European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

1ST TRAINING SCHOOL

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UNIVERSITAT ROVIRA I VIRGILI

COST is supported by the EU Framework Programme

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CARBON NANOMATERIALS

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Outline

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

Trace detection: many challenges

Water

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

Air

-Particulate matter - SOx, NOx, O3, VOCs, CFCs, CH4, Pb, Hg, explosives, warfare agents

Multimedia pollutants:
Heavy metals, Benzene, PCBs,…

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

Soil

Trace detection: many challenges

Air

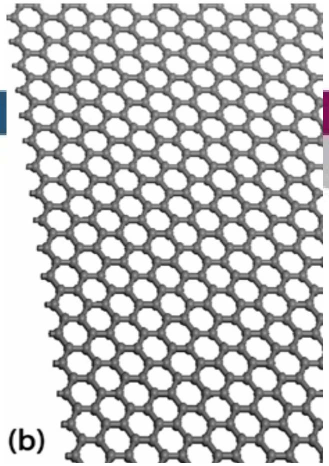
Water

Continuous and ubiquitous monitoring sought

- High sensitivity for ameliorated LOD (ppb, ppt)
- High stability for reliability -
Selectivity -
Humidity and temperature compensation -
Reduced size -
Affordable cost - Low
power -
Distributed sensing

Soil

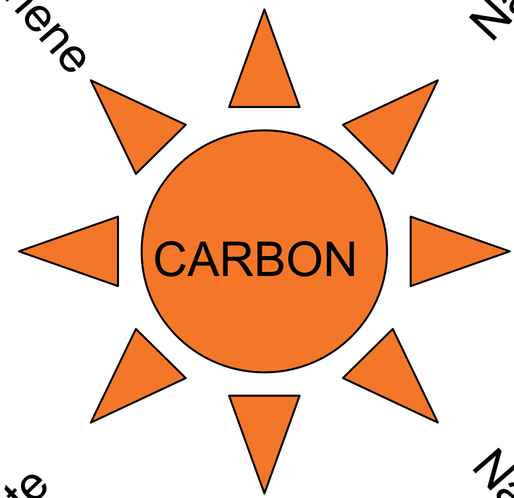
Carbon nanomaterials: a few promises



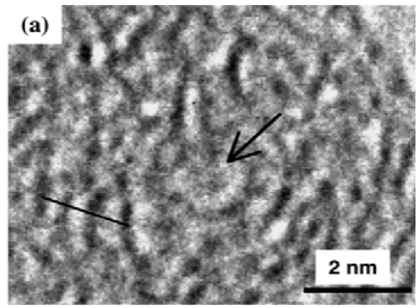
Reduced Graphene oxide

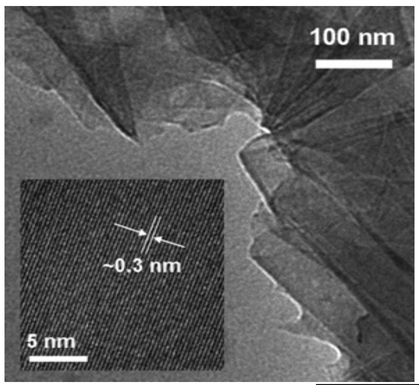
Nanoparticles (Carbon black)

Graphene



Nanoporous carbon

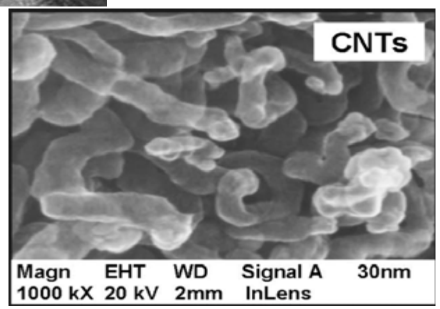


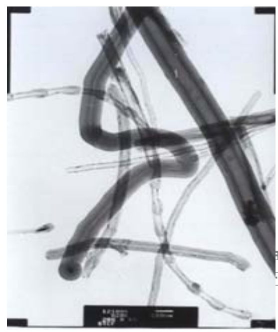


Graphite

Nanotubes

Nanofibres





Carbon nanomaterials: a few promises

NanoMat

- 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

- Avoidance of grain boundary poisoning (such as in polycrystalline metal oxides)

- 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

Carbon nanomaterials: and many issues

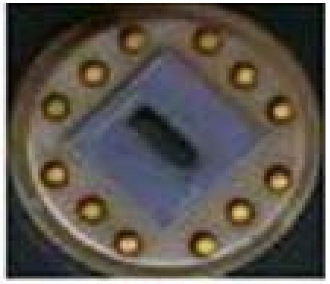
Carbon nanomaterials (CNMATs) show interesting properties for trace detection of ambient pollutants BUT:

- There is a need for cost-effective, scalable production methods that retain the essential properties of such materials …
- … and for tailoring surface properties via functionalization
- Contacting CNMATs is non-trivial (e.g. material contamination, which affects response, reproducibility…)
- High-quality vs low-quality CNMATs dilemma
- The advancement of applications of carbon nanomaterials is hampered by their biopersistence and pro-inflammatory action *in vivo*

Carbon nanomaterials

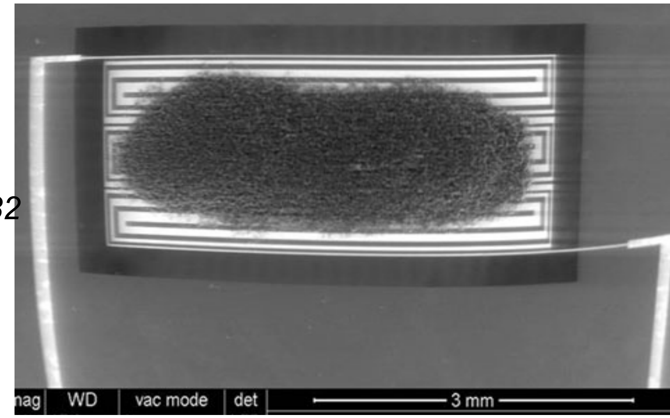
Activated carbon for pre-concentration

Physical reactivation:
Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600–900 °C, in absence of oxygen.
Activation/Oxidation: Raw material to oxidizing atmospheres at temperatures in the range of 600–1200 °C.
Chemical activation: Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base or a salt



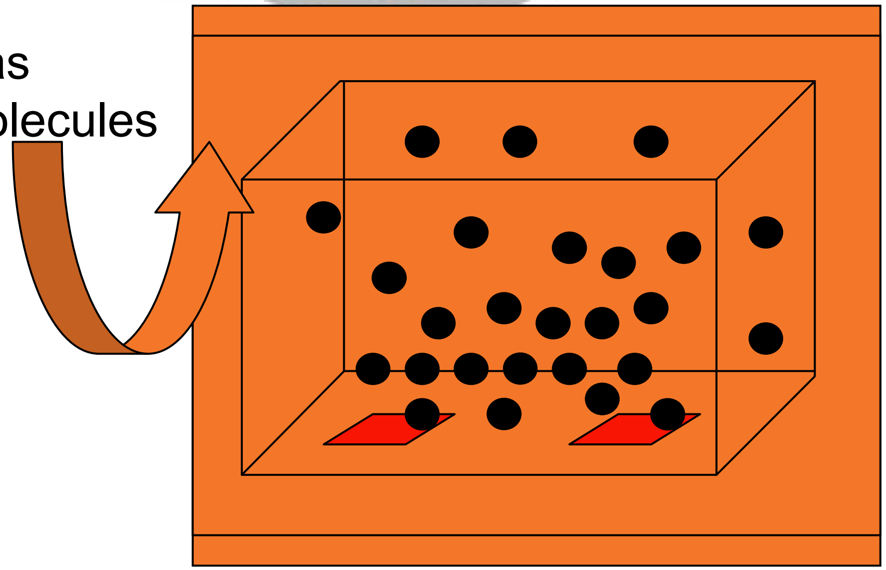
-AC has grain size in the range of microns, surface area of 500 to 1500 m^2/g
- Total carbon content about 60%
- Pores in the 0.5 to 5 nm range
- Concentration factors up to 2000/mg

E. Llobet, Sensors and Actuators B 132 (2008) 90



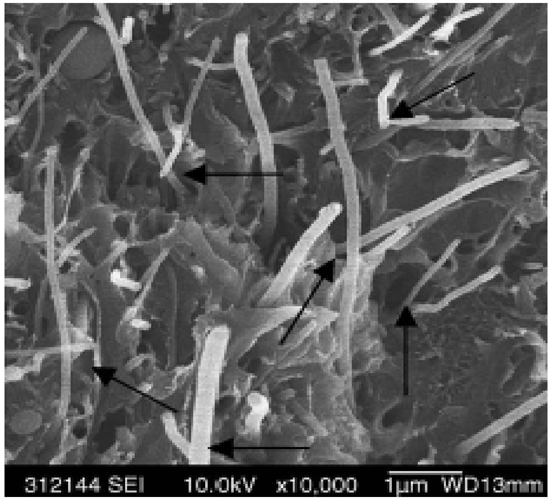
Carbon nanomaterials

Carbon black and carbon nanofibres



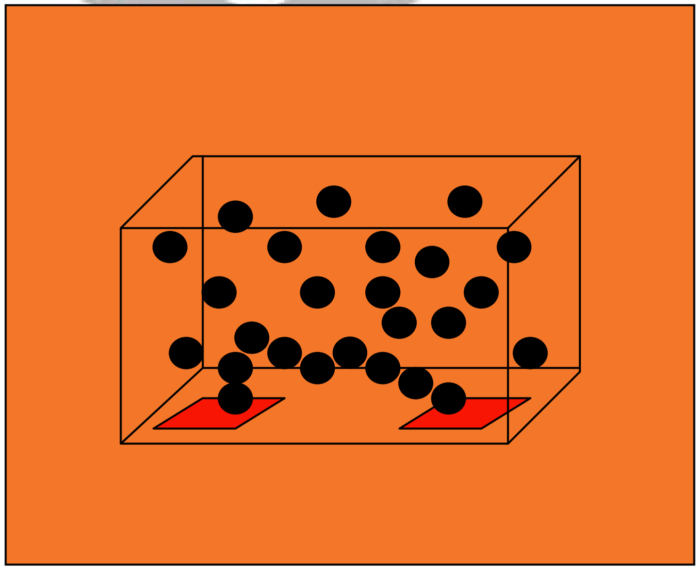
- Produced by the incomplete combustion of heavy petroleum products
-Selectivity tuned by polymer matrix
- Dispersion by solvent/polymer sonication
- Response mechanism explained by percolation theory
- CB: ~ 30 nm, 200 m^2/g
- CNF: 70-250 nm, 70 um

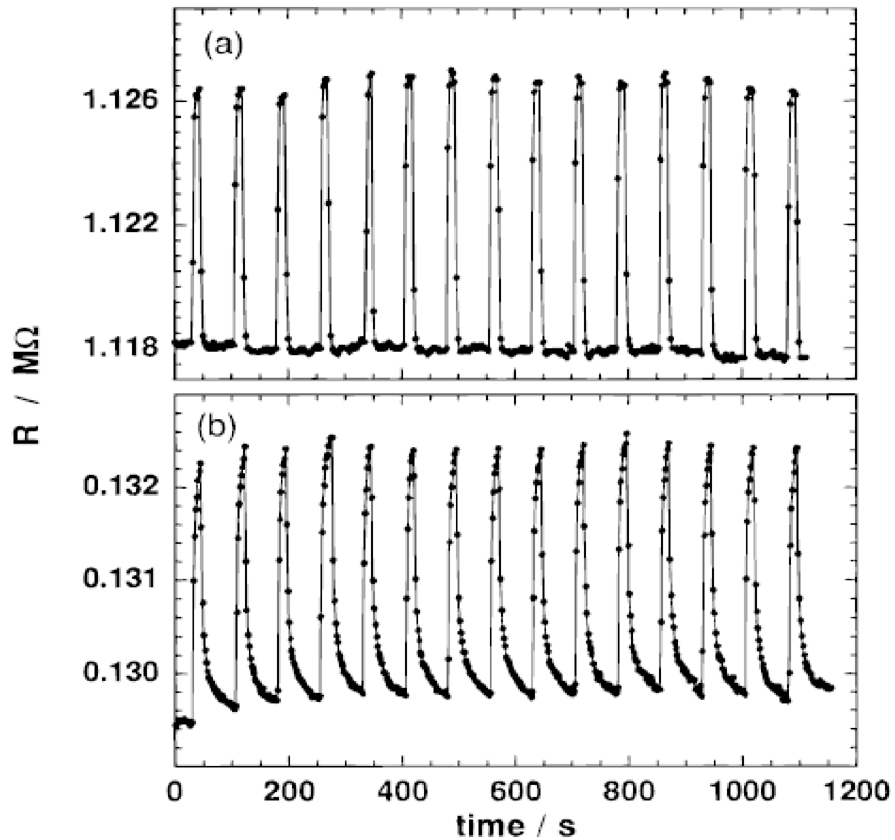
R. Fu, *Mat.Res.Bull.* 41 (2006) 553 S.
Lewis, *Anal. Chem*, 70 (1998) 4177 N.S.
Lewis, *Chem. Mater*. 8 (1996) 2298



Gas sensors employing carbon nanomaterials

Carbon black and carbon nanofibres





a) PVA   b) PVP   Benzene 1.5 ppt

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

Electrospun carbon nanofibers

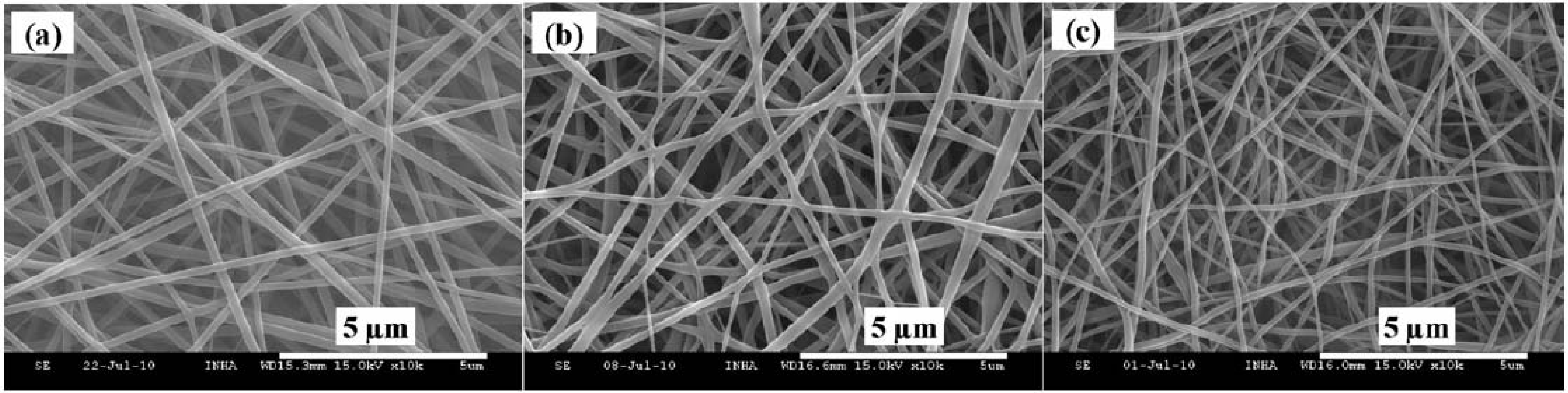


Fig. 1. SEM microphotographs of electrospun (a) pure PVP nanofibers, (b) PEDOT:PSS/PVP nanofibers, and (c) PEDOT:PSS/MWCNT—COOH/PVP nanofibers.

