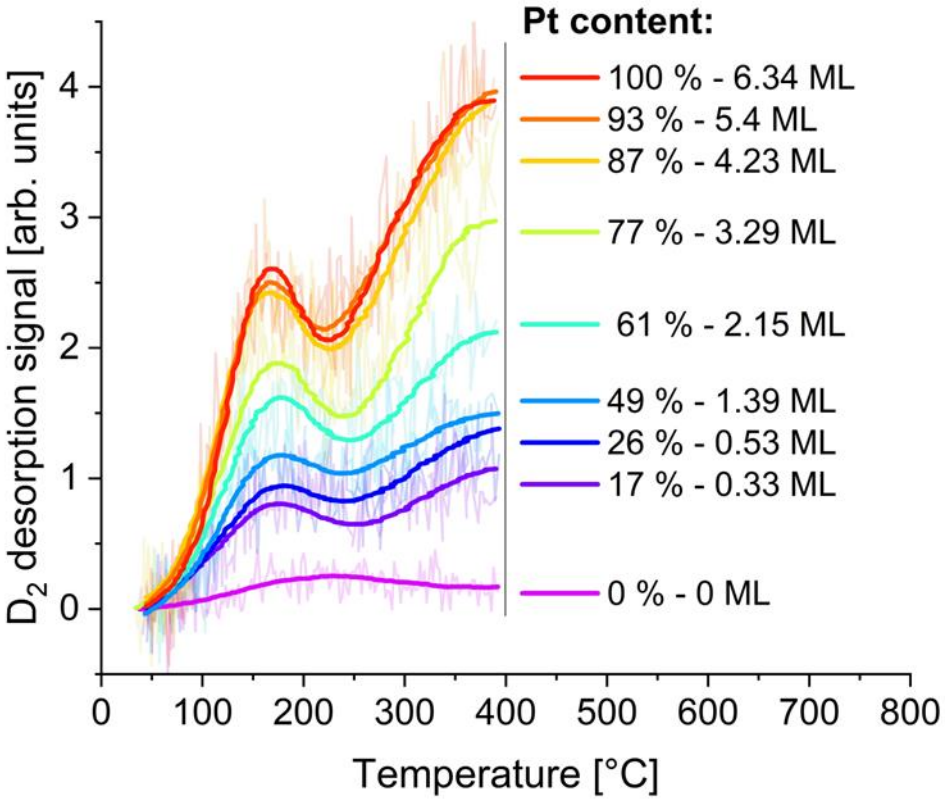

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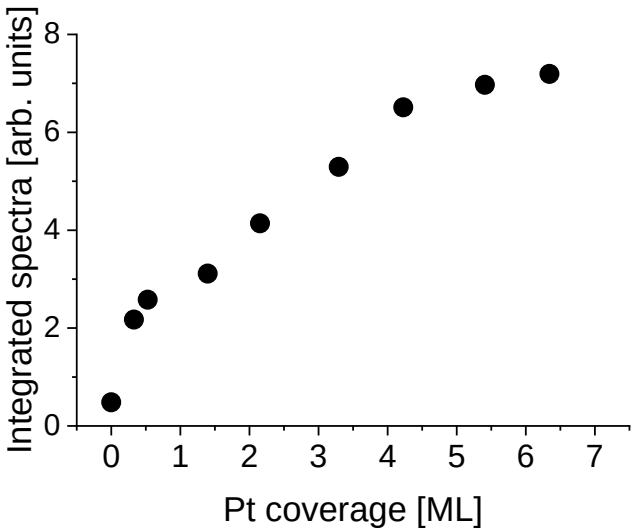
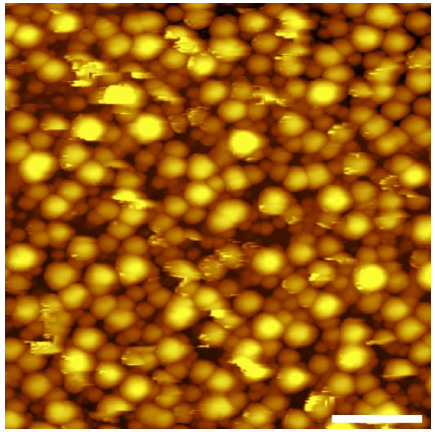


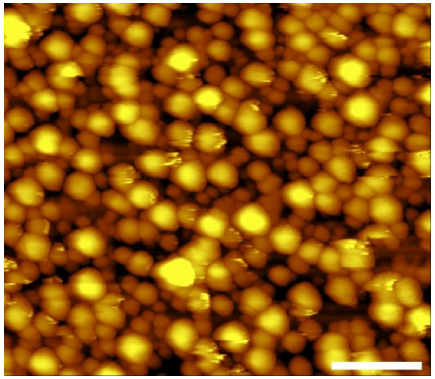
The stored amount increases with the amount of deposited platinum.

