Chemically Derived Graphene For sub-ppm Nitrogen Dioxide Detection

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GraphITA

L'Aquila, 15-18 May 2011

MDB Lab

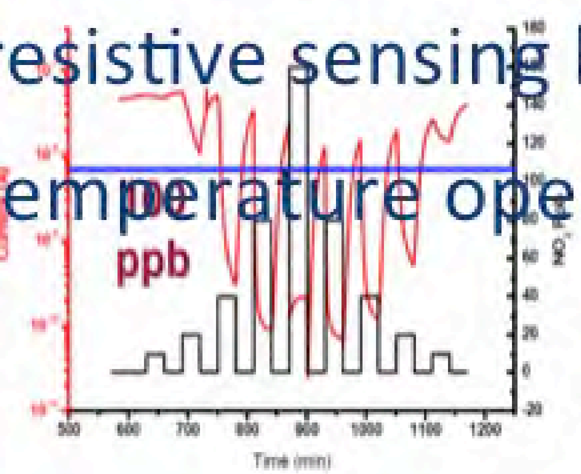
materials and devices basic research

Sensor devices

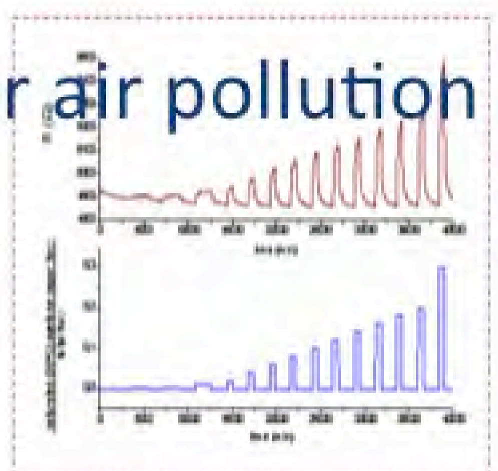
Solar cells

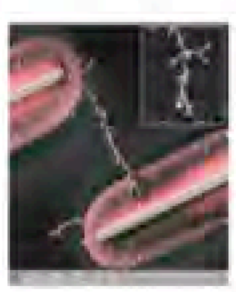
chemiresistive sensing layer for air pollution
room temperature operation

NO2 sensor

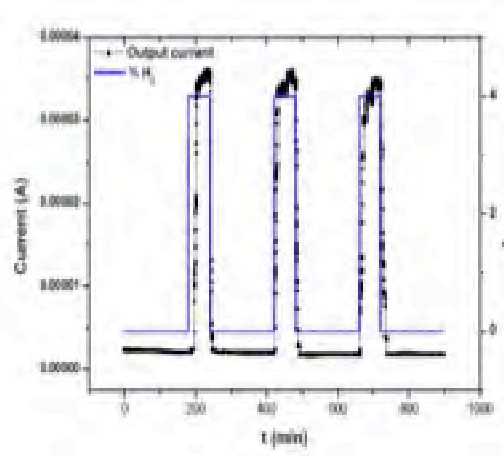


VOC sensor





H2 sensor



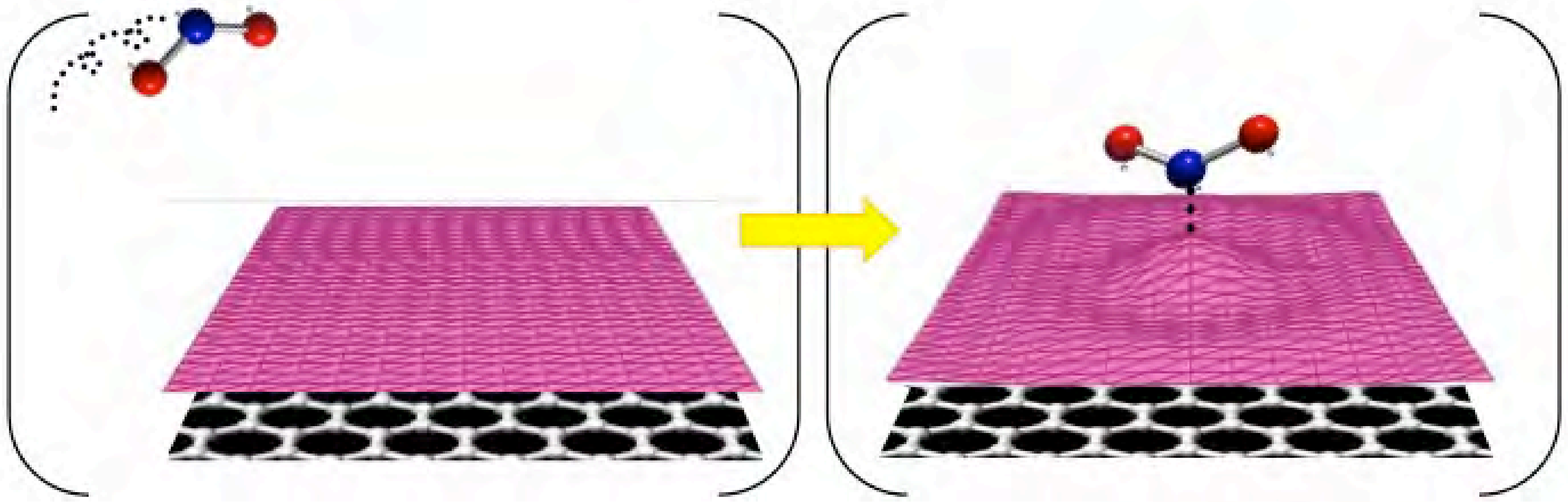
simply to produce and integrate in electronic
cheap and with a low environmental impact
suitable for portable electronic - nose

