Gas sensing with CNTs: false and true stories

Andrea Goldoni

Elettra - Sincrotrone Trieste S.C.p.A., s.s. 14 Km 163,5
Ndwandwe
in Area Science Park, 34149 Trieste, Italy

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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

Silvano Lizzit, Luca Petaccia, Rosanna Larciprete, Luigi Sangaletti, Puleng Mbuyisa, Muzi Ndwandwe, Federica Rigoni, Maria Chiesa, Lorenzo Schiavina, Cinzia Cepek

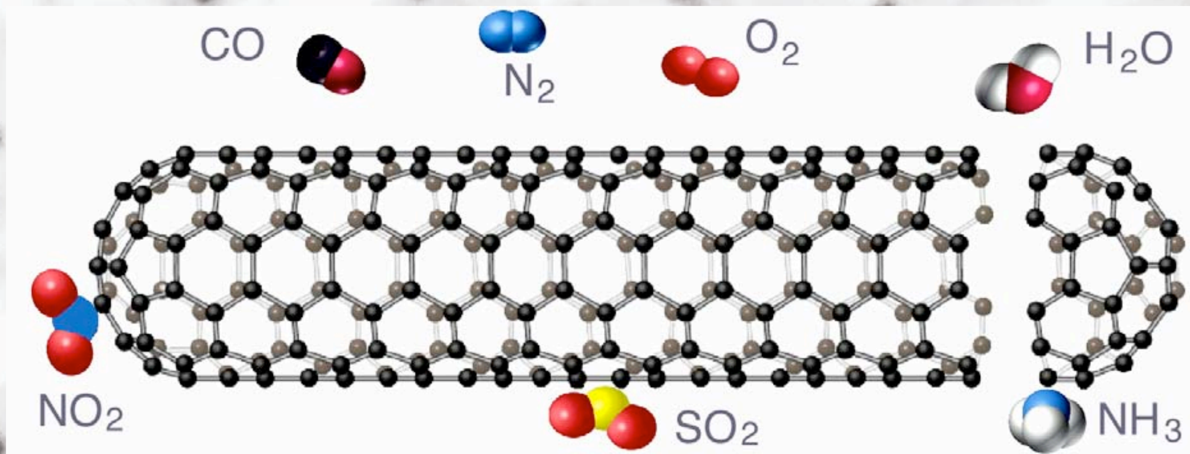
Elettra Synchrotron Light Source

Chemical Sensors with CNTs

Main characteristics that suggest CNTs as promising candidates for extremely sensitive gas sensors:

- High active surface and high aspect ratio

- Large changes in electronic properties due to very tiny external perturbations



Gas Ionization Sensor

- Measures breakdown voltage to identify gas
  - Nanotubes lower breakdown voltage by 65%
- Gas quantities determined by current discharge
- Advantages:
  - Independent of Temp. and Humidity
  - No absorption (quick recovery)
- Disadvantages:
  - Not good at low concentrations (~25ppm when combined with gas chromotography)

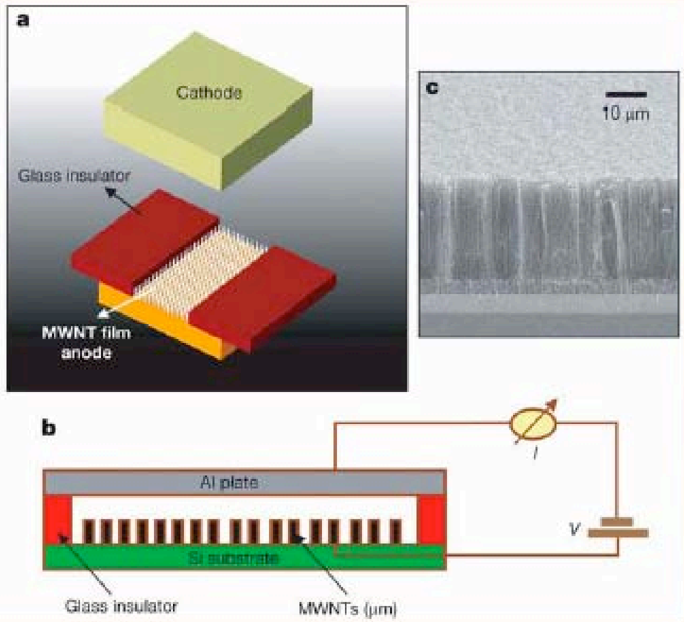
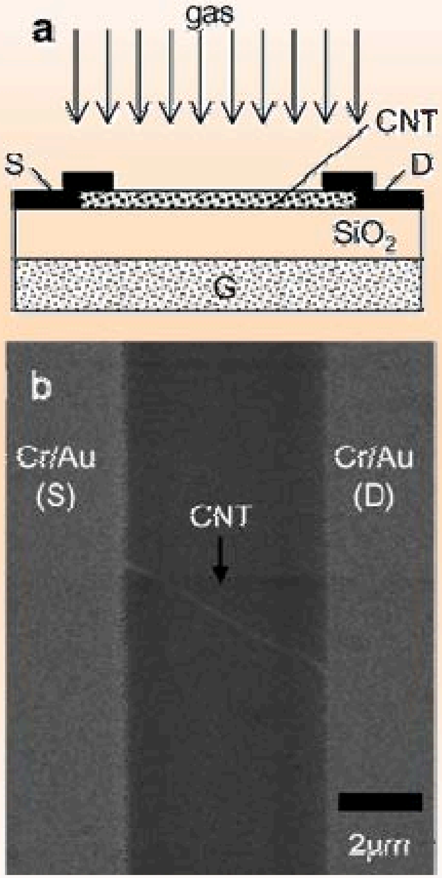


Figure 1 The nanotube sensor device. a, Exploded view of sensor showing MWNT film as the anode, 180-μm-thick glass insulator plates, and Al plate as cathode. b, Diagram of actual test set-up. c, SEM micrograph of a CVD-grown, vertically aligned MWNT film used as the anode.

A. Modi, N. Koratkar, E. Lass, B. Q. Wei and P. M. Ajayan: Nature, 2003, 424, 171–174.

FET- Based Sensor

- Measures drain current with given applied gate voltage
- Sensitivity on the order of ppm has been achieved
- Recovery time ~2 sec when gate voltage is removed
- Disadvantage: difficult to manufacture consistently

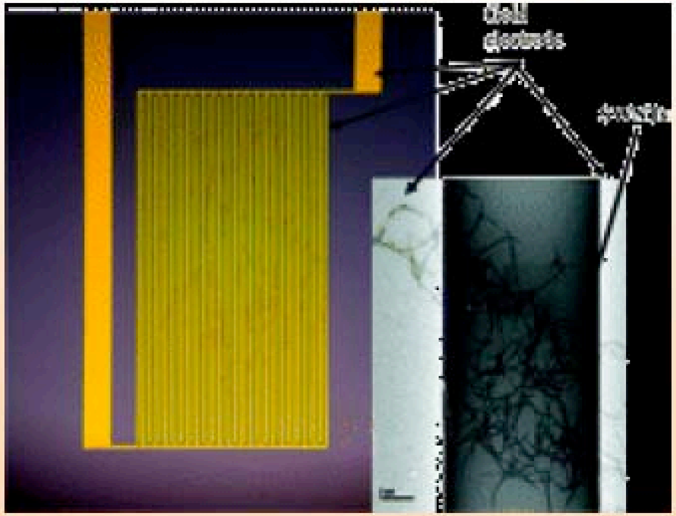


(1) Someya T et al. "Alcohol vapor sensors based on single-walled carbon nanotube field effect" transistors" Nano Letters Vol 3 p.877 2003

(2) Jing Li. et. al. "Carbon nanotube sensors for gas and organic vapor detection" Nano letters Vol. 3, P.929 2003

Chemoresistor

- Measures change in resistance
- CNTs form network on interdigitated electrodes (IDE)
- Enables electric contact between CNTs and electrodes over large areas
- Accessible for vapor adsorption to all CNTs
- Sensitivty:
  - < 44ppb for NO_2
- Recovery:
  - ~4sec

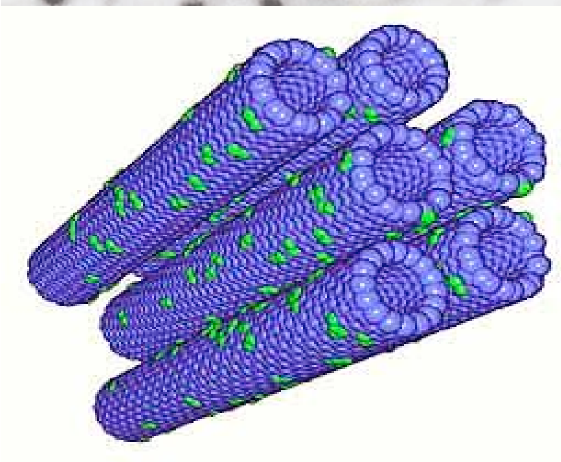


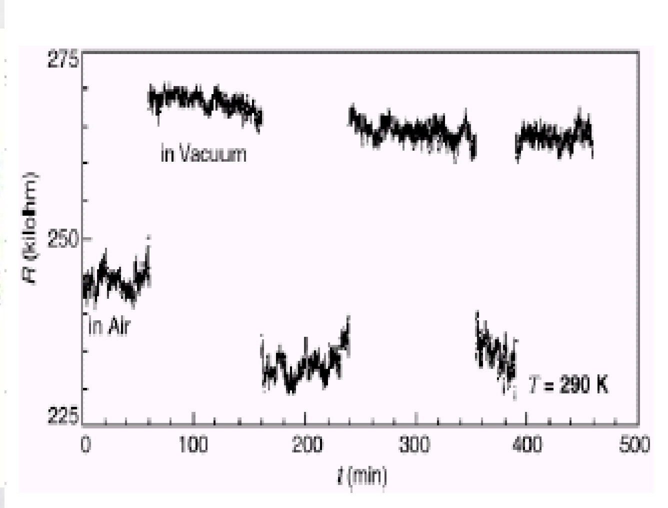
- MUCH cheaper than current solid-state sensors ($100 vs. $1500)
- Scalability limited only by lithography step

