Carbon Nanomaterials for Environmental Monitoring Sensors

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Outline

- Environmental monitoring: many challenges
- Carbon nanomaterials: a few promises
- Gas sensors employing carbon nanomaterials
  - Carbon black and carbon nanofibres
  - Carbon nanotubes
  - Graphene
- Outlook

Environmental monitoring: many challenges

Water

- -Heavy metals: Pb, Hg
- -Endocrine disruptors
- -Microbial pathogens
- -Benzene, PCBs

Air

- -Particulate matter
- -SOx, NOx, O3, VOCs, CO, CO2, CFCs, CH4.
- -Pb, Hg, …

Multimedia pollutants: Heavy metals, Benzene, PCBs,…

- -Heavy metals: Pb, Hg
- -Benzene, Toluene, PCBs, Arsenic, TCE, TetraCE, Radon and other radioactive substances…

Soil

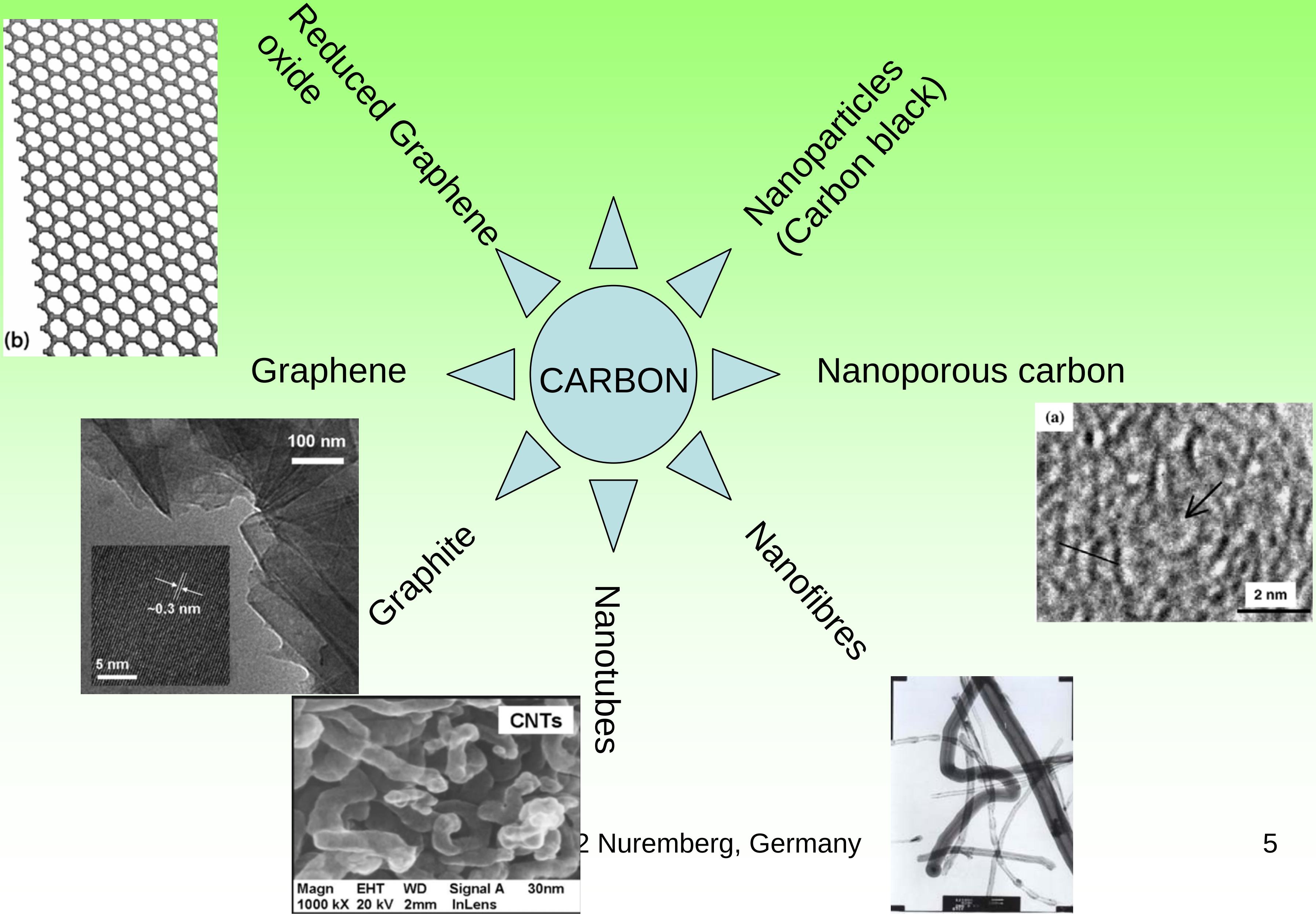
Environmental monitoring: many challenges

Water **Air** **Soil**

Continuous and ubiquitous monitoring sought

- High sensitivity for ameliorated LOD
- High stability for reliability
- Humidity and temperature compensation
- Reduced size
- Affordable cost
- Low power
- Distributed sensing

Carbon nanomaterials: a few promises



Carbon nanomaterials: a few promises

- Low-dimensional structures have most of its atoms exposed to the environment

- Some carbon materials have high quality crystal lattice and show high carrier mobility and low noise

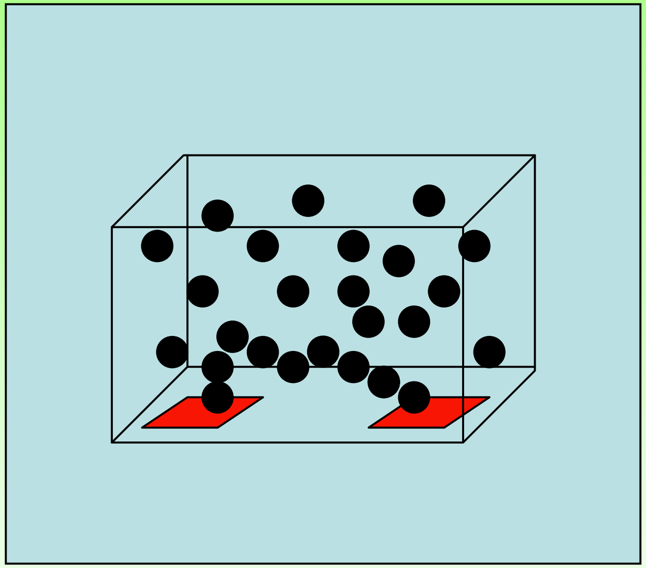
- They are good model materials for computational chemistry studies

- Different techniques can be used both to create defects and graft functional groups to their surface

- Fabricated by different methods, they are often amenable to making devices by conventional methods

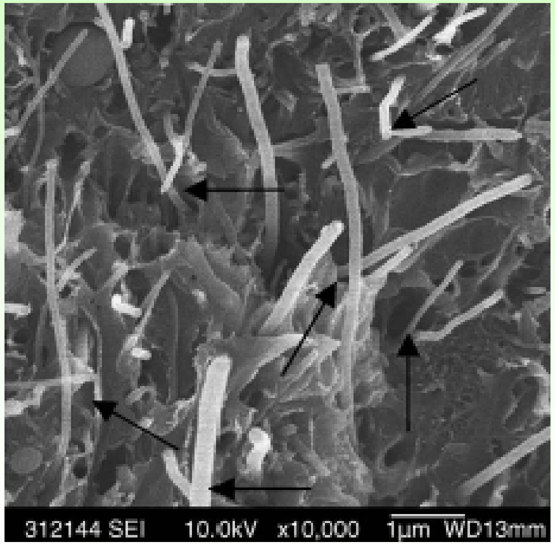
Gas sensors employing carbon nanomaterials

Carbon black and carbon nanofibres



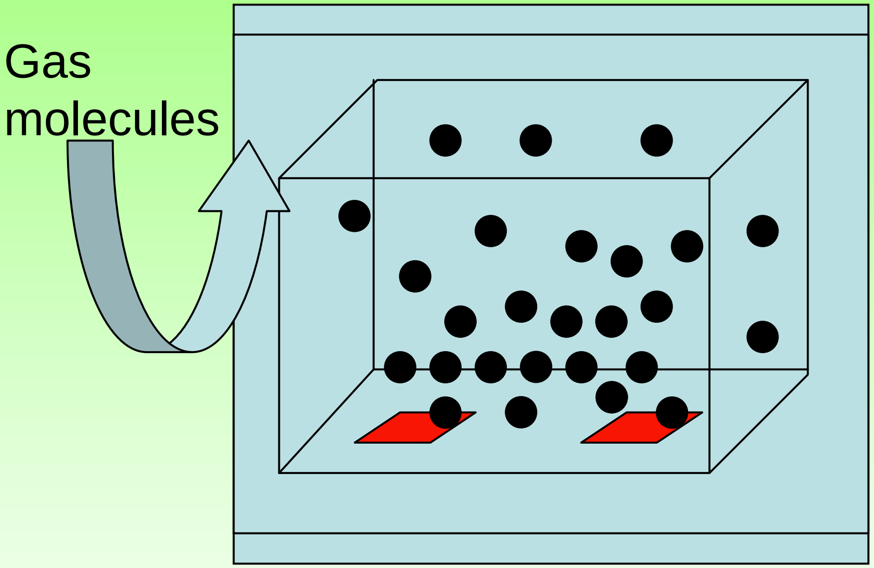
R. Fu, *Mat.Res.Bull.* 41 (2006) 553
S. Lewis, *Anal. Chem*, 70 (1998) 4177
N.S. Lewis, *Chem. Mater*. 8 (1996) 2298

