A novel sensitive calorimetric technique to study energy (heat) exchange at the nano-scale

L. Basta[1], S. Veronesi[1], Y. Murata[1], Z. Dubois[1], N. Mishra[2,3], F. Fabbri[2,3], C. Coletti[2,3], and S. Heun[1]

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NEST

Outline

- Calorimetry

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- Calorimetry
- Calorimetry at the nano-scale

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- New high-sensitive sensor
  - sensor structure
  - thermal model
  - first direct detection of Hydrogen adsorption on Ti-MLG at room temperature

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- Calorimetry
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- New high-sensitive sensor
  - sensor structure
  - thermal model
  - first direct detection of Hydrogen adsorption on Ti-MLG at room temperature
- Conclusions & outlooks

ROAD TO APPLICATIONS...

Design and fabrication of the **SENSOR** → characterization and calibration

Si substrate + Au thermometer

New calorimetric technique → first measurement on a **TEST SAMPLE**

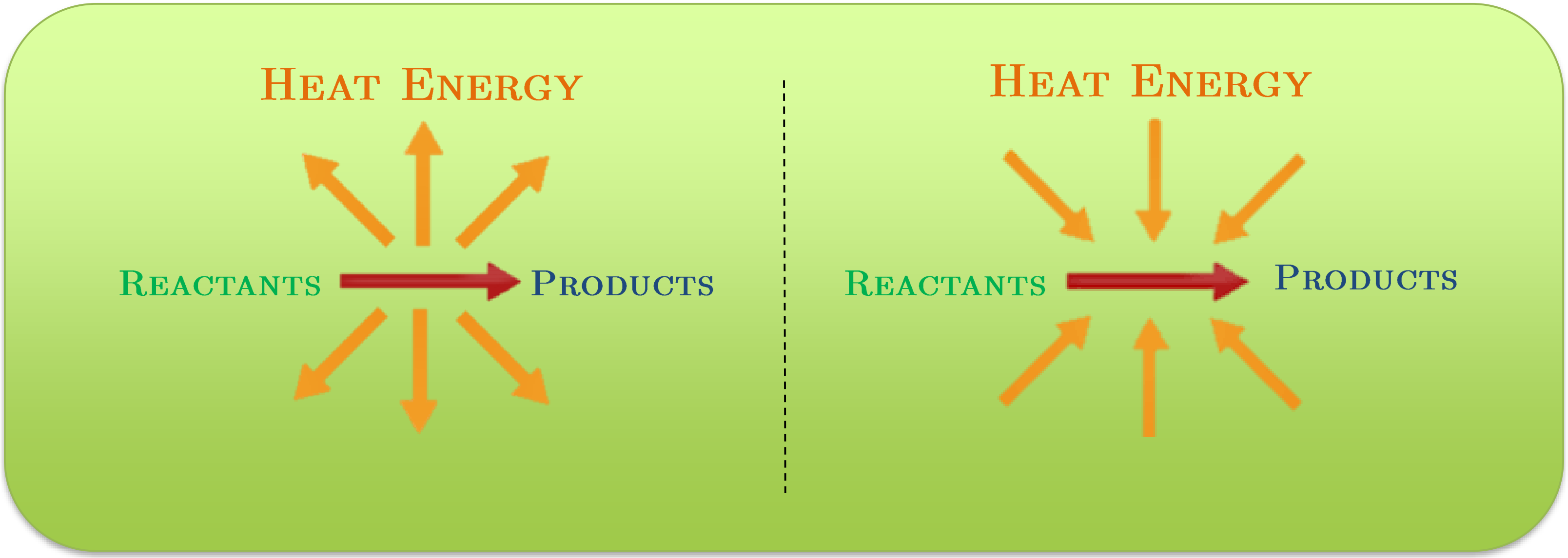
Hydrogenation of Ti-MLG
comparison with TDS

Improvements and implementation → **APPLICATIONS**

investigate novel 2-D materials
sensors and catalyzers
ultra-sensitive thermal imaging
microbolometers

CALORIMETRY

Every time a chemical reaction occurs, an **energy exchange** between reactants and environment occurs



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CALORIMETRY

Every time a chemical reaction occurs, an **energy exchange** between reactants and environment occurs

The study of this energy flux gives invaluable information on the processes underlying the **evolution of the system**

↓

CALORIMETRY

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ENTHALPY VARIATION

While the absolute amount of energy in a chemical system is difficult to measure or to calculate, the **enthalpy variation** is much easier to work with.

ΔH consists in the change in the *internal energy* ΔU plus the *work* L needed to change the system's volume V:

$$\Delta H = \Delta U + L = C_p \cdot \Delta T + V \cdot \Delta P = \delta Q + V \cdot \Delta P$$

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↓ constant pressure

$$\boxed{\Delta H = \delta Q}$$

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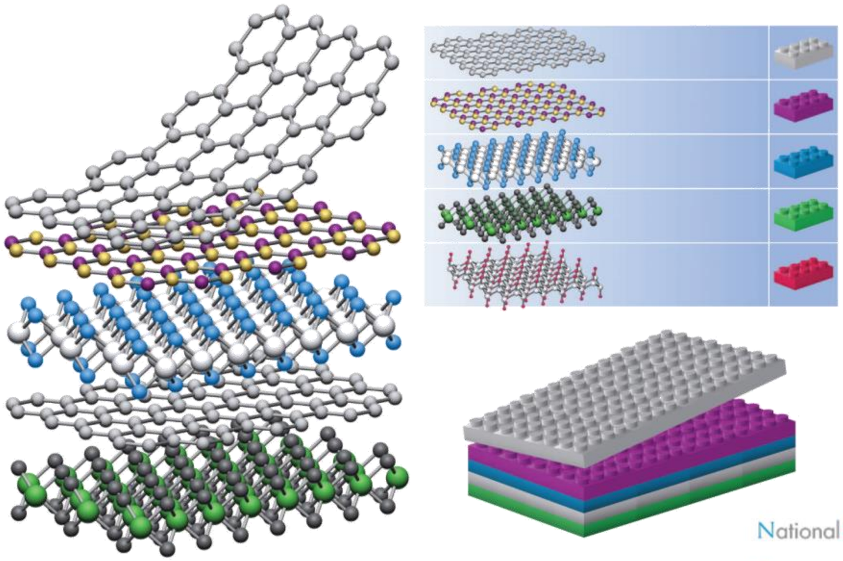
INTO THE NANO-SCALE

In the last decades, research has resulted in an increasing number of devices at the **micro**- or **nano**-scale.

Sensors, catalyzers, and energy storage systems are more and more designed as **nano-devices** which represent the building blocks for commercial "macroscopic" objects.



Geim et al. - Nature 499, 419–425 (2013)

COMMERCIAL CALORIMETERS

So far, several **commercial calorimeters** has been developed to investigate heat exchange in solid or liquid samples.

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Usual requirements of commercial devices are:

- ❖ sample mass in the milligrams range $(10 - 100 \text{ mg})$
- ❖ sensitivity in energy detection $(\boldsymbol{E \geq 1} \textbf{ mJ})$

FROM MACRO TO NANO

In our system, what does it mean to detect the adsorption of 10 mg of H_2 on a monolayer graphene?

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Considering DOE prescriptions of 5.5 wt.%, and the specific surface area of graphene ($\sim$ 2600 m^2/g), we would need $\sim$ **450 m^2** of graphene!