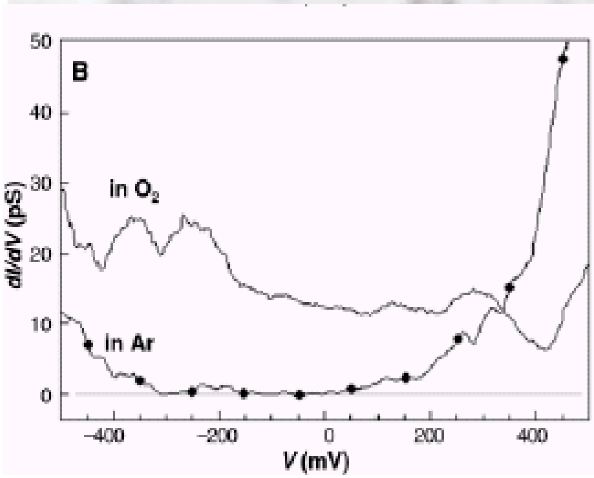
Jing Li. et. al. “Carbon nanotube sensors for gas and organic vapor detection” Nano letters Vol. 3, P.929 2003

O_2 sensitivity of electronic properties of SWCNTs

The electrical resistance of purified SWCNTs reversibly changes when the surrounding medium is cycled between vacuum and air.







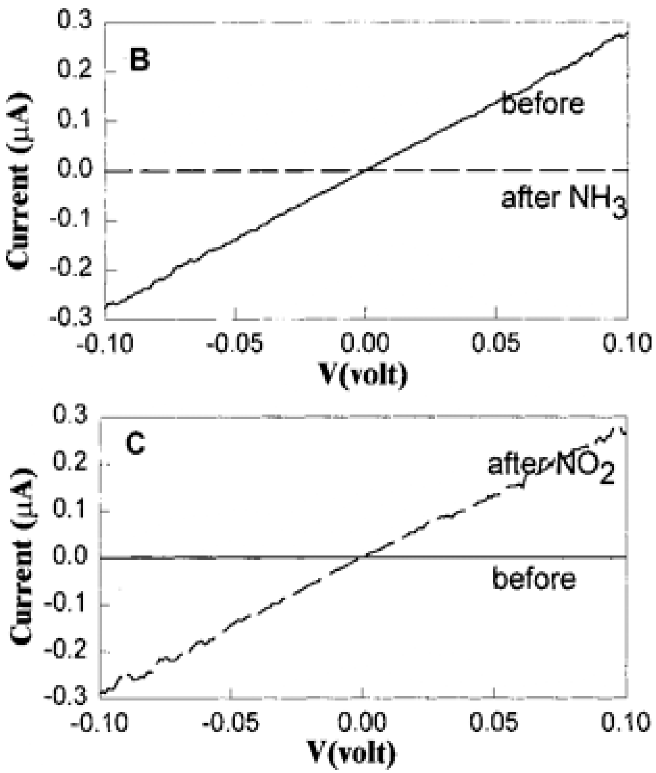
P. G. Collins *et al.*, Science 287 (2000) 1801

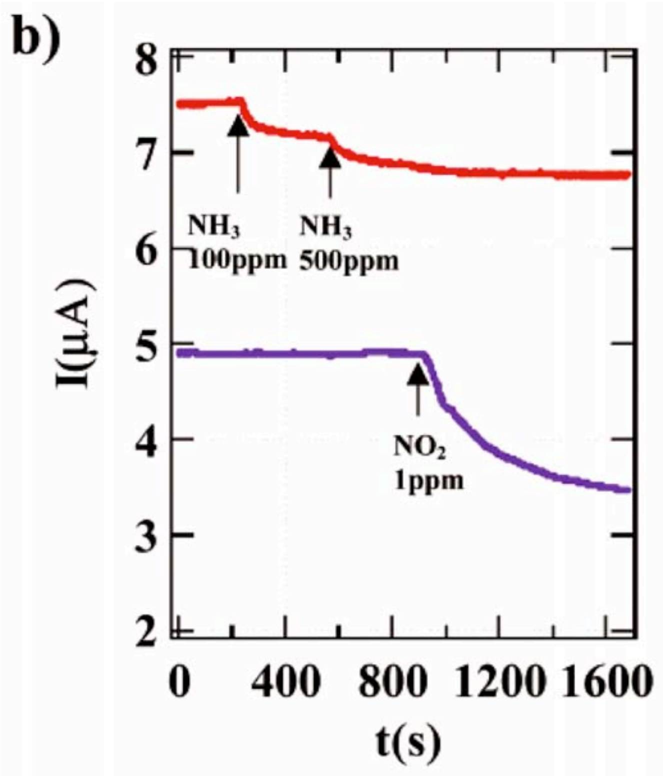
Room temperature exposure to air or oxygen reversibly tunes the electrical resistance and local density of states converting the behaviour of semiconducting tubes into metallic.

SWCNTs sensitivity to toxic molecules

For SWCNTs under NO_2 and NH_3 gas flow, it has been observed a dramatic change in the electrical conductivity.

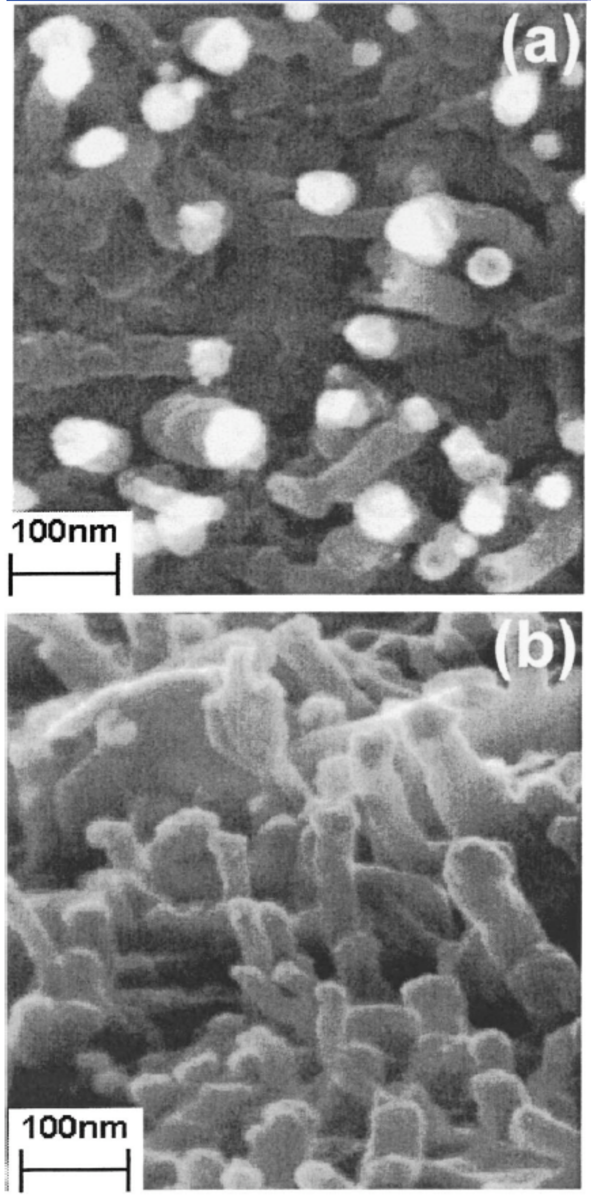
Effects reproducible, reversible and proportional to the amount of adsorbed molecules

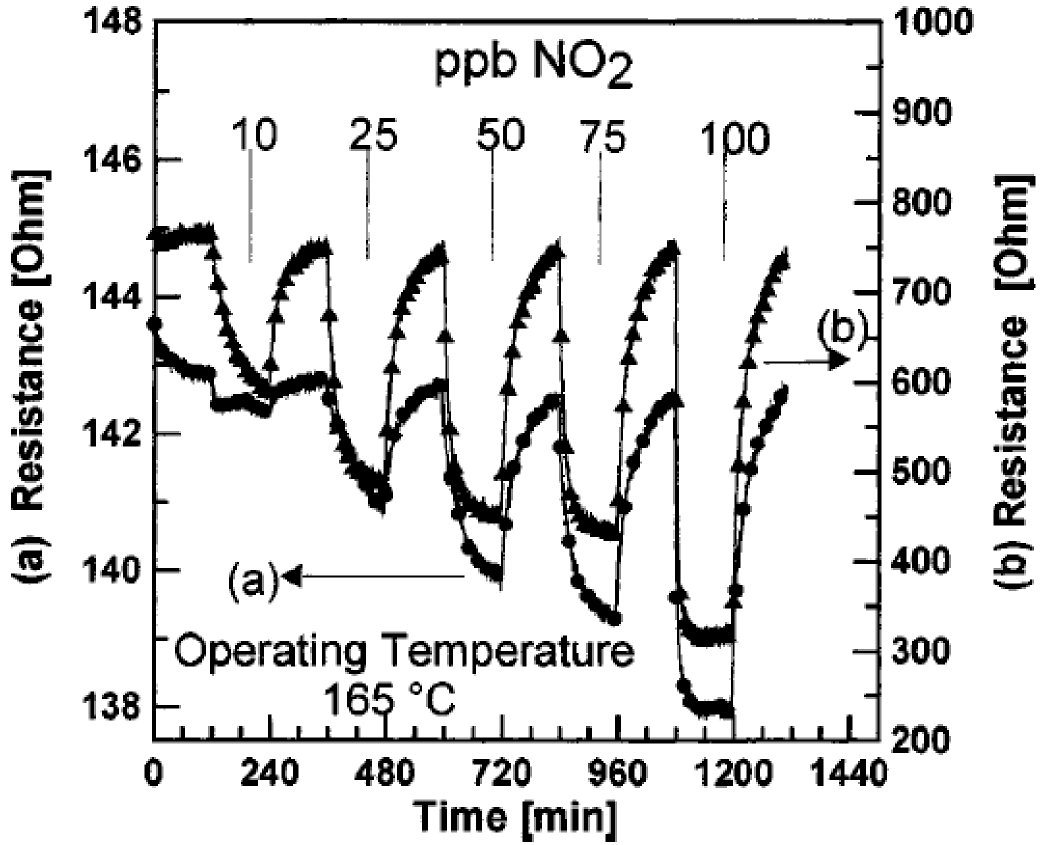




J. Kong *et al.*, Science 287 (2000) 622

As grown MWCNTs: similar behaviour





L. Valentini et al., App. Phys. Lett. 82, 961 (2003)

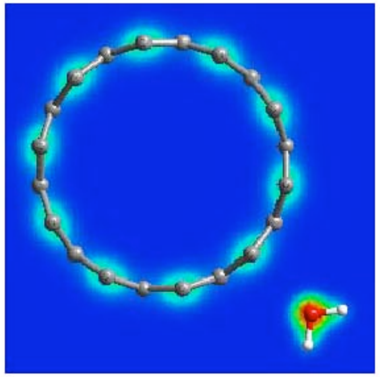
Table 1. Summary of selected sensing performance of pristine CNT chemiresistors and ChemFETs. (Note: N/S = Not-stated.)