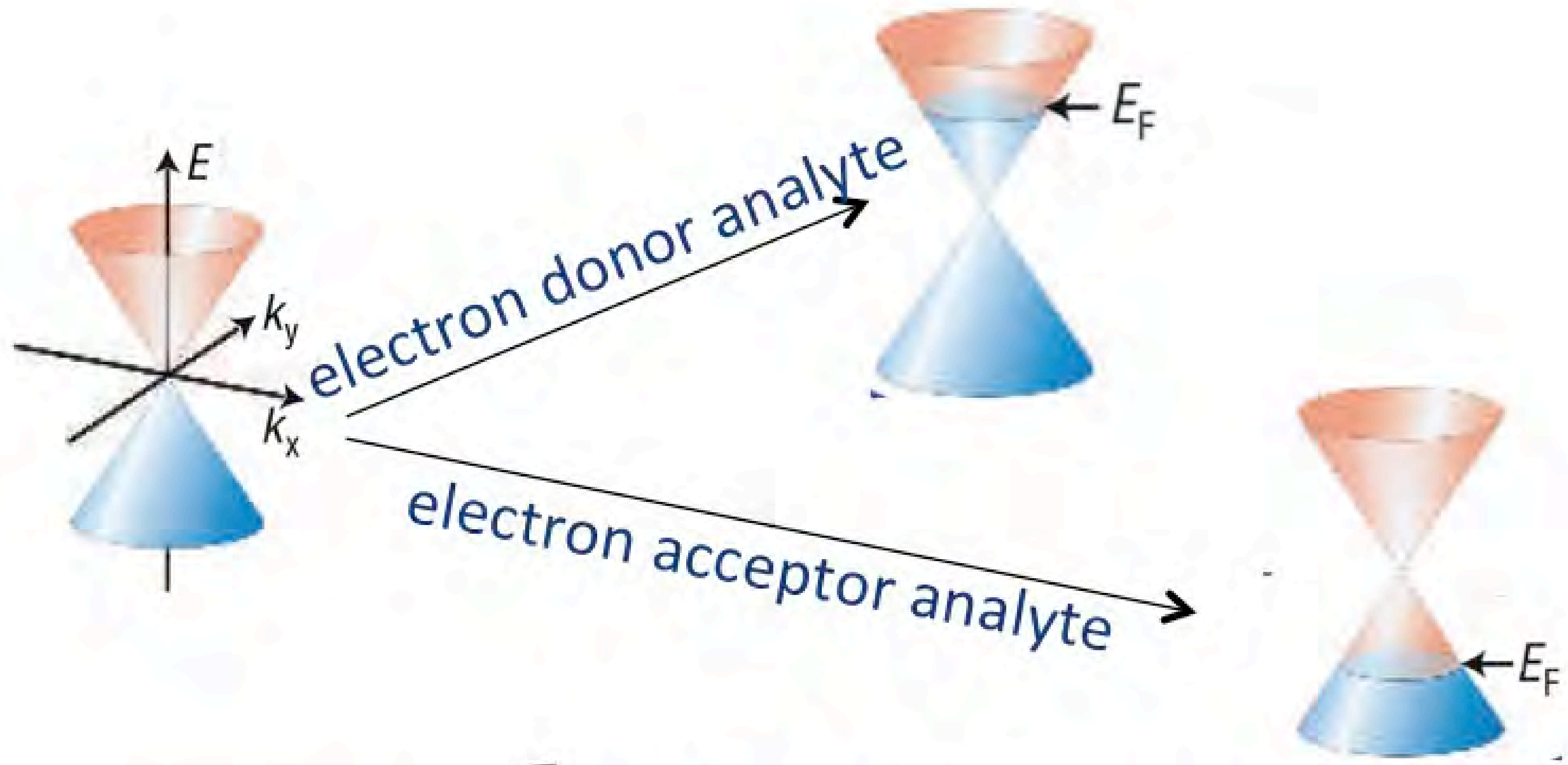
Chemically Derived Graphene For sub-ppm Nitrogen Dioxide Detection

Summary

- The graphene properties for sensing
- Material and devices preparation
- The material characterizations
- Tests towards analytes
- Conclusions

Sensing properties of the graphene





2D material → Analytes only interact with surface atoms
No bulk interaction

The interest in NO_2 detection

NO_2

Originates from the direct reaction between nitrogen and oxygen at high temperature (> 1,200 ° C)

Toxic effects on eyes, mucous membranes and lungs

Average annual limit ➡ 0,02 ppm

Average limit in an hour ➡ 0,01 ppm (not to be exceeded more than 18 times a year)

Many theoretical works predict high sensitivity of graphene to NO_2

Up to now the lowest experimental determined value for NO_2 graphene-based sensor is 500ppb corresponding to a response of less than 1%

Detection of individual gas molecules adsorbed on graphene, F. Schedin et al, Nature mat. , 6, 652-655 (2007)

All- Organic vapor sensor using ink-jet printed reduced graphene oxide, V. Dua et al, Angew. Chem. Int. Ed. 49, 1-5 (2010)

Graphene production

- Mechanical split
  - Micromechanical cleavage
  - Scotch tape technique
- Epitaxial growth on top of other crystals
  - CVD on Ni or Cu
  - Thermal dissociation of the SiC
- Chemical exfoliation

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Graphene production: chemical vs mechanical exfoliation

	Chemical exfoliation	Mechanical exfoliation
Flakes mean size	Hundreds of nanometers	Tens of micrometers
Device patterning	Not necessary	Yes
Electronic quality	Poor	Good
Scalability	Yes	No
Substrate employed for deposition	Any	Limited choice