* Successive Pt evaporation onto the same sample

Why TDS up to 400°C



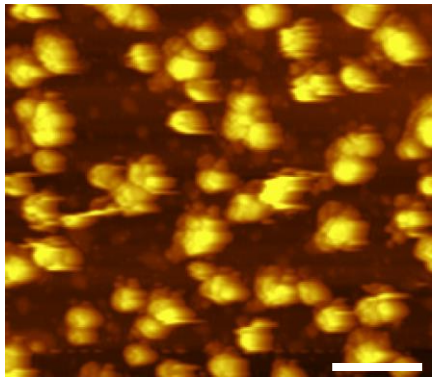
TDS up to 400°C



Area coverage and volume are conserved

No significant changes in the morphology

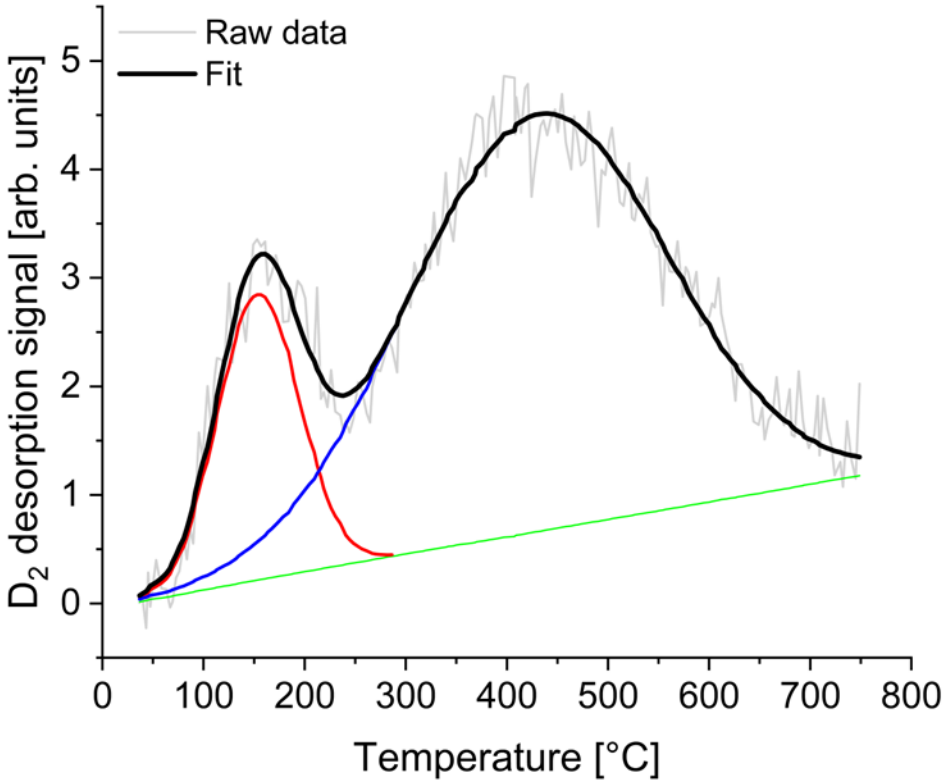
TDS up to 750°C



Area coverage decreases to about 30%, volume is conserved while clusters avg. height and density increases