CNT type	Sensor configuration	Targeted analytes	Detection limit	Response time (s)	Reversibility	Reference
Single SWNT	ChemFET	NO_2, NH_3	2 ppm (NO_2) 0.1% (NH_3)	<600	Irreversible	Kong *et al* [21]
SWNTs	ChemFET	Alcoholic vapors (methanol, ethanol, 1-propanol, 2-propanol, and tert-butanol.)	N/S	5–150	Reversible (−20 V gate bias potential)	Someya *et al* [22]
SWNTs	Chemiresistor	O_2	N/S	N/S	Reversible	Collins *et al* [23]
SWNTs	ChemFET	DMMP	<1 ppb	1000	Reversible (3 V gate bias)	Novak *et al* [24]
MWNTs	Chemiresistor	NO_2	10 ppb	N/S	Reversible (165 °C)	Valentini *et al* [26]
SWNTs	Chemiresistor	NO_2, Nitrotoluene	44 ppb (NO_2), 262 ppb (Nitrotoluene)	600	Reversible (UV)	Li *et al* [27]
MWNTs	Chemiresistor	NH_3	10 ppm	~100	Reversible	Suehiro *et al* [28]
SWNTs	Chemiresistor	$SOCl_2$, DMMP	100 ppm	10	Irreversible	Lee *et al* [29]
SWNTs	Chemiresistor	O_3	6 ppb	<600	Reversible	Wongwiriyapan *et al* [31]
MWNTs	Chemiresistor	NO_2	5–10 ppb	~600 (165 °C)	Reversible (165 °C)	Valentini *et al* [35]
SWNTs	Chemiresistor	methanol, acetone	N/S	~100	N/S	Robinson *et al* [36]
SWNTs	Chemiresistor	H_2O	N/S	10–100	Reversible	Watts *et al* [37]
Carboxylated SWNT	Chemiresistor	CO	1 ppm	~100	Reversible	Fu *et al* [40]

Pristine “pure” CNTs at room temperature are sensitive to the environmental world around them because the molecules are interacting with the nanotube walls. (???)

•Advantages: SWCNT-based chemical sensors

- **High adsorption surface area**
- **Detect very small concentrations (ppb) of O_2, NO_2, NH_3 , etc.**

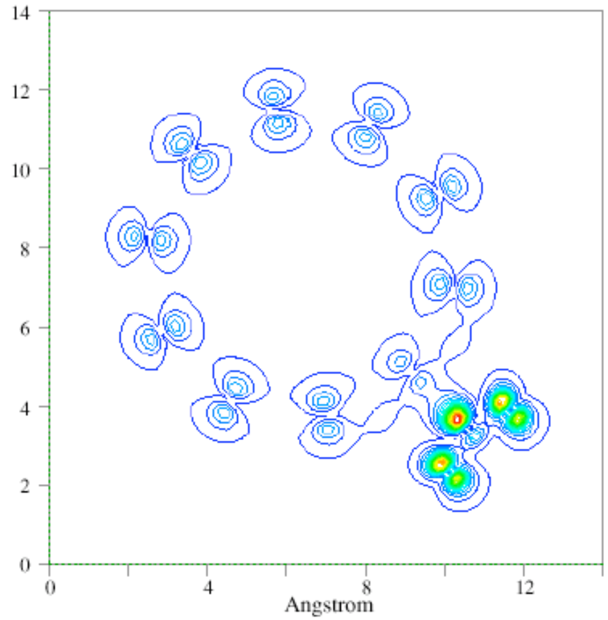


•Disadvantages

•Protection needed for CNTs used in electronic devices because of sensitivity to oxygen/air

How does it work?: charge transfer via direct interaction of the gas molecules with the nanotubes.

Possible artifact: interaction with other molecules (contaminants) or metals (also contacts) already bonded to the nanotubes or defects, may hide or simulate an interaction with the nanotube.



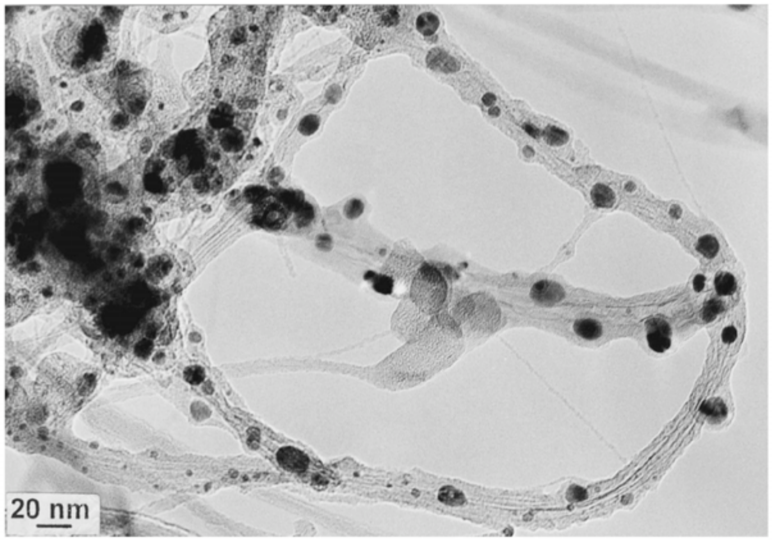
Even in purified SWCNTs there are many contaminants

Purification Method for SWCNTs

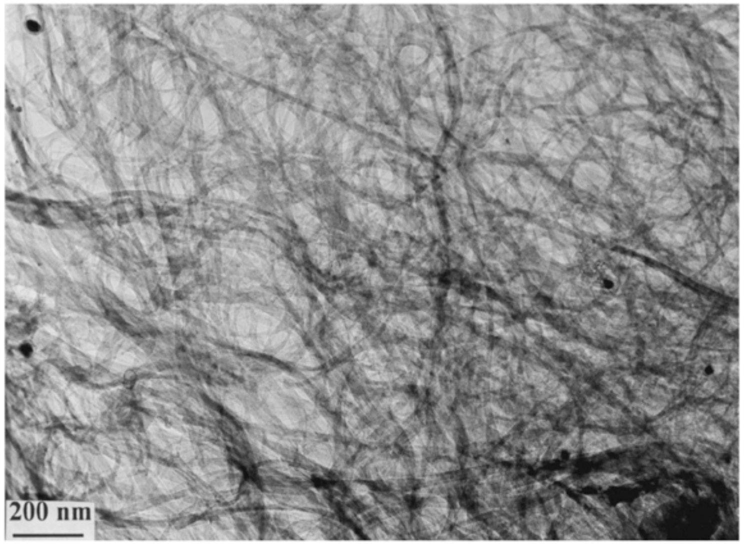
J. Liu *et al.*, Science **280**, 1253 (1998)

Several treatments of the as-grown material in a nitric/sulfuric acid solution to remove the metal catalyst species. Washing in de-ionized water and methanol refluxes. Oxidation in a mixture of sulfuric acid and hydrogen peroxide to burn other carbonaceous material. Washing in NaOH reflux. SWCNTs can be dissolved/dispersed in aqueous solutions containing surfactant (Triton X-100, SDS): filtration gives SWCNT bucky-papers

Before



After



Our experiment

AIM: study of the interaction between SWCNTs and gas phase molecules: O_2, H_2O, SO_2, NH_3, NO_2 …

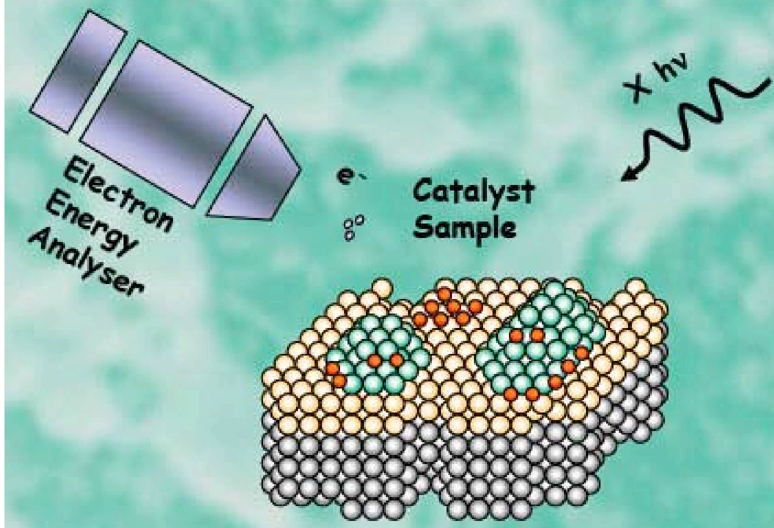
METHODS: x-ray emission, SEM and Raman (ex-situ),