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FROM MACRO TO NANO

We developed a sensor able to measure 10^{-10} mol ($\sim 10^{-10}$ g) of stored hydrogen, in a sample of 5×5 mm^2 size.

THERMOMETRIC SENSOR

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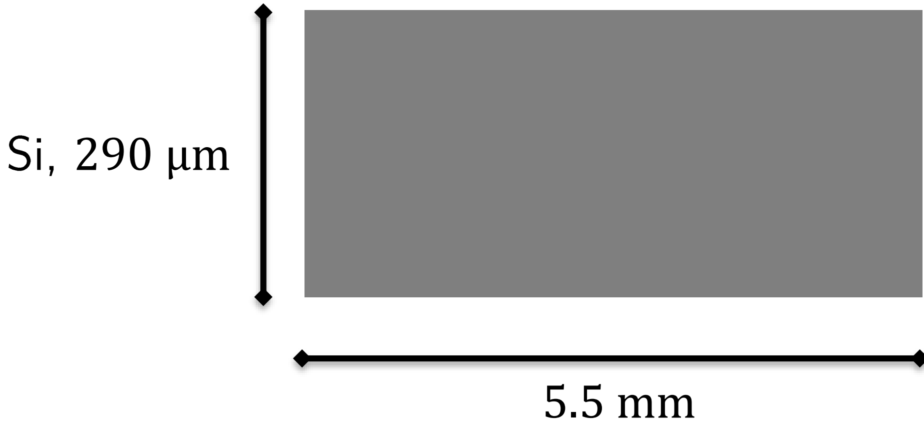
- Si (290 µm), as physical support



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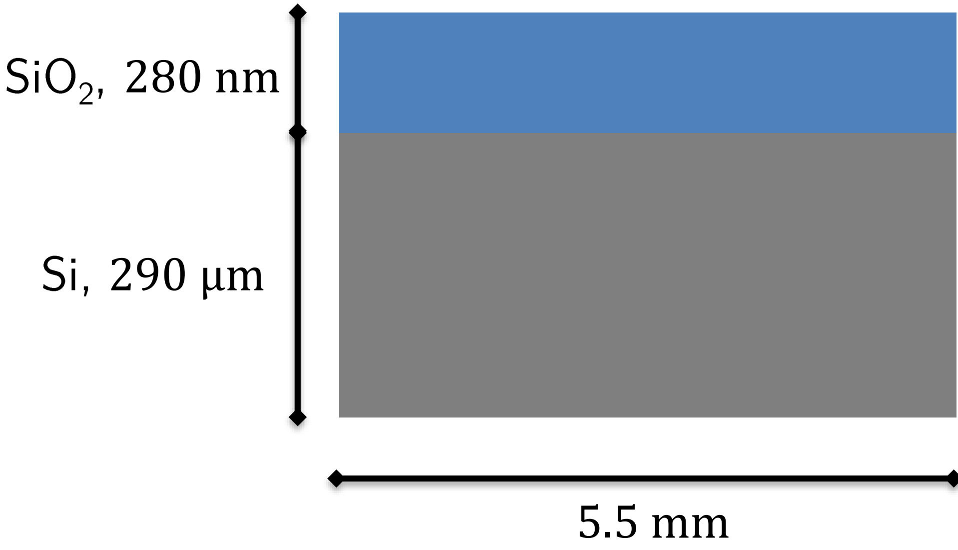

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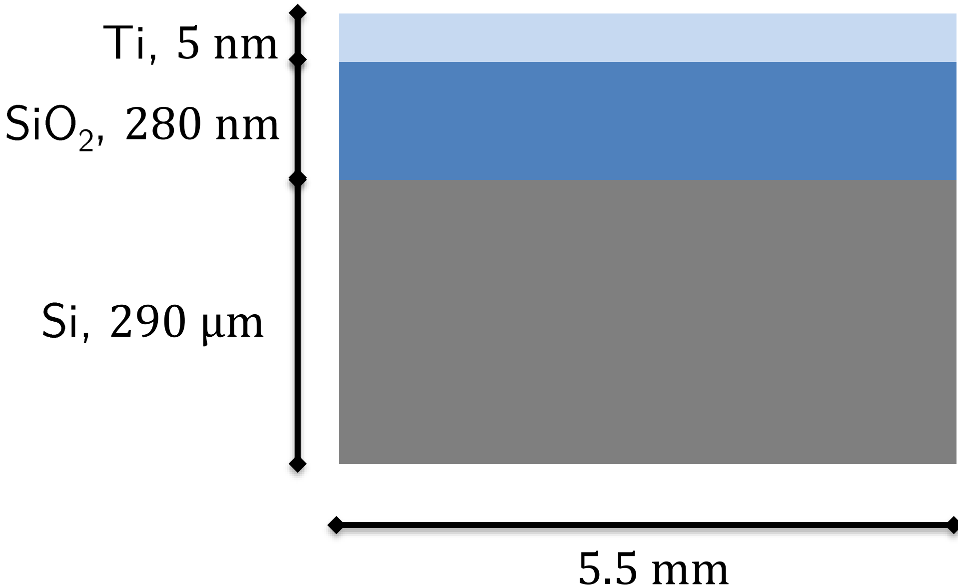
- Ti (5 nm), for the proper sticking of gold



THERMOMETRIC SENSOR

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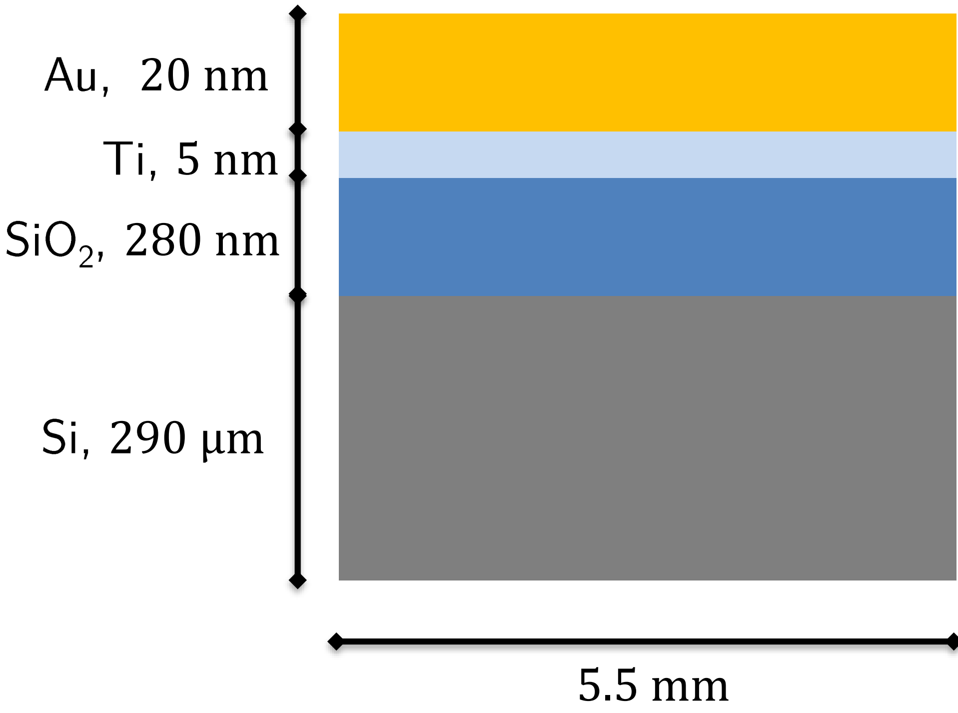
- Ti (5 nm), for the proper sticking of gold
- Au (20 nm), as thermometer



