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COST Action TD1105

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New Sensing Technologies for Indoor and Outdoor Air Quality Control

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GRAPHENE FOR GAS SENSORS

Tiziana Polichetti
WG Participant tiziana.polichetti@enea.it
ENEA - Portici Research Center, Portici (NA), Italy

ENEA
Italian National Agency for New Technologies, Energy and Sustainable Economic Development

Contents

- Introduction on graphene
- State of the art on graphene-based gas sensors
- Graphene-based devices at CR ENEA Portici
- Results
- Conclusions

I would like to introduce myself

I work on graphene since 2009, mainly on gas sensor device applications

Tiziana Polichetti- Physicist

The colleagues which I work with

Girolamo Di Francia- Physicist

Mara Miglietta - Chemist

Filiberto Ricciardella - Physicist

Filippo Fedi- Material Engineer

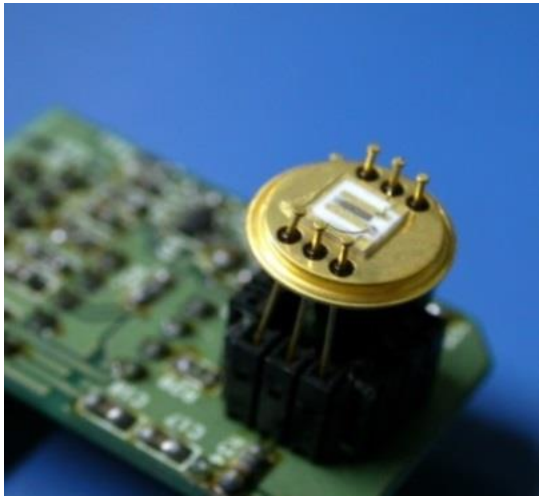
Ettore Massera- Physicist

Who we are

MDB Lab

Materials and **D**evices **B**asic research on sensors and solar cell

Development of sensing layers for air pollution

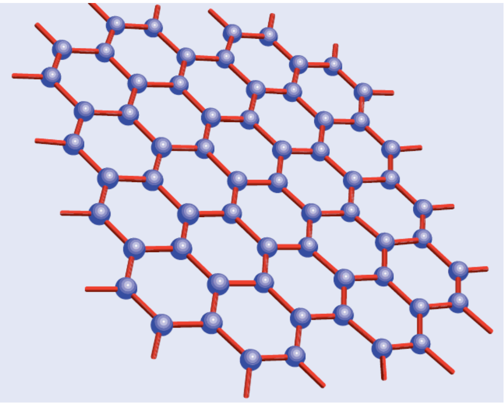


Main requirements:

- **Room T and air operation**
- **Low concentrations**
- **Simple to produce**
- **Integrable in portable devices**
- **Ecologically sustainable**

Introduction on graphene

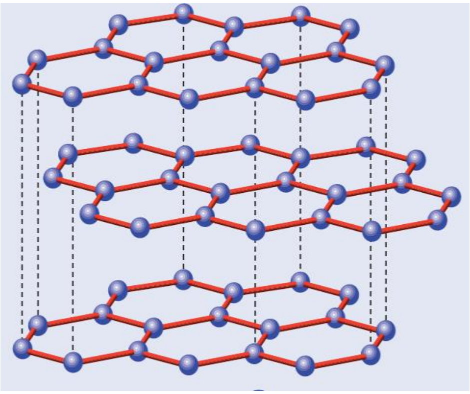
What’s graphene?



Graphene consists of a 2D hexagonal lattice of carbon atoms. Each atom is covalently bonded to 3 others; since carbon has 4 valence electrons, one is left free, allowing graphene to conduct electricity.

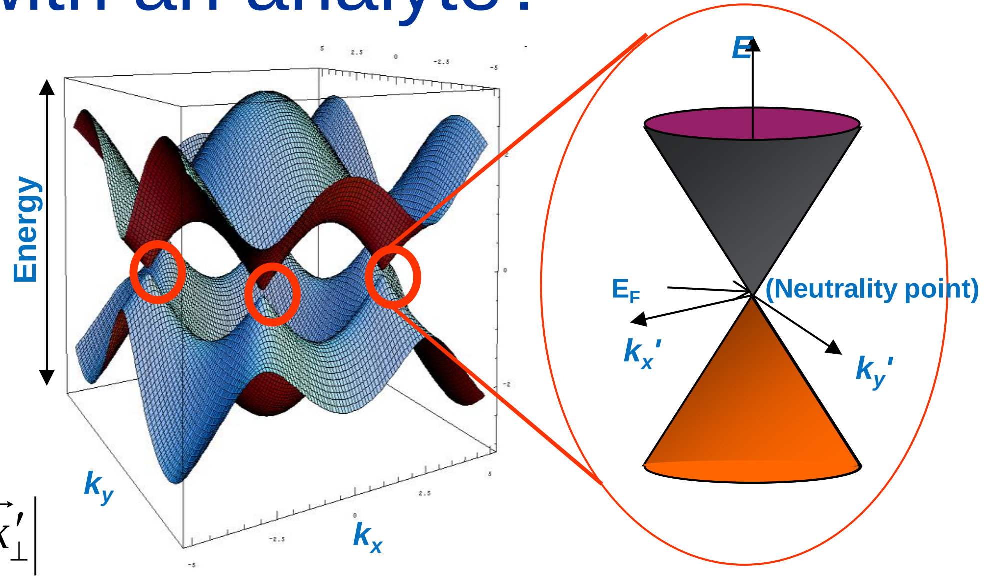
2D crystals are thermodynamically unstable and could not exist except as an integral part of 3D structures

Graphite is a stack of graphene layers.