TDS peaks analysis

Ad-hoc sample with Pt coverage:
49 ± 6 % - 1.4 ± 0.2 ML

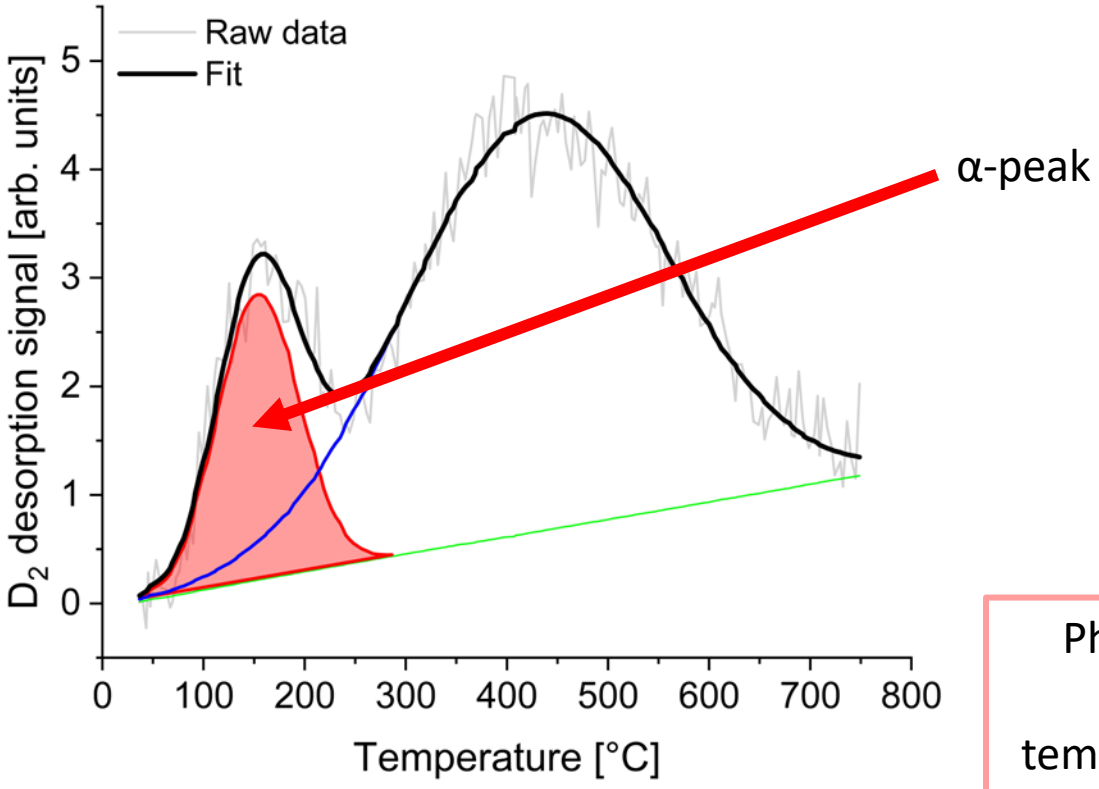


TDS clearly shows the presence of two Gaussian peaks superimposed on a linearly increasing background signal