THERMOMETRIC SENSOR

The idea is to utilize a thin film of gold as a thermometer, exploiting the linear relation (valid from 50 to 900 K):

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Gold has:

- suitable resistance temperature coefficient
- good thermal and electrical conductivities
- low chemical reactivity

THERMAL MODEL

In our thermal model we consider the thermometer heated by the absorption of a **thermal power** $P(t) \longrightarrow \Delta T(t) = T(t) - T_0$

$$C\frac{d\Delta T(t)}{dt} = P(t)$$

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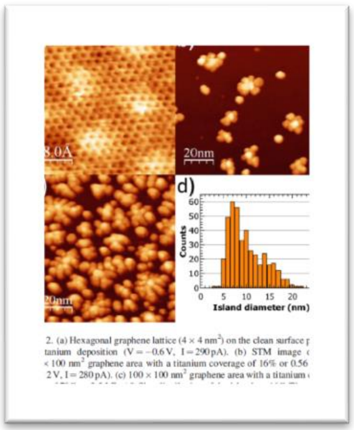
$$C \frac{d\Delta T(t)}{dt} = P(t) - \lambda\, \Delta T(t)$$

$$\boxed{\Delta T(t) = \frac{P}{\lambda}\left(1 - e^{-t/\tau}\right)}$$

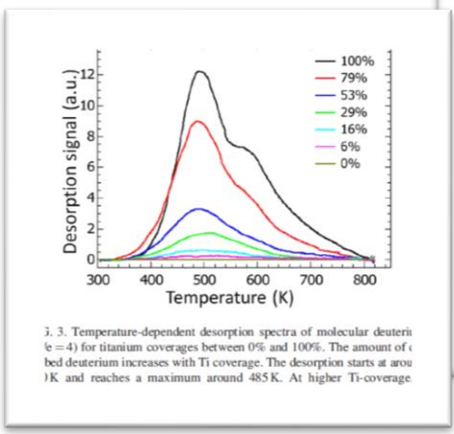
$$\tau = \frac{C}{\lambda} \qquad\qquad P(t) = P \ (\text{fixed}) \longrightarrow \lambda$$

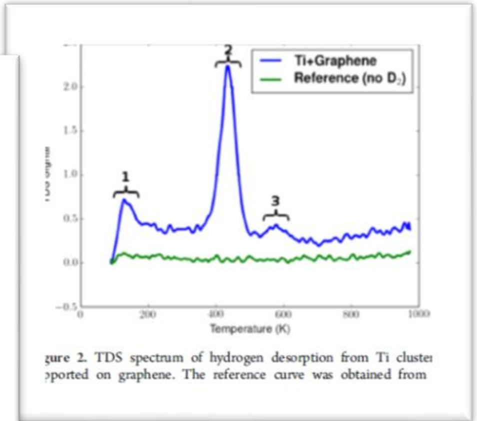
WHY Ti-MLG?

In the hydrogen storage field solid-state graphene-based devices are under **extensive investigations**. We chose Ti-functionalized monolayer graphene because:

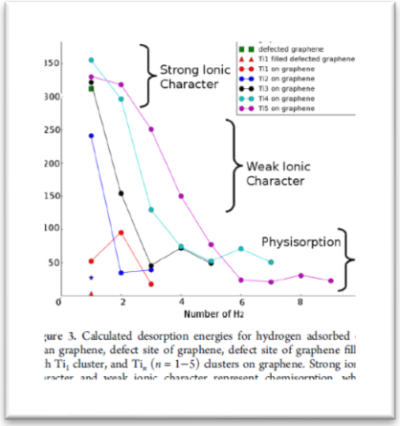


STM study





TDS measurements



theoretical investigation

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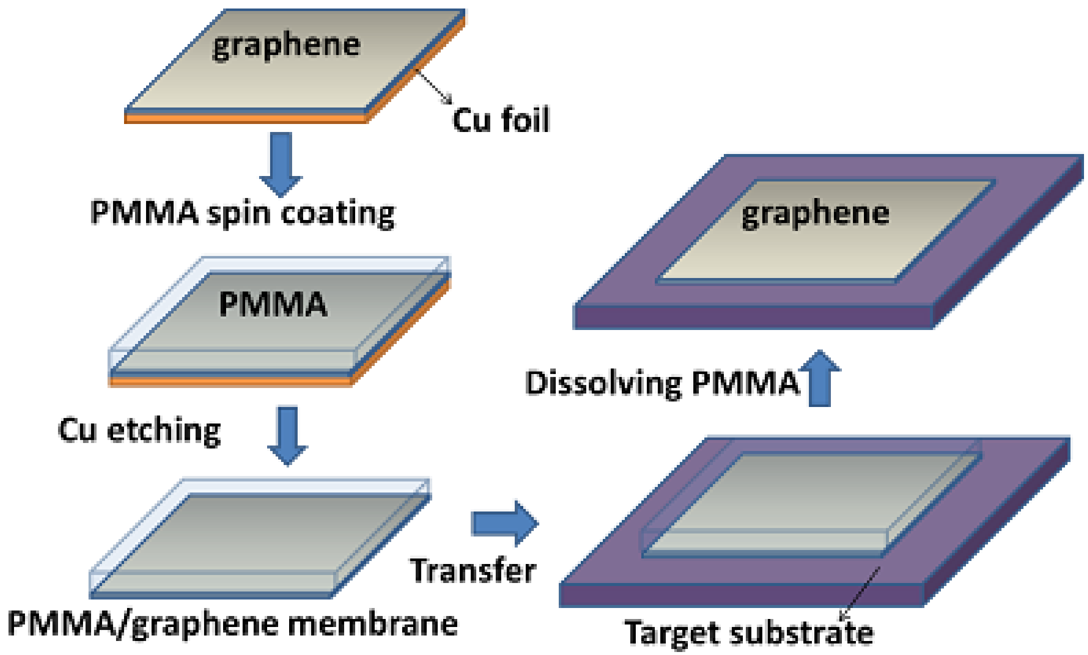
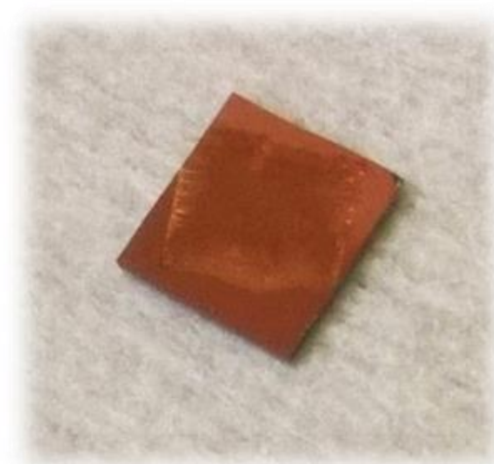
Mashoff et al. – Appl. Phys. Lett. 103, 013903 (**2013**); Takahashi et al. - J. Phys. Chem. C, **2016**, 120, 12974–12979

GRAPHENE TRANSFER

Using a standard PMMA–assisted transfer process we transferred MLG onto the gold-coated SiO_2/Si substrates