Room temperature detection of aromatic VOCs at ppm level

J. Choi et al., *Synthetic Metals* 162 (2012) 1513

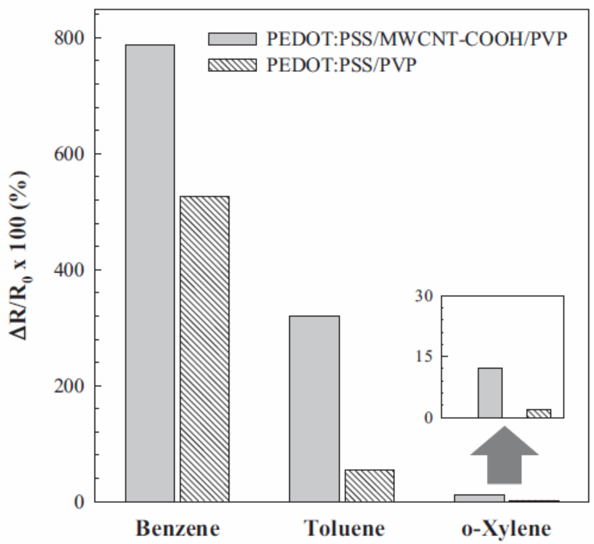


Fig. 4. Response magnitude of electrospun PEDOT:PSS/MWCNT—COOH/PVP and PEDOT:PSS/PVP nanofibers to the aromatic VOCs at room temperature.

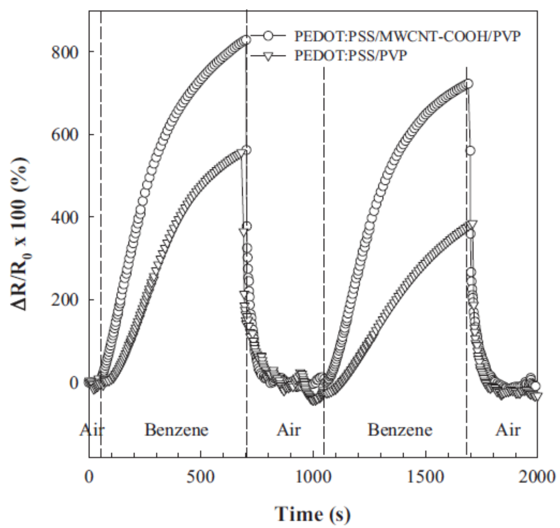


Fig. 5. Response of electrospun PEDOT:PSS/MWCNT—COOH/PVP and PEDOT:PSS/PVP nanofibers upon cyclic exposure to benzene vapor at room temperature.

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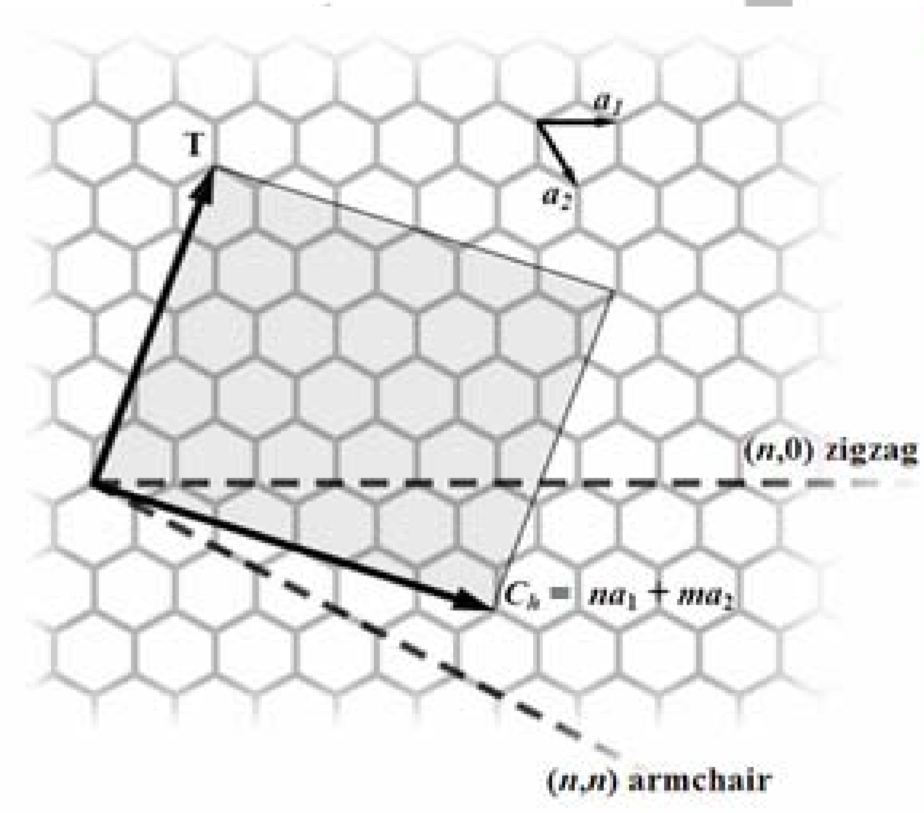
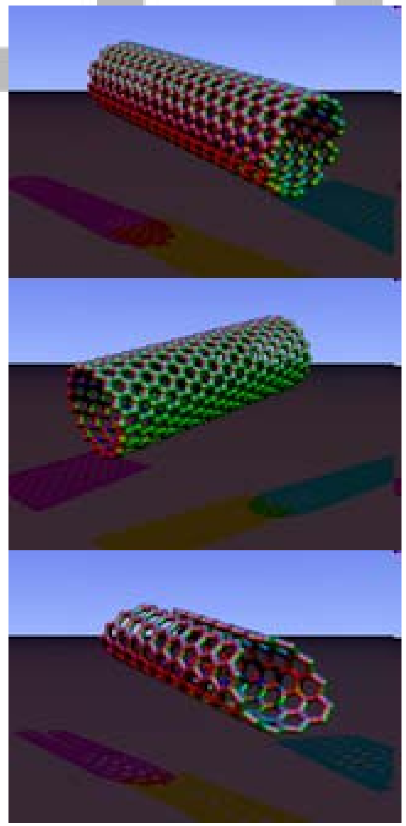
Carbon nanomaterials

Carbon nanotubes





Armchair

ZigZag

Chiral

For a given (n,m) nanotube, if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor.

Carbon nanomaterials

Carbon nanotubes

Synthesis methods

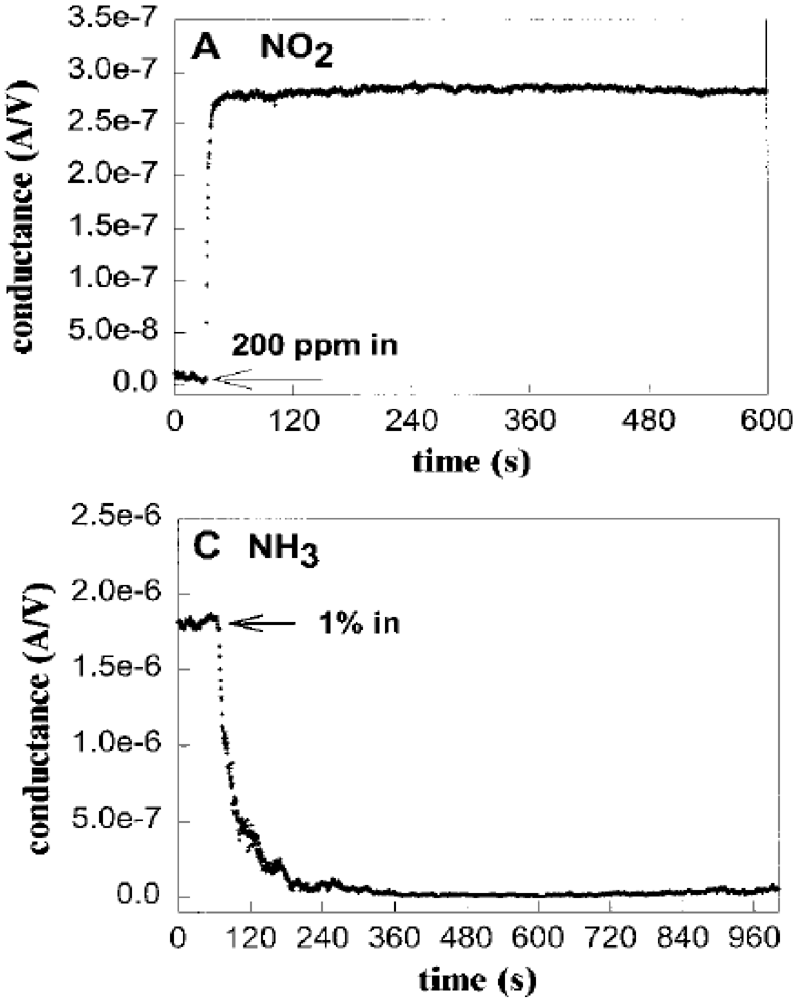
• Arc discharge: Nanotubes were observed in 1991 in the carbon soot of graphite electrodes during an arc discharge. Yield: 30% of both SWNT and MWNT with few defects

• Laser ablation: A pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Co+Ni catalysts increase yield to 70% mostly SWNT (expensive)

• Chemical vapor deposition: During CVD, a substrate is prepared with a layer of metal catalyst particles. The substrate is heated to approximately 700°C and a process gas (such as ammonia, nitrogen or hydrogen) and a carbon-containing gas (such as acetylene, ethylene, ethanol or methane) are bled onto the reactor. Nanotubes grow at the sites of the metal catalyst. (Most promising technique for commercial production)

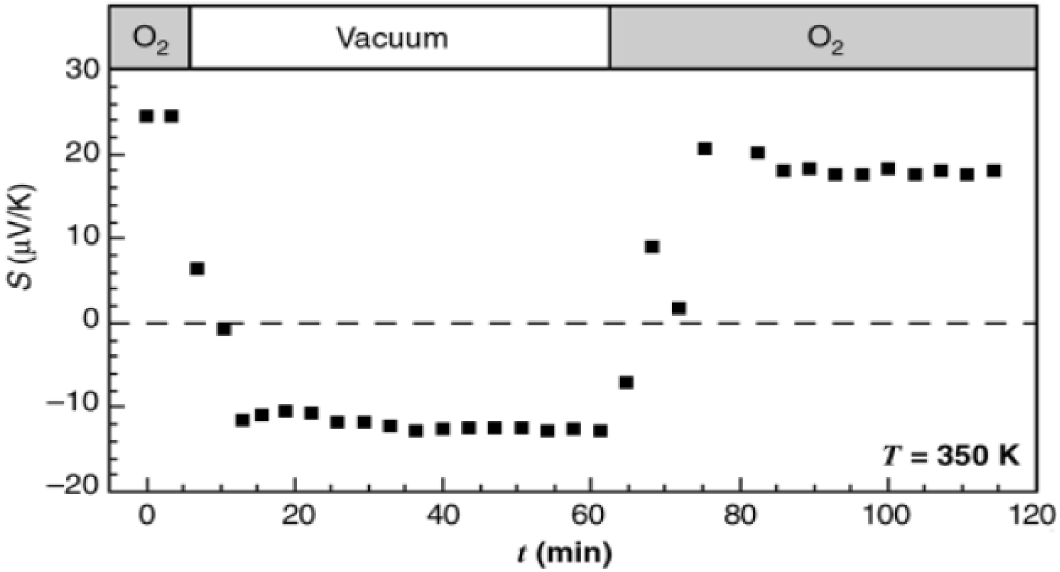
Carbon nanomaterials

Carbon nanotubes



J. Kong, Science 287 (2000) 622

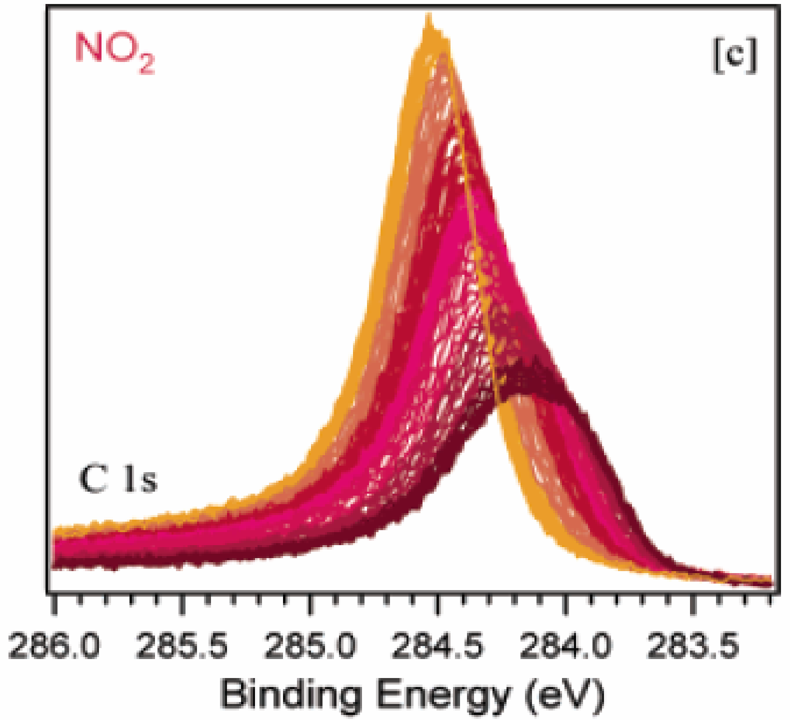
Electronic properties of SWCNTs are found extremely sensitive to chemical environment