*First TDS experiment

TDS peaks analysis

Ad-hoc sample with Pt coverage:
49 ± 6 % - 1.4 ± 0.2 ML



Desorption temperature
$T_\alpha = 155 \pm 7$ °C

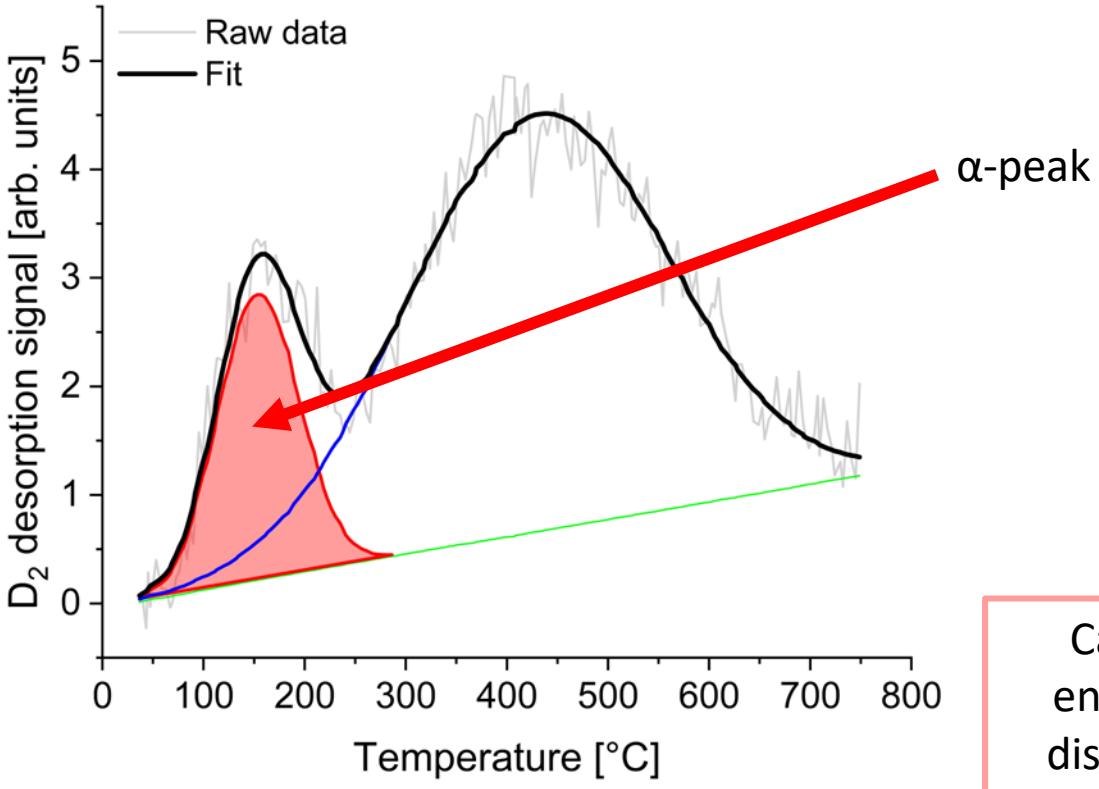
Desorption energy barrier
$E_\alpha \sim 1.14$ eV/molecule

Physisorption of H_2 molecules on Pt(111) showed desorption temperature between 150 and 200°C

Baldwin et al., *J. Vac. Sci. Tech.* **8**, 49-52 (1971)
Craig et al., *Surf. Sci.* **127**, 175-181 (1983)

TDS peaks analysis

Ad-hoc sample with Pt coverage:
49 ± 6 % - 1.4 ± 0.2 ML



Desorption temperature
$T_\alpha = 155 \pm 7$ °C

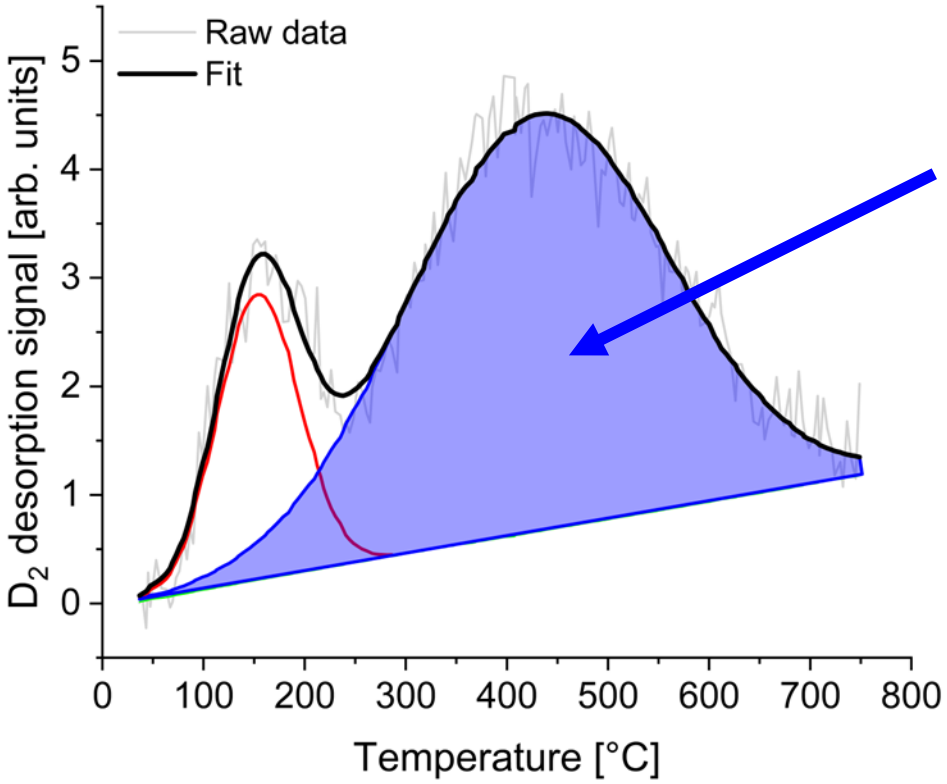
Desorption energy barrier
$E_\alpha \sim 1.14$ eV/molecule