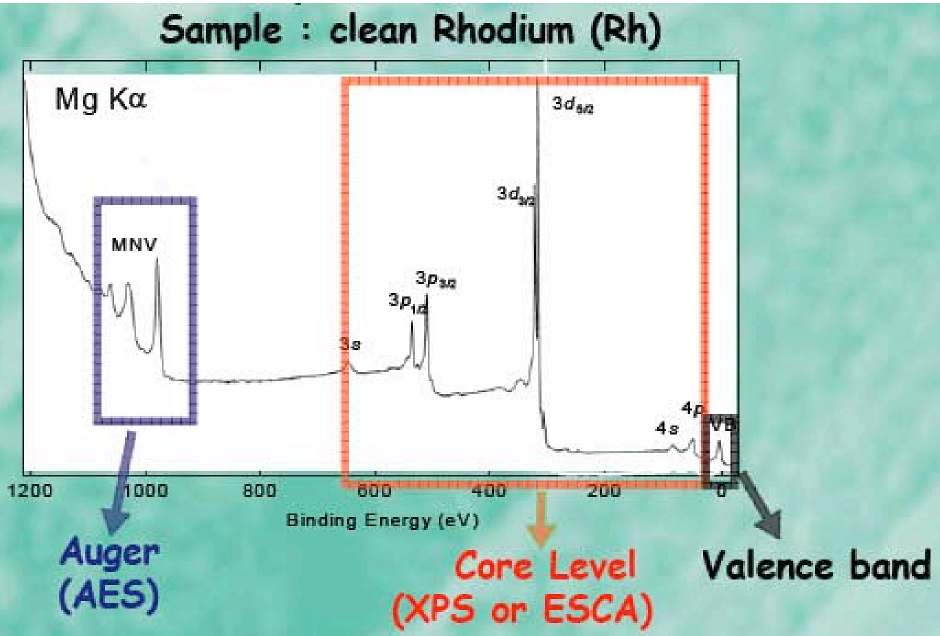
EELS & fast- photoemission spectroscopy

@ SuperESCA beamline, ELETTRA (Trieste, Italy)

SAMPLE: commercial *bucky paper* (purity > 90% vol. according to the producer) made of single-walled nanotubes with an average diameter of 1.2-1.3 nm

Photoemission Spectroscopy





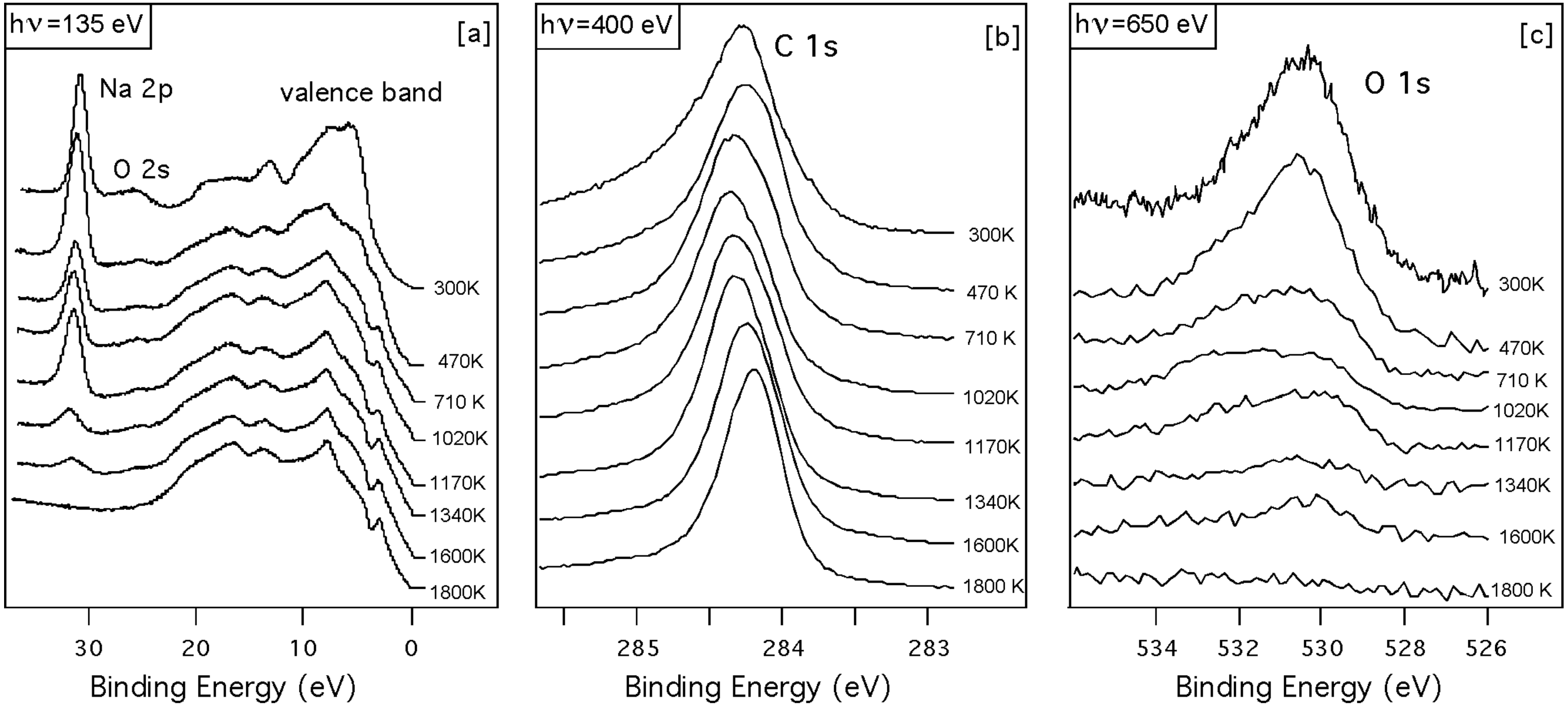
Advantages of XPS

1. Atomic and molecular species sensitivity
2. Quantitative analysis: chemical species population directly on catalyst surface
3. BE variations or Chemical Shifts ⇒ oxidation state, chemical environment, nanoparticles and/or support geometric/electronic structure changes.

With Synchrotron Radiation

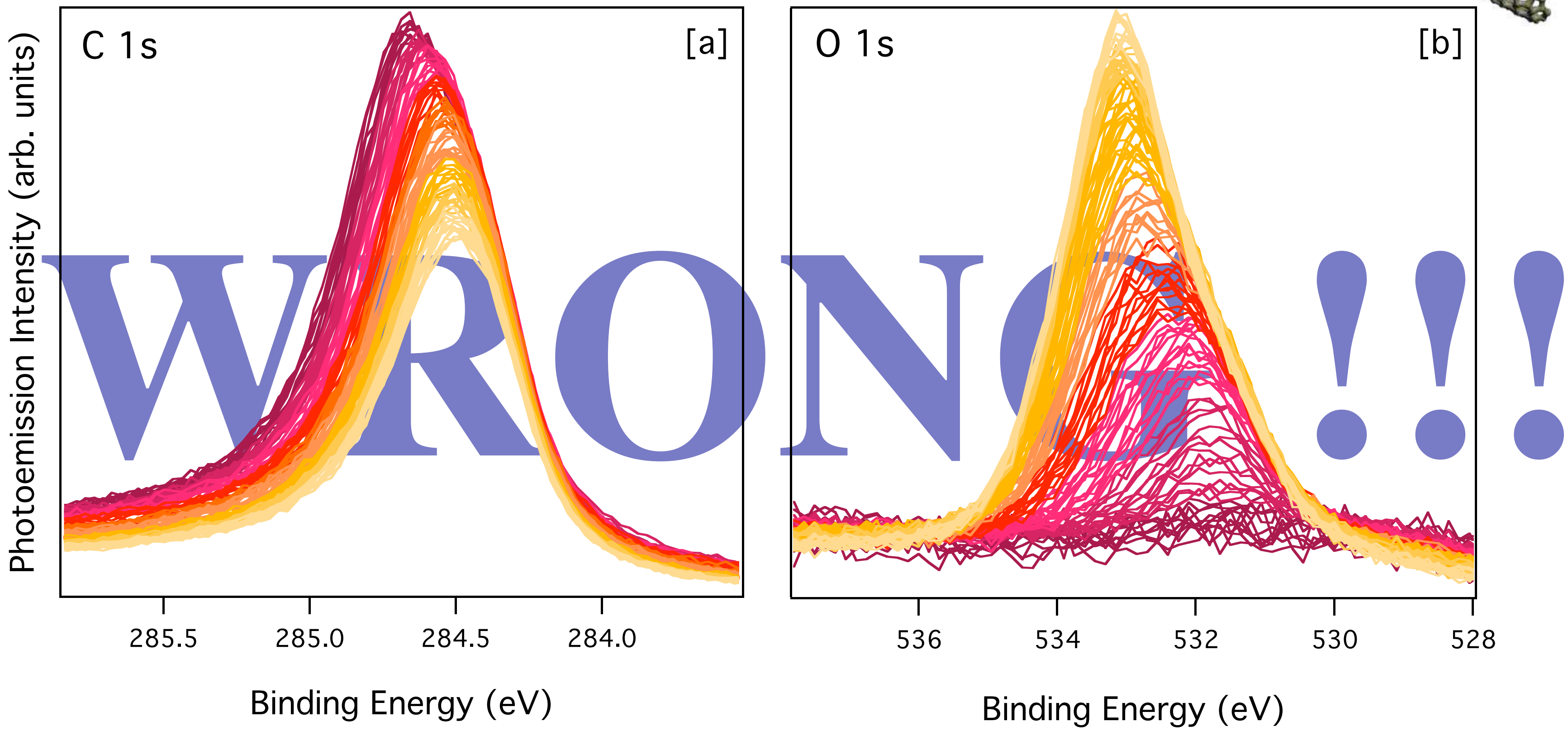
1. Tunability, Photon flux, Energy resolution available at the same time
2. Higher sensitivity to elemental composition (<1% ML), higher surface sensitivity, acquisition times <100 ms/spectrum) to follow surface time-dependent phenomena in RealTime.
3. Well suited for the study of low atomic density systems like nano-catalysts