- Selectivity tuned by polymer matrix
- Dispersion by solvent/polymer sonication
- Response mechanism explained by percolation theory
- CB: ~ 30 nm, 200 m^2/g
- CNF: 70-250 nm, 70 um



Gas sensors employing carbon nanomaterials

Carbon black and carbon nanofibres



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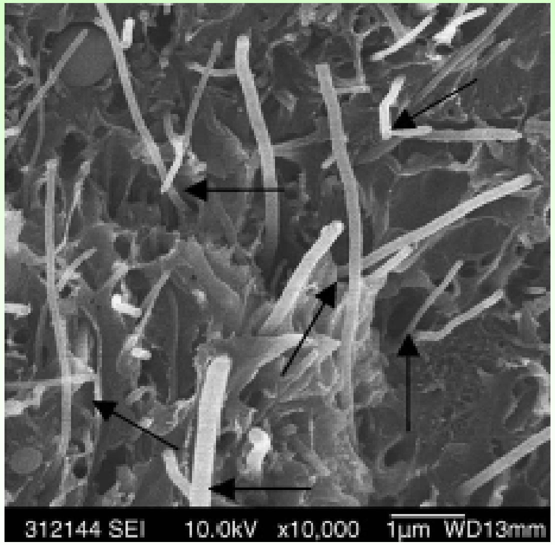

Gas sensors employing carbon nanomaterials

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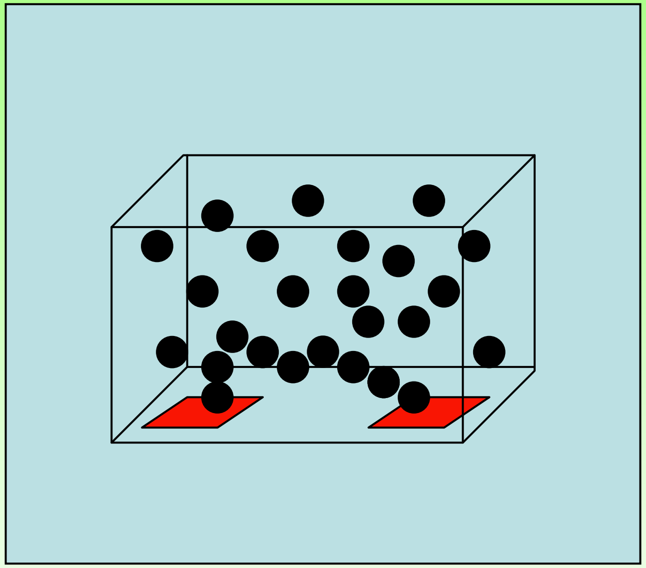

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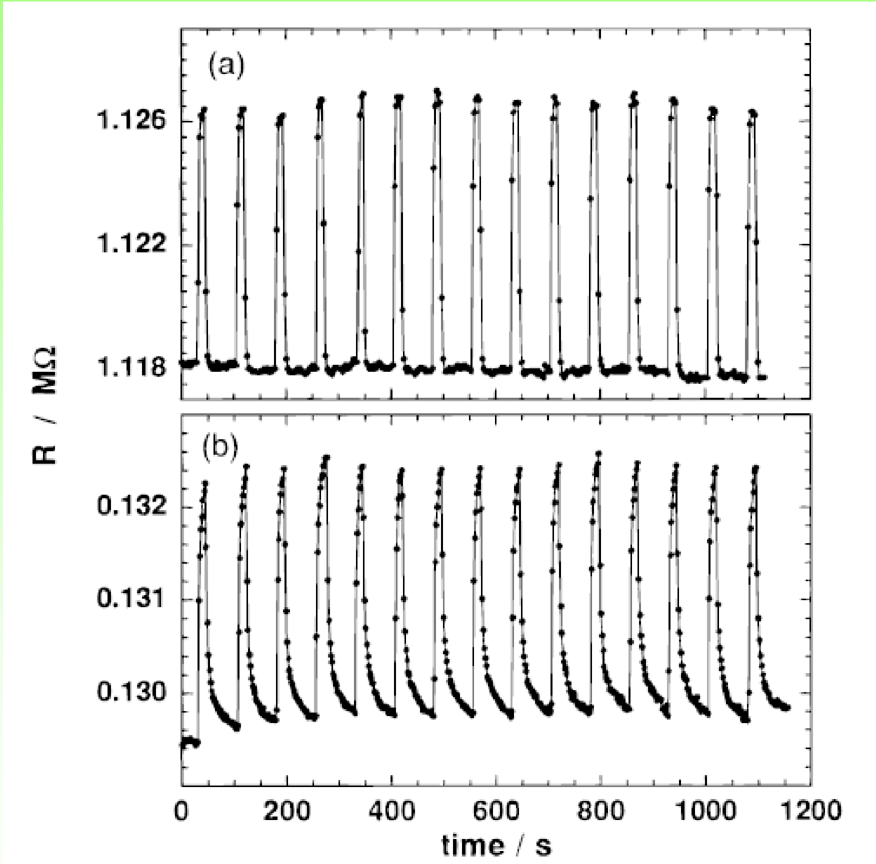
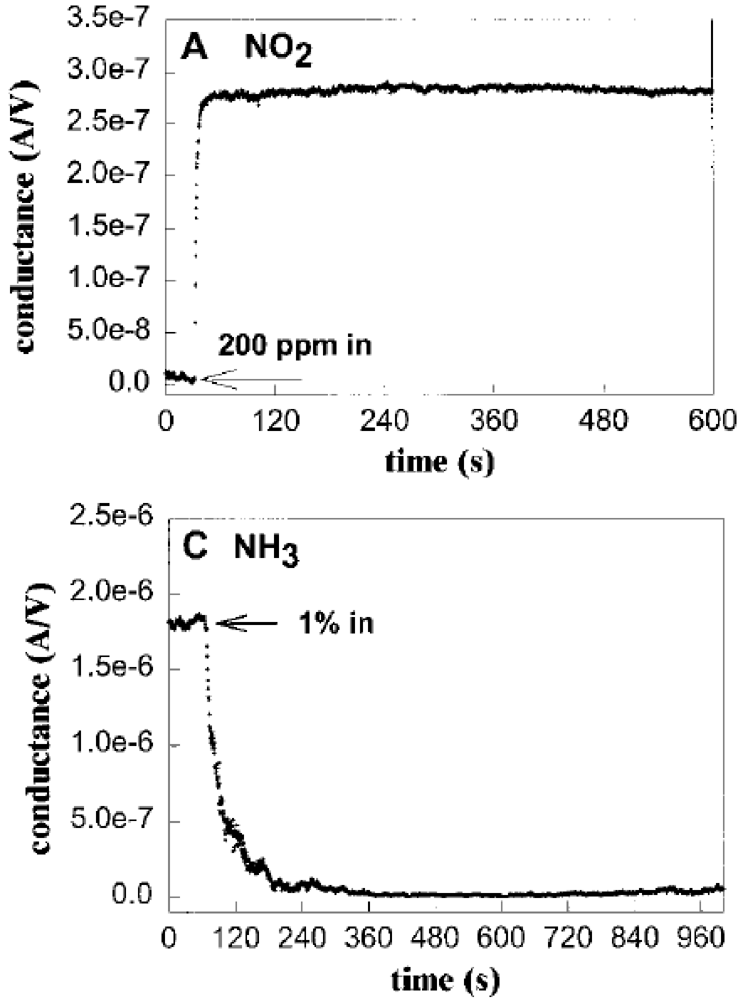


a) PVA b) PVP Benzene 1.5 ppt

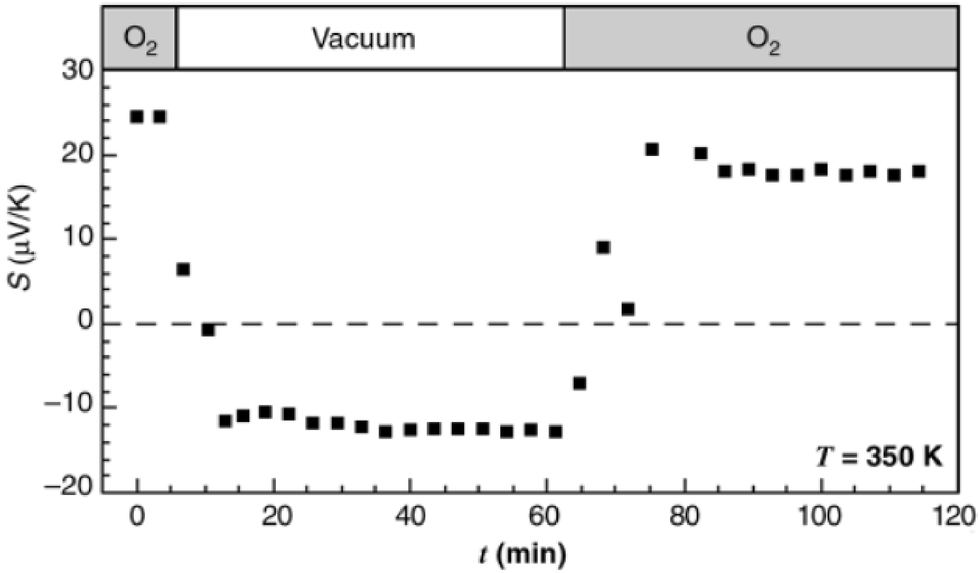
Gas sensors employing carbon nanomaterials

Carbon nanotubes



J. Kong, Science 287 (2000) 622

Electronic properties of SWCNTs are found extremely sensitive to chemical environment