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

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

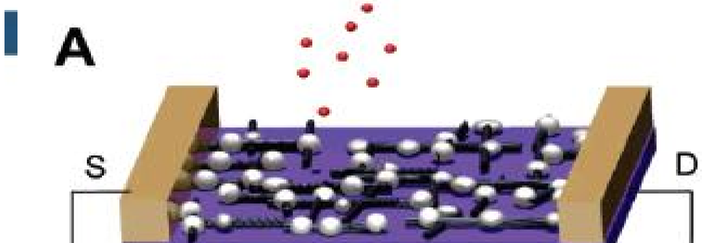
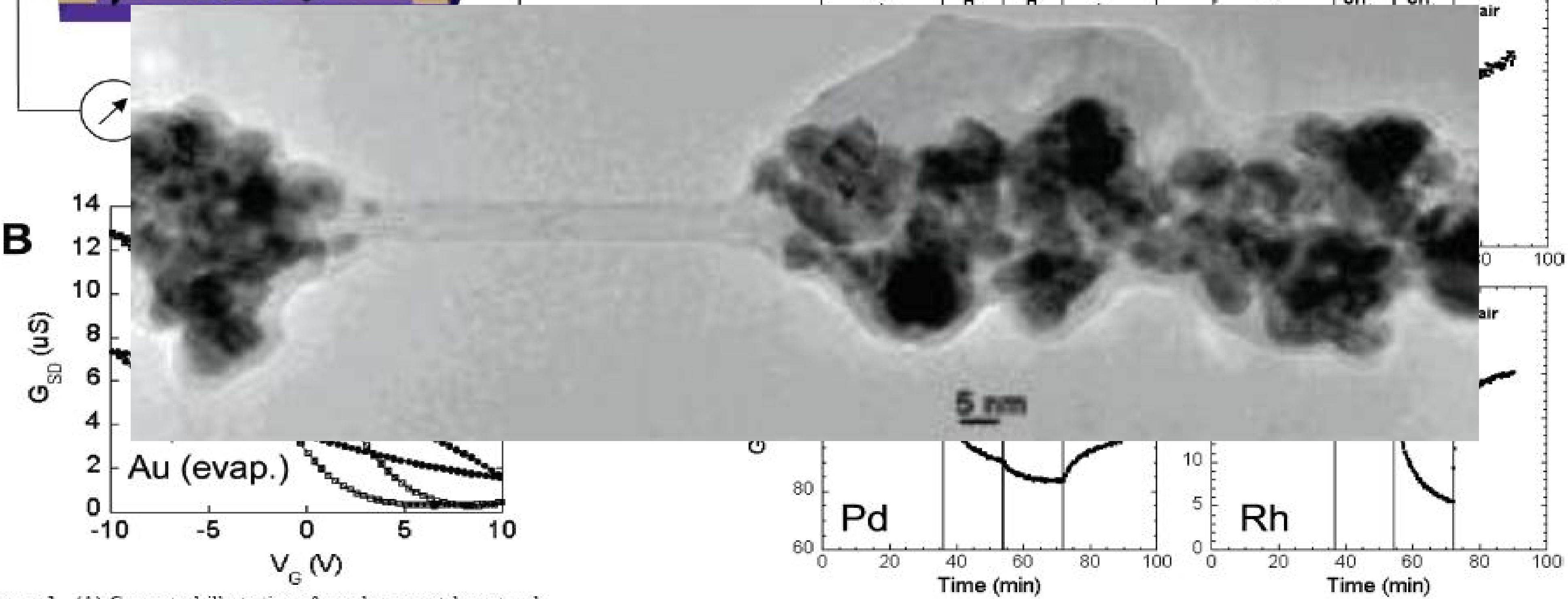


Figure 1. (A) Conceptual illustration of a carbon nanotube network connecting source (S) and drain (D) electrodes of a FET. SWNTs are decorated with metal nanoparticles (silver bullets) for selective detection of analyte gases (red dots). (B) Electronic measurements, such as source-drain conductance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

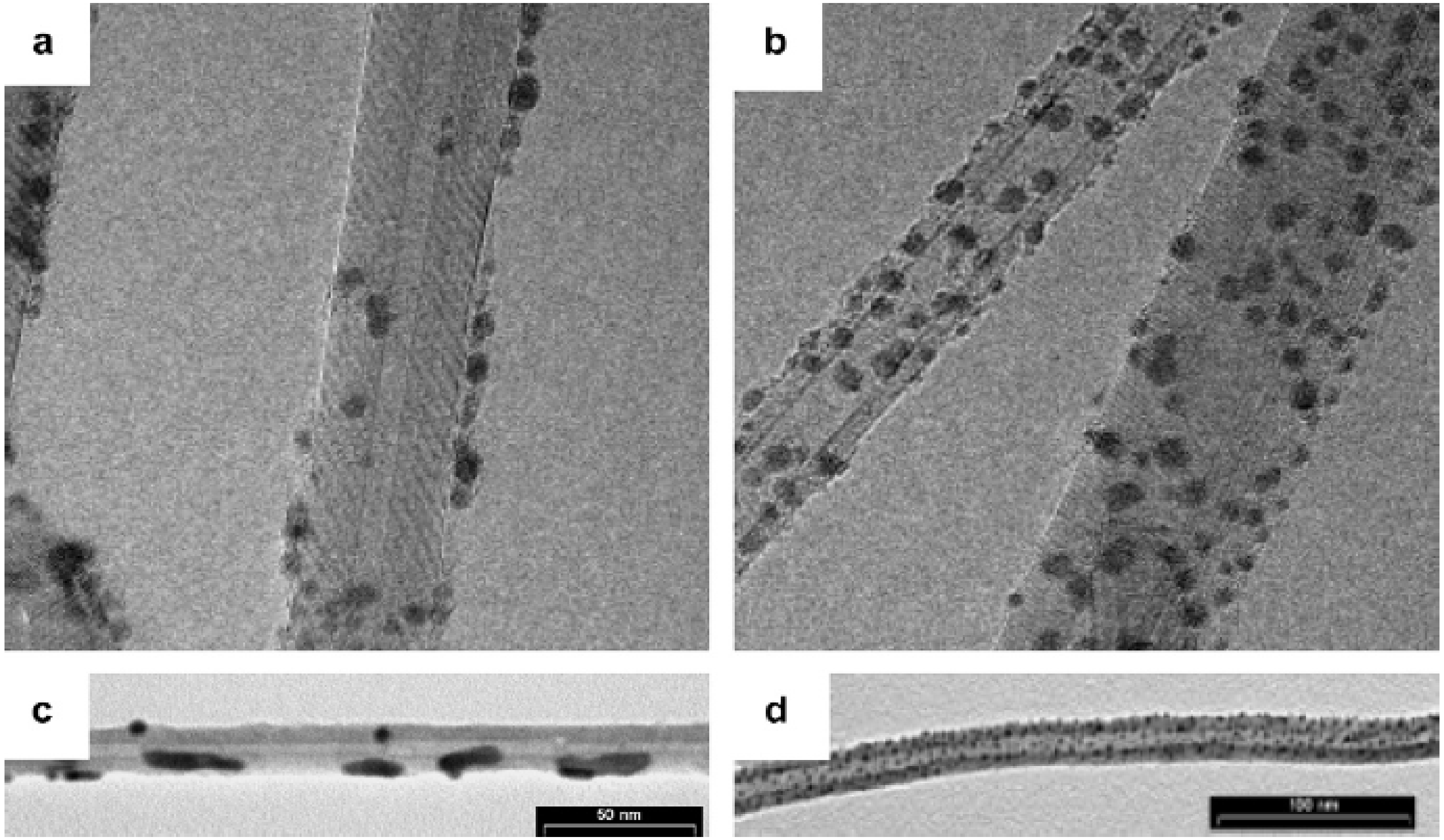
SWNT decorated with Pd, Pt, Rh, Au, Sn, Mg, Fe, Co, Ni, Zn, Mo, W, V, Cr



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

Carbon nanomaterials

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

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Gas sensors employing carbon nanomaterials

Carbon nanotubes

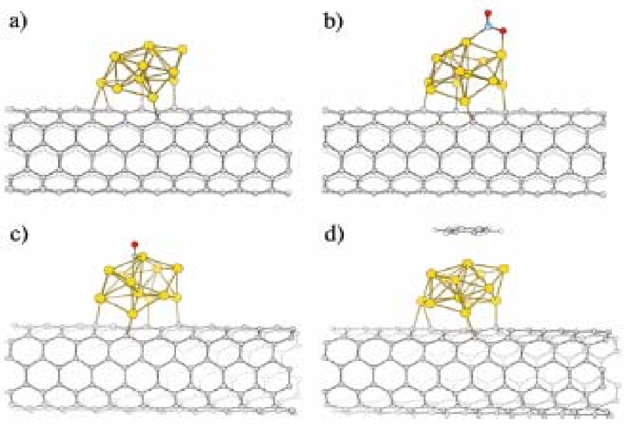
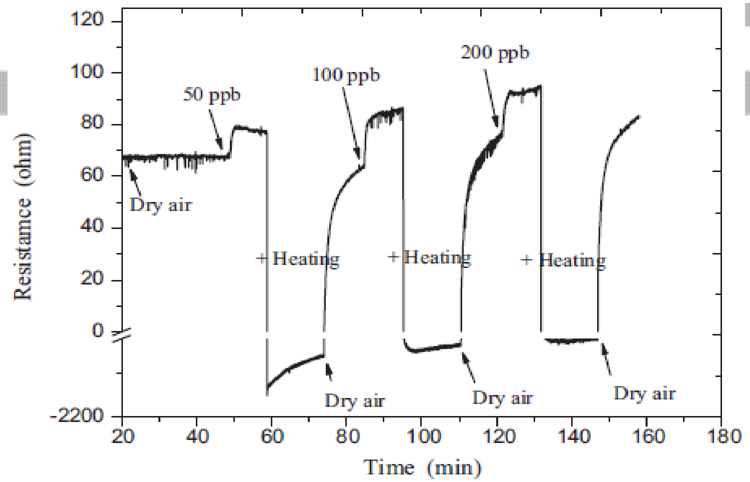


Figure 4. Ball-and-stick models illustrating fully *ab initio* optimized atomic structures of a (5,5) SWNT decorated with a Au_{13} nanocluster (a) and with various adsorbed molecules: NO_2 (b), CO (c), and C_6H_6 (d).