The first (not complete) cleaning procedure



Flash @ 1800 K in UHV for t ~ 60 s

Exposure to O_2 at 150 K

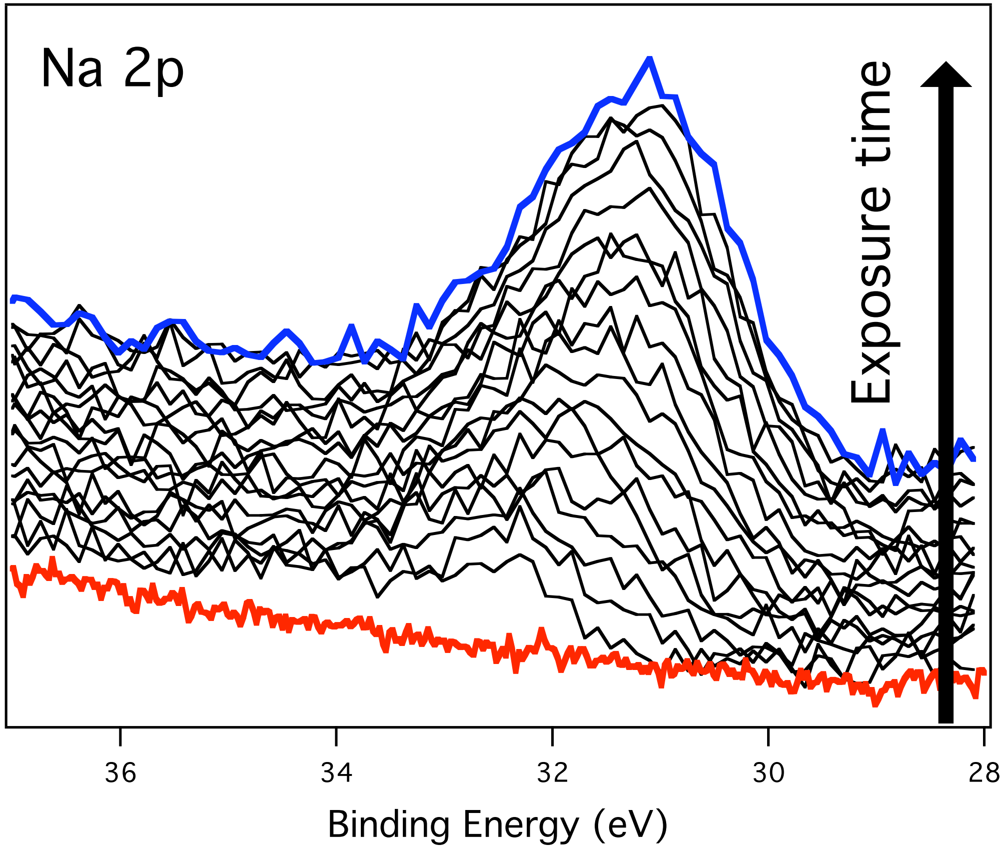


peak shifts and line shape modifications are reversible

Oxygen reversibly influences the electronic properties of SWCNTs ?

Same suggestion as Collins *et al.*, *Science* (10 March 2000)

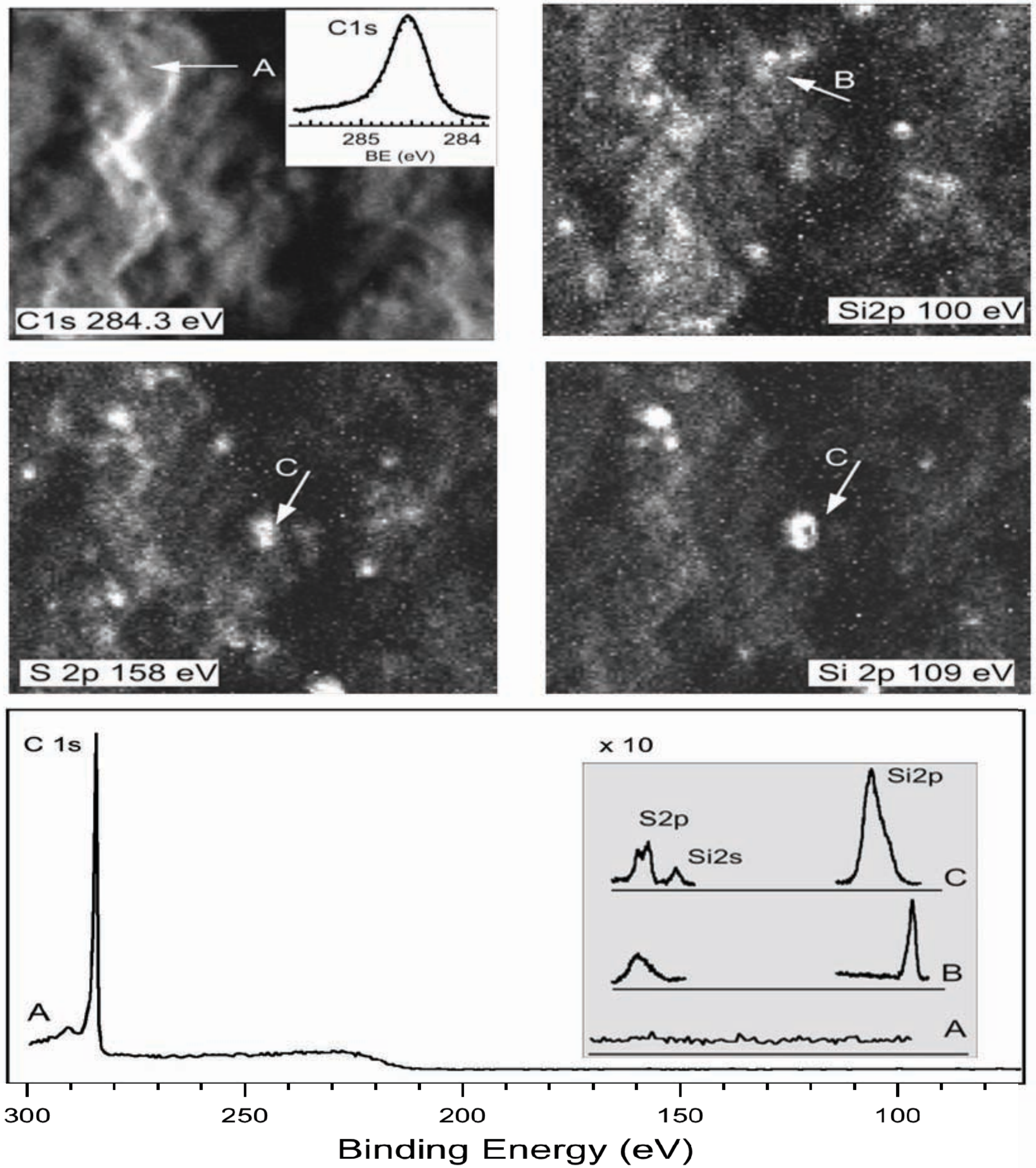
Flashes at 1800 K are effective in removing Na from the near surface layer, but after that new Na impurities segregate from the bulk under the x-ray beam



Sodium from purification (SDS surfactant, NaOH bath)

Sodium atoms diffuse toward the surface under the beam

The correct cleaning procedure



After the flash at 1800 K needed to remove Ni, Na is completely removed by annealing at 1270 K in UHV for t > 2 h