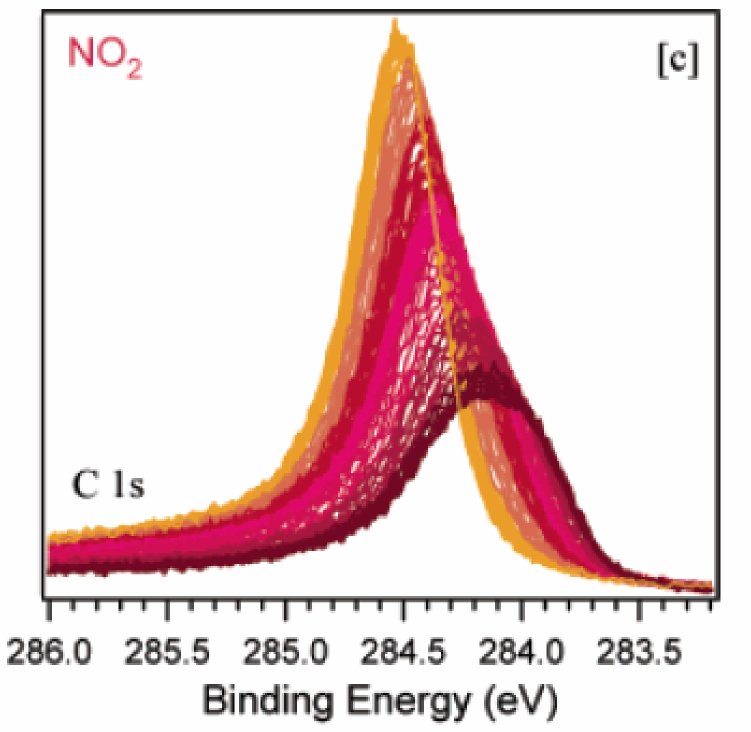


P.G. Collins, Science 287 (2000) 1801

L. Valentini, Appl. Phys. Lett. 82 (2003) 961

Gas sensors employing carbon nanomaterials

Carbon nanotubes



Electronic spectra affected by NO_2 as revealed by photoemission spectra

Sensitivity to O_2, H_2O and CO may be induced by the presence of contaminants (Na), catalysts or defect sites and open tube caps.

Cleaning process: Annealing at 1270 K in ultra high vacuum: Removes impurities, restores nanotube structure and closes nanotube caps.

A. Goldoni, JACS 125 (2003) 11329

Cleaning of CNT surface and control of surface defects needed for consistent sensitivity

Gas sensors employing carbon nanomaterials

Carbon nanotubes

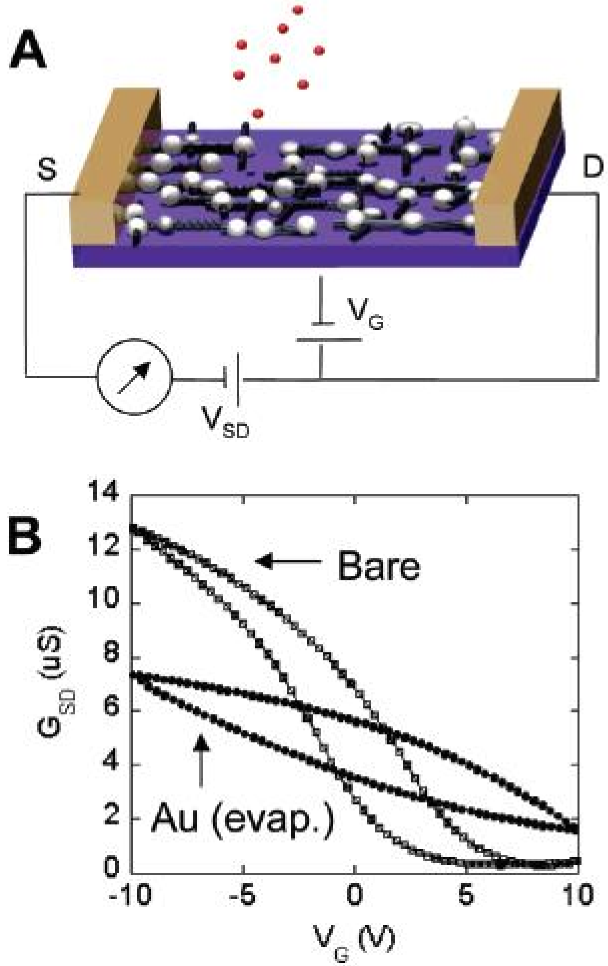
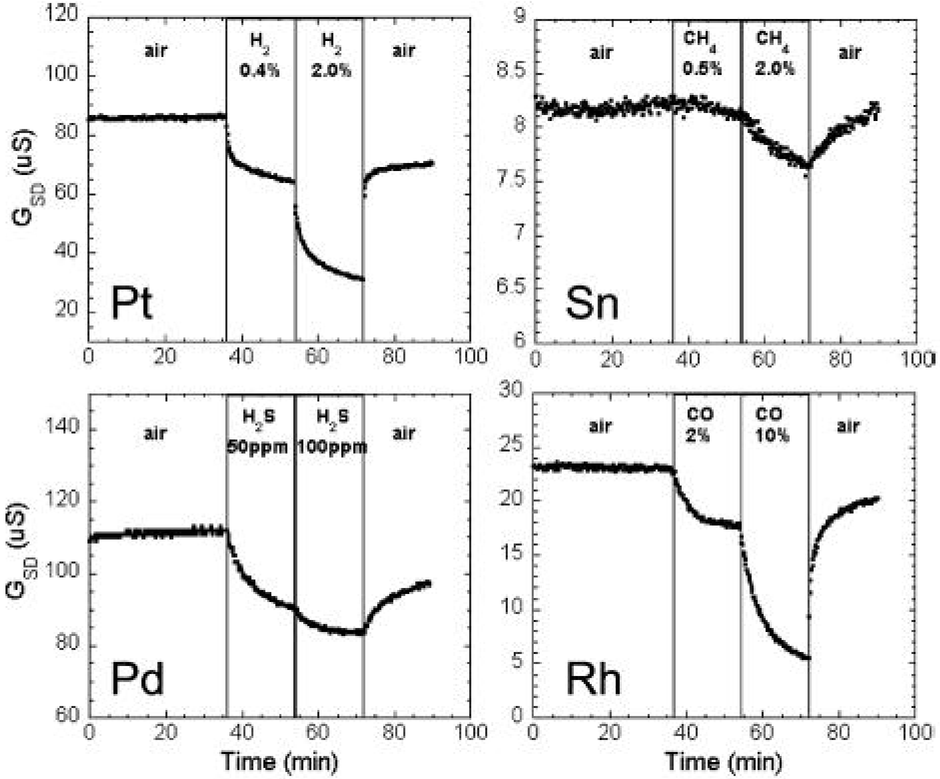


Figure 1. (A) Conceptual illustration of a carbon nanotube network connecting source (S) and drain (D) electrodes of a FET. SWNTs are decorated with metal nanoparticles (silver bullets) for selective detection of analyte gases (red dots). (B) Electronic measurements, such as source-drain conductance (G_{SD}), as a function of gate voltage (V_g) before (bare) and after thermal evaporation of discontinuous layer of gold (Au evap).

SWNT decorated with Pd, Pt, Rh, Au, Sn, Mg, Fe, Co, Ni, Zn, Mo, W, V, Cr



A. Star, *J. Phys. Chem. B*, 110 (2006) 21014.

Gas sensors employing carbon nanomaterials

Carbon nanotubes

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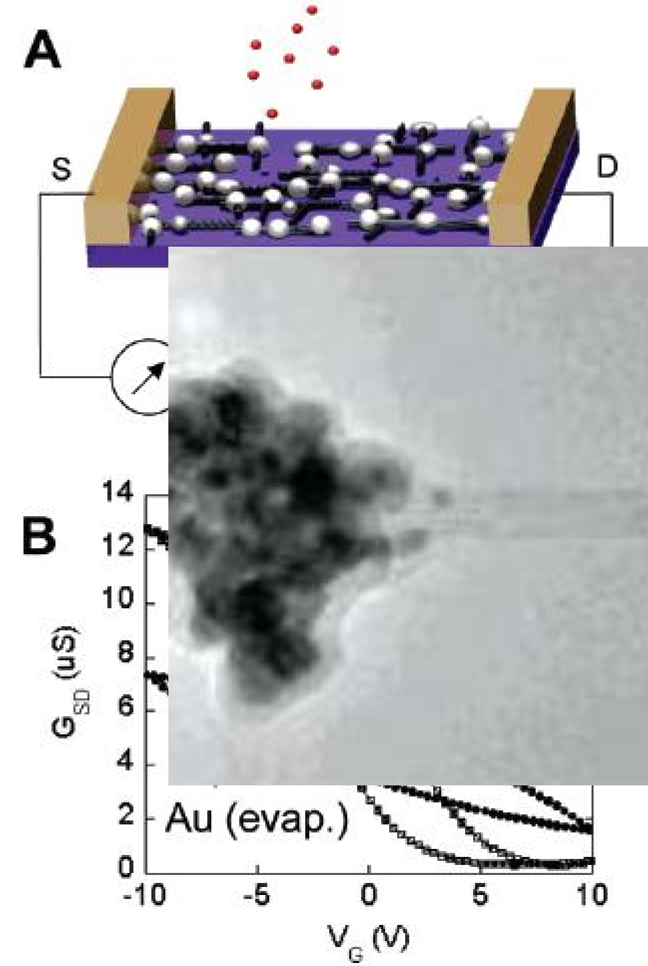