Graphene by chemical exfoliation: the procedure

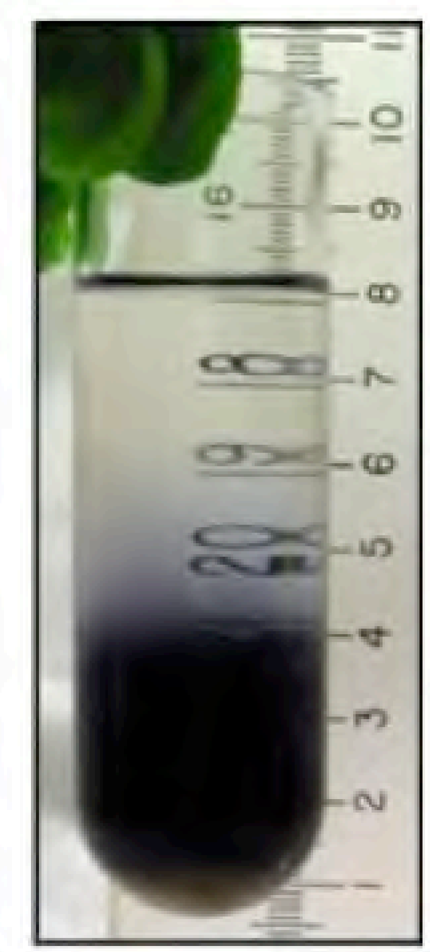
Graphite flakes
From Sigma-Aldrich

+

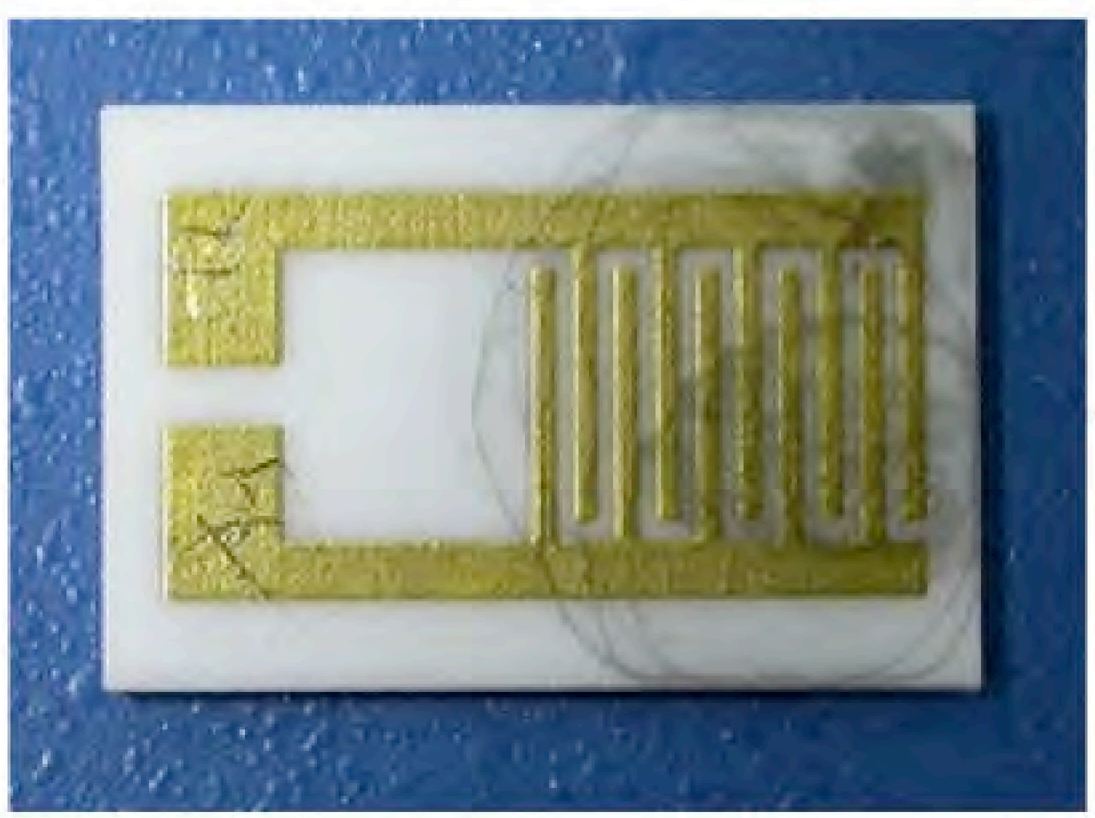
NMP (N-Methylpyrrolidone)
or
DMF (dimethylformamide)

+

- sonication for 3 h at 50 W
- centrifuged at 500 rpm for 30 min.