Calculations report a desorption energy barrier for an H_2 molecule dissociated on Pt and adsorbed on graphene of ~ 1 eV

L. Chen et al., *J. Phys. Chem. C* **111**, 18995-19000 (2007)

TDS peaks analysis

Ad-hoc sample with Pt coverage:
49 ± 6 % - 1.4 ± 0.2 ML



Desorption temperature
$T_\beta = 432 \pm 13$ °C

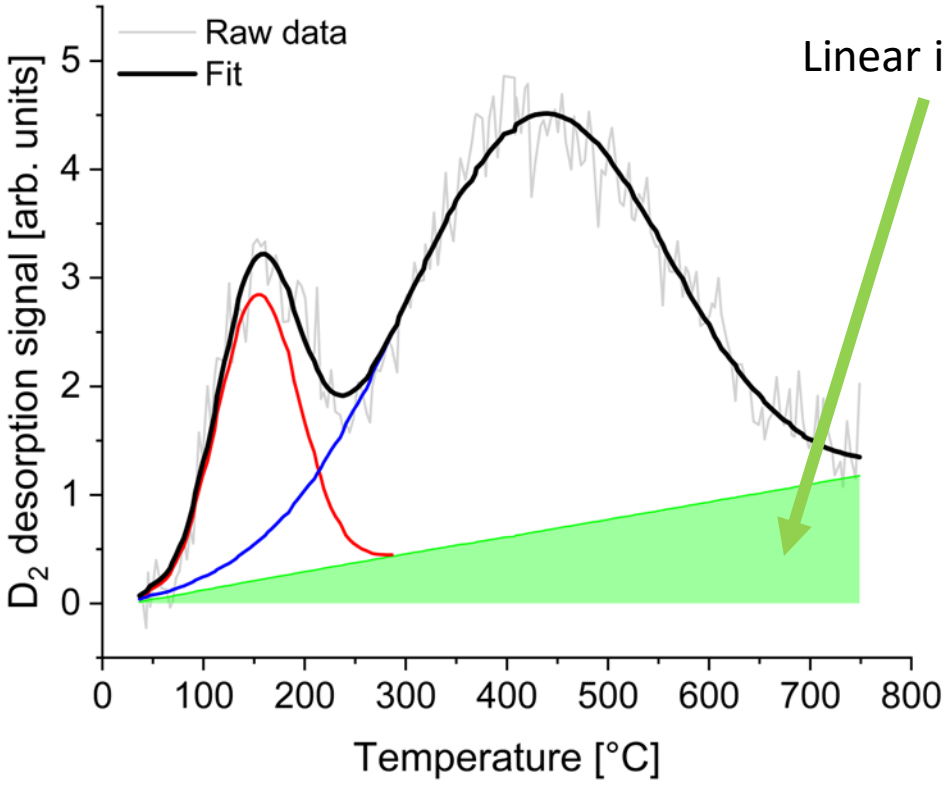
Desorption energy barrier
$E_\beta \sim 1.96$ eV/molecule

Calculations report a binding energy for an H_2 molecule dissociatively chemisorbed on Pt of 1.85 eV