Only S and Si are left as localized clusters that do not interfere with SWCNTs

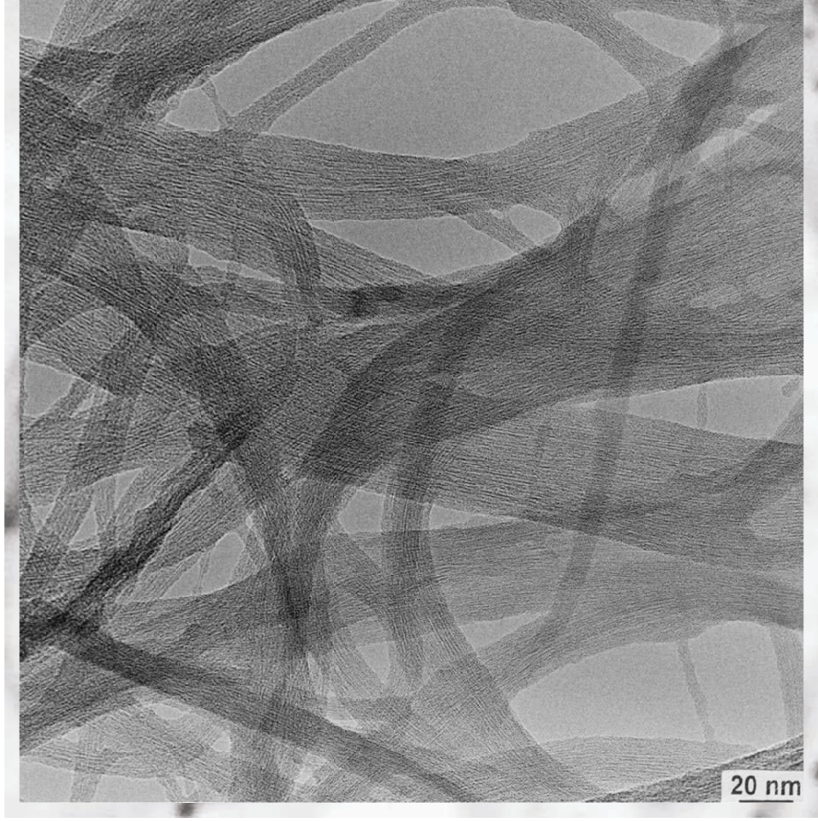
We consider these SWCNTs as clean

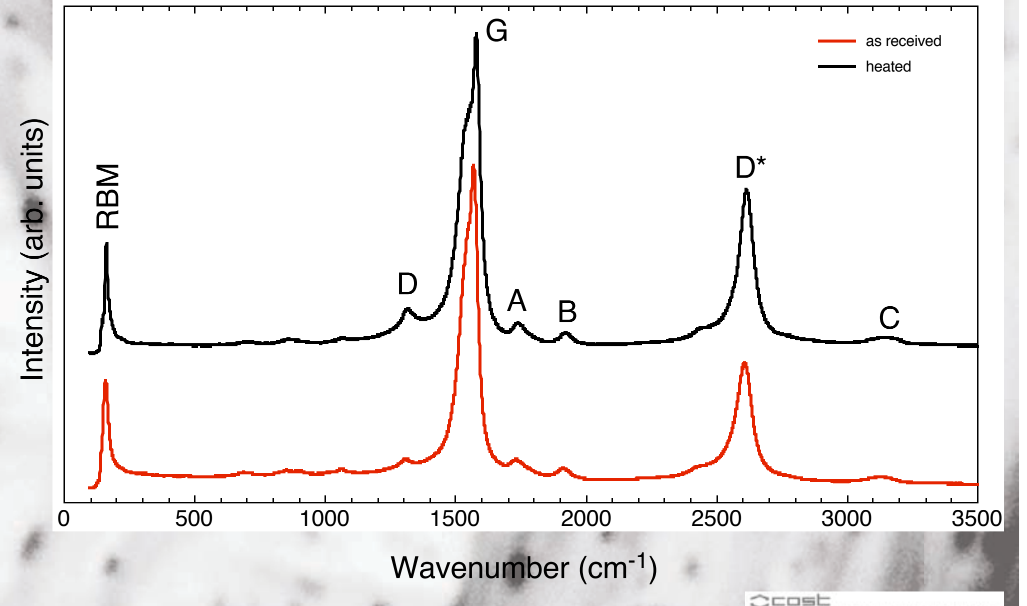
After the high-temperature UHV annealing (removal of contaminants)

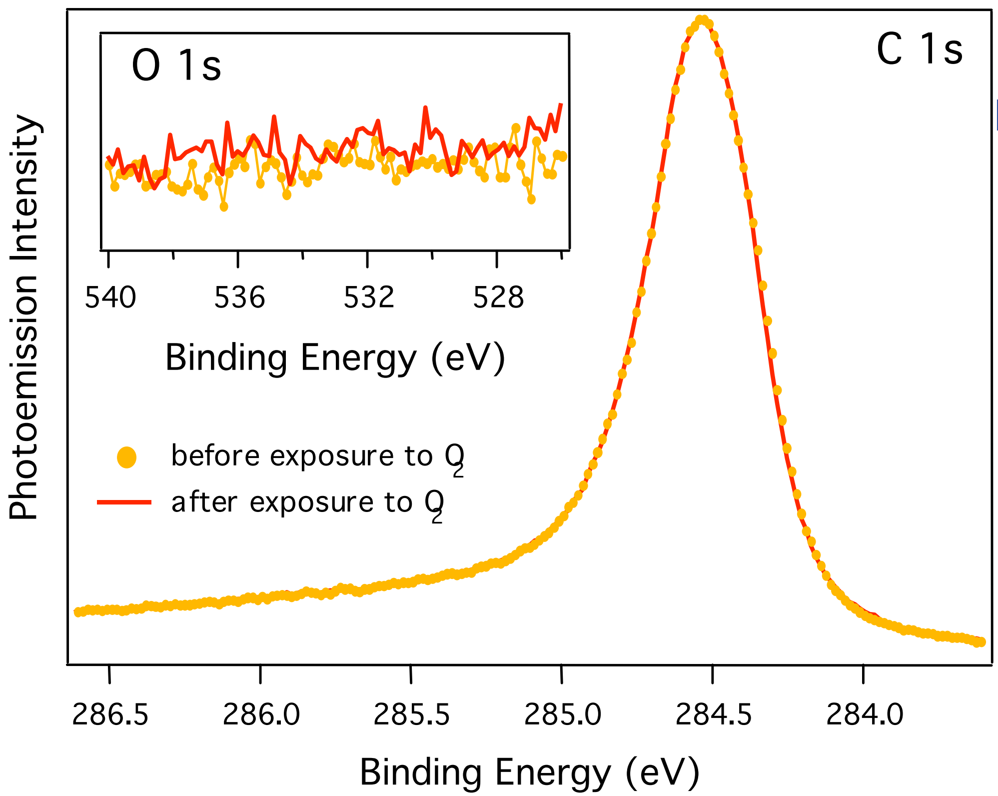
Annealing-out of defects
Improved SWCNT network
Closed caps

(M. Monthioux et al., Carbon 39 (2001) 1251)

No significant changes in Raman and EEL spectra compared to the pristine sample: no formation of graphitic material or merging in multi-walled structures







O_2 exposure @ 150 K

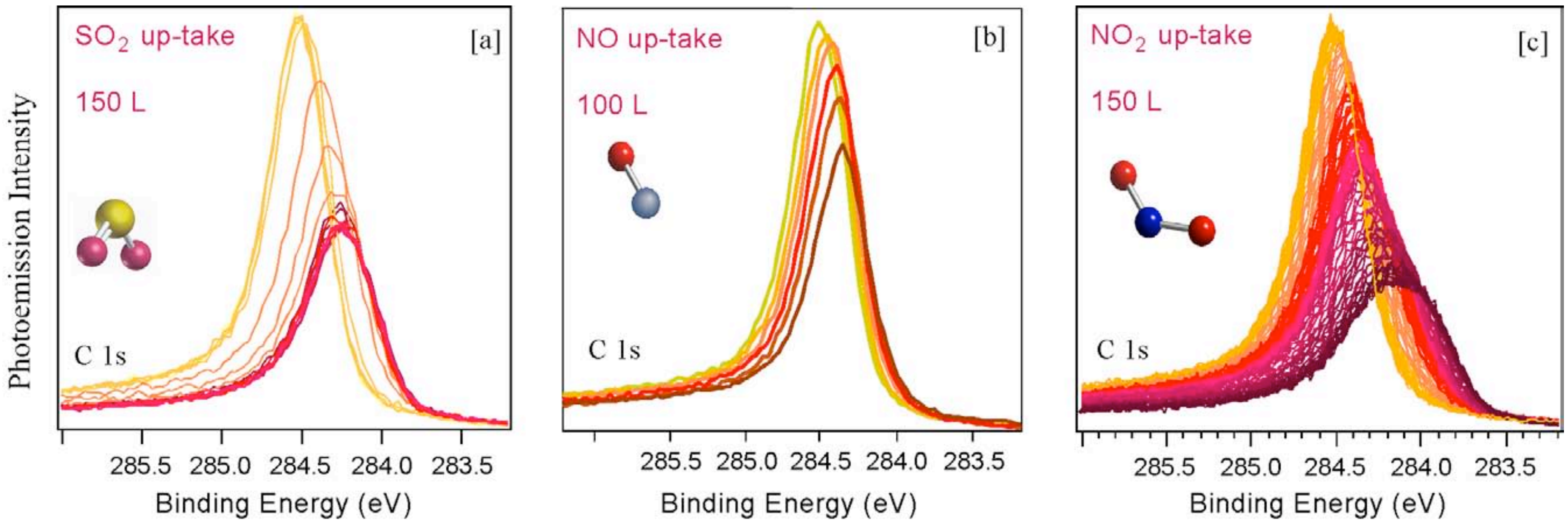
After accurate cleaning from contaminants (mainly Ni and Na) no oxygen adsorption or oxygen effect on the C 1s.

The same is true for N_2, H_2O, CO and air.

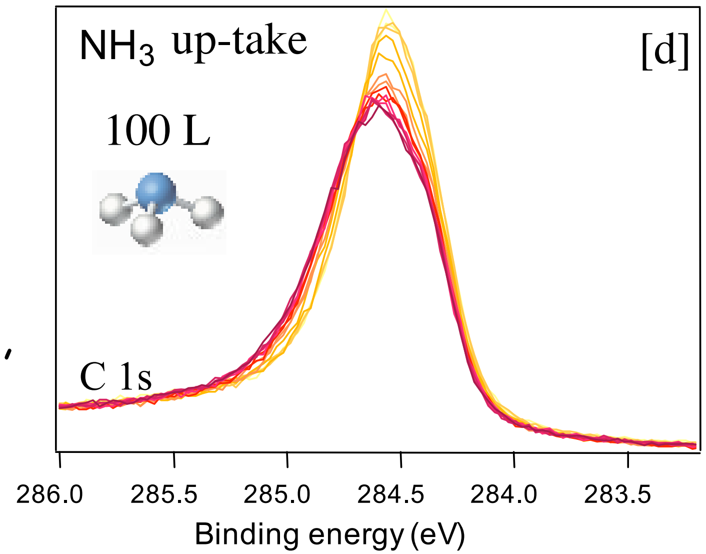
Agreement with other experiments [H. Ulbricht et al , *Phys*. *Rev*. *B* **66**, 075404 (2002)] and calculations [P. Giannozzi et al., *J*. *Chem Phys*. **118**, 1003 (2003)].