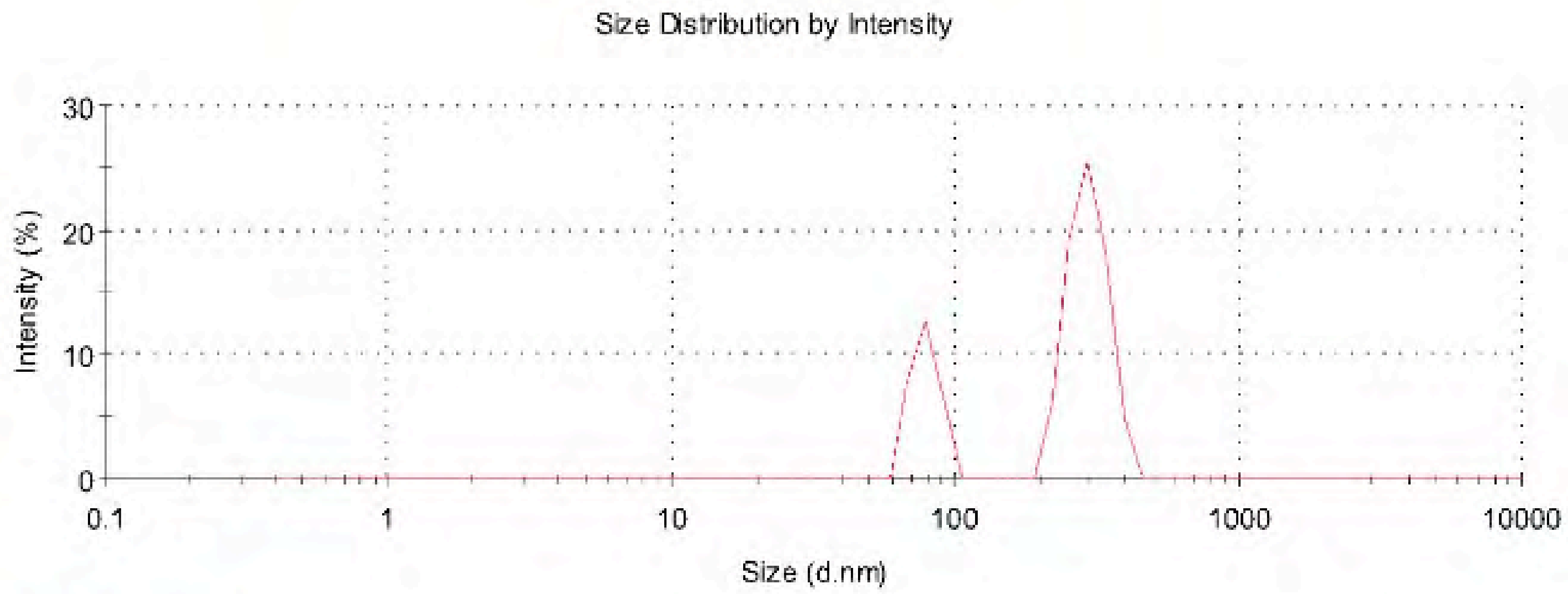


rough alumina substrate with interdigitated Au electrodes



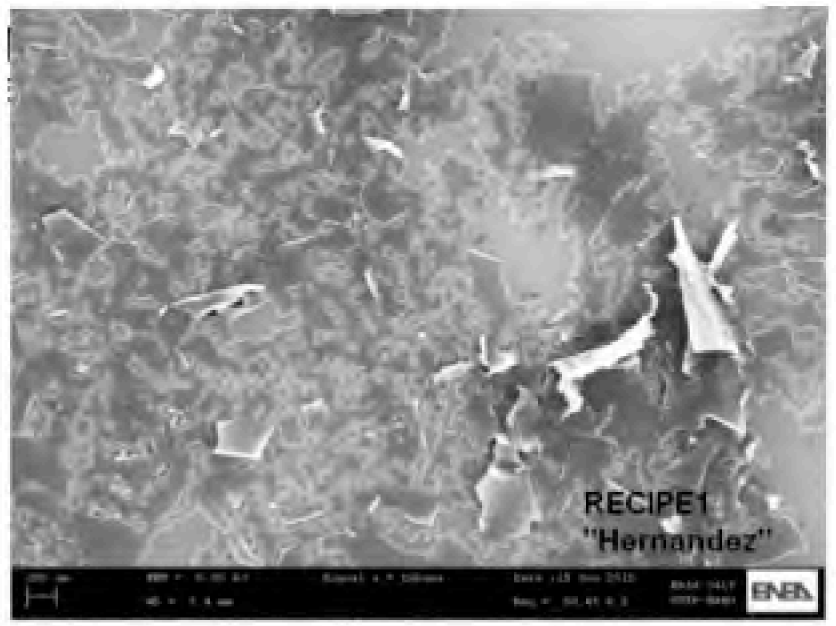
The material characterizations

DLS

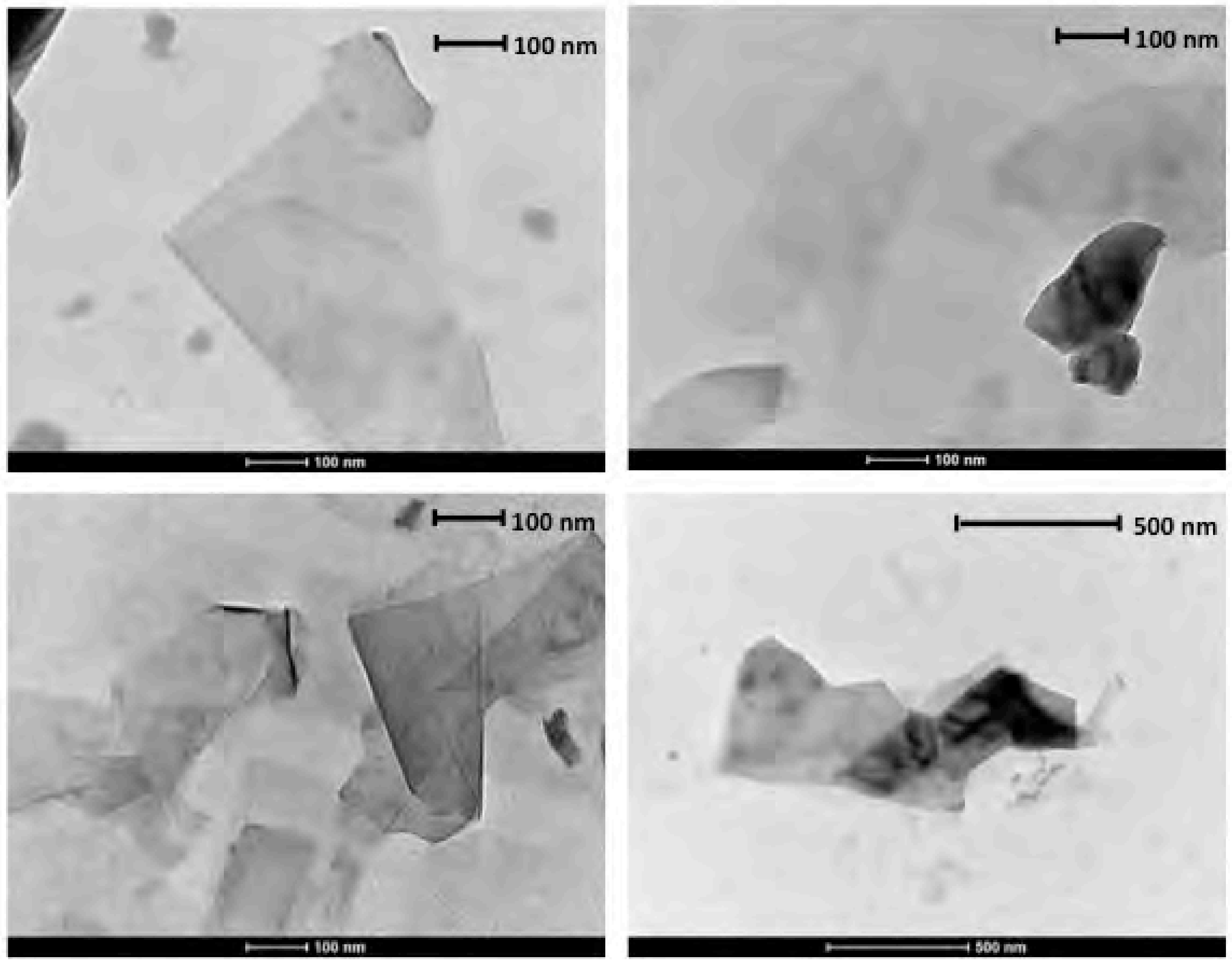


Average size :
200 nm

SEM



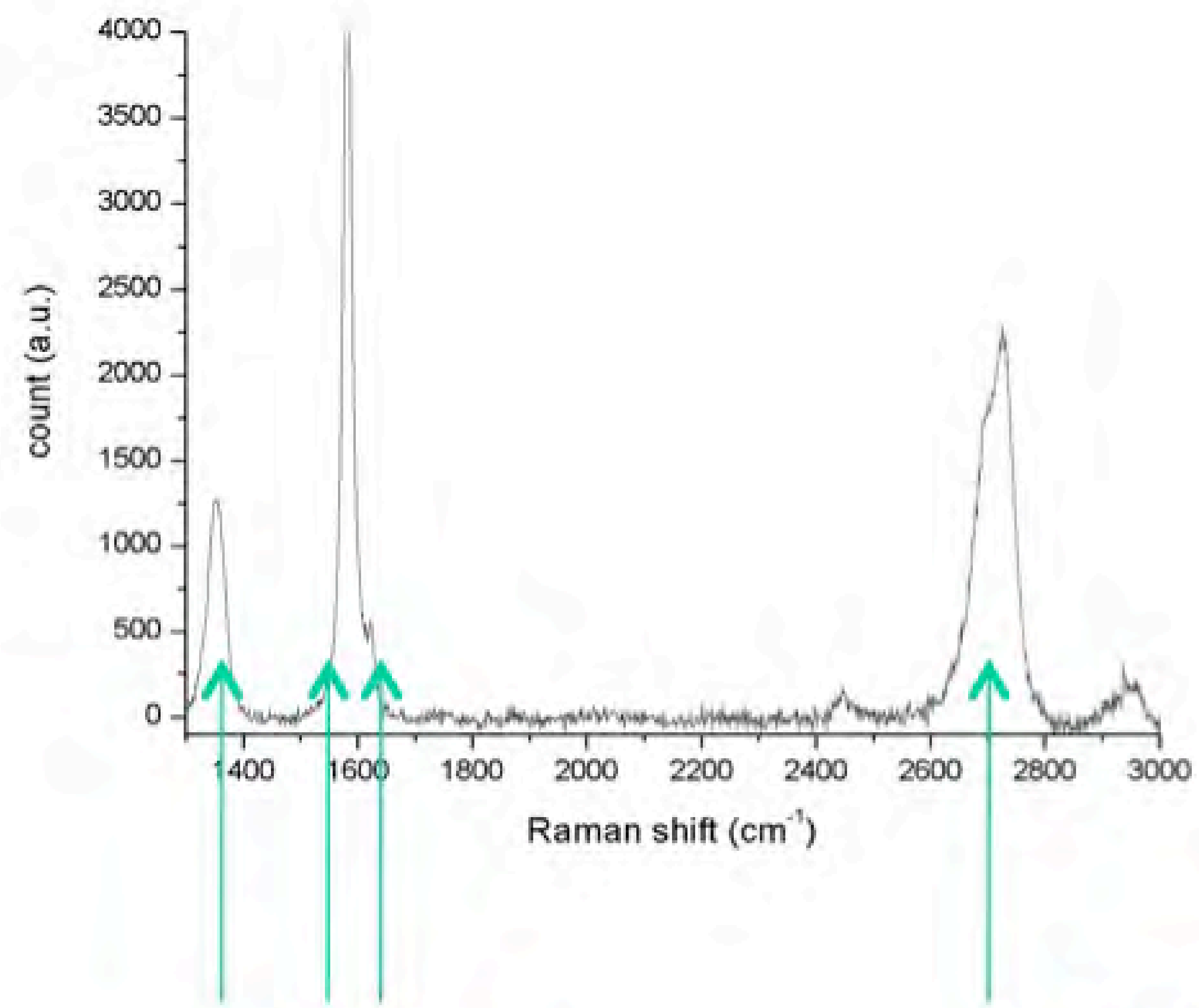
TEM



The material characterizations

Raman analysis

λ=514 nm



D G D'

G' (2D)