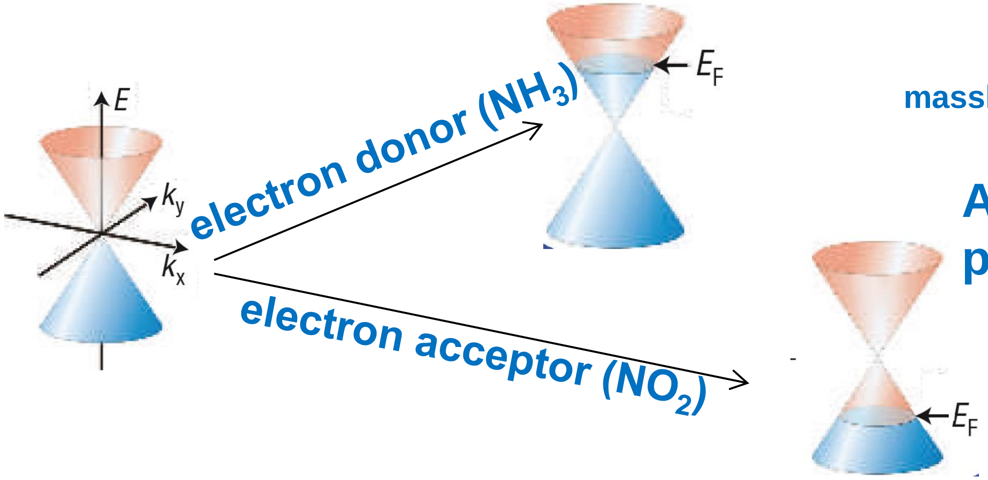
How does graphene work during the interaction with an analyte?

Electronic structure of graphene



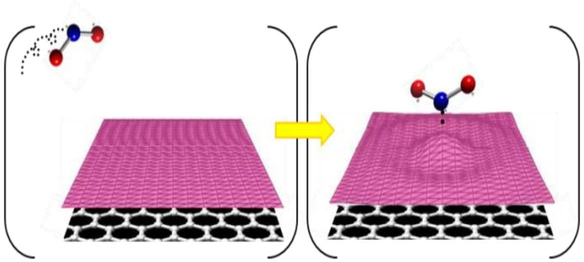
$$E \approx \hbar v_F \left|\vec{k}'_\perp\right|$$

massless Dirac particles with effective speed of light v_F.



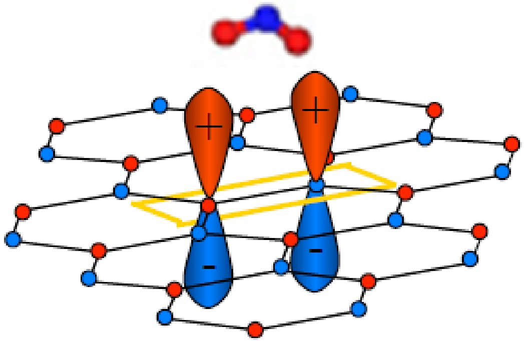
Adsorption/desorption changes electrical properties

Why graphene in sensing field?

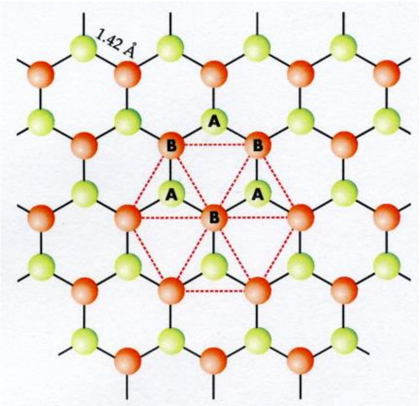


➢ HIGHEST SURFACE VOLUME RATIO

- two-dimensional material
- Interaction on surface, no bulk



➢ GAS-MOLECULES JOIN TO π-BONDS



➢ LOWEST SIGNAL-TO-NOISE RATIO

local concentration less than one electron charge at room temperature

F. Schedin et al., Nature 6, 652 (2007).

Top down and bottom up techniques for fabricating graphene

TOP-DOWN approach

- Mechanical cleavage
  - Rubbing
  - Scotch-tape method
- Liquid-phase exfoliation
  - GRAPHITE
    - Dispersion in organic solvents
    - Dispersion in water + surfactants
  - GRAPHITE OXIDE
    - Exfoliation and next reduction

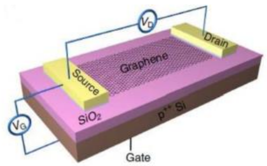
BOTTOM-UP approach

- Thermal decomposition of SiC
- CVD

State of the art on graphene-based gas sensors

The very first graphene based gas sensor

F. Schedin et al., Nature 6, 652 (2007).



Field effect transistors (FET) realized starting from mechanical exfoliated graphene; the device was realized by e-beam lithography.