It suggests that the presence of contaminants bonded to SWCNTs may simulate a strong sensitivity to oxygen (Collins *et al., Science (2000)*) and other gases

SO_2 , NO, NH_3 and NO_2 exposure @ 150 K



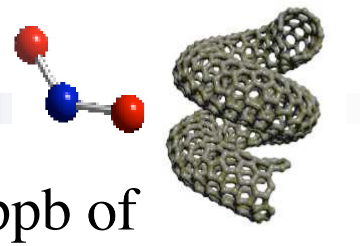
SO_2, NO and NO_2 are strong oxidizer,
charge is moved from NTs to molecules,
shift of C1s toward low BE

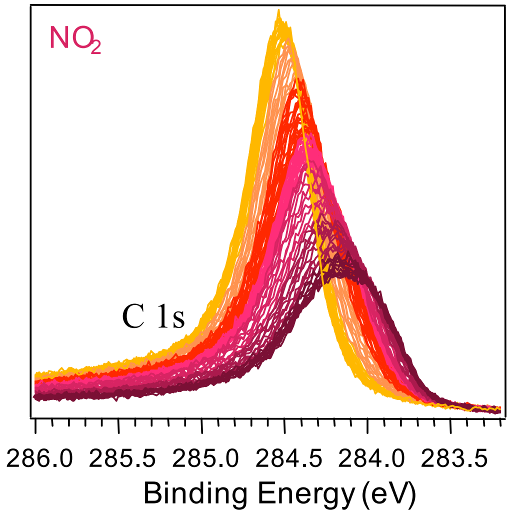


NH_3 has a lone pair that can be donated to NTs,
shift of C1s toward high BE

A. Goldoni et al., J. Am. Chem. Soc. 125, 11329 (2003)

NO_2 exposure @ 150 K

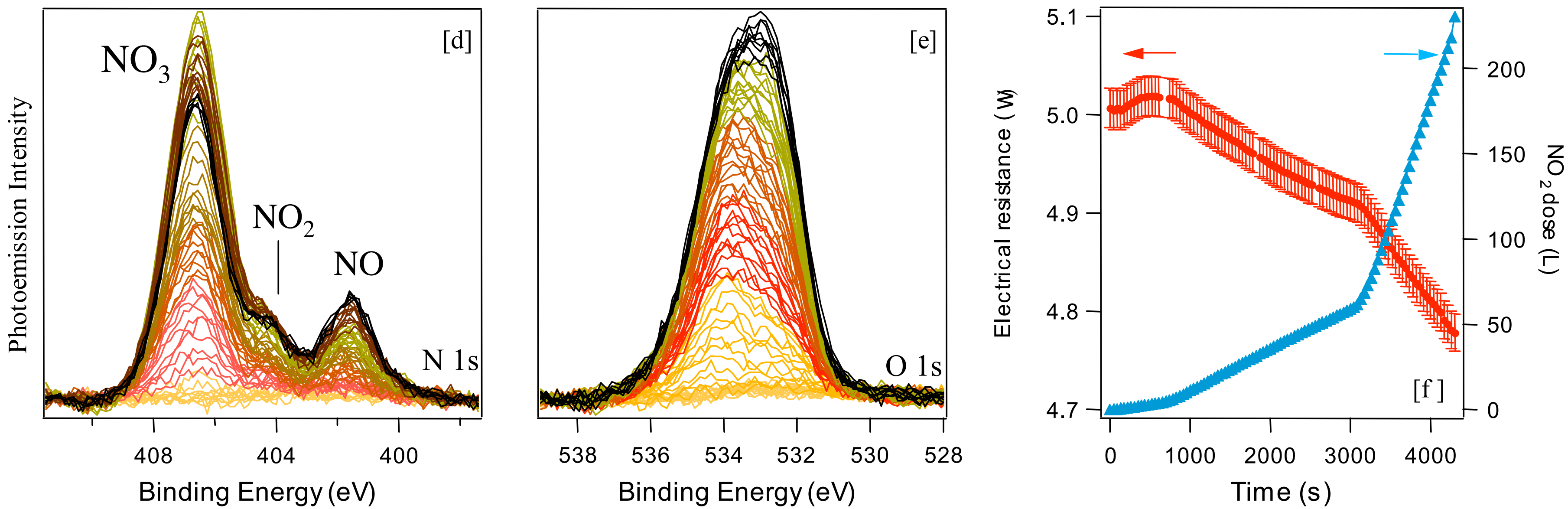




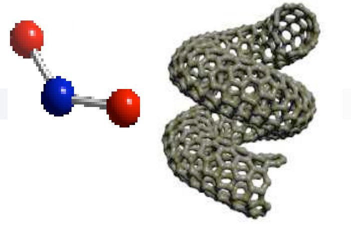
2% of variation after ~ 40 L, i.e. 10 ppb of toxic molecules in 4 sec.

(same as P. Qi et al., Nano Lett. 3 (2003) 347)

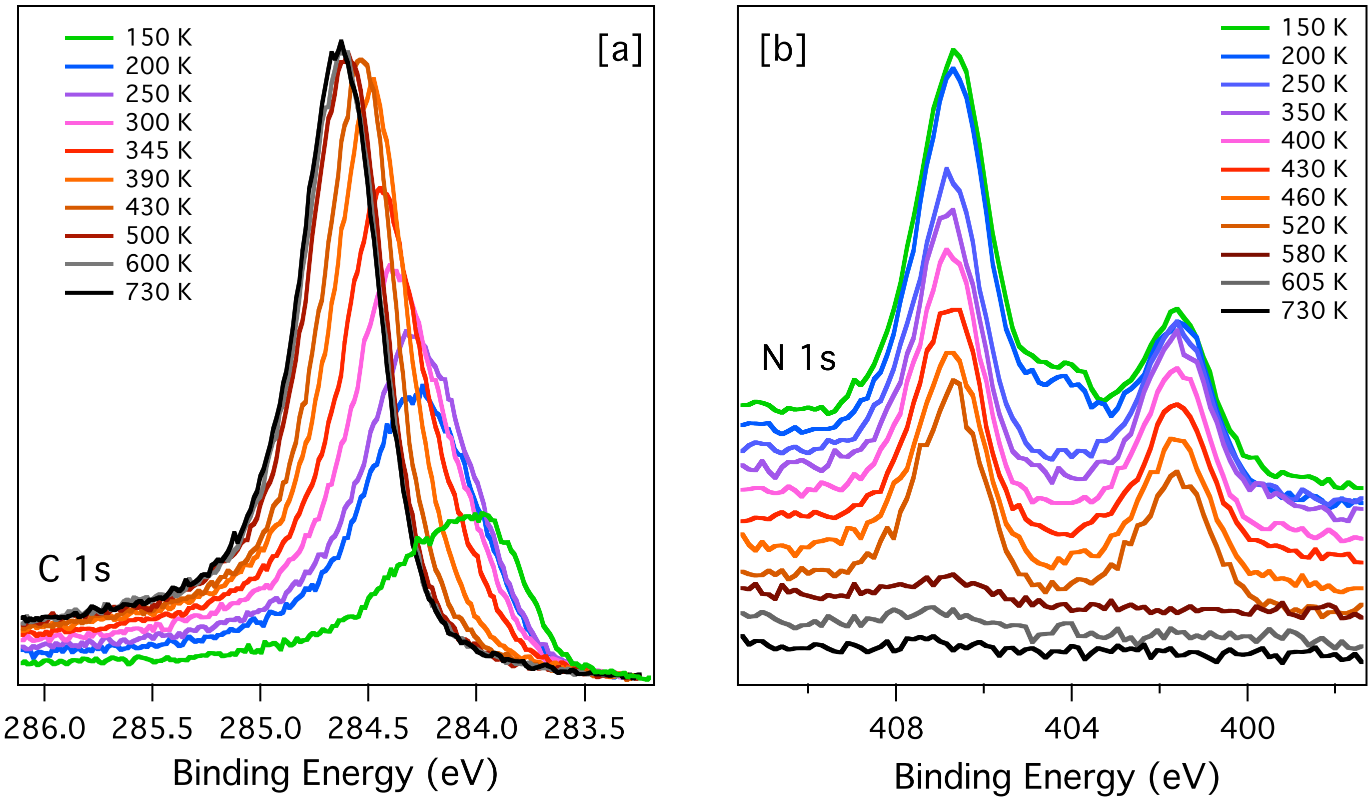
Typical polymer-based or SnO_2-based detectors: a few ppm in 1 min.



Thermal desorption of NO_x species



Reversible

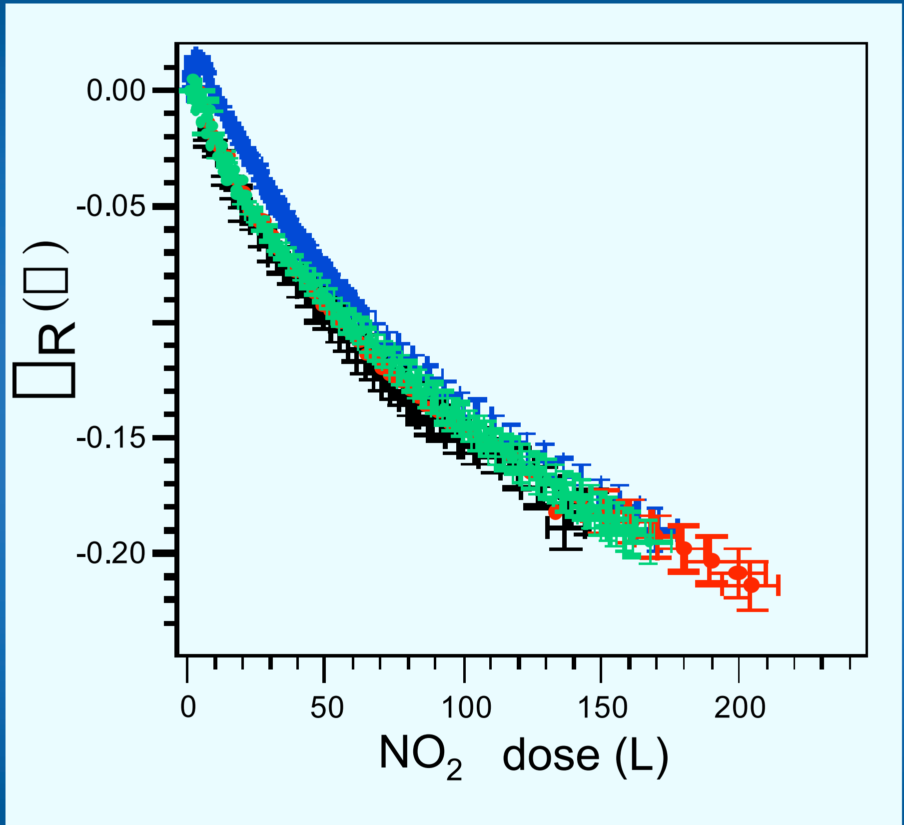


NO_3 and NO chemisorbed, NO_2 physisorbed

A. Goldoni et al., Carbon 42, 2099 (2004)

Later confirmed by calculations (S. Peng et al. Chem Phys. Lett. 387, 271 (2004))