Barin et al. - Carbon (2015) 84, 82–90

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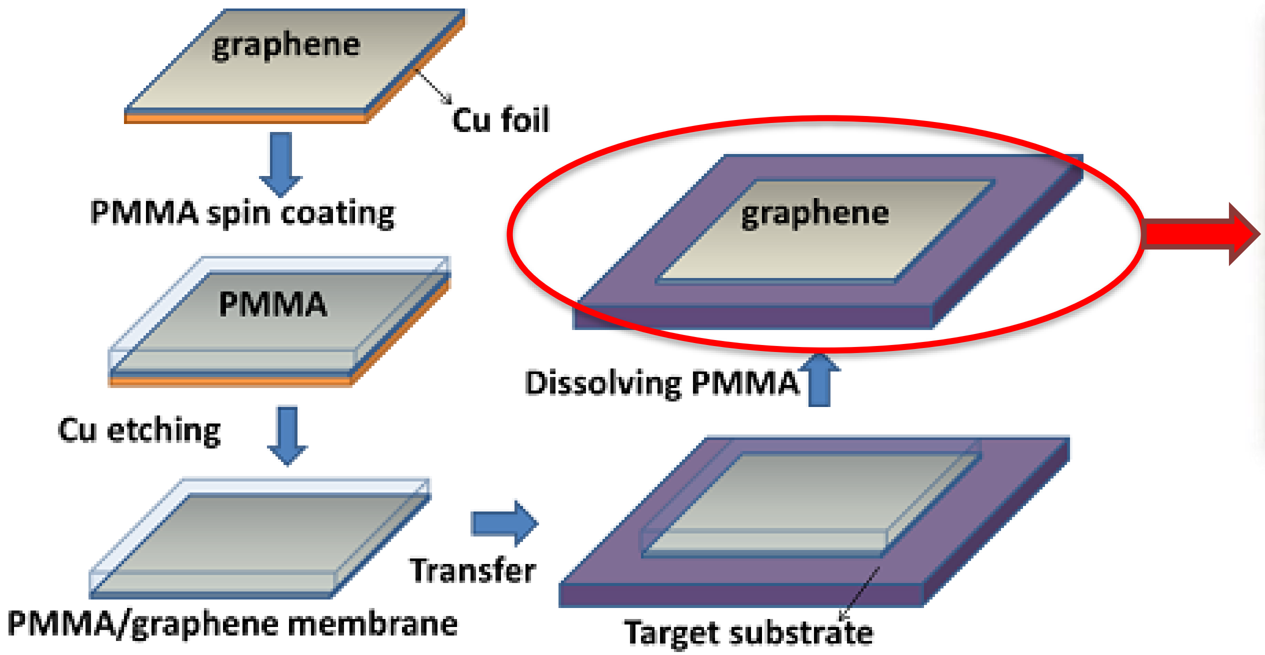

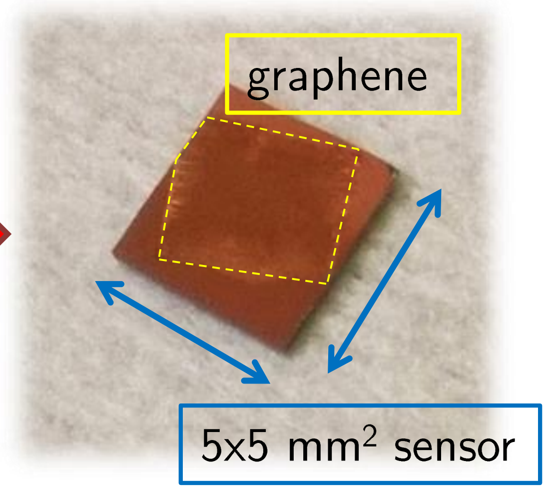

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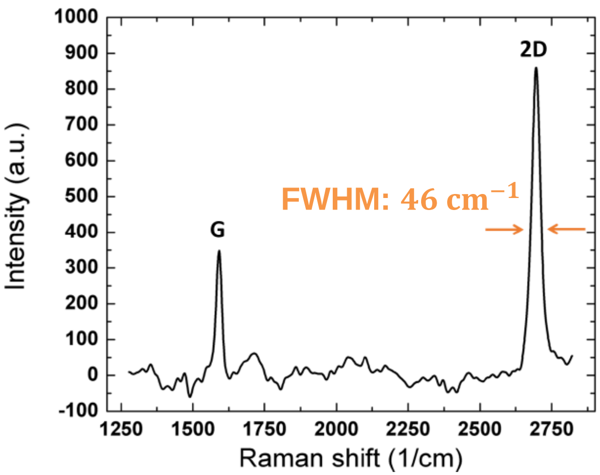
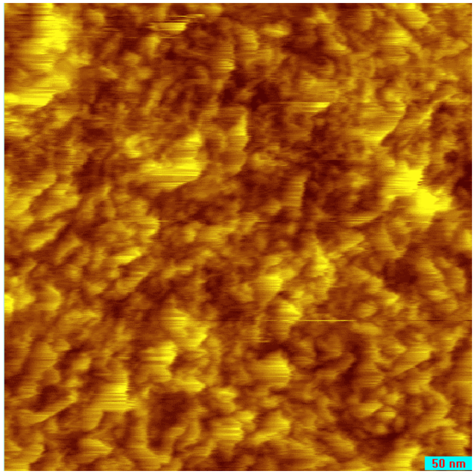
SAMPLE CHARACTERIZATION

Using a standard PMMA–assisted transfer process we transferred MLG onto the gold-coated SiO_2/Si substrates

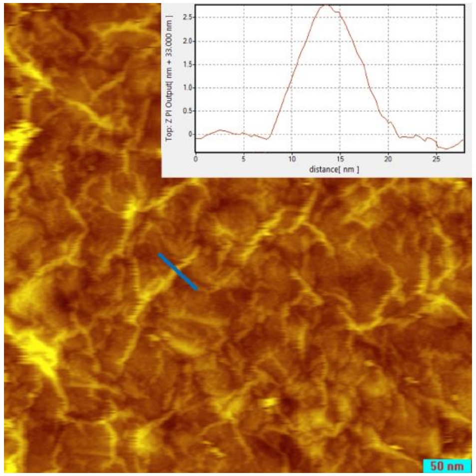
We performed *Raman Spectroscopy* and *STM*, in order to properly characterize the sample



Raman spectrum of MLG



STM on Au



STM on MLG

Basta et al. - Nanoscale, 2018, 10, 10079-10086

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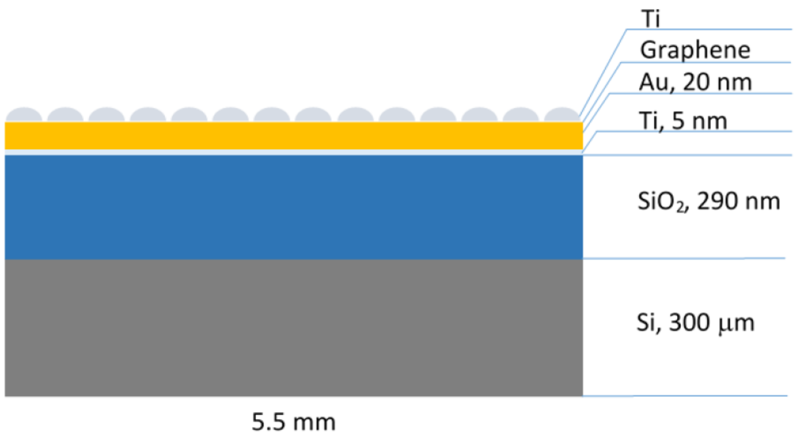
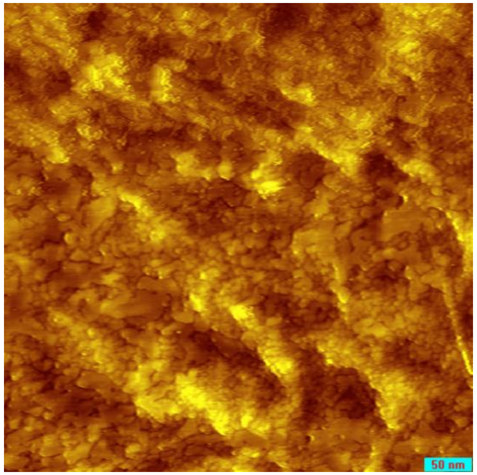
Finally we deposited Ti, reaching a 100% coverage