S. Lamichane et al., *Bibechana* **11**, 113-122 (2014)

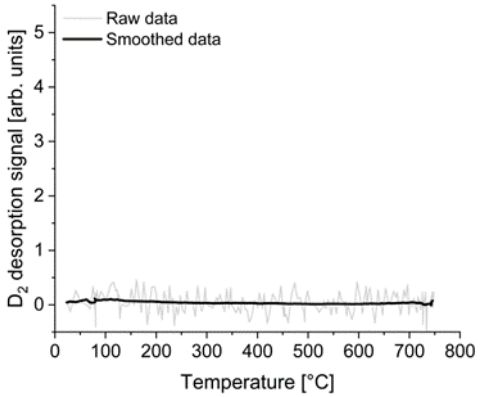
TDS peaks analysis

Ad-hoc sample with Pt coverage:
49 ± 6 % - 1.4 ± 0.2 ML



This cannot be regarded as a simple baseline

Pristine graphene showed little to no D_2 uptake



TDS peaks analysis

Ad-hoc sample with Pt coverage:
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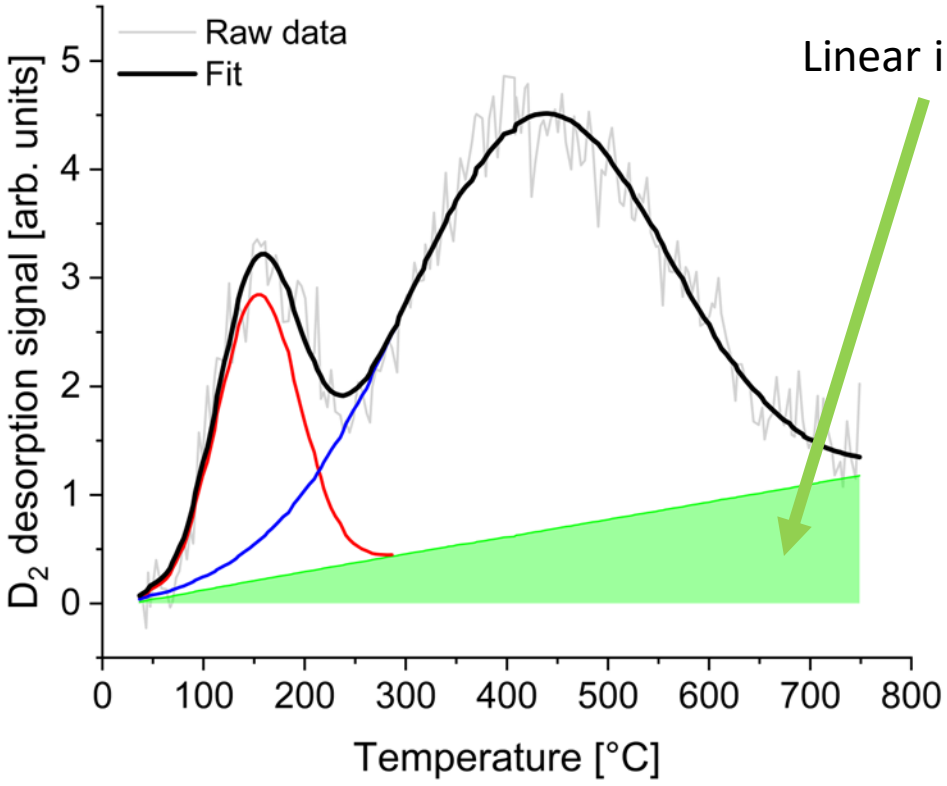
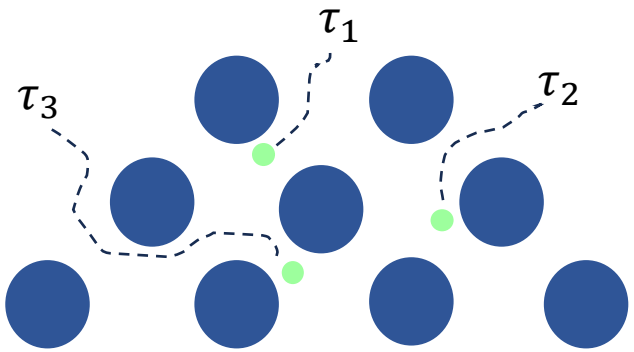


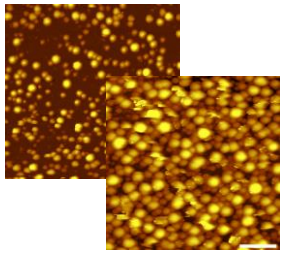
«Retarded effect» of hydrogen bonded in the volume of the cluster