Working principle

the number of the carriers of the drain current depends on the gate bias:

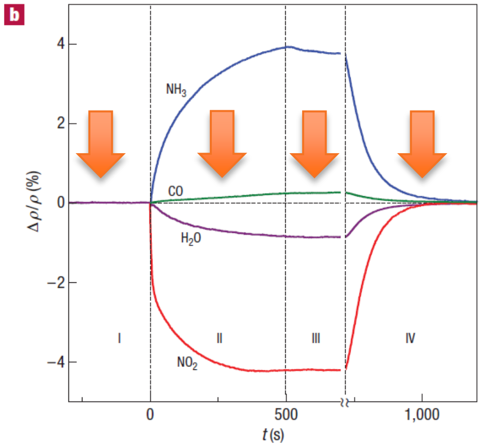
$$n = \varepsilon_0 \varepsilon V_g / e\, t$$

t = dielectric thickness; e = electron charge

Fixing V_g, the change of the drain current is exclusively due to the exposure to the target gas.

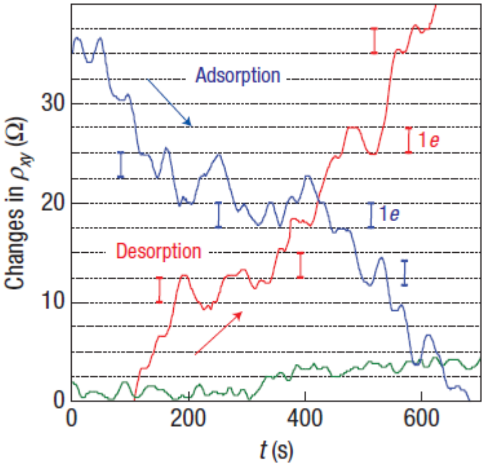
Main achievements :
- Material fabrication technique easy and cheap
- Detection of single molecules.

Main drawbacks:
- identification and alignment of the flakes, required for device realization by lithography, are very hardworking.
- Tests were not performed in real environmental conditions (dry nitrogen or dry helium environment).
- Recovery is achieved after evacuation and annealing at 150°C.



Exposure to 1 ppm of different analytes.

Resistance variation upon exposure.
- Region I: the device is in vacuum before its exposure;
- II: exposure to diluted chemical;
- III: evacuation of the experimental set-up;
- IV: annealing at 150 °C.



Detection of single molecules

Changes in Hall resistivity during adsorption of 1 ppm of NO_2 (blue curve) and its desorption in vacuum at 50 °C (red curve).
The grid lines correspond to changes in ρ_{xy} caused by adding one electron charge, e ($\delta R \approx 2.5\ \Omega$);
The green curve is a reference, the same device thoroughly annealed and then exposed to pure He.

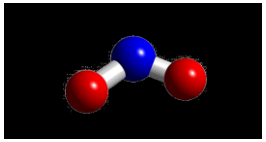
This paper has got around 2700 citations!!

State of the art

After the first experimental evidence that a graphene flake can detect the presence of even a single interacting molecule, many theoretical and experimental studies have shown that graphene-based chemisensors operating at room temperature possess pronounced sensitivity to certain analytes (e.g., NH_3, CO, NO_2, SO_2, H_2O).

Interaction of the graphene with analytes

NO_2 molecule orientation

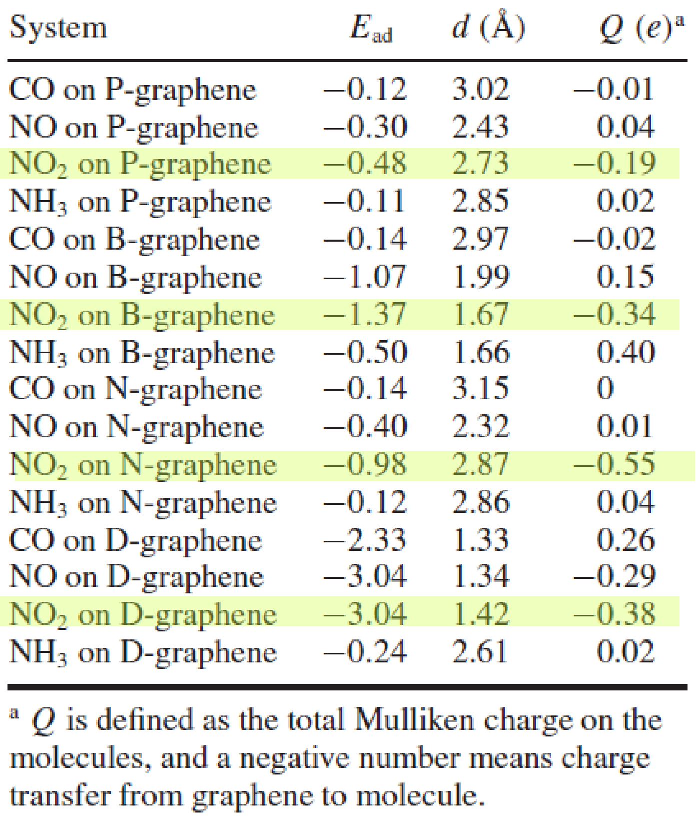


N-O bonds points up with respect to the surface
N-O bonds points down with respect to the surface
N-O bonds is parallel to the graphene surface