The D band is related to the number of structural defects that fall within the laser spot area

Nanostructured graphite

+

graphene multi layer

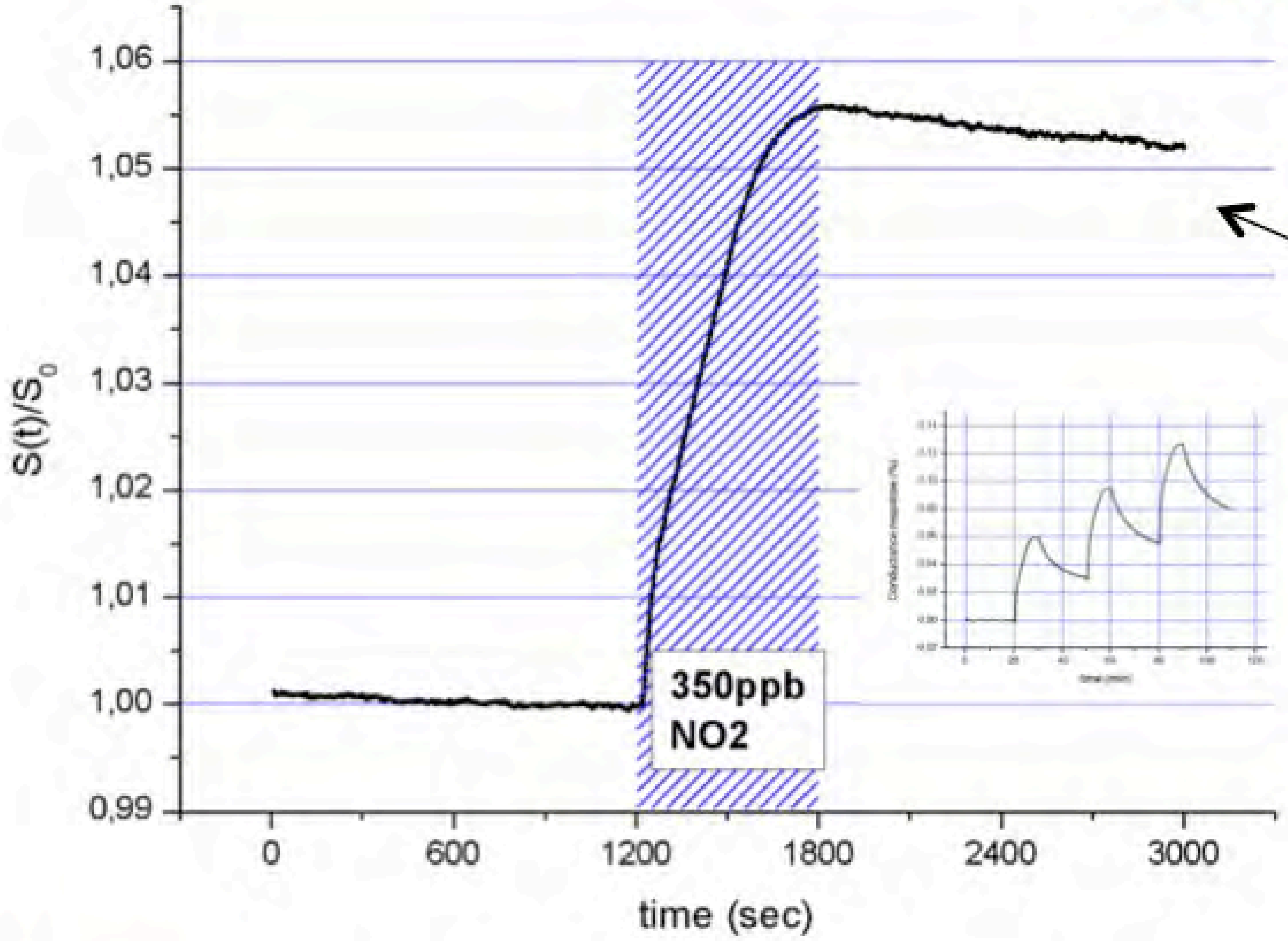
Studying disorder in graphite-based systems by Raman spectroscopy
M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cancado, A. Jorio and R. Saito Phys. Chem. Chem. Phys., 2007, 9, 1276–1291