J. Guterl et al., *J. of Appl. Phys.* **118**, 043302 (2015)
A. Macili et al., *Appl. Surf. Sci.* **615**, 156375 (2023)

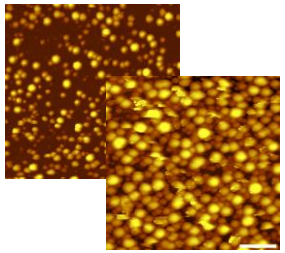
Conclusion and Outlook

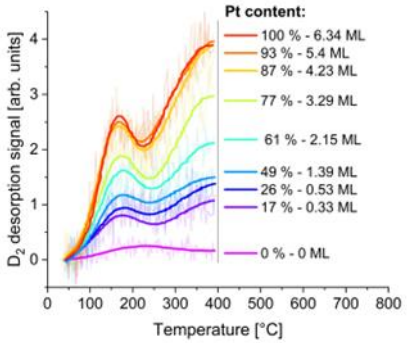
Insights in the Pt growth mechanism on epitaxial graphene



Conclusion and Outlook

Insights in the Pt growth mechanism on epitaxial graphene

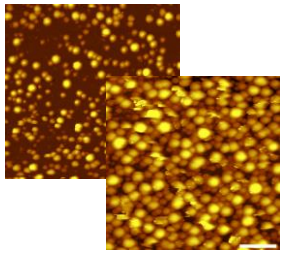


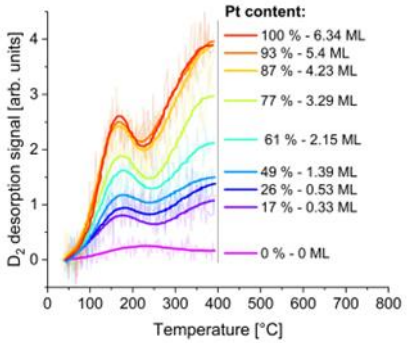


Experimental demonstration of molecular hydrogen storage at room-temperature in Pt-functionalized graphene

Conclusion and Outlook

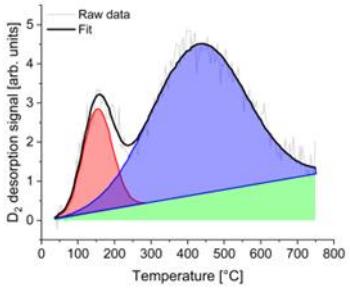
Insights in the Pt growth mechanism on epitaxial graphene





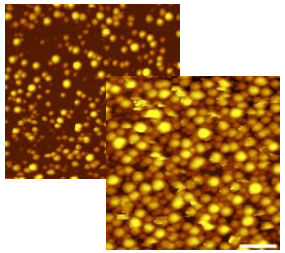
Experimental demonstration of molecular hydrogen storage at room-temperature in Pt-functionalized graphene

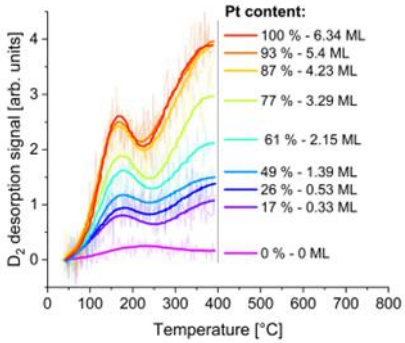
Demonstration of three different hydrogen adsorption mechanisms on Pt functionalized graphene at moderate temperature



Conclusion and Outlook

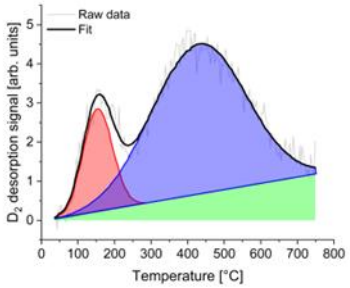
Insights in the Pt growth mechanism on epitaxial graphene





Experimental demonstration of molecular hydrogen storage at room-temperature in Pt-functionalized graphene

Demonstration of three different hydrogen adsorption mechanisms on Pt functionalized graphene at moderate temperature



Further measurements are in order to better understand the nature of the hydrogen adsorption sites

Thank you all

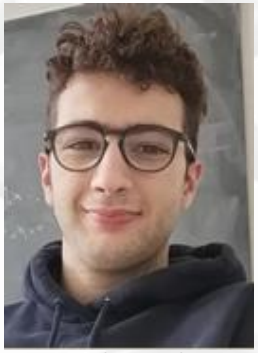
for your attention !

Stefano Veronesi

Ylea Vlamidis

Stefan Heun

Antonio Rossi



Leonardo Sabattini

Camilla Coletti

ECOSS 36

28 Aug - 1 Sep 2023, Lodz, Poland