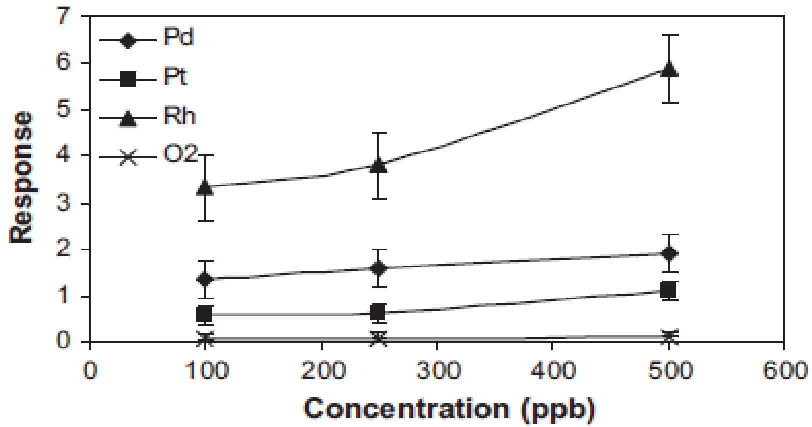
TABLE 1. Computed Binding Energies (E_B, eV), Charge Transfer (Δq, $|e|$), Au_{13}—SWNT Bond Length (d_{Au}, Å), and Molecule—Au_{13} Bond Length (d_{gas}, Å)

	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

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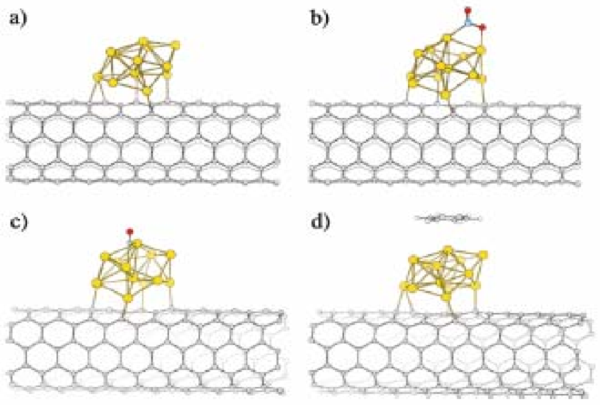
Carbon nanomaterials

Carbon nanotubes



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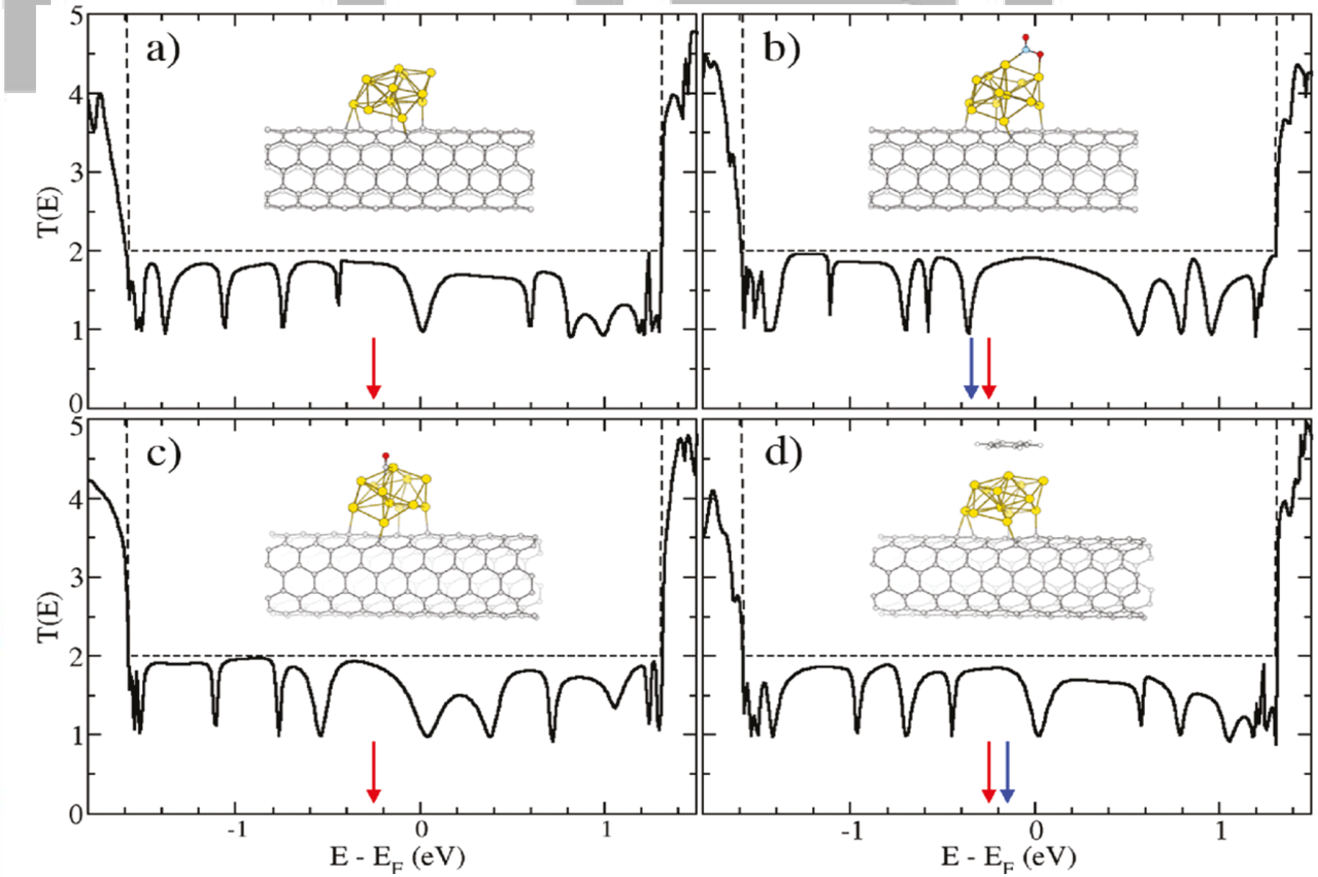
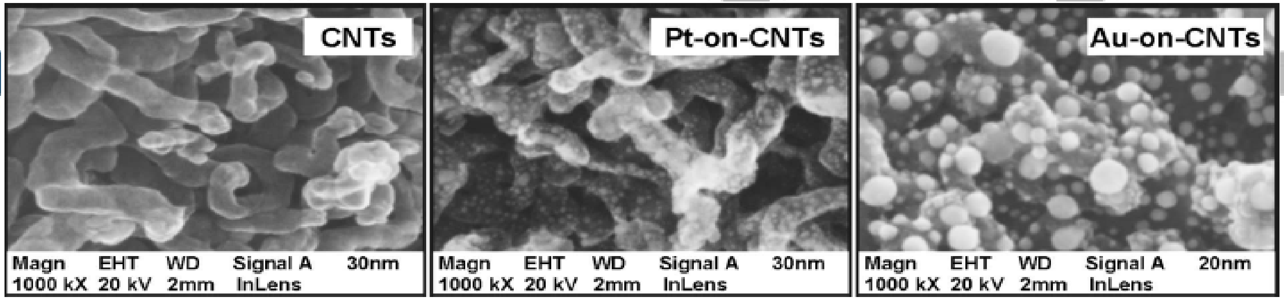


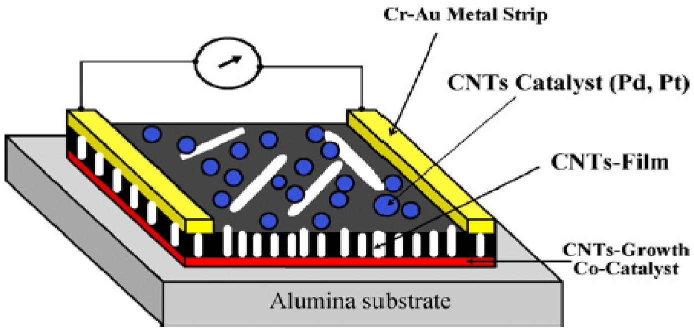
a) Au b) Au+NO2, c) Au+CO, d) Au+C6H6

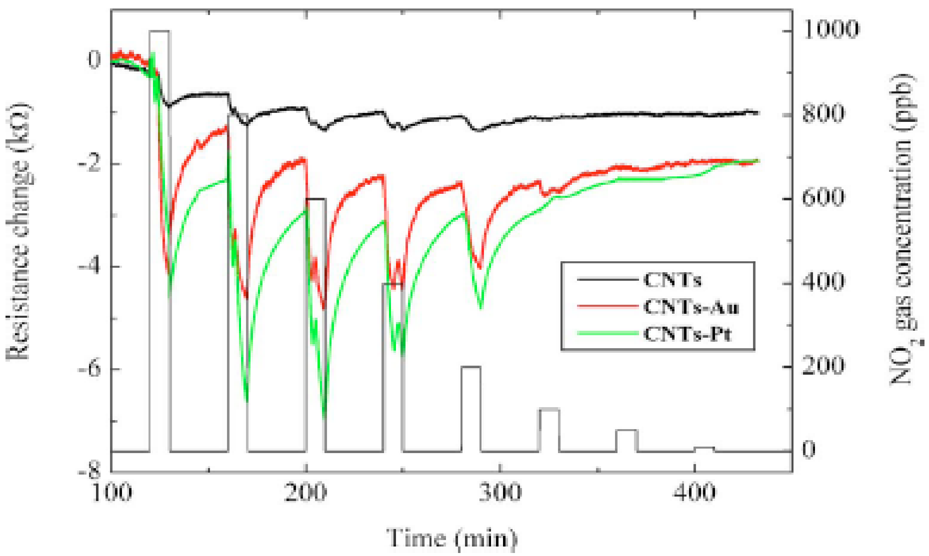
E. Llobet, *ACS Nano*, 6 (2011) 4592

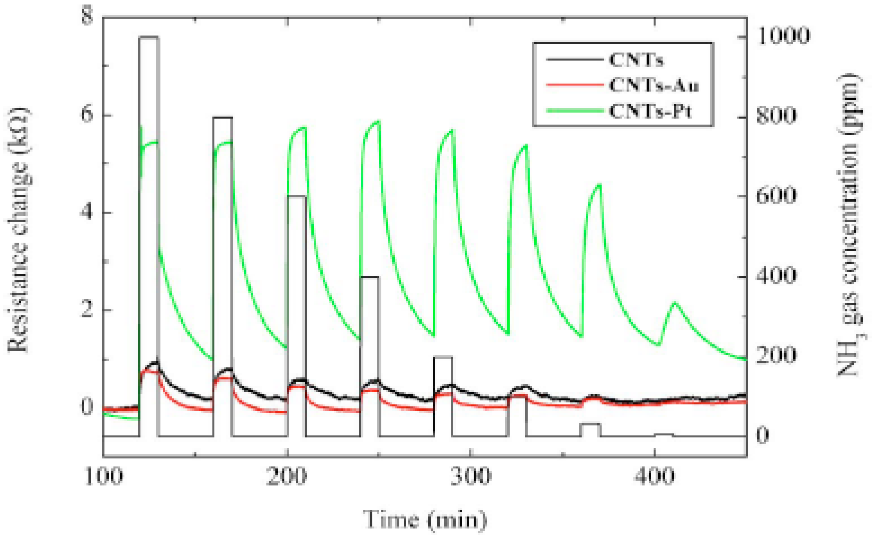
Gas sensors employing carbon nanomaterials

Carbon nanotubes





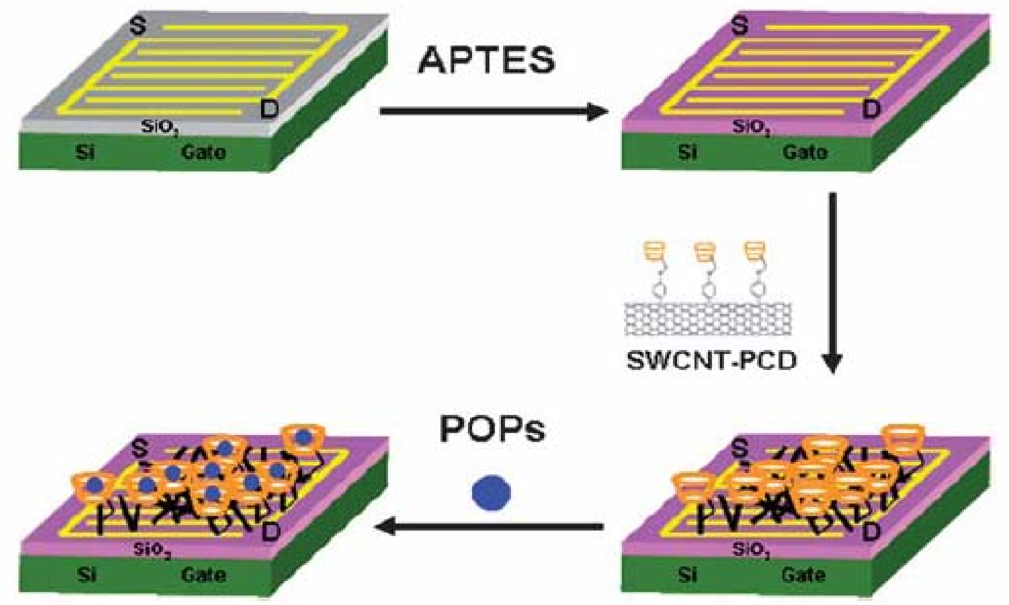


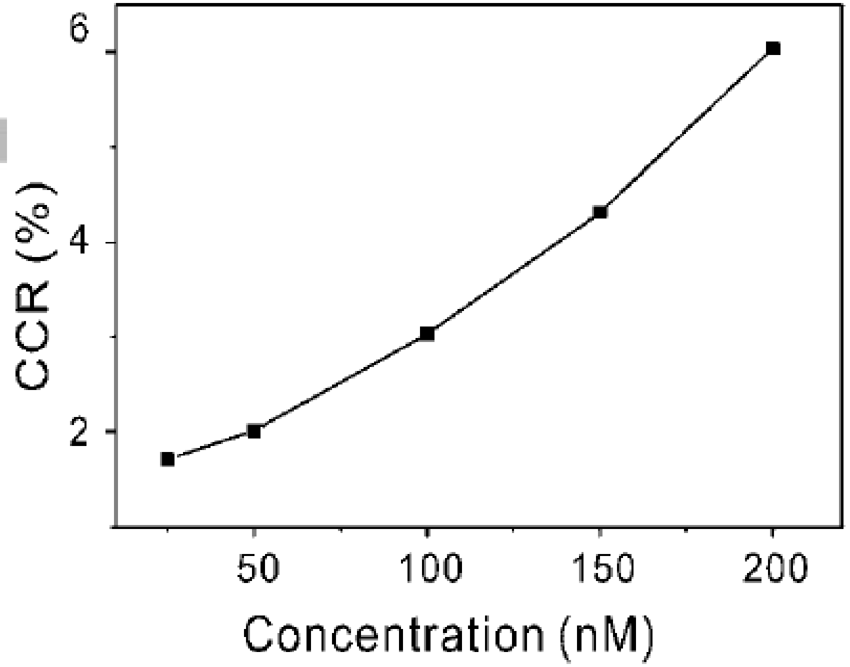


M. Penza, *APL*, 90 (2007) 173123 M. Penza, *Sens. Actuators B* 135 (2008) 289 M. Penza, *Thin Solid Films* 517 (2009) 6211