Tests towards NO_2

Test upon exposure to NO_2 in wet N_2 (500sccm)

device is biased at 1V

20°C
Sensor response 4%



slow recovery time

- Fast response < 120 s
- High sensitivity to NO_2
- Calculated detection limit down to 2 ppb
- Responses are also very reproducible.

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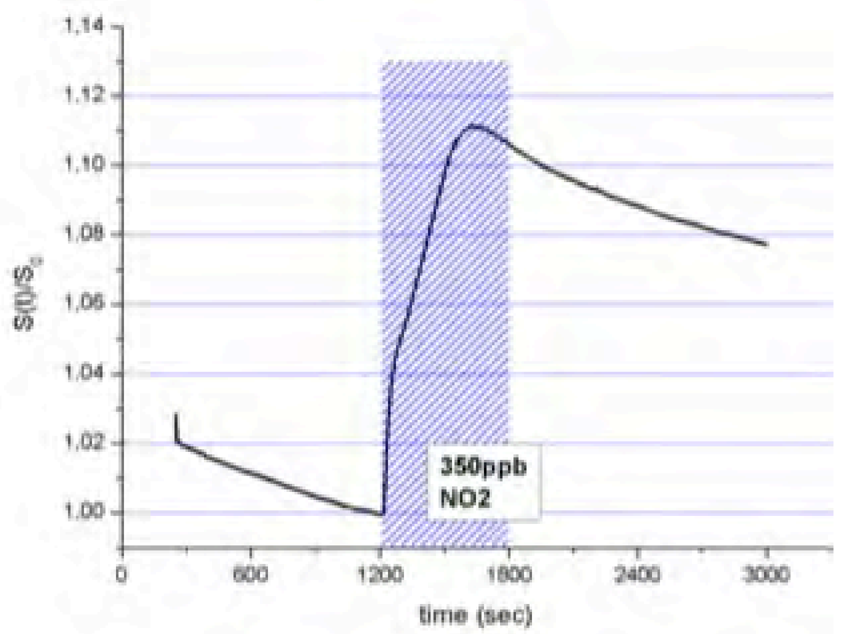
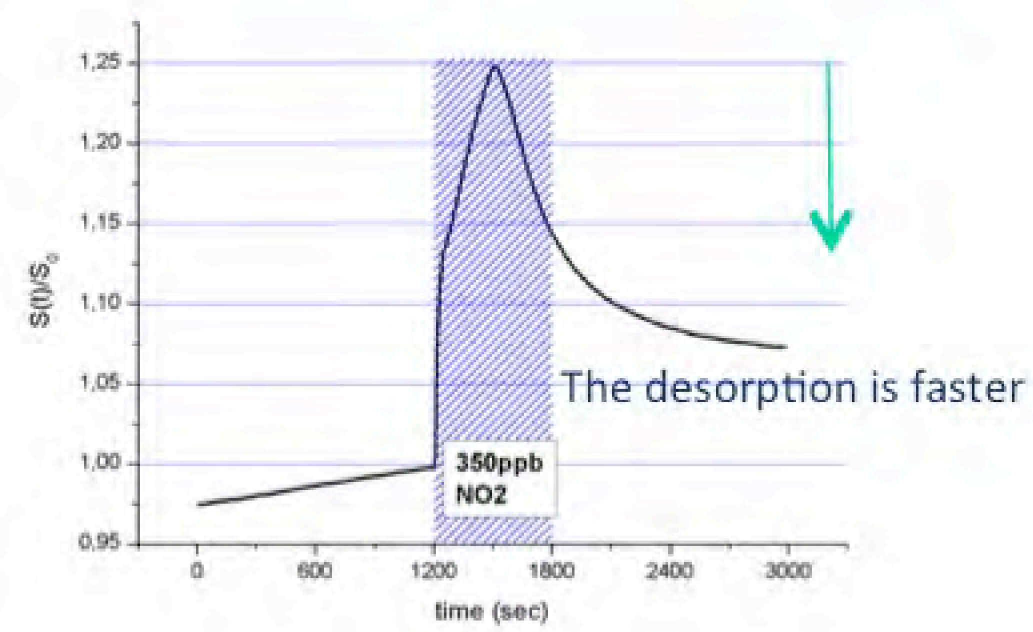
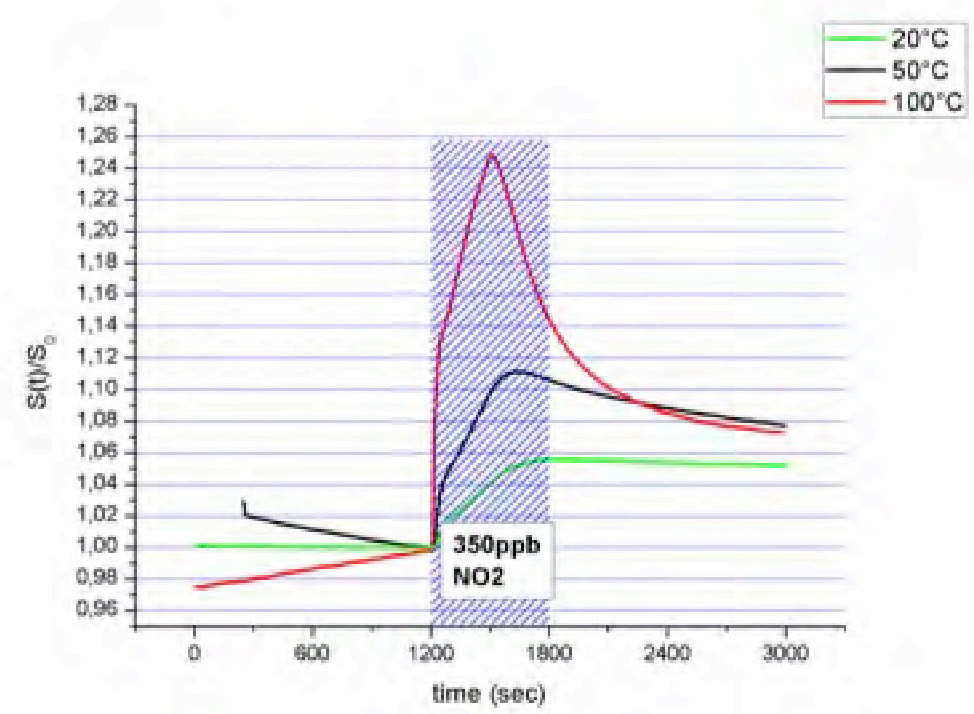
Recovery at different temperature