P-graphene stands for pristine graphene
B-graphene stands for boron-doped graphene
N-graphene stands for nitrogen-doped graphene
D-graphene stands for defective graphene

Adsorption energy

$E_{ad}=E_{graphene+molecule}-E_{graphene}-E_{molecule}$



System	E_{ad}	d (Å)	Q (e)[a]
CO on P-graphene	−0.12	3.02	−0.01
NO on P-graphene	−0.30	2.43	0.04
NO_2 on P-graphene	−0.48	2.73	−0.19
NH_3 on P-graphene	−0.11	2.85	0.02
CO on B-graphene	−0.14	2.97	−0.02
NO on B-graphene	−1.07	1.99	0.15
NO_2 on B-graphene	−1.37	1.67	−0.34
NH_3 on B-graphene	−0.50	1.66	0.40
CO on N-graphene	−0.14	3.15	0
NO on N-graphene	−0.40	2.32	0.01
NO_2 on N-graphene	−0.98	2.87	−0.55
NH_3 on N-graphene	−0.12	2.86	0.04
CO on D-graphene	−2.33	1.33	0.26
NO on D-graphene	−3.04	1.34	−0.29
NO_2 on D-graphene	−3.04	1.42	−0.38
NH_3 on D-graphene	−0.24	2.61	0.02

[a] Q is defined as the total Mulliken charge on the molecules, and a negative number means charge transfer from graphene to molecule.

Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study, Y.H. Zhang, Y.B. Chen, K.G. Zhou, C.H. Liu, J. Zeng, H.L. Zhang and Y. Peng, Nanotechnology 20 (2009) 185504

Interaction of the graphene with analytes

Summarizing:

The defects in graphene sheets are important for gas sensing.
The results indicate that defective graphene interacts strongly with CO, NO or NO_2, but weakly with NH_3.
Nitrogen-doped (N-doped) graphene shows strong binding with NO_2.
Boron-doped (B-doped) graphene exhibits enhanced interactions with NO, NO_2, and NH_3.

State of the art

Being a defective material, reduced graphene oxide (RGO) is very promising in sensing applications.
In fact, most of the papers found in the literature, concerning the graphene-based gas sensors, use the oxidation of graphite to produce the graphite-oxide which, in turn, can be easily exfoliated in liquid media such as water with a very high yield of mono-layer graphene oxide (GO).

1. Lu, Ganhua, Leonidas E. Ocola, and Junhong Chen. "Reduced graphene oxide for room-temperature gas sensors." *Nanotechnology* 20.44 (2009): 445502.
2. Hu, Nantao, et al. "Ultrafast and sensitive room temperature NH3 gas sensors based on chemically reduced graphene oxide." *Nanotechnology* 25.2 (2014): 025502-025502.
3. Tran, Quang Trung, et al. "Reduced graphene oxide as an over-coating layer on silver nanostructures for detecting NH< sub> 3</sub> gas at room temperature." Sensors and Actuators B: Chemical 194 (2014): 45-50.
4. Muhammad Hafiz, Syed, et al. "A practical carbon dioxide gas sensor using room-temperature hydrogen plasma reduced graphene oxide." Sensors and Actuators B: Chemical 193 (2014): 692-700.
5. Su, Pi-Guey, and Hung-Chiang Shieh. "Flexible NO< sub> 2</sub> sensors fabricated by layer-by-layer covalent anchoring and in situ reduction of graphene oxide." Sensors and Actuators B: Chemical 190 (2014): 865-872.
6. Zhang, Hao, et al. "SnO< sub> 2</sub> nanoparticles-reduced graphene oxide nanocomposites for NO< sub> 2</sub> sensing at low operating temperature." Sensors and Actuators B: Chemical 190 (2014): 472-478.
7. Wang, Zhenyu, et al. "Humidity sensing properties of urchin-like CuO nanostructures modified by reduced graphene oxide." ACS applied materials & interfaces (2014).
8. Zhou, Xiaoqing, et al. "Preparation, characterization and NH< sub> 3</sub>-sensing properties of reduced graphene oxide/copper phthalocyanine hybrid material." Sensors and Actuators B: Chemical 193 (2014): 340-348.
9. Ghosh, Ruma, et al. "Humidity Sensing by Chemically Reduced Graphene Oxide." Physics of Semiconductor Devices. Springer International Publishing, 2014. 699-701.
10. Yao, Yao, et al. "Investigation of the stability of QCM humidity sensor using graphene oxide as sensing films." Sensors and Actuators B: Chemical 191 (2014): 779-783.

And so on……

The processability of GO in a common and simple solvent as water is undoubtedly an advantage since it is suitable for industrial, large scale applications, but requires toxic and costly chemicals for pre- and post-treatments.