Gas sensors employing carbon nanomaterials

Carbon nanotubes





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

Gas sensors employing carbon nanomaterials

Carbon nanotubes

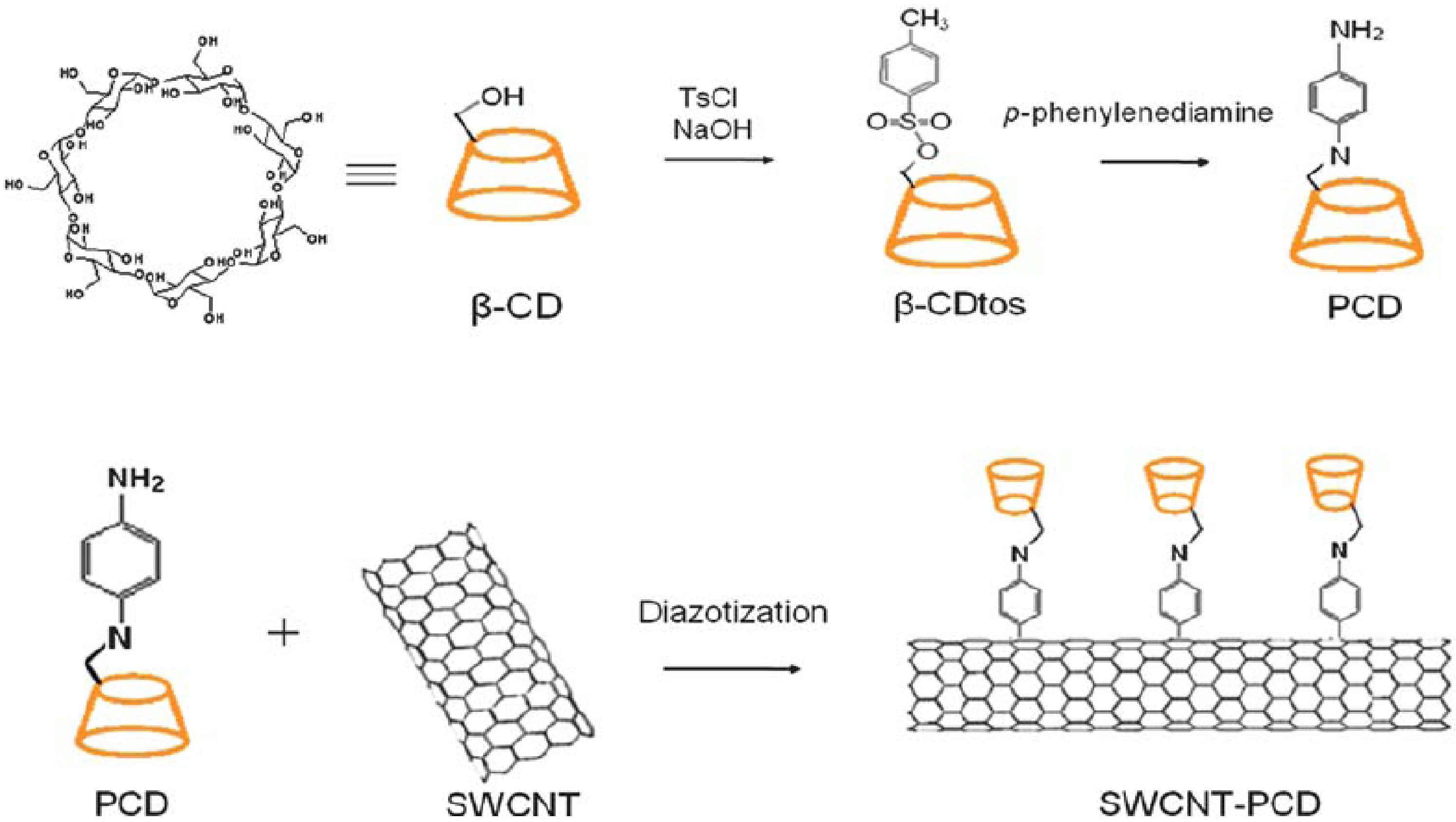


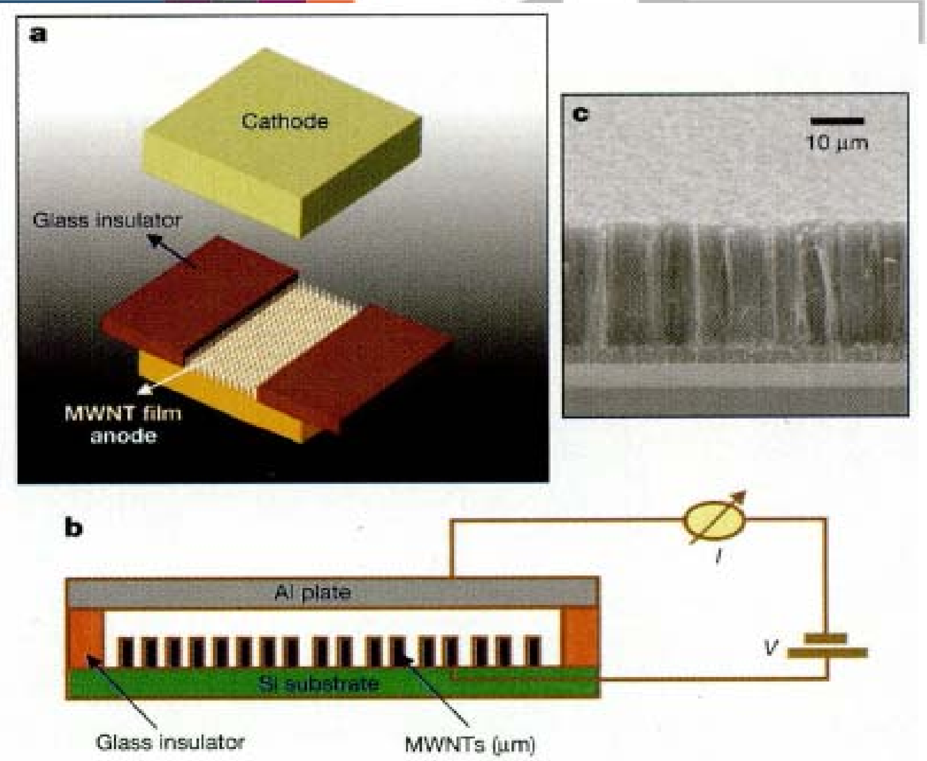
Fig. 1 Schematic representation of synthesis of PCD and preparation of SWCNT–PCD hybrids.

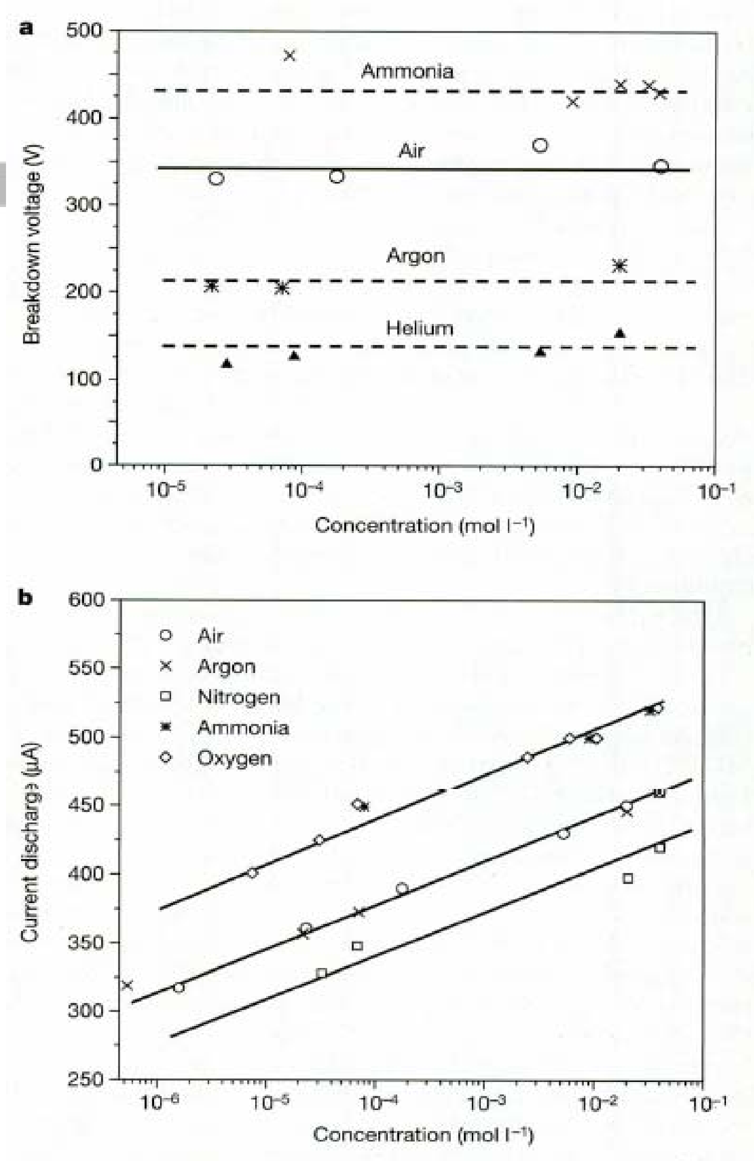
SWCNT decorated with an aminophenylamino cyclodextrin (PCD) for detection of persistent organic compounds