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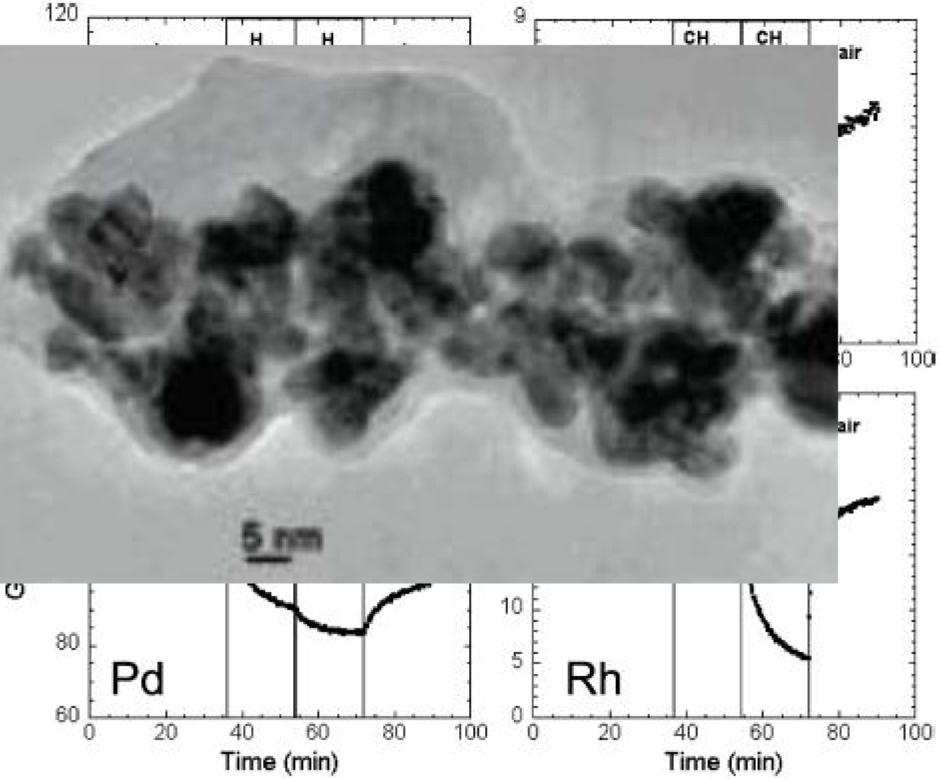

A. Star, *J. Phys. Chem. B*, 110 (2006) 21014.

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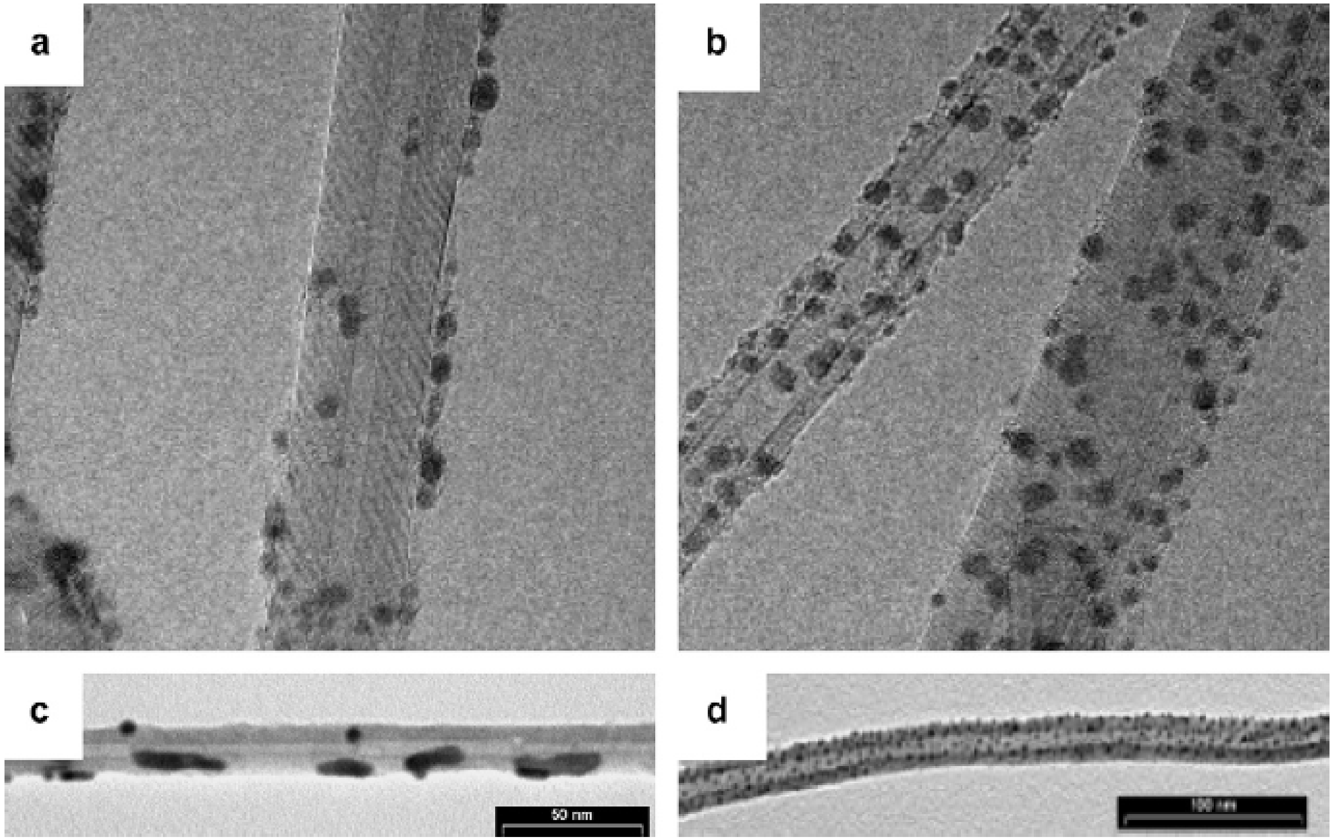
Carbon nanotubes



Au binding energy:

Pristine CNT: 0.73 eV

Isolated Au pair: 1.39 eV

VO_2: 1.29 eV.

Pd (top) and Au (bottom) decorated MWCNTs
a) & c) pristine; b) & d) oxygen plasma treated

E. Llobet, *Sens. Actuators B*, 113 (2006) 36.
E. Llobet, *Nanotechnology* 20 (2009) 375501
E. Llobet, Carbon 48 (2010) 3477

Gas sensors employing carbon nanomaterials

Carbon nanotubes

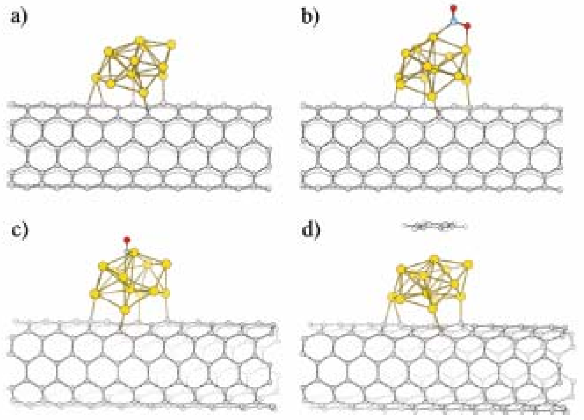
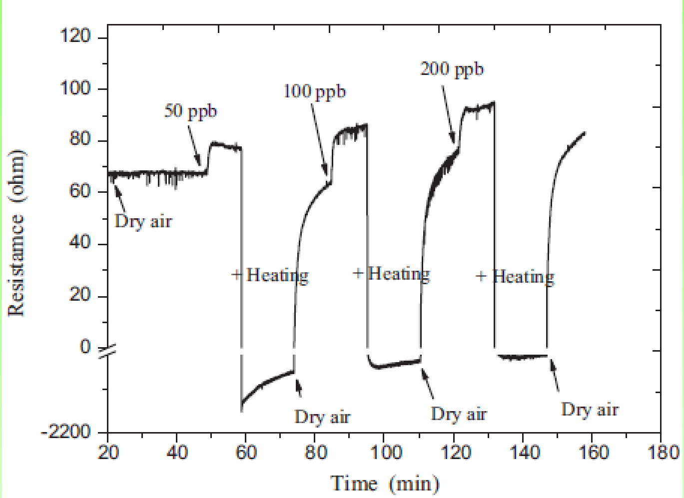


Figure 4. Ball-and-stick models illustrating fully *ab initio* optimized atomic structures of a (5,5) SWNT decorated with a Au_{13} nanocluster (a) and with various adsorbed molecules: NO_2 (b), CO (c), and C_6H_6 (d).

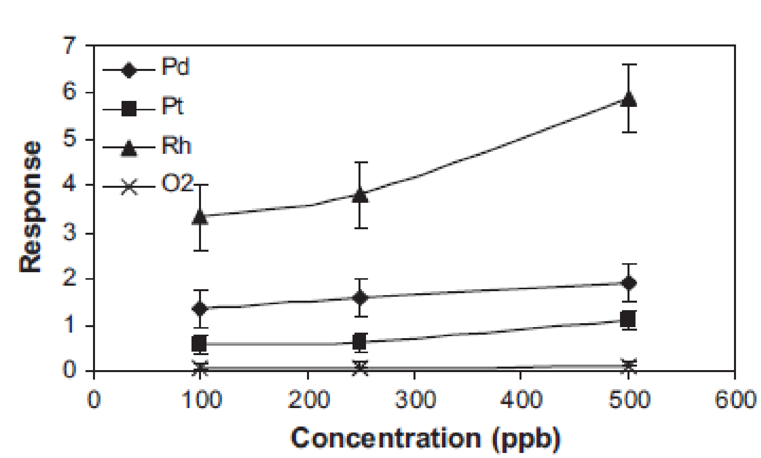
TABLE 1. **Computed Binding Energies (E_B, eV), Charge Transfer (Δq, $|e|$), Au_{13}—SWNT Bond Length (d_{Au}, Å), and Molecule—Au_{13} Bond Length (d_{gas}, Å)**

	Au_{13}	NO_2	CO	C_6H_6
E_B	−2.444	−3.257	−1.821	−0.193
d_{Au}	2.38	2.39	2.35	2.38
d_{gas}		2.13	2.10	3.88
Δq^a	0.06	0.506	0.164	~0.0

[a] Positive (negative) values of Δq denote an acceptor (donor) character of the corresponding adsorbed molecule.