State of the art

F. Yavari et al., *Appl. Phys. Lett.* 100 (2012) 203120.

Chemiresistor is the most widely used configuration of gas sensors.
In this case, graphene film was grown by CVD on Cu and then transferred onto a Si/SiO$_2$ substrate. Gold contact pads were deposited on the film in the Van Der Pauw configuration.

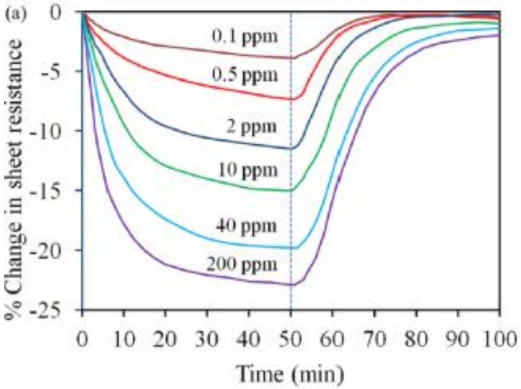
Working principle
The gaseous analytes were detected by measuring the resistance changes of sensing layers induced by adsorbing the gas molecules.

Main achievements :

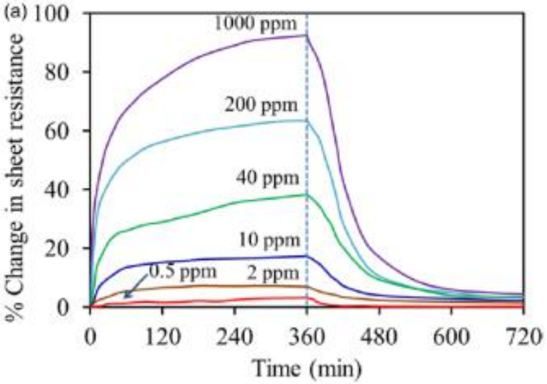
- Sub- ppm detection of NO$_2$ and NH$_3$

Main drawbacks:

- Material fabrication technique energy-consuming.
- Tests not performed in real environmental conditions (dry air).
- Duration of exposure to analyte on the order of hours.
- Recovery is achieved after evacuation and annealing at 200°C.



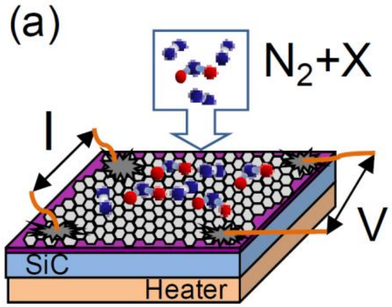
NO$_2$ detection at room temperature and atmospheric pressure.
After 50 min the samples were exposed to vacuum desorption conditions and heated to 200 C using a hot plate.



NH$_3$ detection at room temperature and atmospheric pressure.
After 360 min the samples were exposed to vacuum desorption conditions and heated to 200 °C using a hot plate.

State of the art

I. Iezhokin et al., *Appl. Phys. Lett.* 103 (2012) 053514.



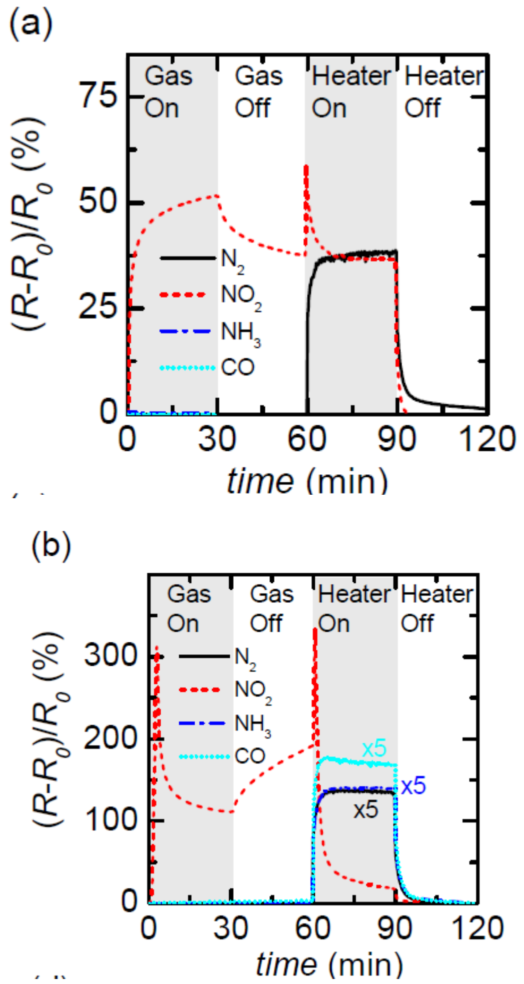
Chemiresistor based on epitaxial graphene (eG) and quasi free standing epitaxial graphene (QFeG). eG was grown by thermal decomposition of SiC at 1450°C.
In a second step the buffer layer is intercalated by hydrogen in order to obtain QFeG**.**

Main achievements :

- Sub-ppm detection and specificity to NO_2

Main drawbacks:

- Material fabrication technique energy-consuming.
- Tests not performed in real environmental conditions (dry nitrogen).
- Recovery is achieved after annealing at 150°C.