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

Gas sensors employing carbon nanomaterials

Carbon nanotubes

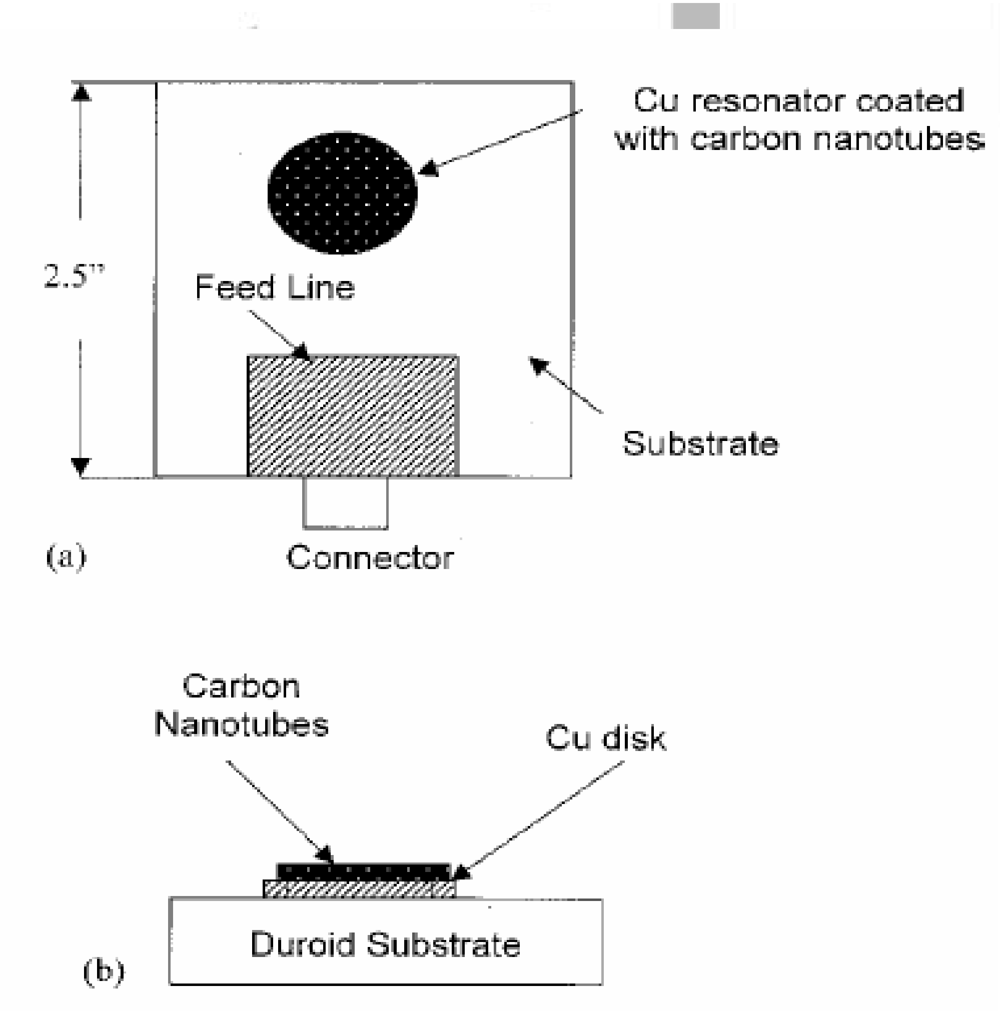


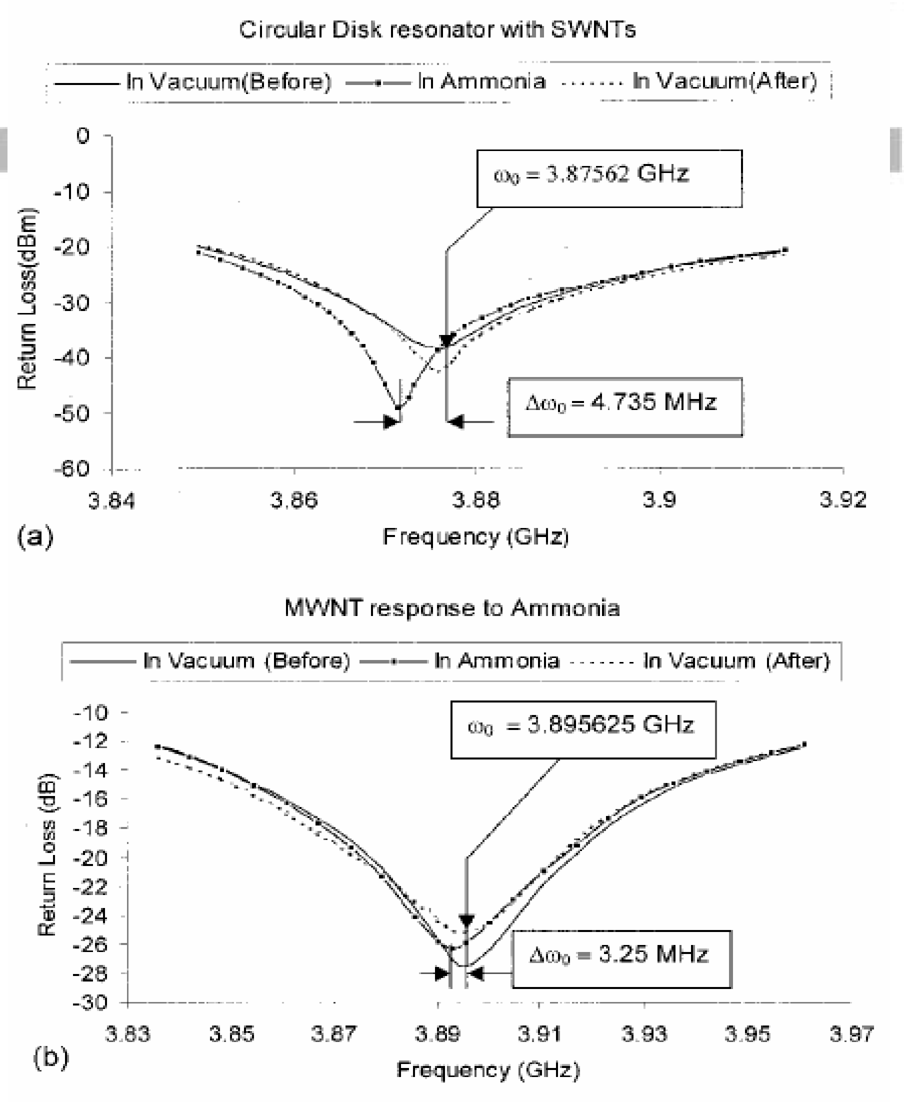


A. Modi, *Nature*, 424 (2003) 171

Gas sensors employing carbon nanomaterials

Carbon nanotubes





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

Flexible CNT sensors

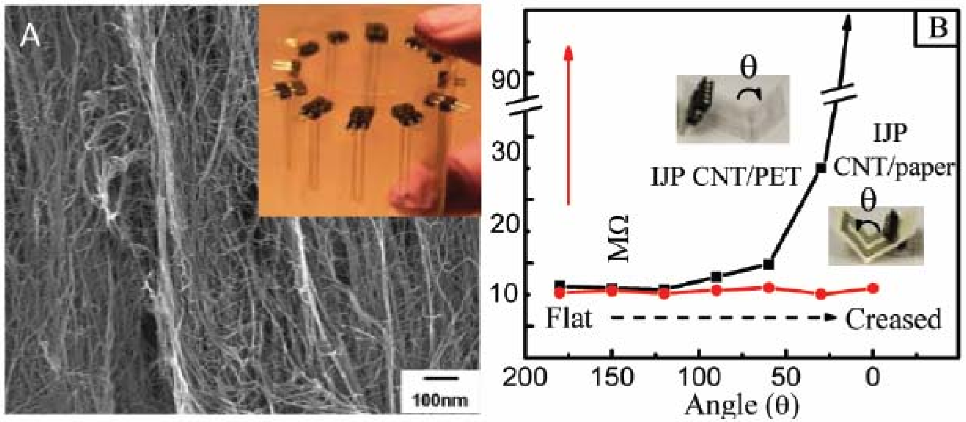


Figure 1. (A) Field-effect SEM image of inkjet-printed CNTs on PET (CNT/PET). The inset shows an array of 10 inkjet-printed CNT/PET sensors. (B) Plot of resistance vs bending angle for CNT/PET and CNT/paper sensors.

Room temperature detection of NO_2 at ppm-ppb level

A. Ammu et al., *JACS* 134 (2012) 4553

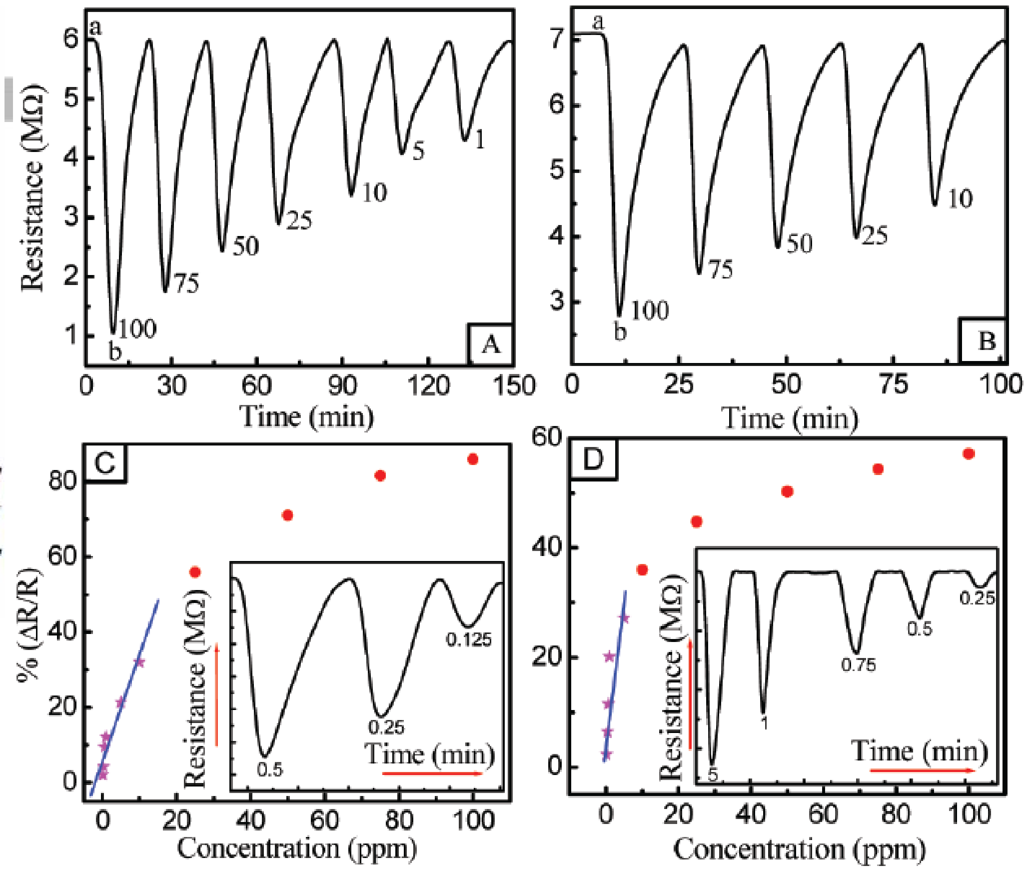


Figure 2. (A, B) Plots of resistance (*R*) vs time for successively decreasing concentrations of NO_2 vapor for inkjet-printed (A) CNT/PET and (B) CMT/paper films. NO_2 vapor was present at point "a" and removed at point "b". Numbers on valleys represent the vapor concentrations in ppm. (C, D) Plots of $\Delta R/R$ vs concentration for inkjet-printed (C) CNT/PET and (D) CNT/paper films. The insets show plots of resistance vs time at low concentrations.

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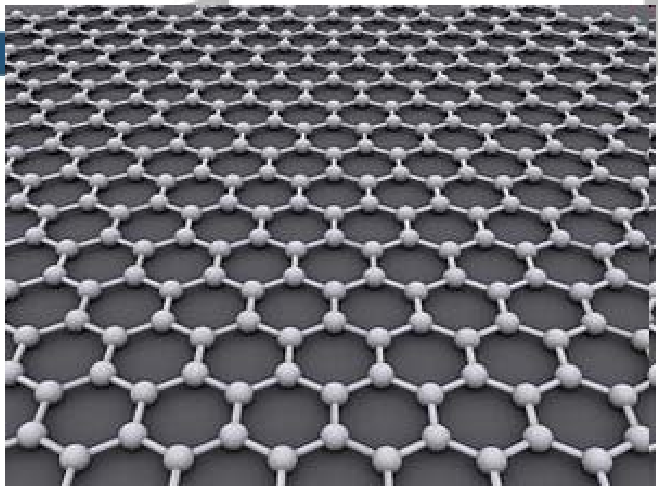
Carbon nanomaterials

Graphene



Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities.

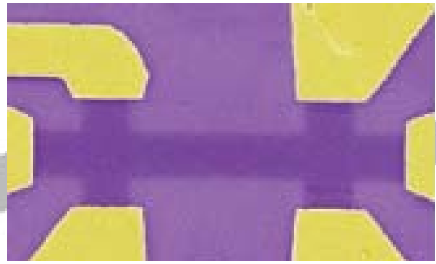
K.S. Novoselov, *Nature Mat*, 6 (2007) 183

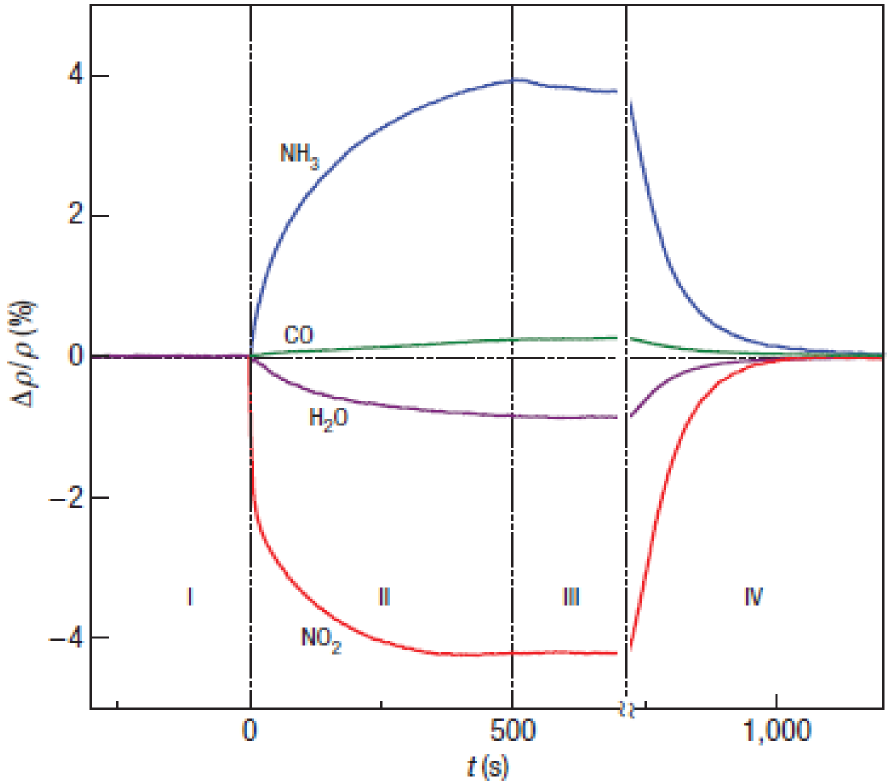
Graphene can be obtained by exfoliation of graphite, by epitaxial growth on SiC substrates, graphite oxide reduction, from graphite by sonication, …

Graphene shows very high carrier mobility and very low noise

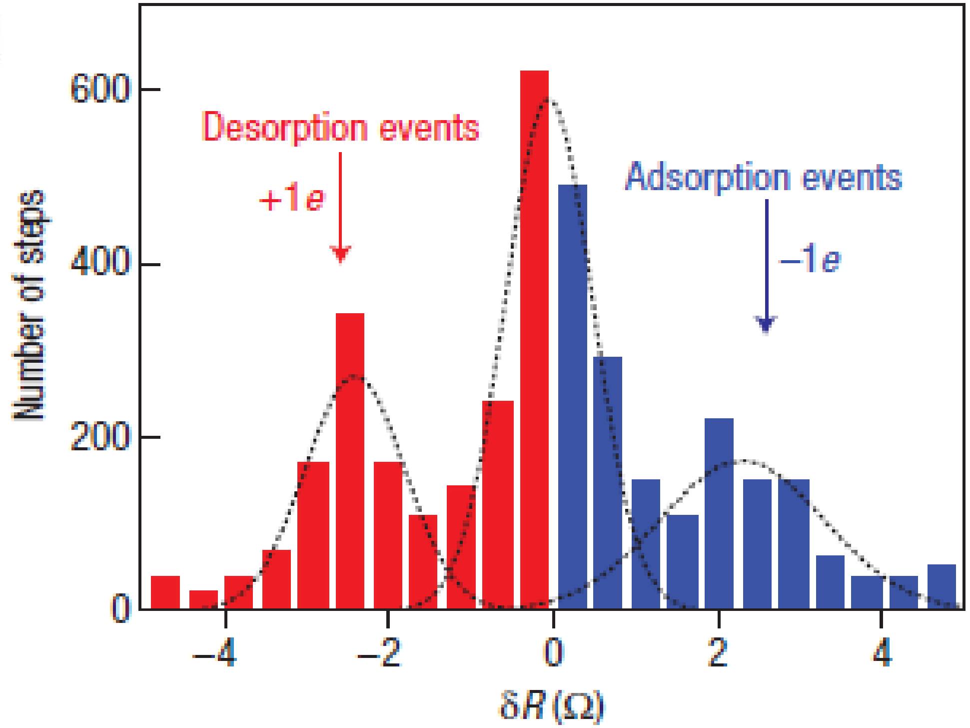
Carbon nanomaterials

Graphene





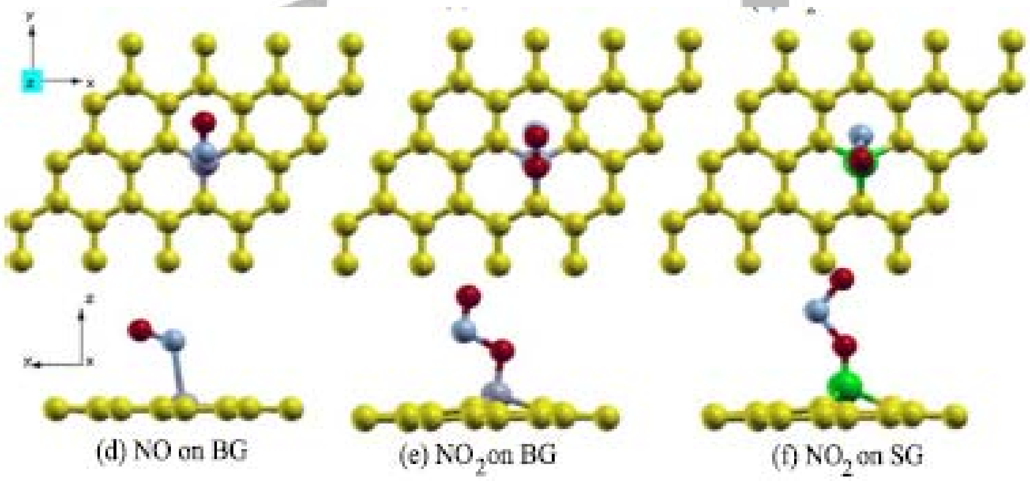
K.S. Novoselov, *Nature Mat*, 6 (2007) 652