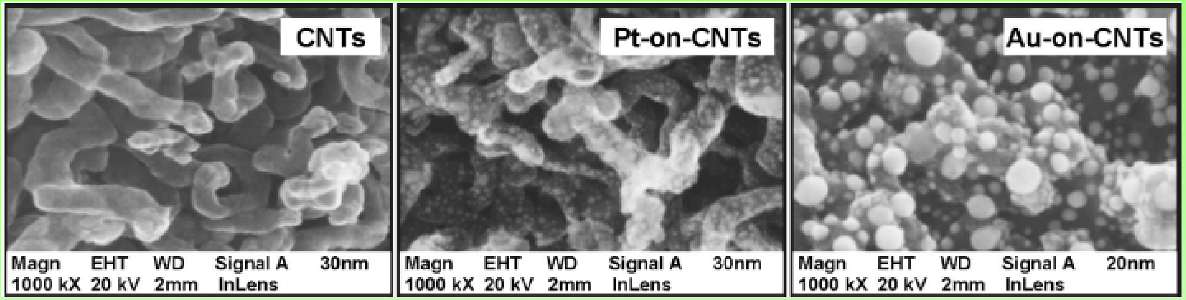
Rh-CNT sensor response to benzene

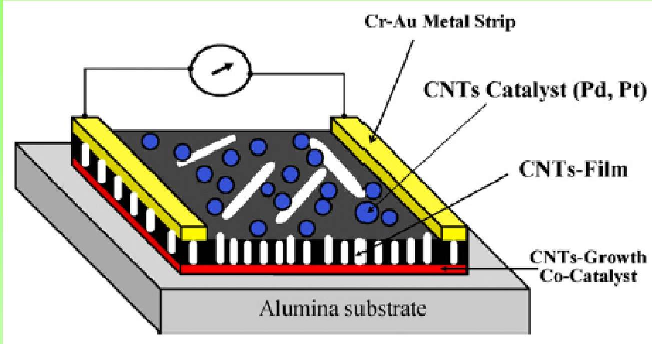


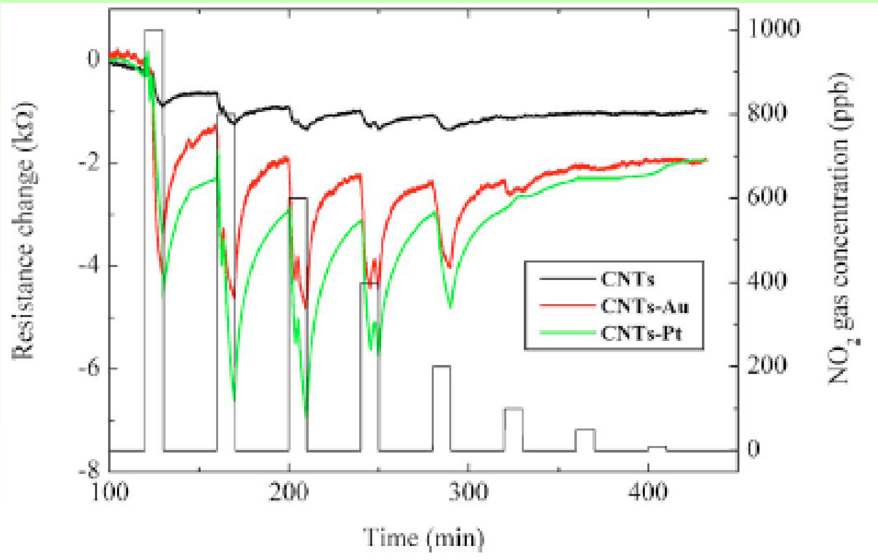
E. Llobet, *ACS Nano*, 6 (2011) 4592
E. Llobet, *Anal.Chim.Acta* 708 (2011) 19

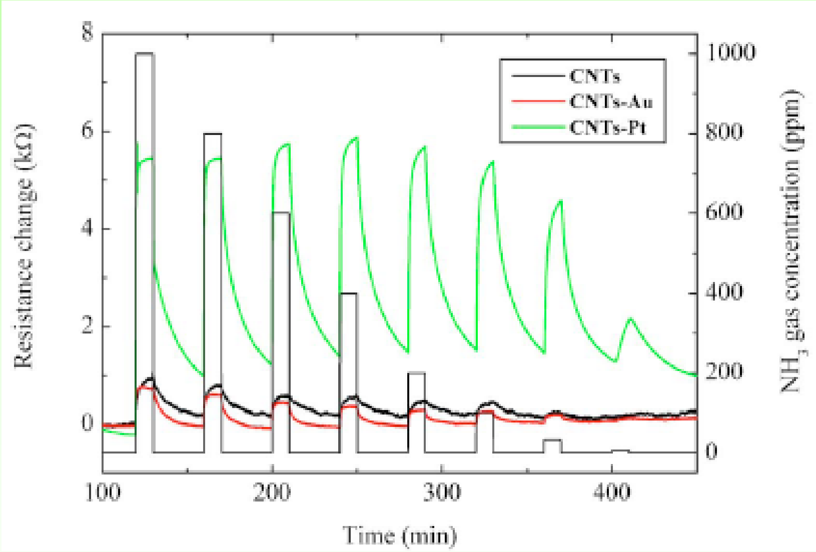
Gas sensors employing carbon nanomaterials

Carbon nanotubes









M. Penza, *APL*, 90 (2007) 173123
M. Penza, *Sens. Actuators B* 135 (2008) 289
M. Penza, *Thin Solid Films* 517 (2009) 6211

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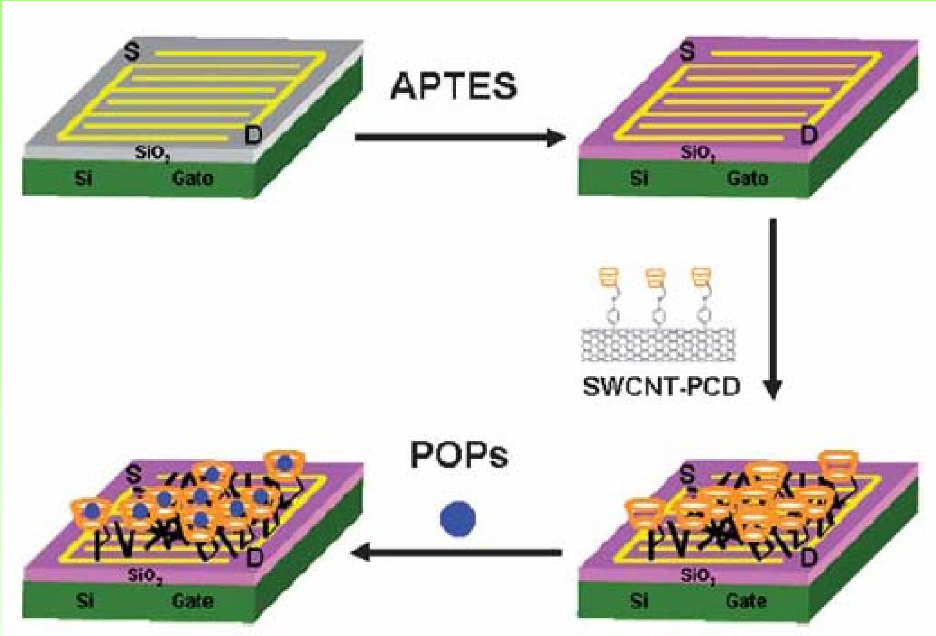

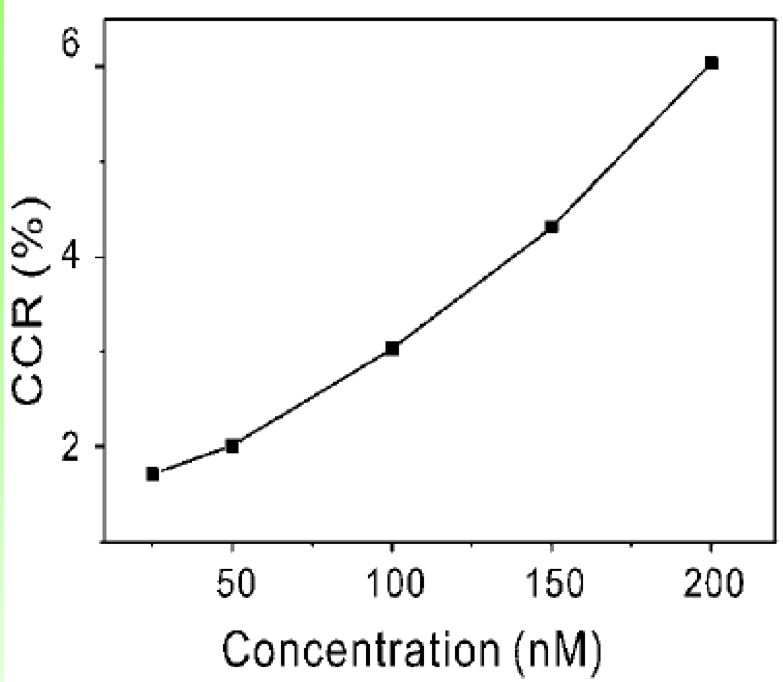

POPs	CCR/%
TCB	12.5
Aldrin	5.6
CD-68	3.8
Mirex	3.3
HCB	1.6

SWCNT decorated with an aminophenylamino cyclodextrin (PCD) for detection of persistent organic compounds