50°C
Sensor response 8%



100°C
Sensor response 27%





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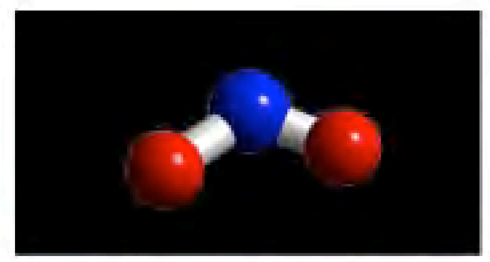
Interaction of the graphene with NO_2

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

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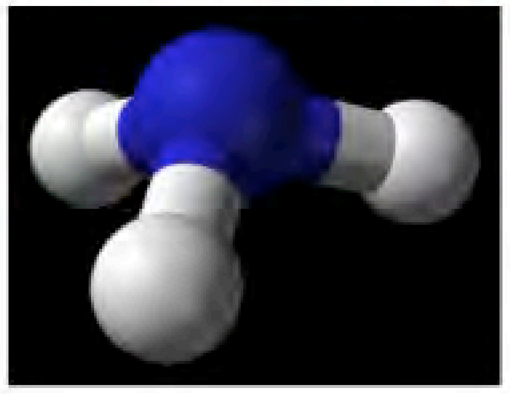
Tests towards NH_3

NH_3



-u, the H atoms point away from the surface
-d, the H atoms point to the surface

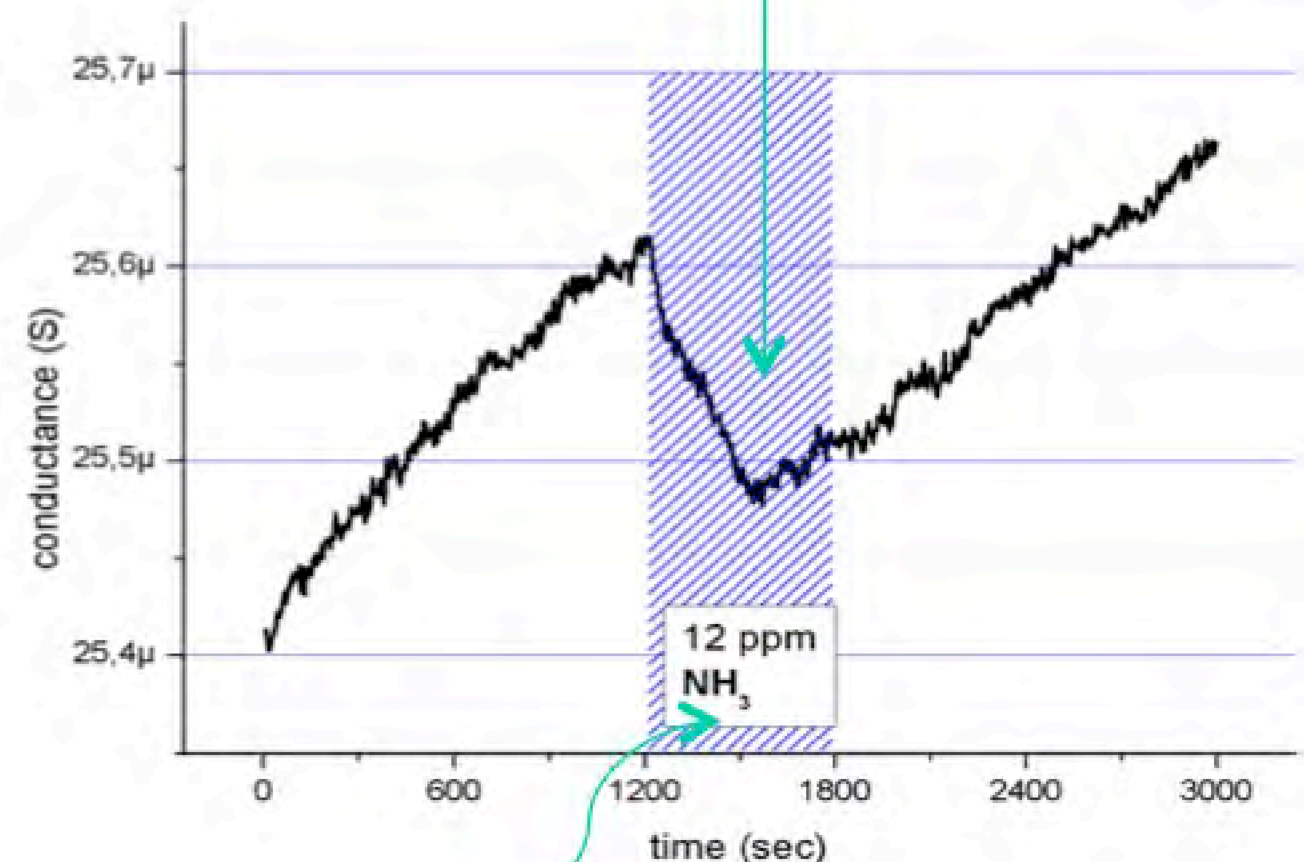
Absorption energy

u energetically favoured

Lower charge transfer

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
B	u	21	3.86	0.026
T	u	20	3.86	0.026
C	u	31	3.81	0.027
B	d	15	4.08	0.001
T	d	16	3.97	0.000
C	d	25	3.92	−0.001

The conductance decreases



The response is poor

Adsorption of H2O, NH3, CO, NO2, and NO on graphene: A first-principles study
O. Leenaerts,B. Partoens,and F. M. Peeters, PHYSICAL REVIEW B 77, 125416 2008

NH_3 behaves like a donor

Tests towards analytes

- sensitive to NO_2
- in presence of NO_2 the conductance increases
- in presence of NH_3 the conductance decreases

↓

the material is p-doped

The p doping of the chemical exfoliated graphite was confirmed by Seebeck effect measurement.