Resistance change of (a) eG and (b) QFeG exposed to

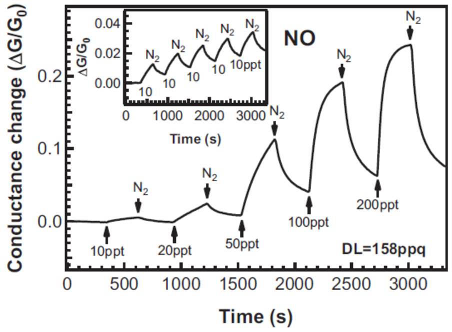
pure N_2,
100 ppb NO_2 (for eG),
40 ppb NO_2 (for QFeG),
300 ppm NH_3
3000 ppm CO.

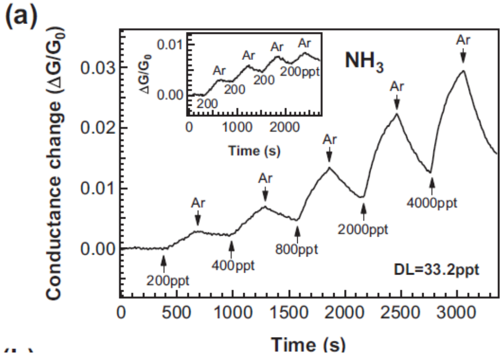
During anneal the sample was heated to 150°C.

State of the art

G. Chen et al., *Appl. Phys. Lett.* 101 (2012) 053119

Chemiresistor based on pristine graphene, synthesized by chemical vapor deposition, can detect gas molecules at extremely low concentrations with detection limits as low as 158 parts-per-quadrillion (ppq) for a range of gas molecules at room temperature. This sensitivity was achieved by applying continuous *in situ* cleaning of the sensing material with ultraviolet light.



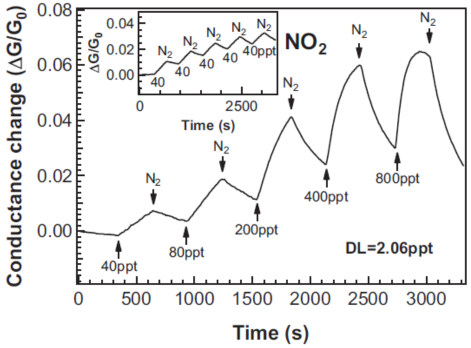


Main achievements :

- Sub-ppm and sub-ppt detection of NO, NO_2 and NH_3

Main drawbacks:

- Material fabrication technique energy-consuming.
- Tests not performed in real environmental conditions (dry nitrogen).
- Complicated and unwieldy device structure.



State of the art

Summarizing:

- The detection of NO_2 has achieved an extremely low limit, below the sub-ppm (parts per million) range.
- In many cases graphene is prepared by laborious and expensive techniques, such as chemical vapour deposition or epitaxial growth, or by chemically exfoliating graphite oxide, which requires toxic and costly chemicals for pre- and post-treatments.
- In other cases, specific measures, for instance continuous exposure of the sensitive material to ultraviolet light, were adopted to reach an even lower limit, in the range of ppt (parts per trillion).
- In any cases is paid the price of employing time- and energy-consuming systems and/or a more complicated and unwieldy device structure.

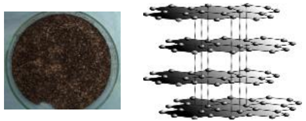
State of the art

Summarizing:

- Tests are generally performed in dry environment.
- The recovery is always achieved through annealing of the device.

Graphene-based devices at CR ENEA Portici

Our recipe: liquid phase exfoliation in green solvents



Natural Graphite

+

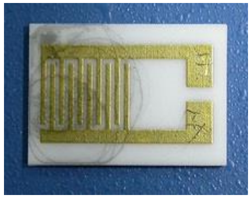
Dispersion of flakes in solvents (H_2O-IPA)