STM on Ti-MLG

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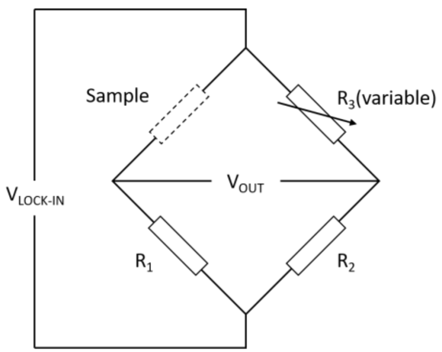
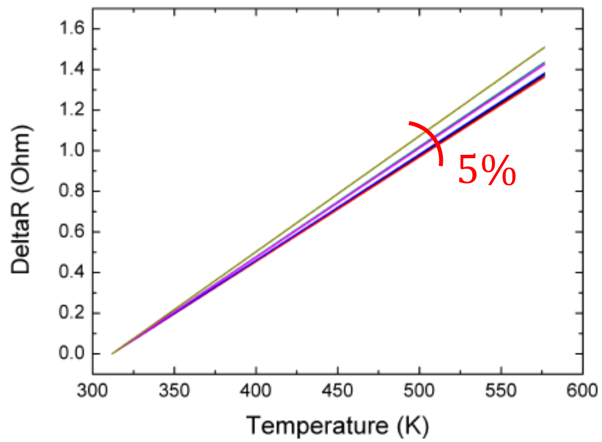
SAMPLE CALIBRATION

To enhance the sensitivity, we use a **Wheatstone bridge** setup, and we perform a final calibration of the sample, obtaining the effective parameters α_{eff} (*temperature coefficient of resistance*) and ρ_{eff} (*electrical resistivity*)



$$R_1 = R_2 = 1\text{K}\Omega$$
$$R_3 \approx R_S\,(T_0)$$



calibration ramps

$$\alpha_{eff} = (1.8 \pm 0.3)10^{-3}\text{K}^{-1}$$

$$\rho_{eff} = (3.6 \pm 0.4)10^{-8}\Omega\text{m}$$

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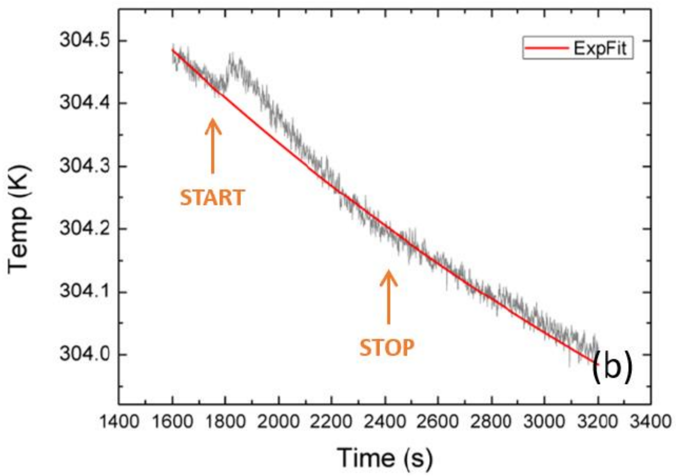
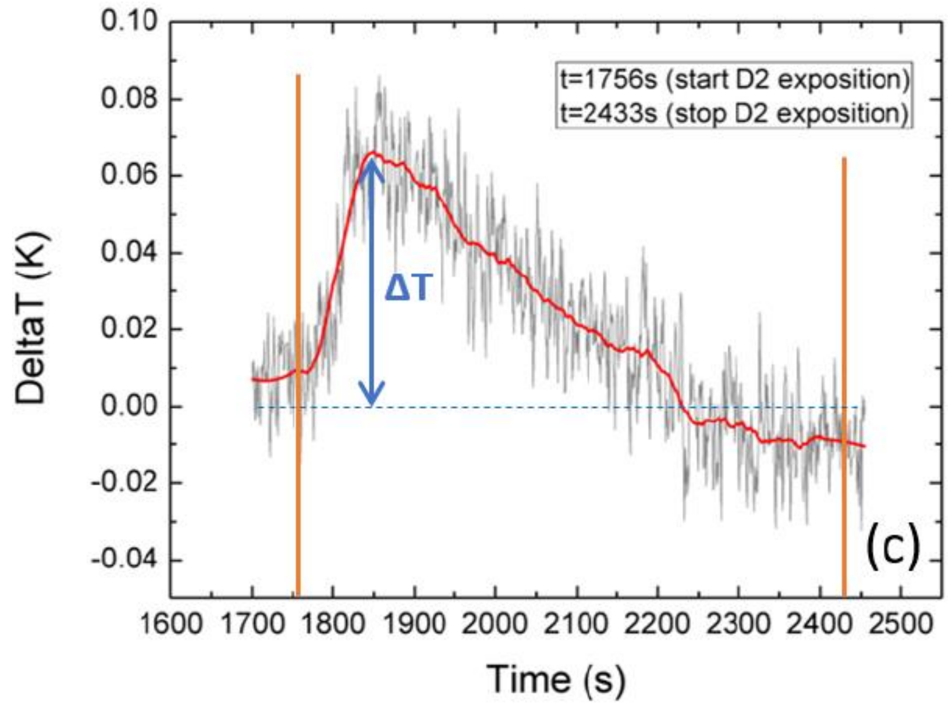
CALORIMETRY DURING HYDROGENATION

During the exposure of the sample to D_2 (better signal-to-noise ratio in the mass spectrometer for the TDS), at a pressure of $\sim 1 \cdot 10^{-7}$mbar, for 5 min, we record the temperature of the sensor



exponential fit of the cooling after the Ti deposition



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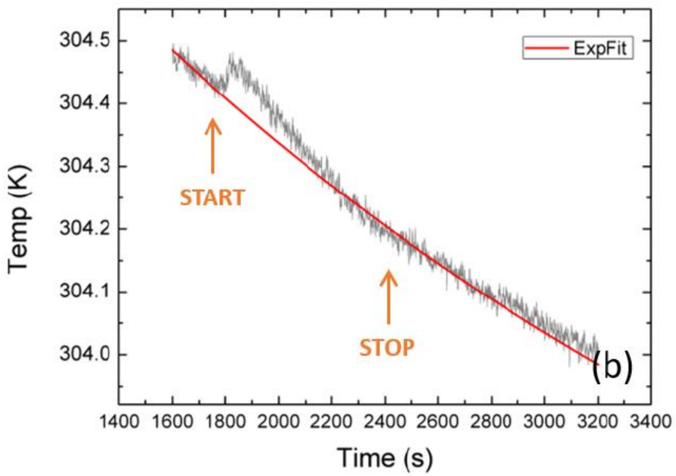