Conclusions

- material produced with a low cost and simple process
- the sensing layer in nanostructured made by few layer graphene mixed to graphitic material
- the device is very sensitive towards NO_2 (down to 2 ppb)
- fast and reproducible response

- slow desorption of the nitrogen dioxide

Acknowledgements

MDB Group involved in the graphene activity

Ettore Massera
Mara Miglietta
Ivana Nasti
Filiberto Ricciardella
Silvia Romano
Girolamo Di Francia

Gennaro Gentile - CNR-ICTP
For TEM Imaging

………… thank you for the attention

Tests towards NO_2

Test upon exposure to NO_2 in wet N_2 :

$V_{chamber}$=38 cl

- Baseline: 20 min → 500 sccm of wet N_2
- 15 s at 2.5 ppm of NO_2 → 800 ppb in the chamber
- 5 min → 250 ppb of NO_2 → 270 ppb of NO_2
- 5 min → 0 ppb of NO_2 → 270 ppb of NO_2
- Recovery : 20 min → 500 sccm of wet N_2

device is biased at 1V

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Tests towards NO_2

NH_3 in wet N_2 :

- Baseline: 20 min ⟶ 500 sccm of wet N_2
- 15 s at 100 ppm of NH_3 ⟶ 33 ppm of NH_3
- 5 min ⟶ 10 ppm of NH_3 ⟶ 11 ppm of NH_3
- 5 min ⟶ 0 ppm of NH_3 ⟶ 11 ppm of NH_3
- Recovery : 20 min ⟶ 500 sccm of wet N_2

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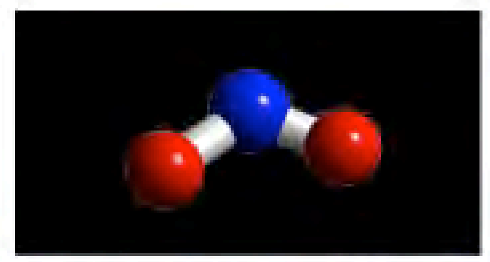
Interaction of the graphene with NO_2

Adsorption energy

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

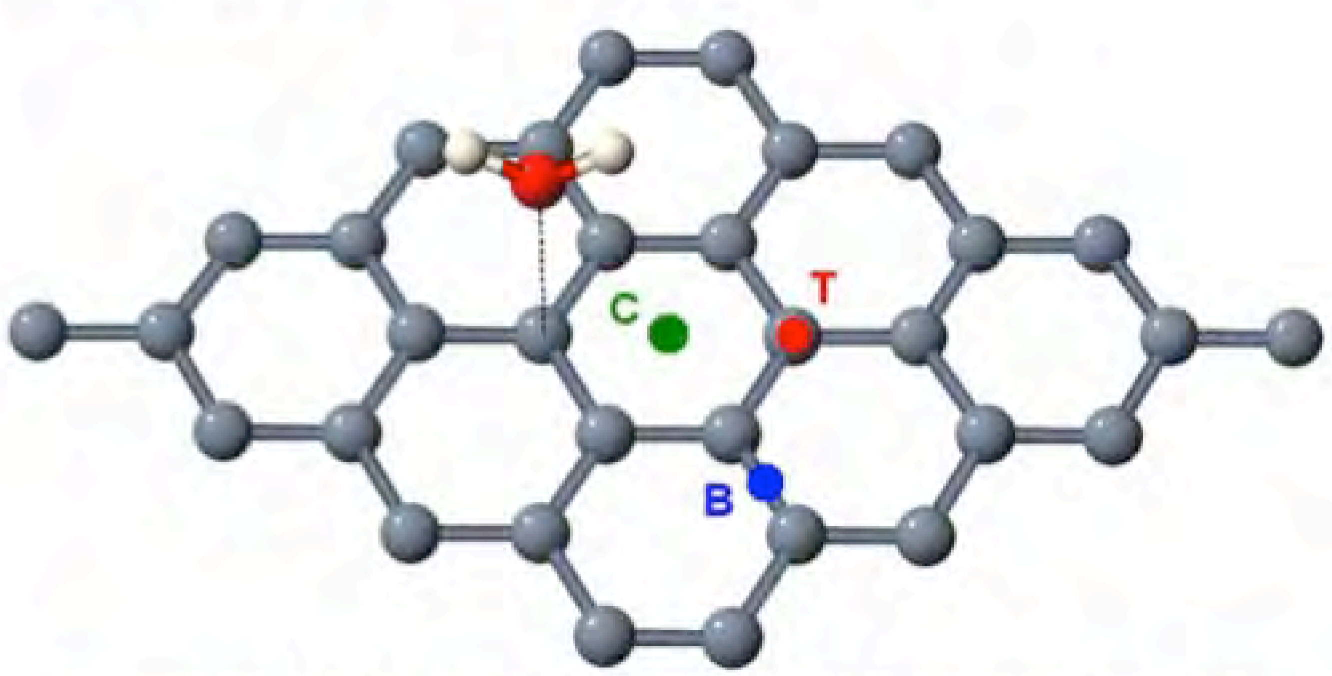
NO_2 molecule orientation



-u, N-O bonds points up with respect to the surface
-d, N-O bonds points down with respect to the surface
-n, N-O bonds is parallel to the graphene surface

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
B	d	67	3.61	−0.099
T	d	65	3.61	−0.099
C	d	63	3.64	−0.098
B	u	55	3.83	−0.089
T	u	55	3.93	−0.090
C	n	67	3.83	−0.102

Adsorption sites



Adsorbate	Theory	E_a (meV)	ΔQ (e)
H_2O	Acceptor	47	−0.025
NH_3	Donor	31	0.027
CO	Donor	14	0.012
NO_2	Acceptor	67	−0.099
NO	Donor	29	0.018

Adsorption of H2O, NH3, CO, NO2, and NO on graphene: A first-principles study
O. Leenaerts,B. Partoens,and F. M. Peeters, PHYSICAL REVIEW B 77, 125416 2008

Interaction of the graphene with NO_2

The slow recovery time was theoretically predicted

$$\tau = \nu_0^{-1} e^{(-E_B/K_B T)}$$

T is temperature, K_B the Boltzmann's constant and v_0 the attempt frequency

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