Sonication (~16W)
- **Energy for exfoliation**
- **Low power: no flake cracks**

Centrifugation
- **Separation of exfoliated and thicker flakes**

Colloidal dispersion of graphene

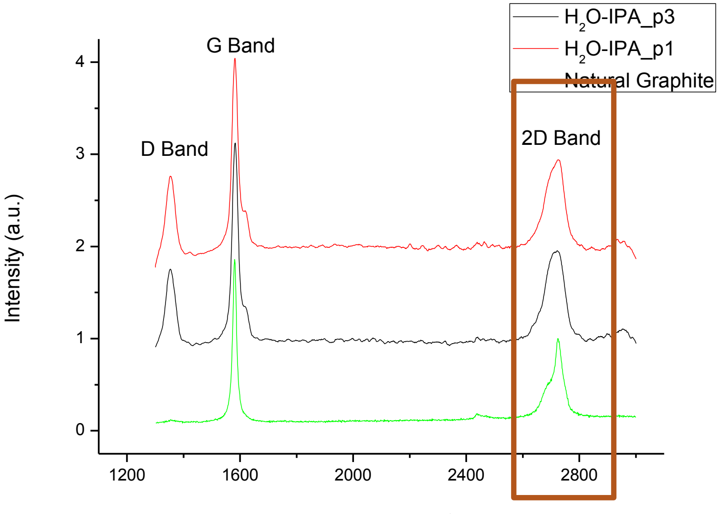
Drop casting of surnatant

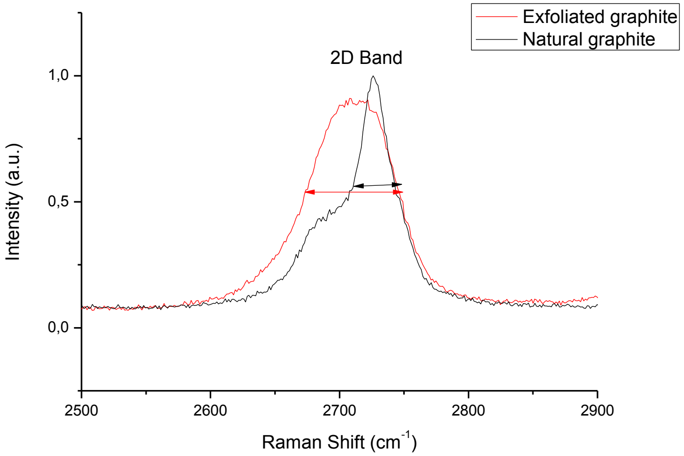


Graphene based chemiresistors

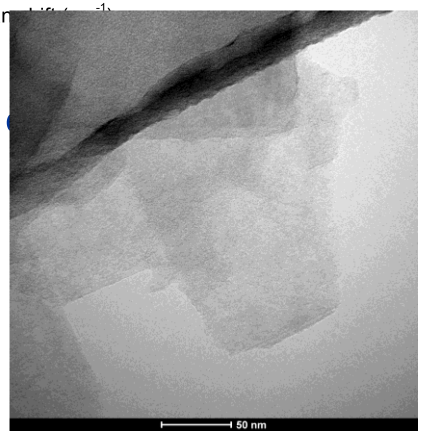
F. Fedi et al: paper in preparation

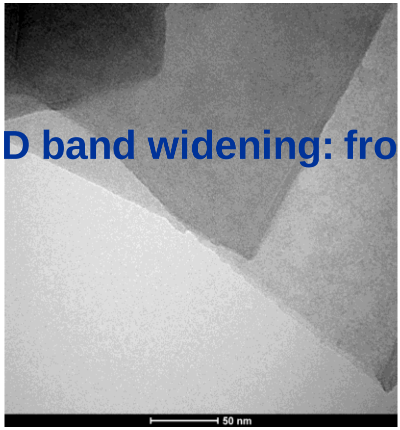
Material characterizations





Homogeneity





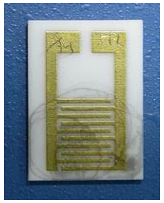
2D band widening: from graphite to oligolayered flakes