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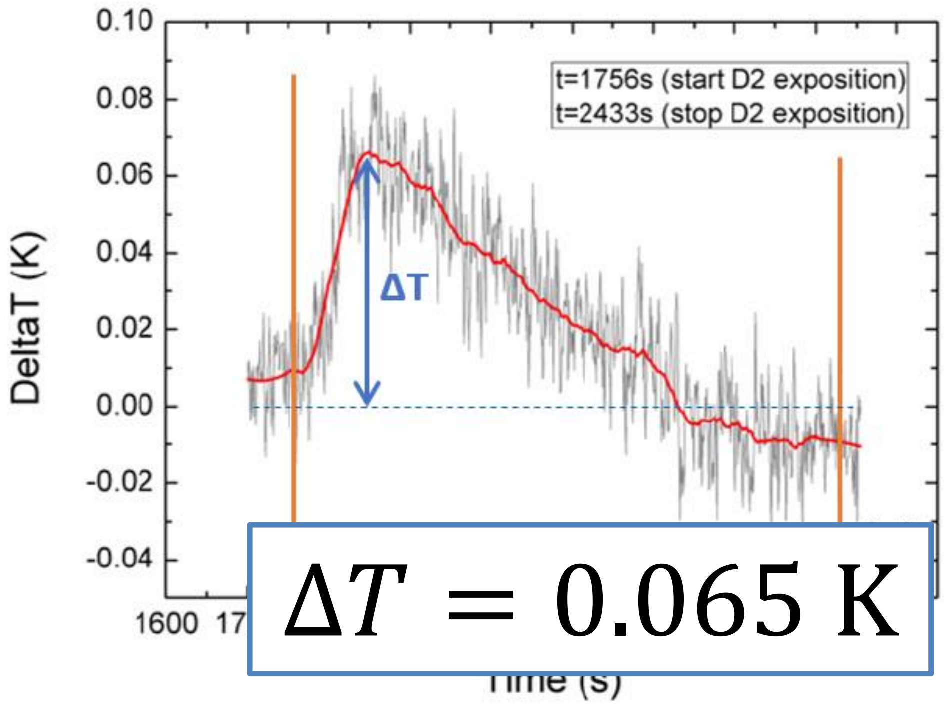

$$\Delta T = 0.065 \text{ K}$$

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ENTHALPY FROM CALORIMETRY

In that case $P(t) = \frac{\delta H_r(t)}{\delta t}$, with H_r the total heat release

$$\frac{\delta H_r(t)}{\delta t} = C\,\frac{\delta \Delta T(t)}{\delta t} + \lambda\,\Delta T(t)$$

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Ti-MLG + Au/Ti sensor + SiO_2 substrate

$C = (15.0 \pm 0.2) \cdot 10^{-6}$ J/K

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Ti-MLG + Au/Ti sensor + SiO_2 substrate

$C = (15.0 \pm 0.2) \cdot 10^{-6}$ J/K

$\tau = (2.9 \pm 0.6)$ s

$\lambda = (5.1 \pm 1.1) \cdot 10^{-6}$ W/K

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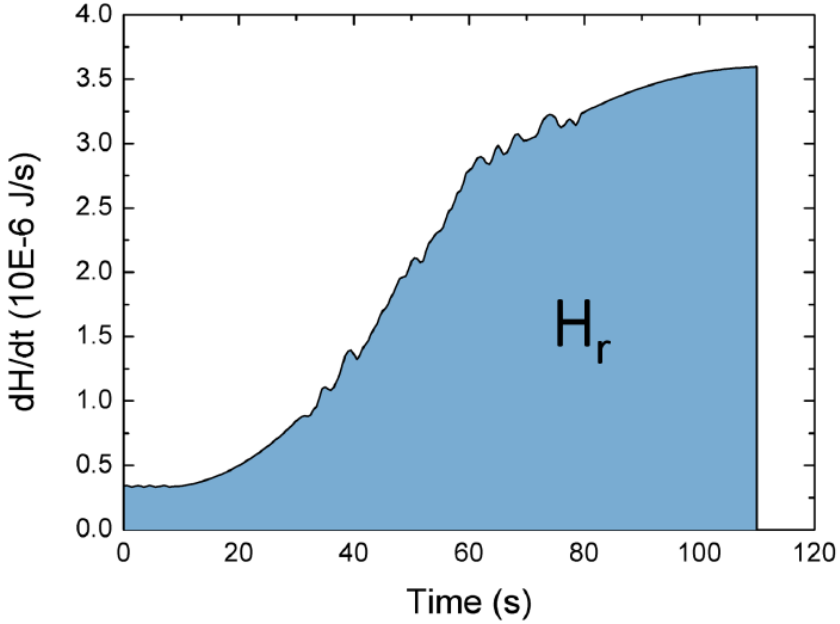

$$H_r = (23.4 \pm 4.7)\ \mu J$$

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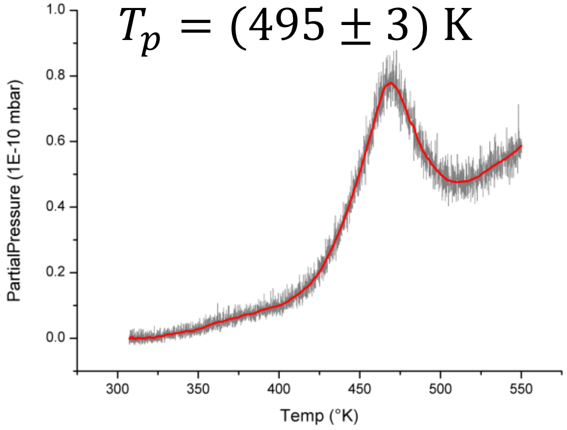
ENTHALPY FROM TDS ANALYSIS



$T_p = (495 \pm 3)$ K

TDS vs Temperature

$$\frac{E_d}{k_B T_p} = A\,\tau_m \exp\left(-\frac{E_d}{k_B T_p}\right)$$

$$E_d = (1.32 \pm 0.07)\ \text{eV/molecule}$$

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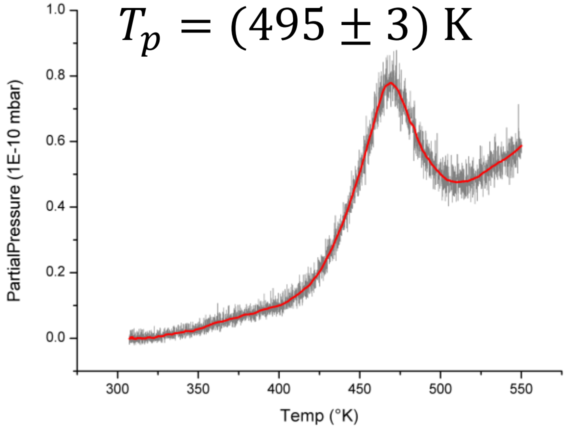