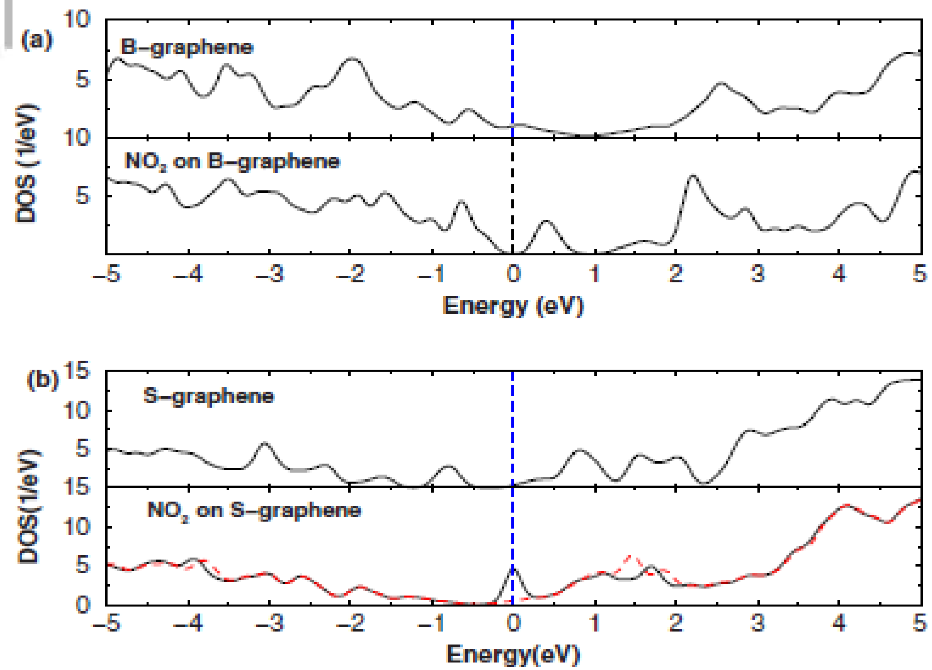


Statistical distribution of step changes in device resistance, *δR*, during the slow desorption of NO2. The side peaks are evidence for detection of adsorption or desorption of individual gas molecules

Gas sensors employing carbon nanomaterials

Graphene



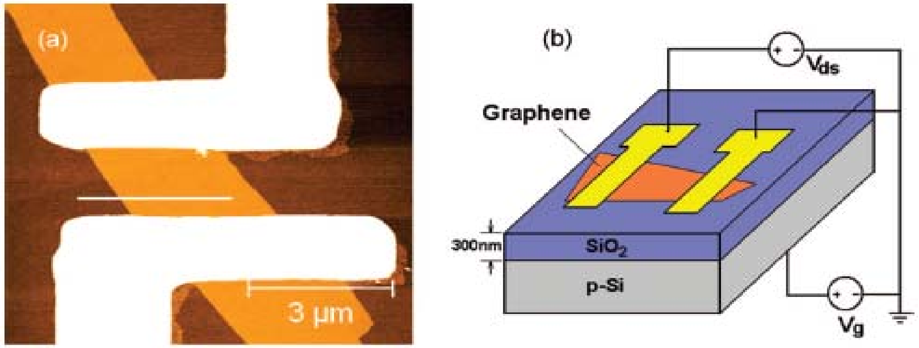


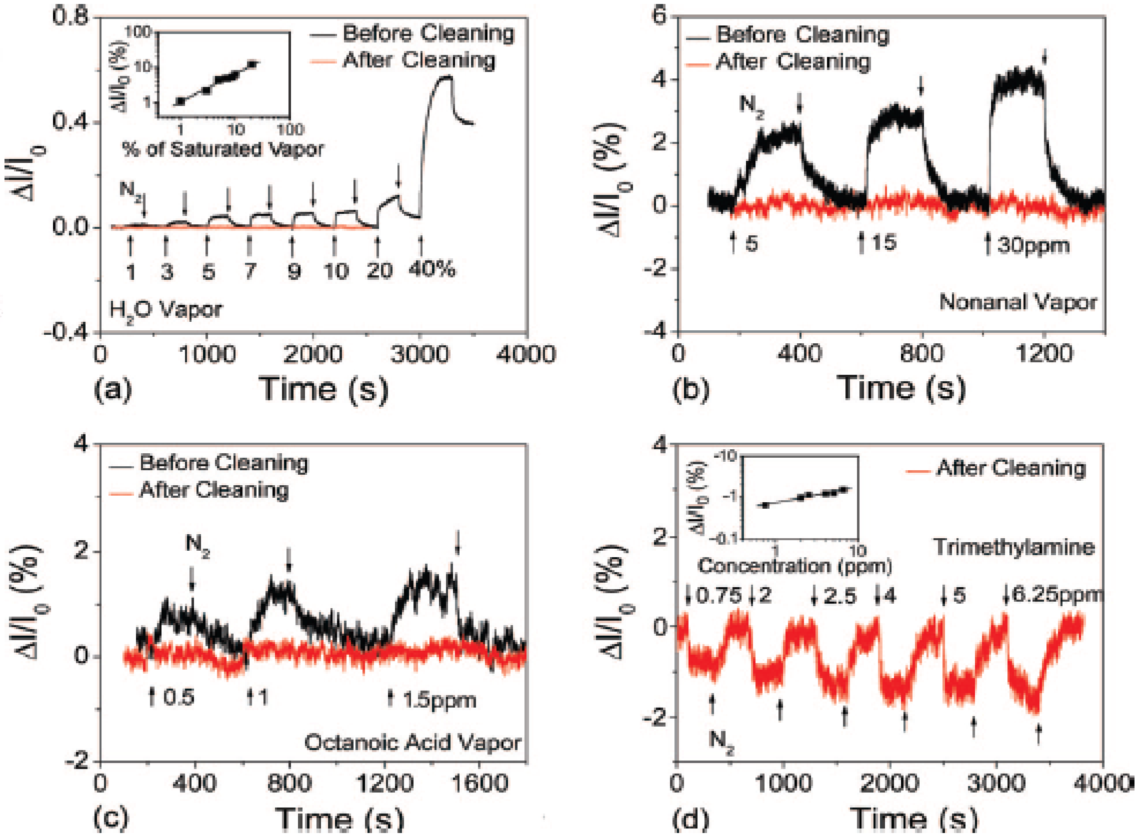
Substitutional doping of graphene enhances changes upon NO2 or NO adsorption

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

Gas sensors employing carbon nanomaterials

Graphene





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

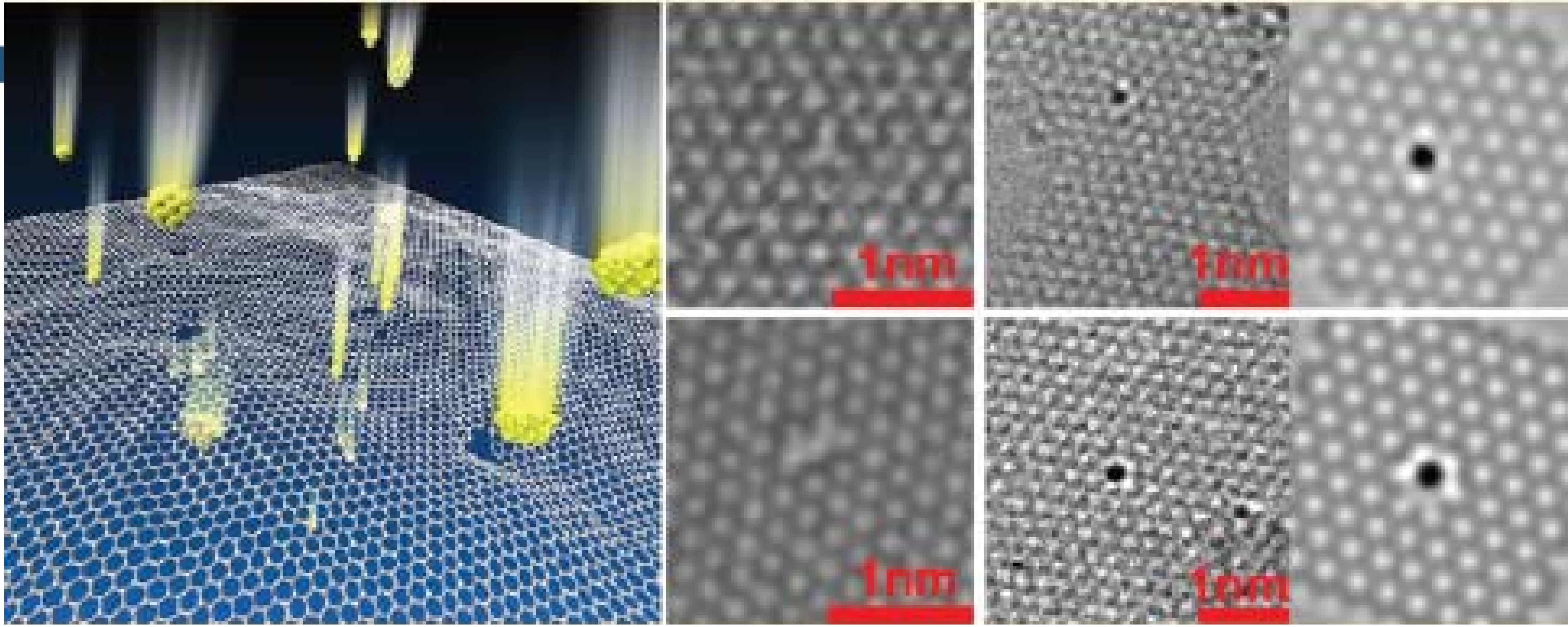
Graphene shows low response to gases!

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

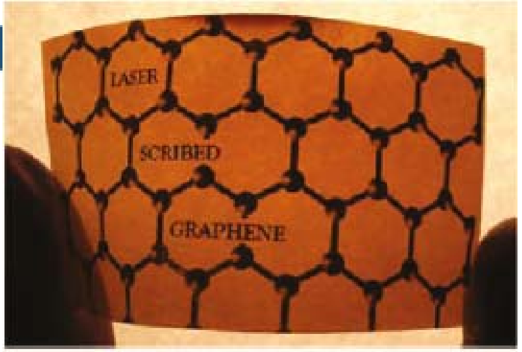
Single atom substituted graphene

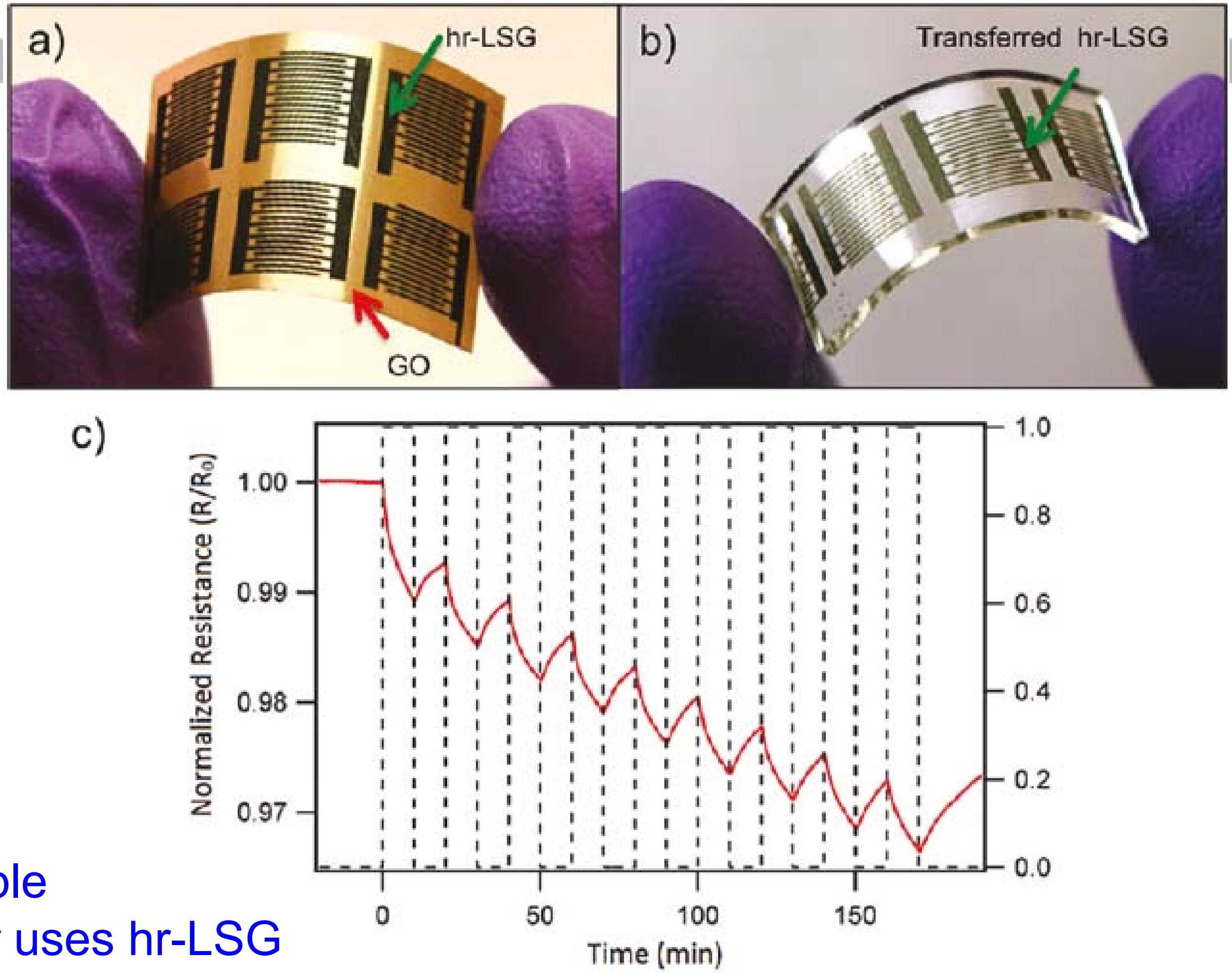


1. **Create vacancies by high-energy atom bombardment (Au). Monovacancies, bivacancies selectively created by confining the kinetic energy of incoming atoms**
2. **Vacancy filling with different dopants (N, B, Pt, Co, In) by ion beam or sputtering**