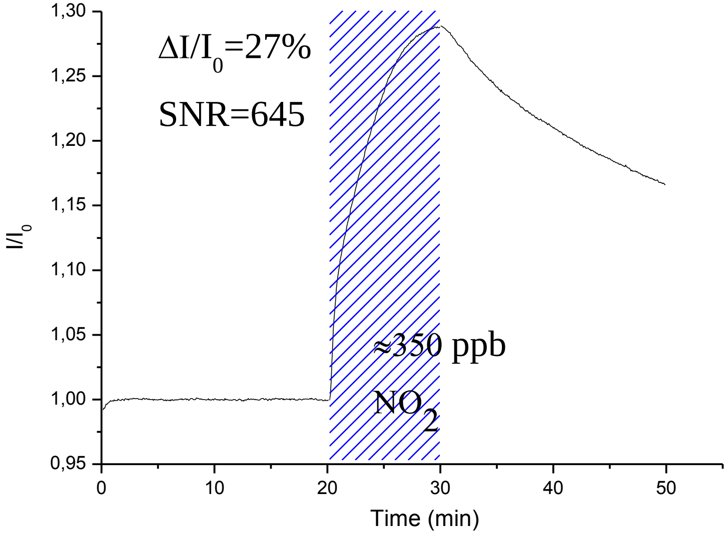
Our device

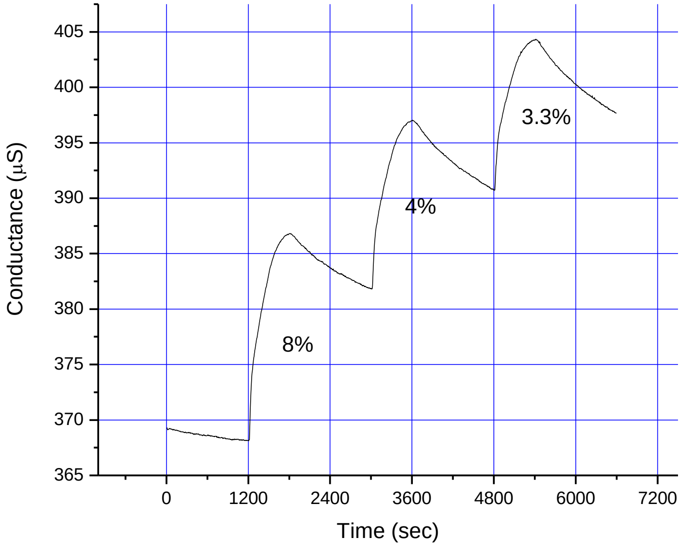
Graphene based chemiresistor

DEVICE DATA

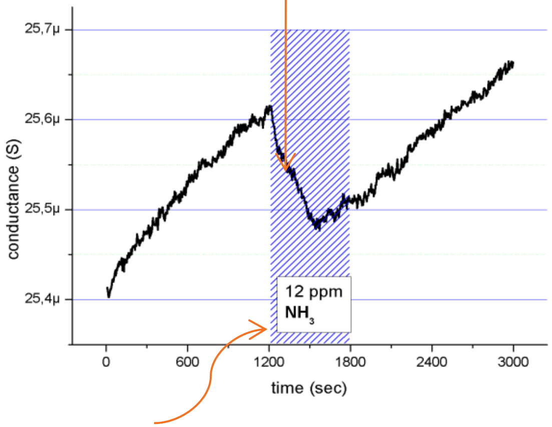
- R ~10 kΩ
- Bias=1 V
- Carrier: Air
- T=22°C
- RH=50%







The conductance decreases



The response is poor

Main achievements:

- ✓ Response time at gas inlet: 4 sec
- ✓ $\Delta I/I_0$ and SNR remarkable in environmental conditions
- ✓ Specificity to NO_2

Main drawbacks:

- ✓ Partial Recovery: solid state sensor bottleneck
- ✓ Worsening of the response

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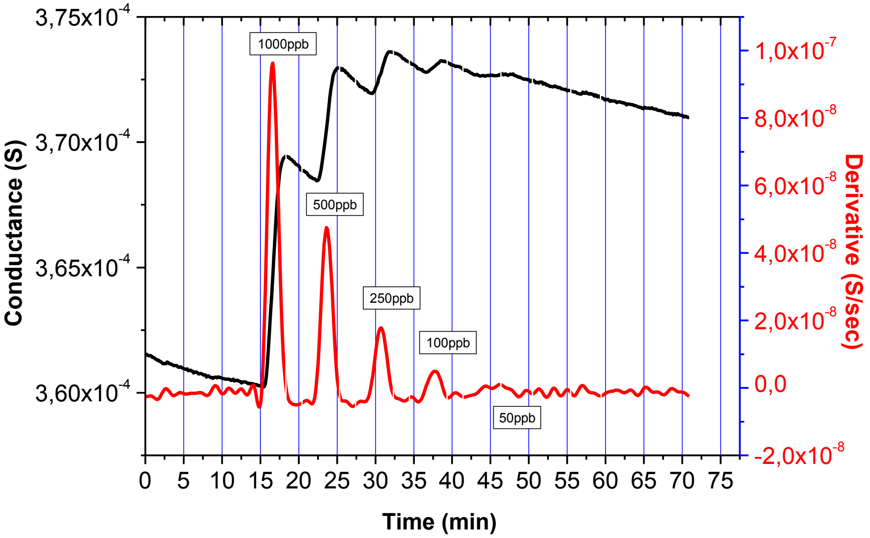
How to overcome the drawbacks?

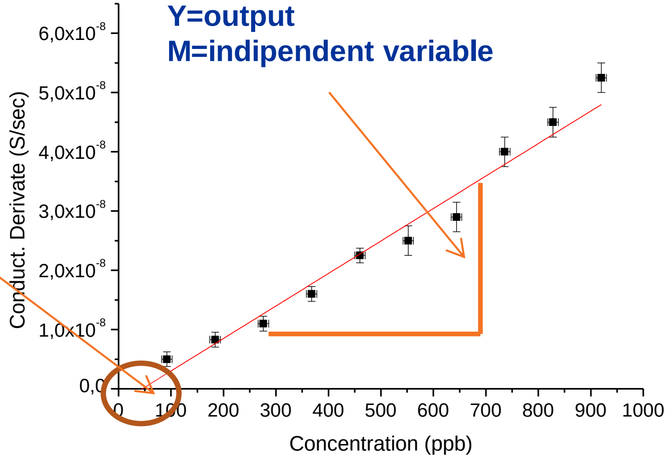


Derivative of the signal allows to overcome drawbacks

$S=\Delta Y/\Delta M$

S=sensitivity
Y=output
M=indipendent variable

LOD (Limit of Detection): 50 ppb



F. Ricciardella, E. Massera, T. Polichetti, M. L. Miglietta, G. Di Francia: Appl. Phys. Lett. under revisions

CONCLUSIONS

- A cheap and easy method to produce graphene has been presented.
- Device fabricated using such material is able to detect NO_2 in real environmental condition down to tens of ppb.
- The recovery problems and the worsening of the response upon cyclic exposure to the analyte have been solved by using the derivative of the conductance signal.
- Next goal will be the tuning of the selectivity towards other analytes.

Thank you for your kind attention!!!