J. Liu, *J Mater. Chem.*, 21 (2011) 11109

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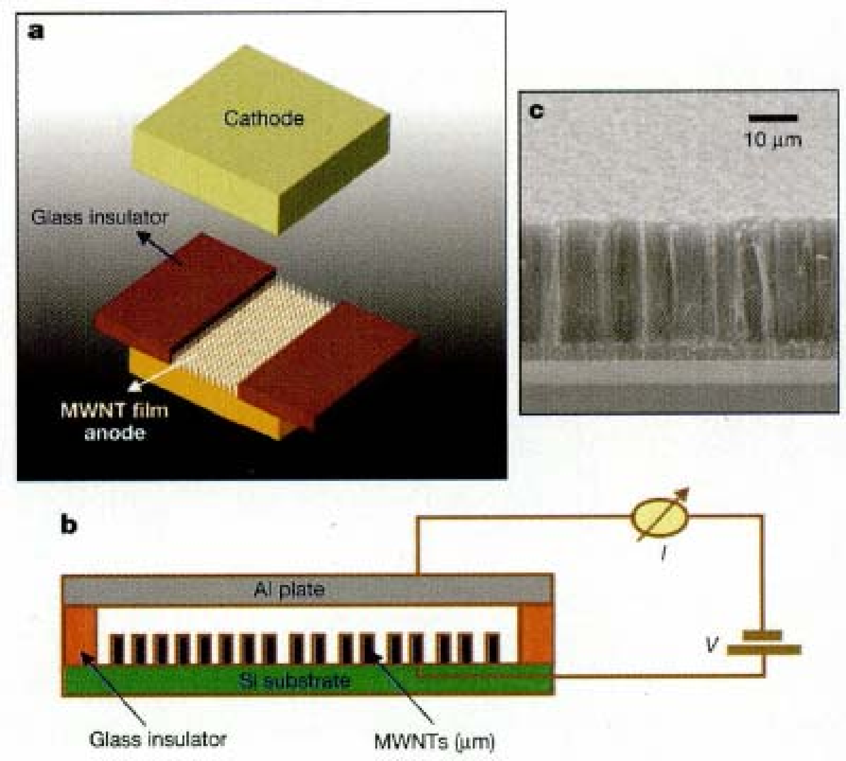

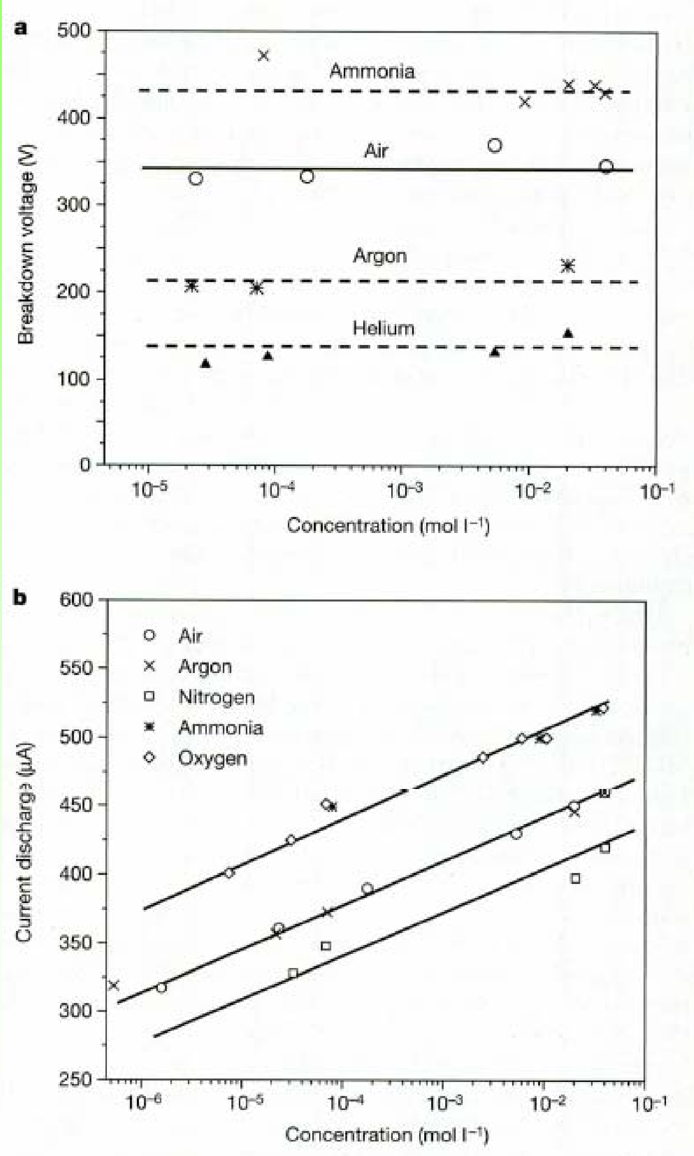

A. Modi, *Nature*, 424 (2003) 171

Gas sensors employing carbon nanomaterials

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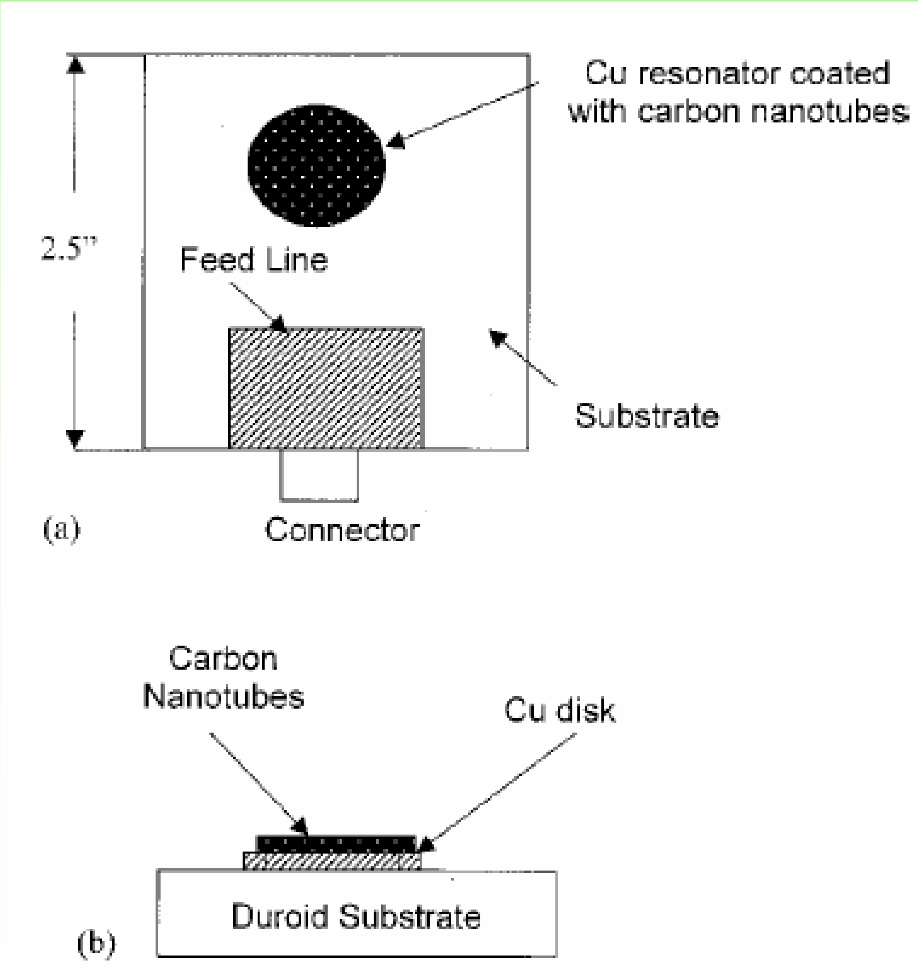
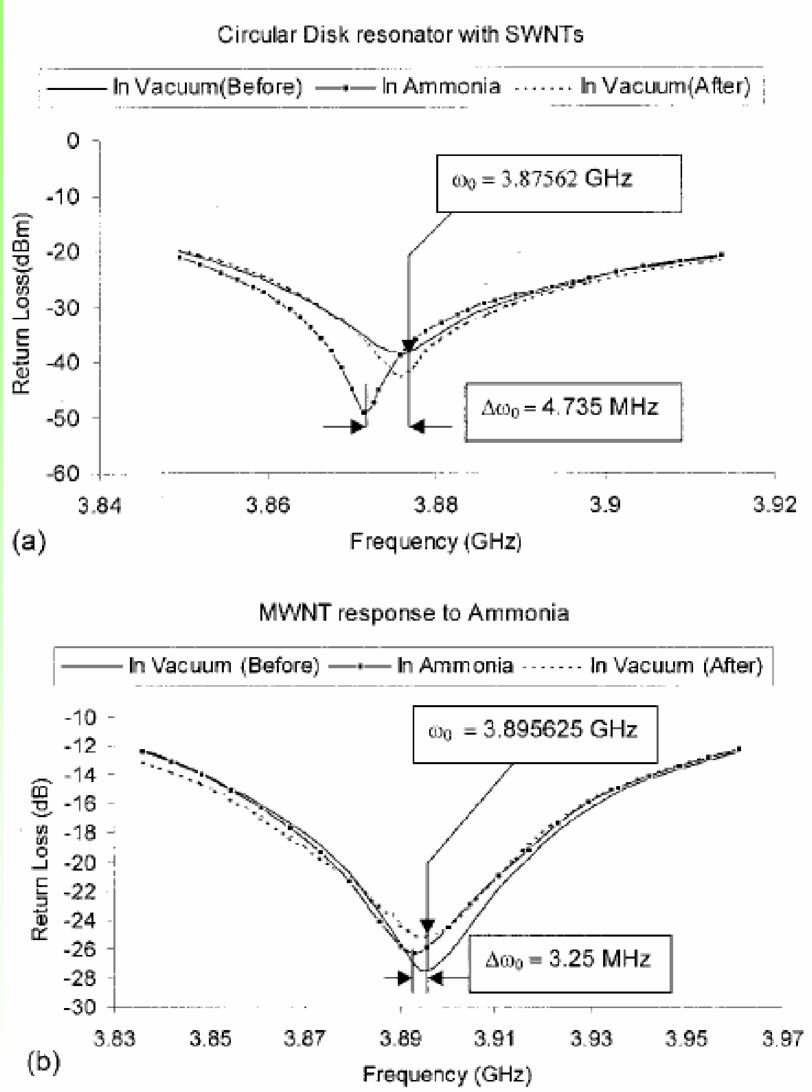
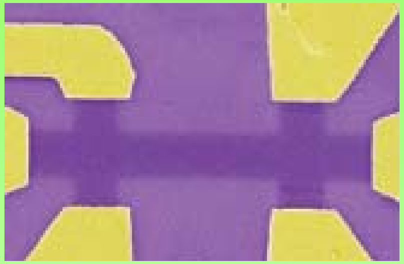