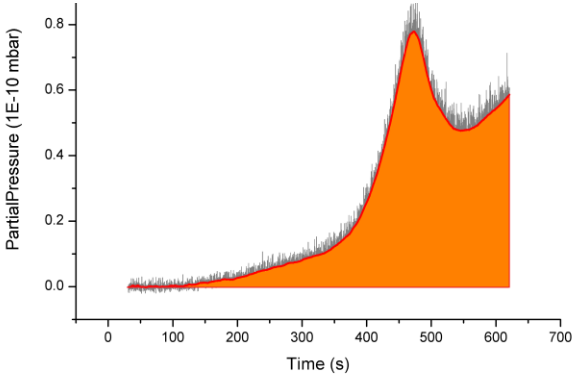

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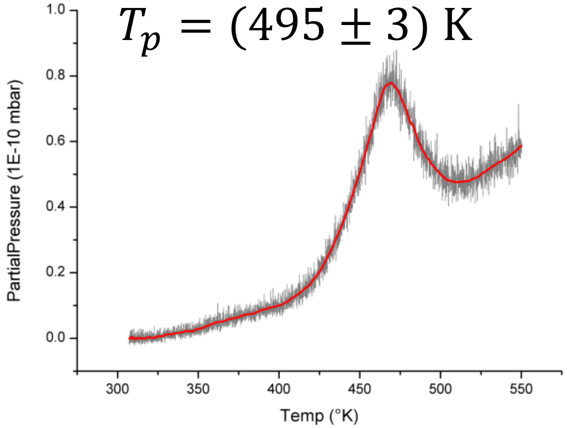

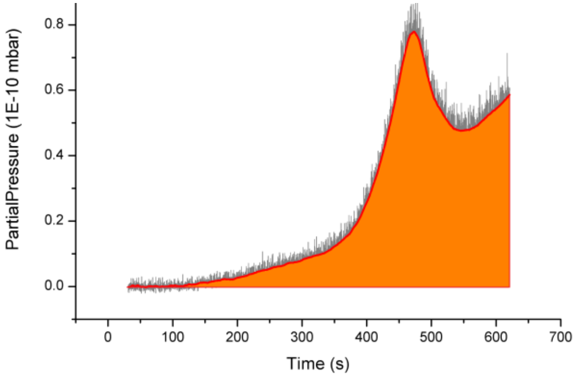

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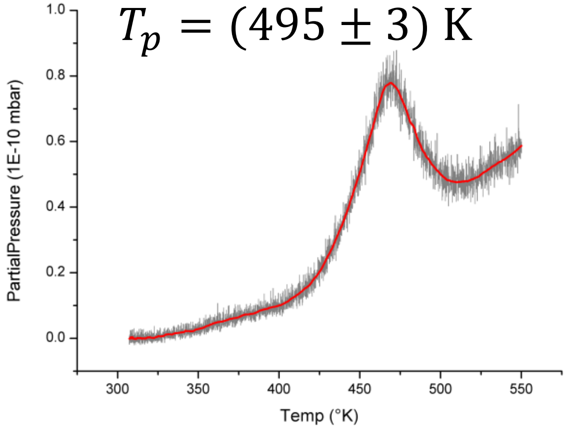

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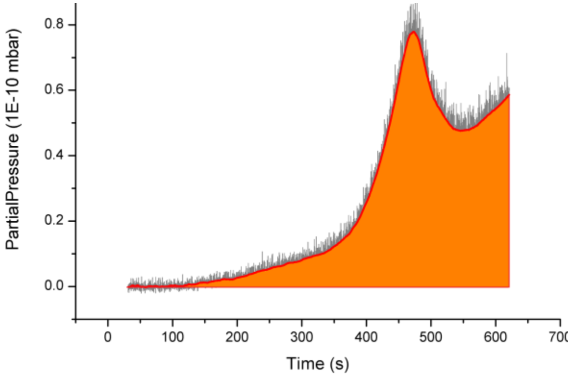

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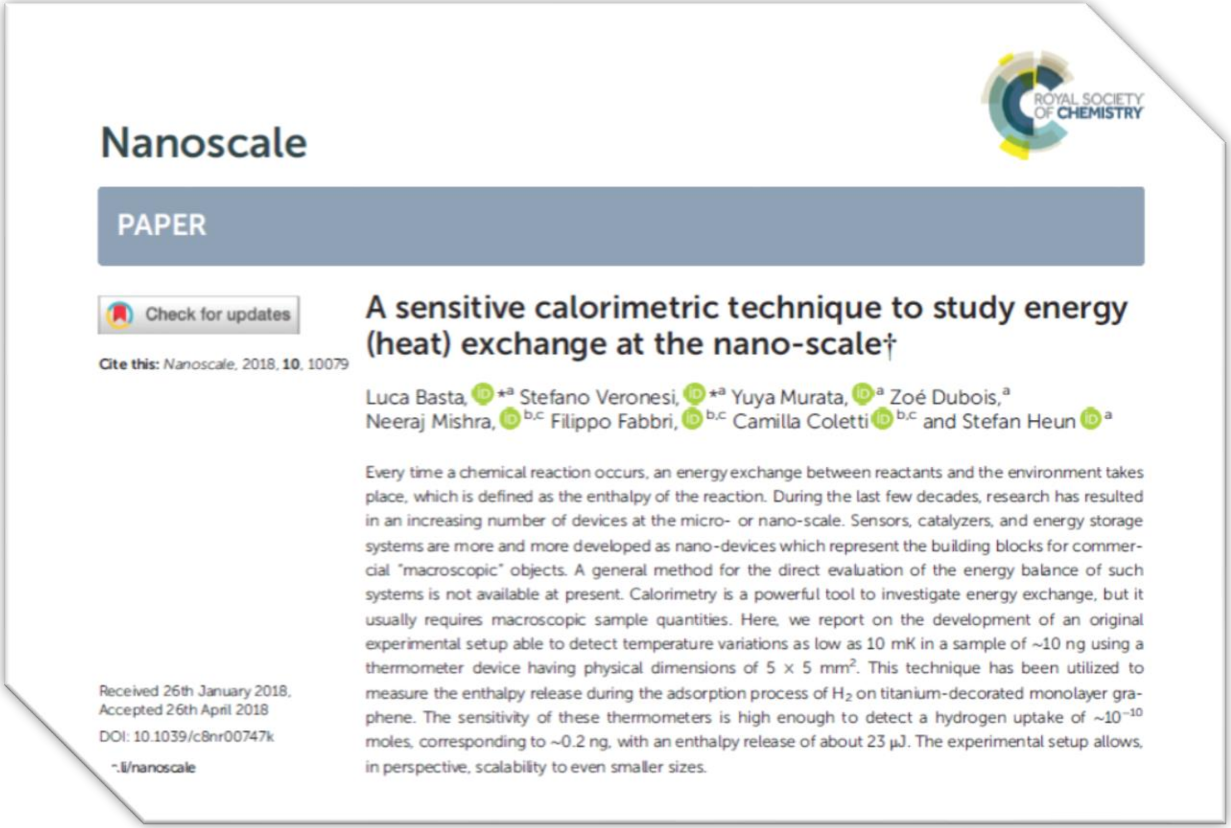
  - detection of ~ 0.2 ng / $1.7 \cdot 10^{-10}$ mol
  - energy sensitivity ~ 5 μJ
- ***Direct*** and ***non-destructive*** technique (compared to the standard TDS method)

Conclusions

➢ Paper published: « *Nanoscale*, 2018, **10**, 10079 »



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PAPER

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A sensitive calorimetric technique to study energy (heat) exchange at the nano-scale†

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Every time a chemical reaction occurs, an energy exchange between reactants and the environment takes place, which is defined as the enthalpy of the reaction. During the last few decades, research has resulted in an increasing number of devices at the micro- or nano-scale. Sensors, catalyzers, and energy storage systems are more and more developed as nano-devices which represent the building blocks for commercial "macroscopic" objects. A general method for the direct evaluation of the energy balance of such systems is not available at present. Calorimetry is a powerful tool to investigate energy exchange, but it usually requires macroscopic sample quantities. Here, we report on the development of an original experimental setup able to detect temperature variations as low as 10 mK in a sample of ~10 ng using a thermometer device having physical dimensions of 5 × 5 mm^2. This technique has been utilized to measure the enthalpy release during the adsorption process of H_2 on titanium-decorated monolayer graphene. The sensitivity of these thermometers is high enough to detect a hydrogen uptake of ~10^{-10} moles, corresponding to ~0.2 ng, with an enthalpy release of about 23 μJ. The experimental setup allows, in perspective, scalability to even smaller sizes.