H. Wang et al., *Nano Lett.* 12 (2012) 141

Laser scribed graphene





LSG is produced and patterned (mask less) from direct laser irradiation of graphite oxide films under ambient conditions

NO_2 detection using all-organic flexible interdigitated electrodes. The sensor uses hr-LSG as the active electrodes and marginally laser-reduced graphite oxide as the detecting media. The NO_2 concentration is 20 ppm in dry air gas.

V. Strong et al., *ACS Nano*, 6 (2012) 1395

Pristine graphene transistor

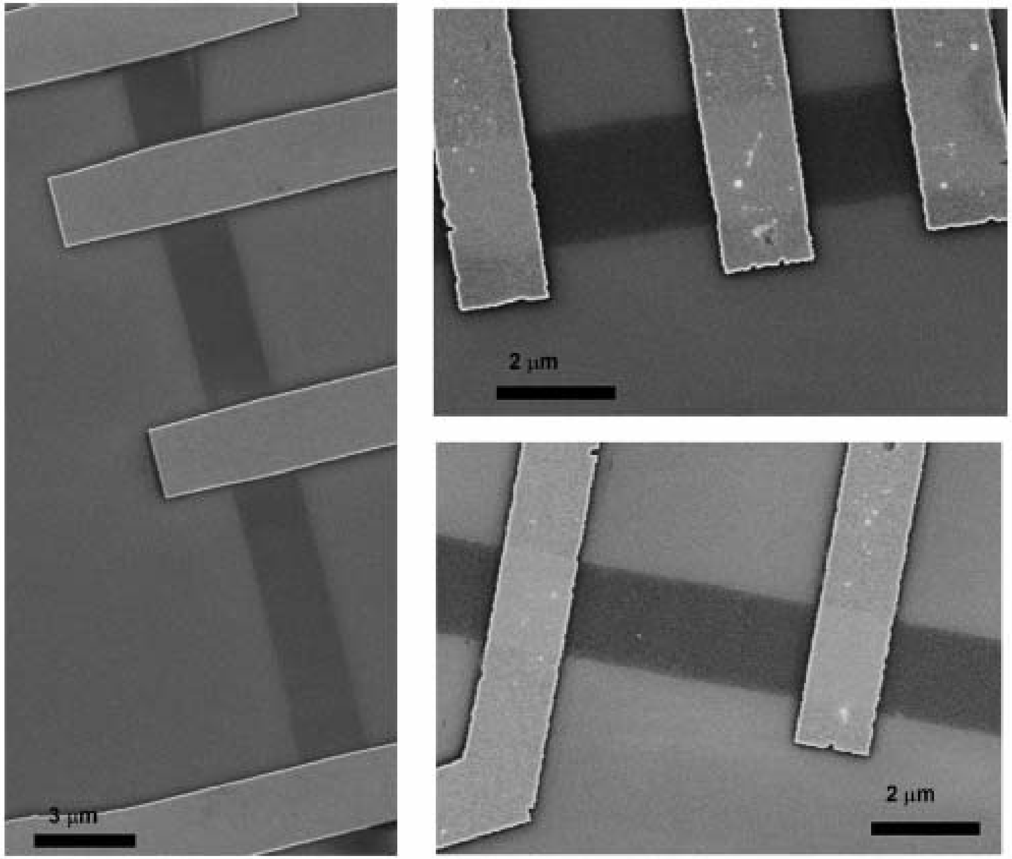
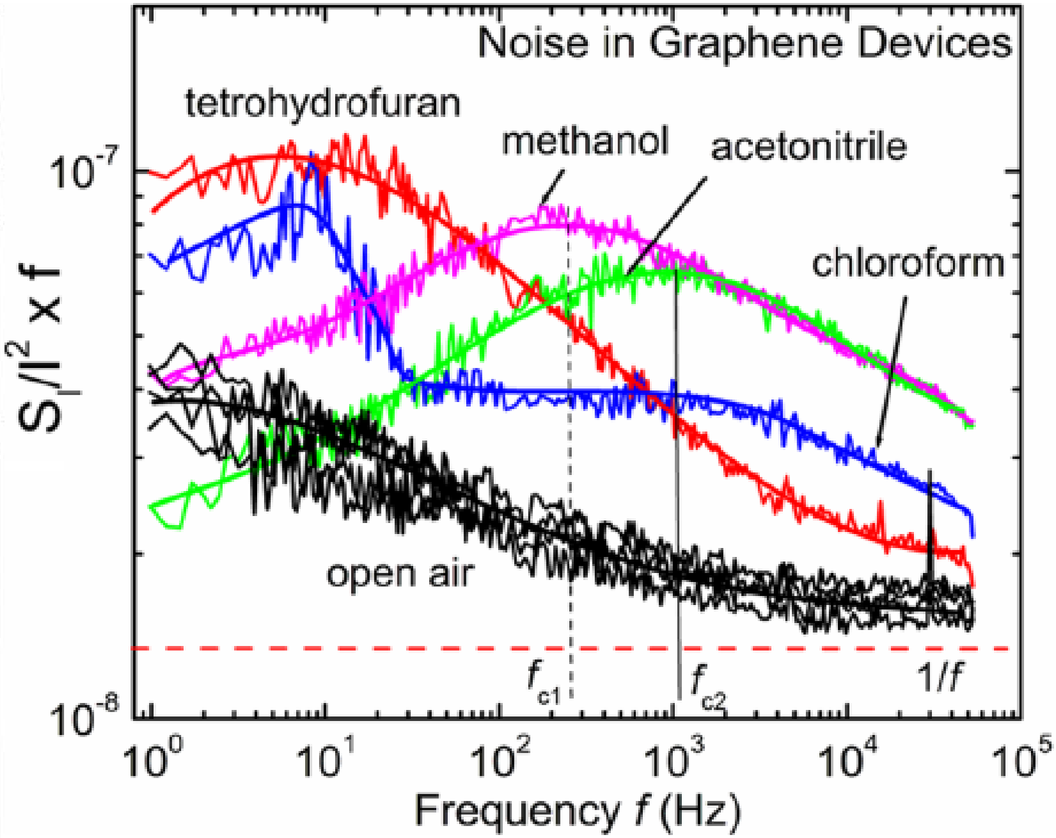


Figure 1. Scanning electron microscopy images of back-gated graphene devices with different number of top electrodes. In the



The low-frequency noise spectra of graphene is affected by vapors of different chemicals by inducing Lorentzian components with distinctive features.

S. Rumuantsev et al., *Nano Lett.*, 12 (2012) 2294

Polycrystalline graphene ribbons

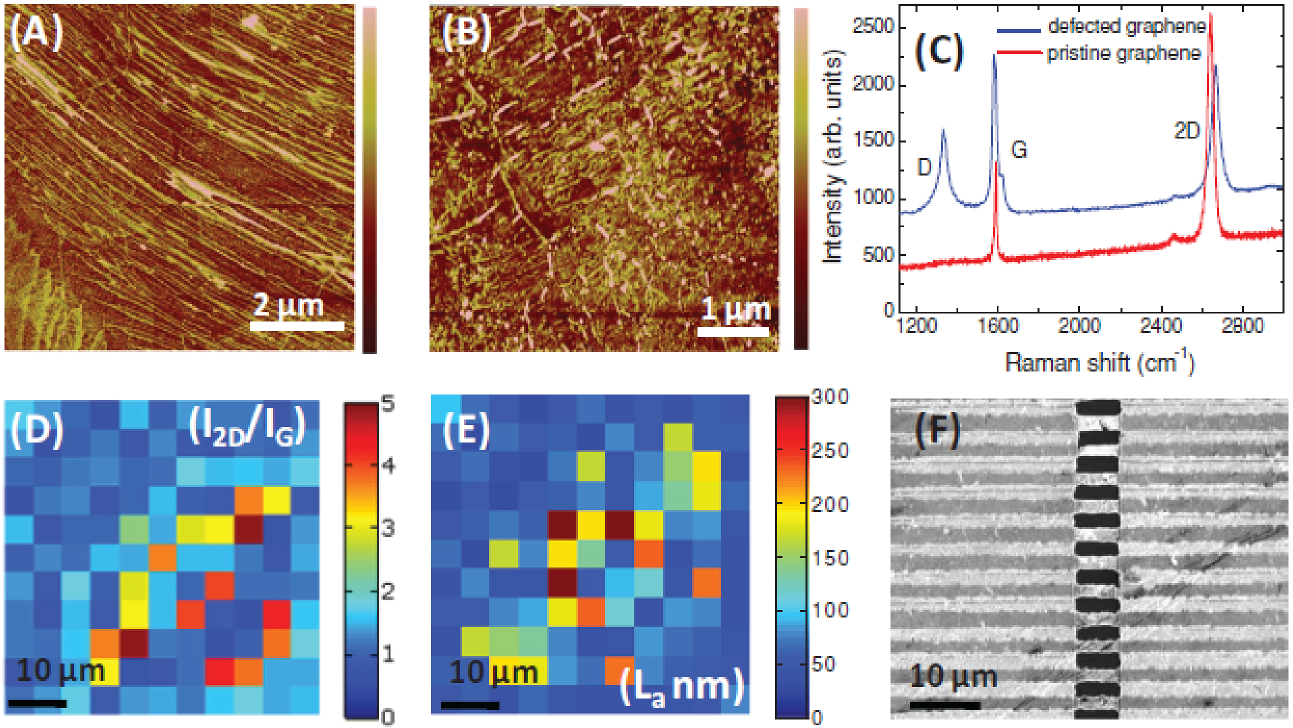
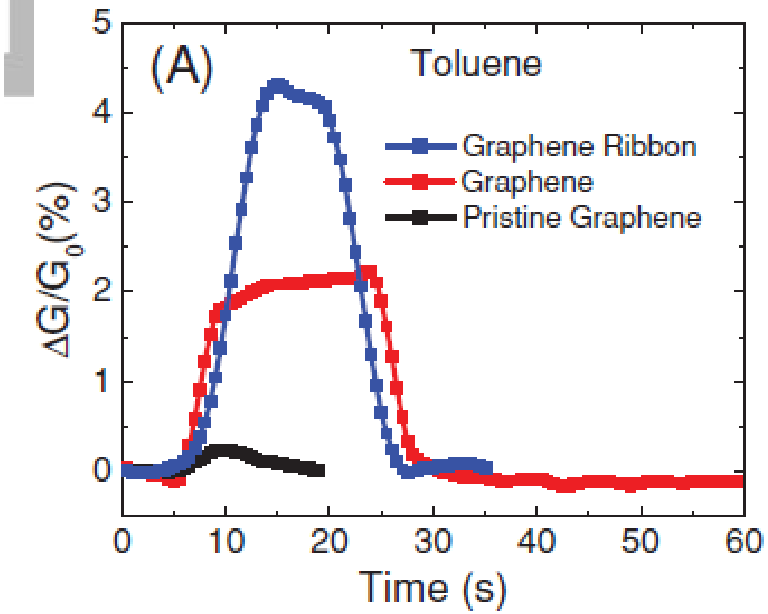


Figure 1. (A and B) AFM images of CVD graphene used for sensors, color scales are 10 and 5 nm, respectively, (C) Raman spectra of pristine and CVD-based "defective" graphene samples, (D) map of I_{2D}/I_G ratio indicating our CVD process produces mono to few layer graphene, (E) map of crystallite size indicative of 30 to >300 nm distance between line defects with an average L_a ~ 80 nm (see text), and (F) Scanning electron microscopy image of CVD graphene ribbons.



Cutting graphene in ribbons the width of which is comparable to the dimensions of line defects increases sensitivity to ppb levels.

A. Salehi-Khojin et al., *Adv. Mat.*, 24 (2012)

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

Conclusions and outlook (II)

- Single atom substitution brings about accurate control of surface properties of graphene
- Electrospinning of carbon nanofibers or laser scribed graphene are scalable techniques for producing unexpensive AQC sensors for mass market applications
- The previous techniques are well adapted for producing sensors on flexible substrates
- The analysis of low-frequency noise in carbon nanomaterials and, particularly, in graphene can be of interest for increasing selectivity