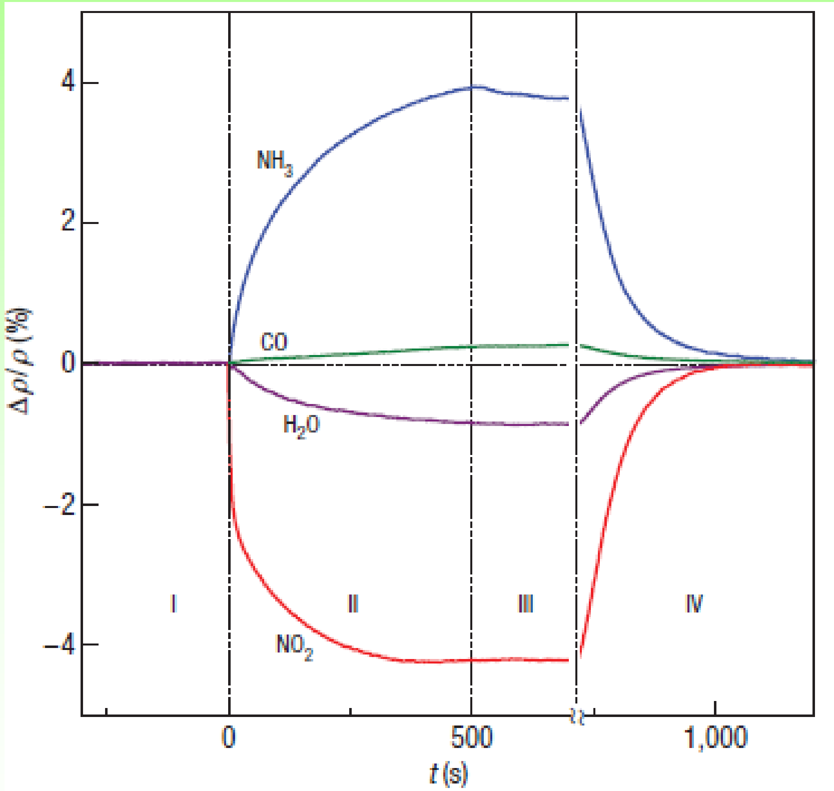


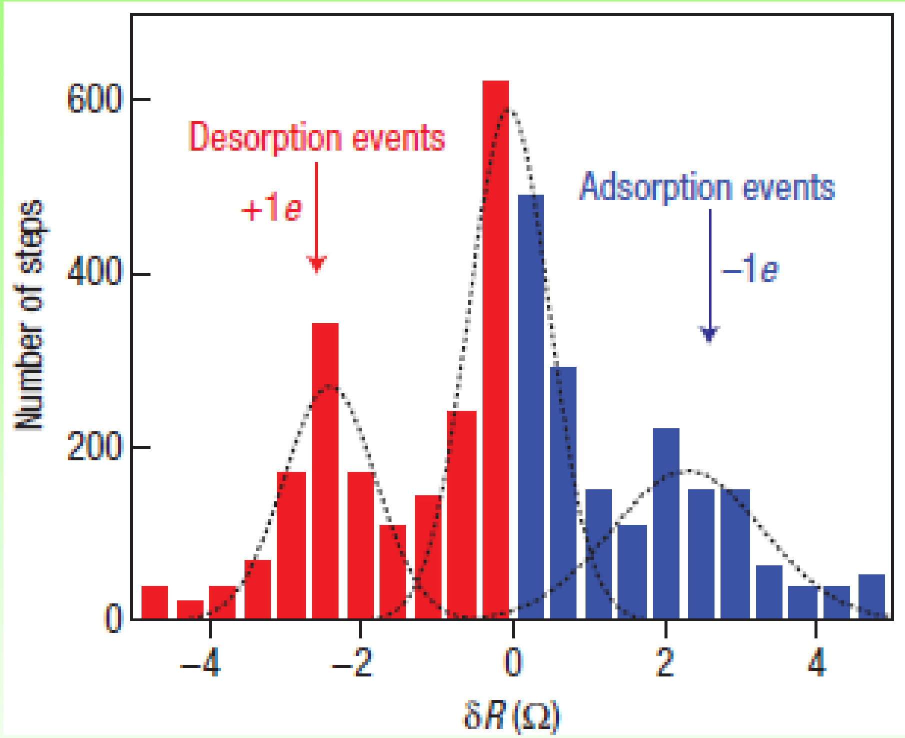
A. Pham, *APL*, 80 (2002) 4632

Gas sensors employing carbon nanomaterials

Graphene







Statistical distribution of step changes in device resistance, δR, during the slow desorption of NO2. The side peaks are evidence for detection of adsorption or desorption of individual gas molecules

K.S. Novoselov, *Nature Mat*, 6 (2007) 652

Gas sensors employing carbon nanomaterials

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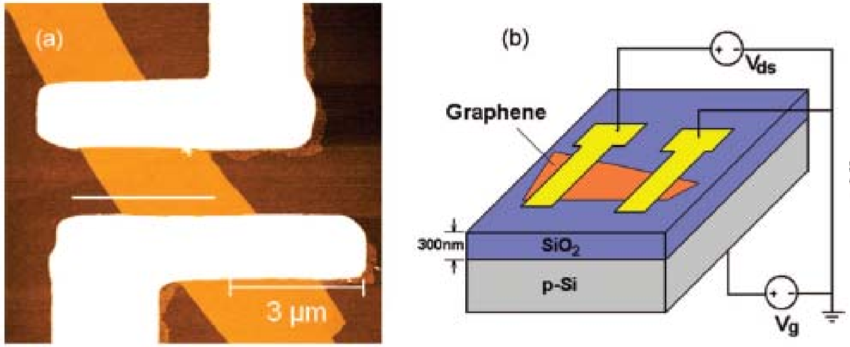
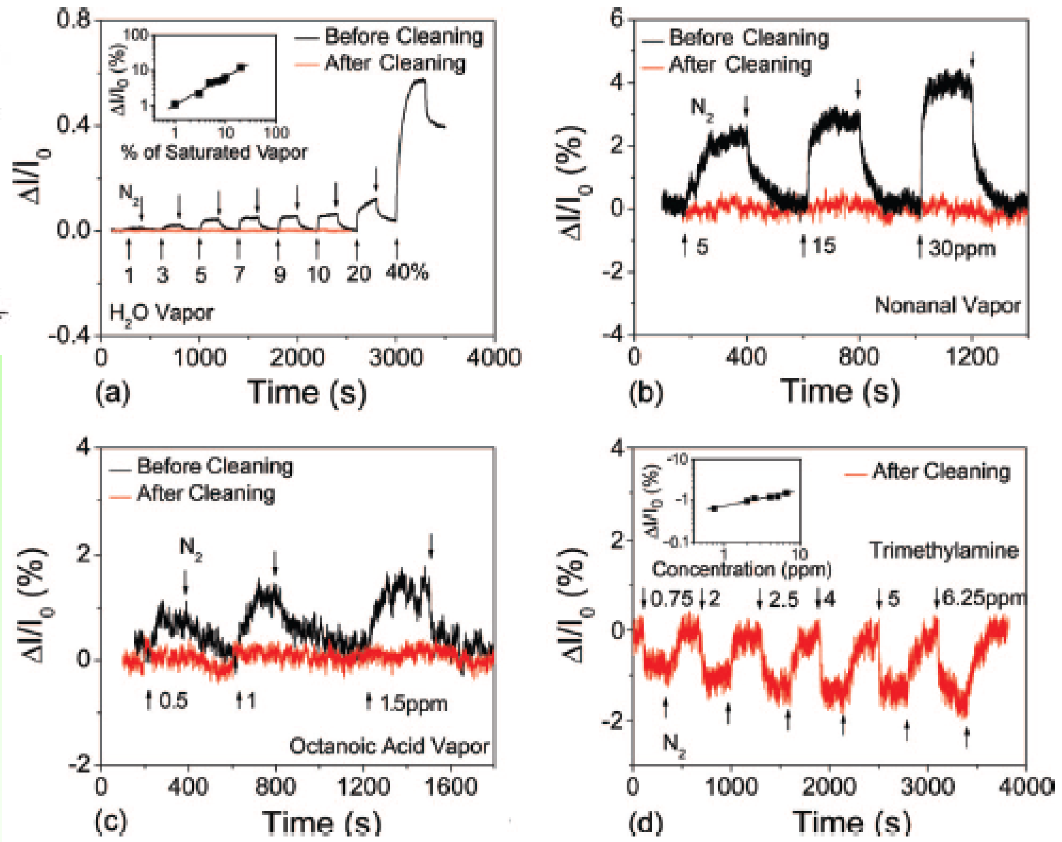