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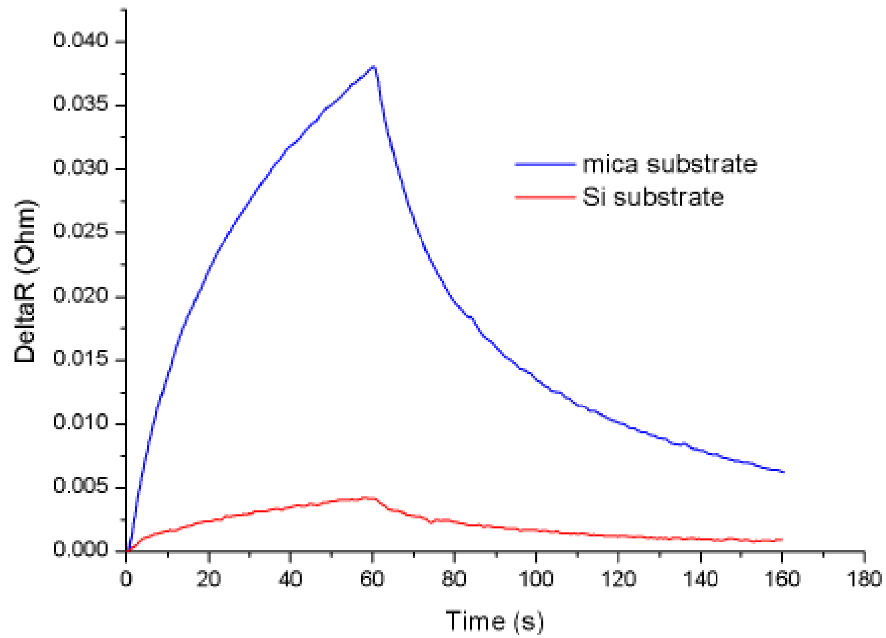
Outlooks

➢ Better sensitivity using Mica instead of Si as substrate

- $\lambda_{mica} \sim 2 \cdot 10^{-7}$ W/K vs $\lambda_{Si} \sim 5 \cdot 10^{-6}$ W/K



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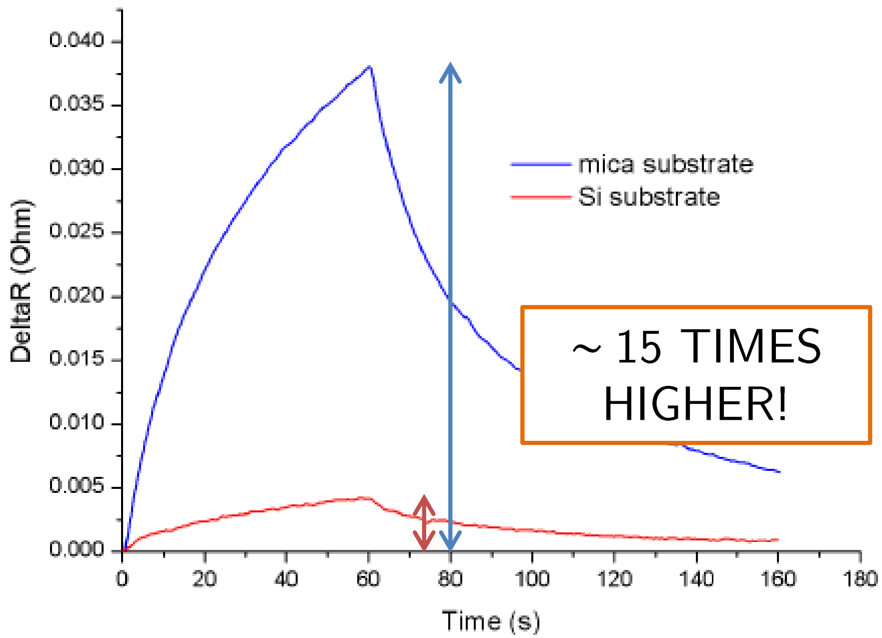

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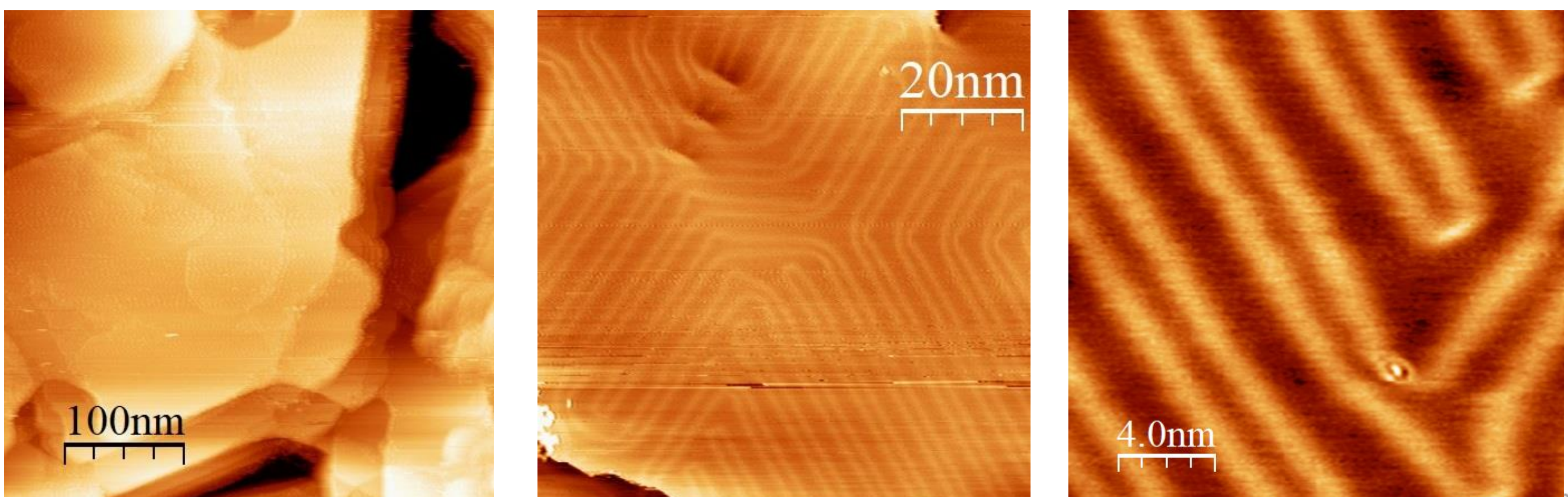
- Gold surface re-crystallization → atomically flat surface → atomic resolution with STM



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