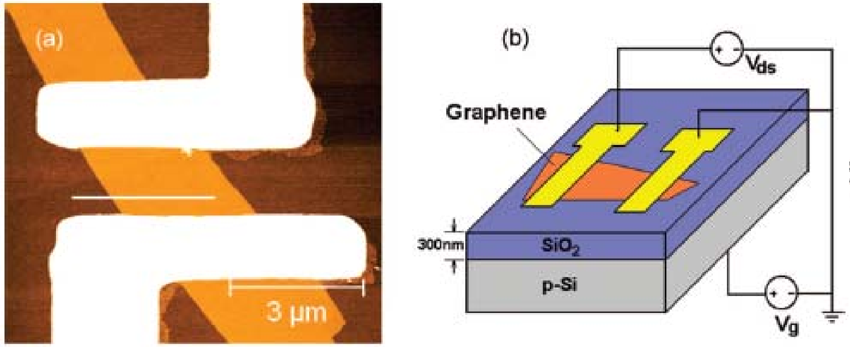
Conventional nanolithography (EBL) leaves residues that influence response. Cleaning in H2/Ar reveals the properties of pristine devices.

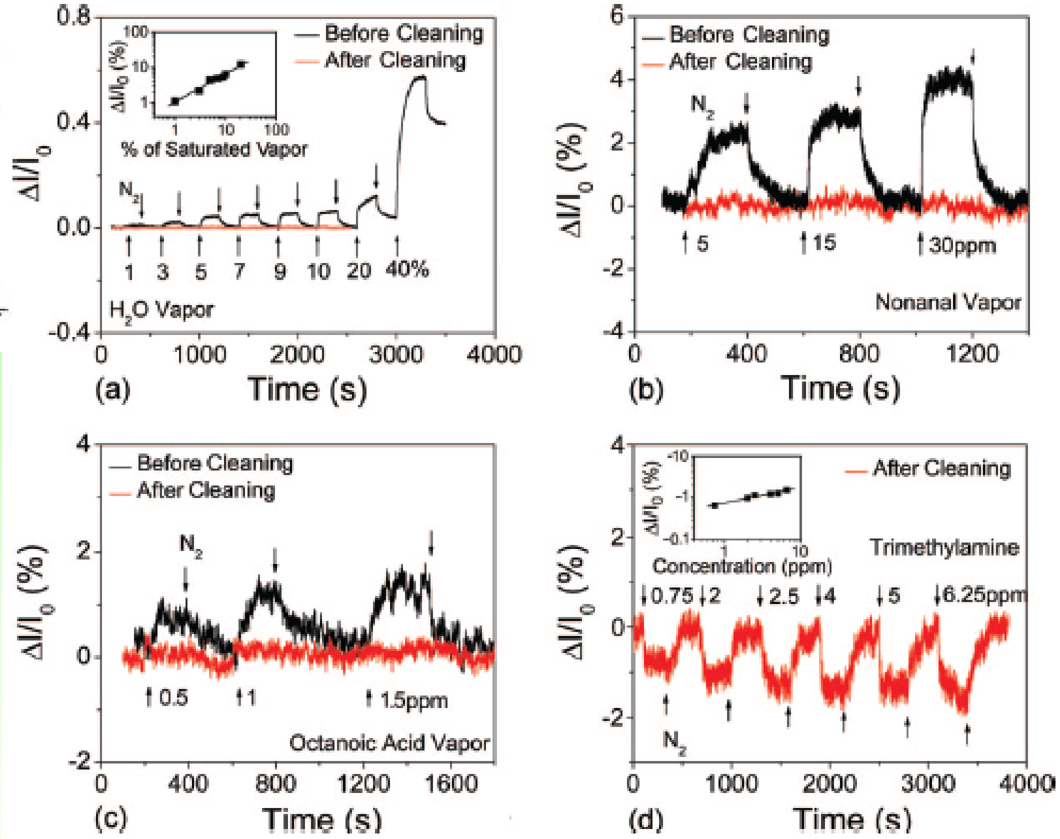
Graphene shows low response to gases!

A.T.C. Johnson, *Nano Letts*, 9 (2009) 1472

Gas sensors employing carbon nanomaterials

Graphene





Conventional nanolithography (EBL) leaves residues that influence response. Cleaning in H2/Ar reveals the properties of pristine devices.

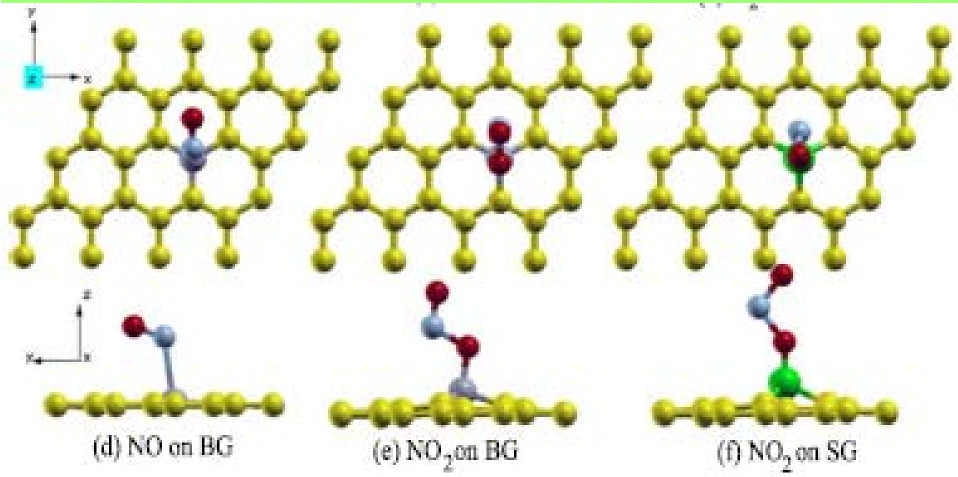
Graphene shows low response to gases!
e.g. Reduced graphene oxide shows ppb sensitivity to warfare agents,explosives and NO

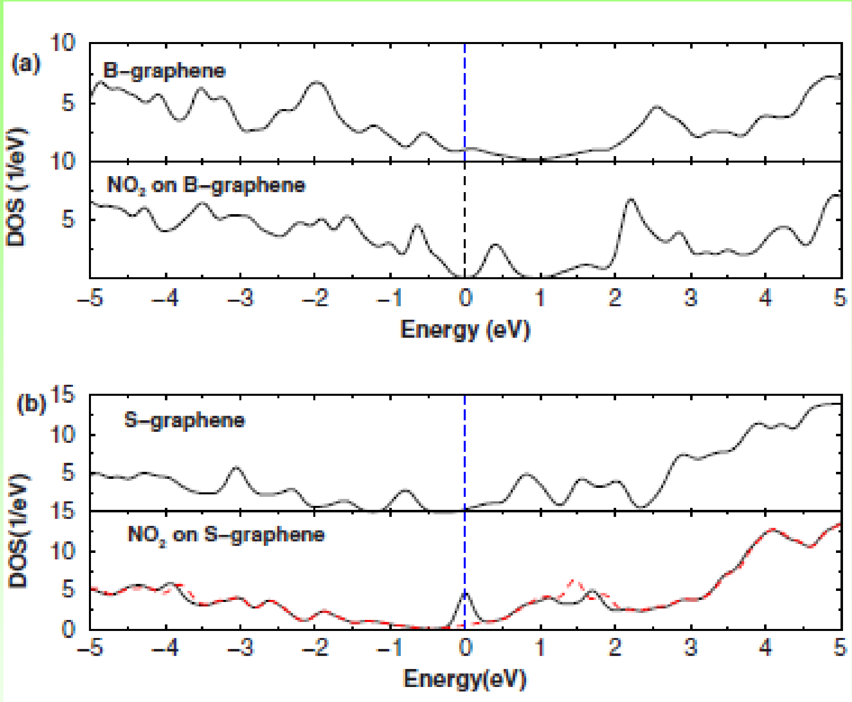
(J.T. Robinson, *Nano Lett.,* 8 (2008) 3137
R.B. Kaner, *ACS Nano*, 3 (2009) 301
L. Liu, ACS Nano 5 (2011) 6955)

A.T.C. Johnson, *Nano Lett.*, 9 (2009) 1472

Gas sensors employing carbon nanomaterials

Graphene





Substitutional doping of graphene enhances changes upon NO2 or NO adsorption

J. Yuan, *APL.*, 95 (2009) 232105

Conclusions and outlook

- Carbon nanomaterials show interesting properties for trace detection of ambient pollutants
- There is a need for cost-effective, scalable production methods that retain the essential properties of such materials
- Functionalisation (surface engineering) is the way to increase sensitivity and minimize unwanted effects
- Carbon nanomaterials could be used in ultra-low power RFID tags for ubiquitous environmental monitoring
- Nanometer sized resonators based on carbon nanomaterials could reach (theoretically) zeptogram sensitivities.

Acknowledgements MINOS group:

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