SO_2, NO_2 adsorption on SWCNTs at 150 K

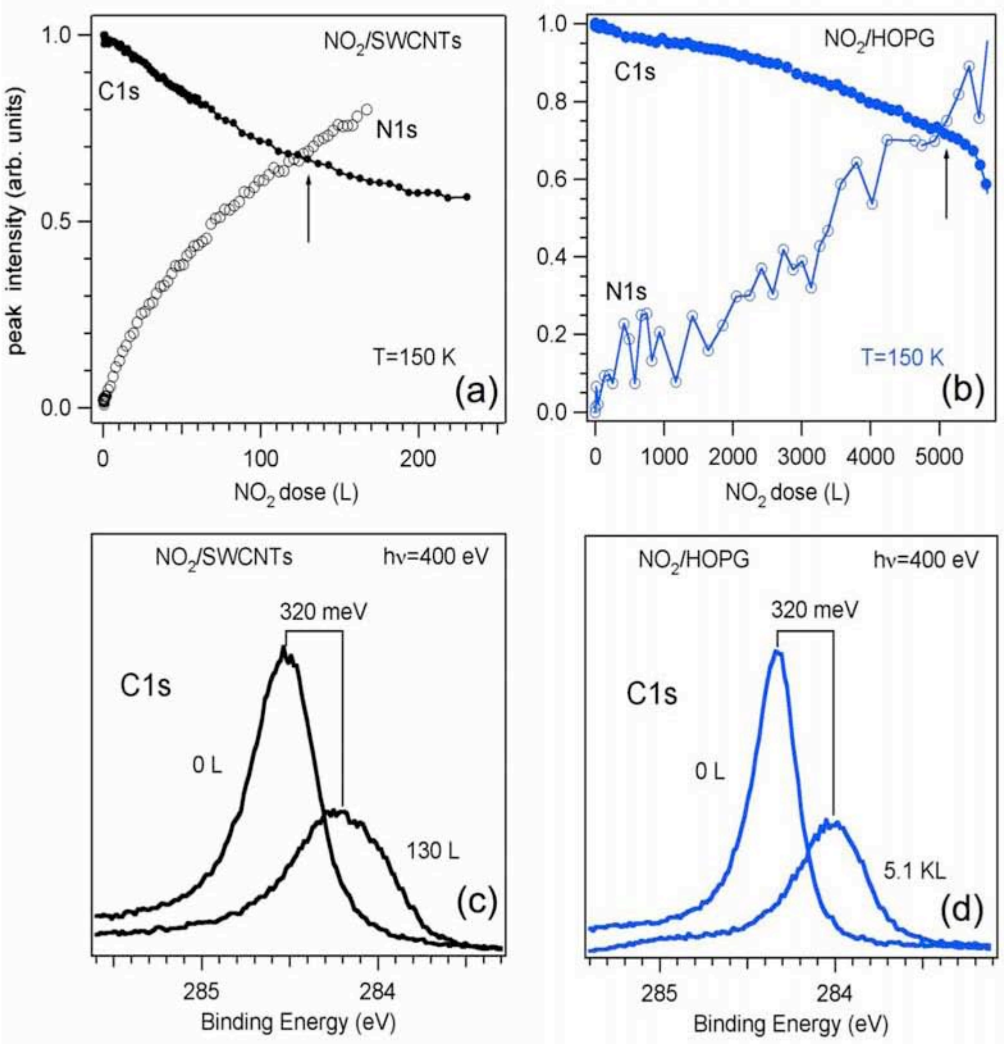


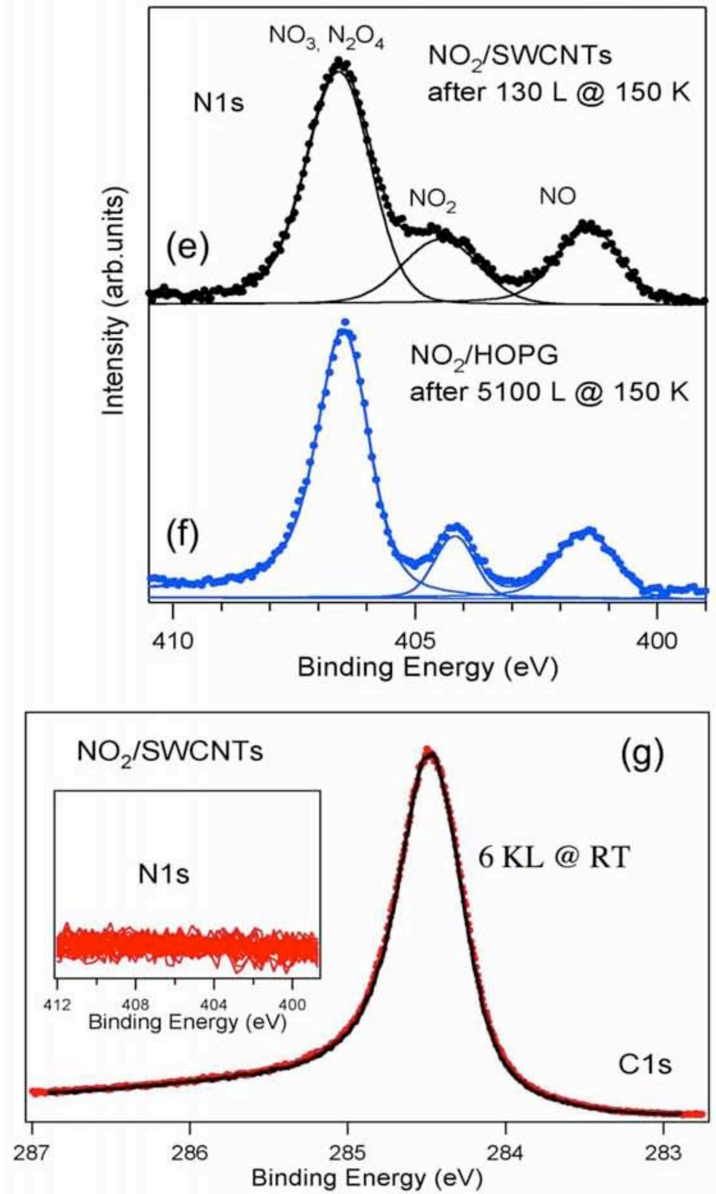
SENSITIVITY

variation in the transport properties of SWCNTs are detectable well above the noise level after exposing the sample to 40 L of toxic gas

40 L means an exposure to a partial pressure of 10^{-5} mbar (i.e. 10 ppb of toxic molecules in air at atmospheric pressure) for about 4 s

Nanotubes and Graphite HOPG

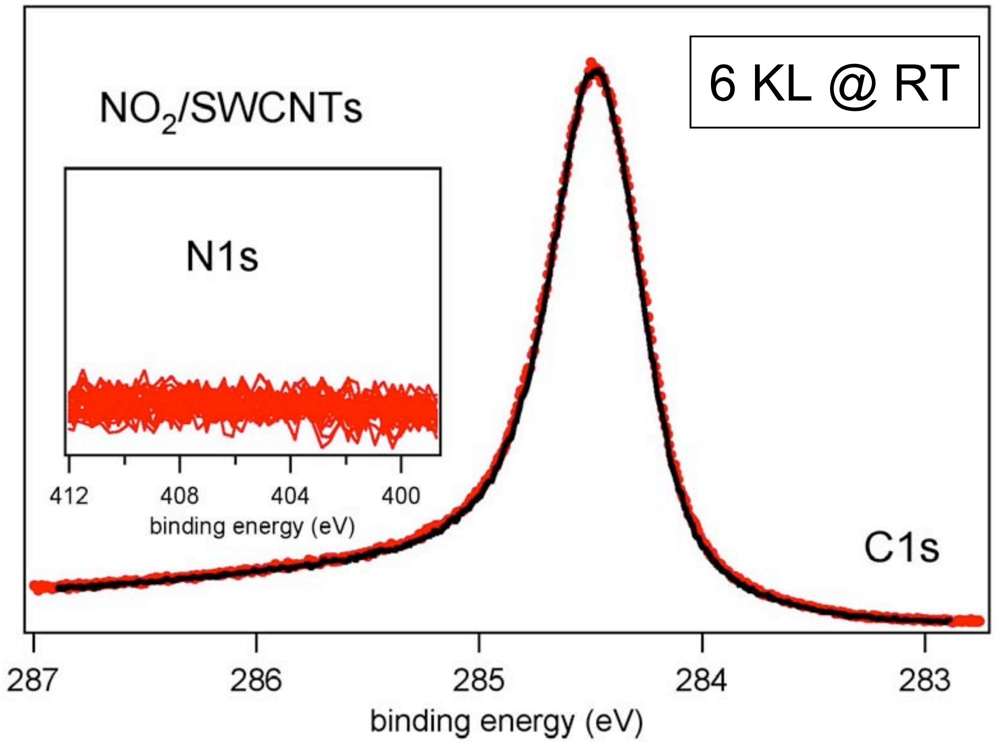




Apart sensitivity CNTs behave like graphite

Nanotubes and Graphite

The same kind of NO_x molecular species, i.e. the same kind of chemical interactions. Apart sensitivity CNTs behave like graphite

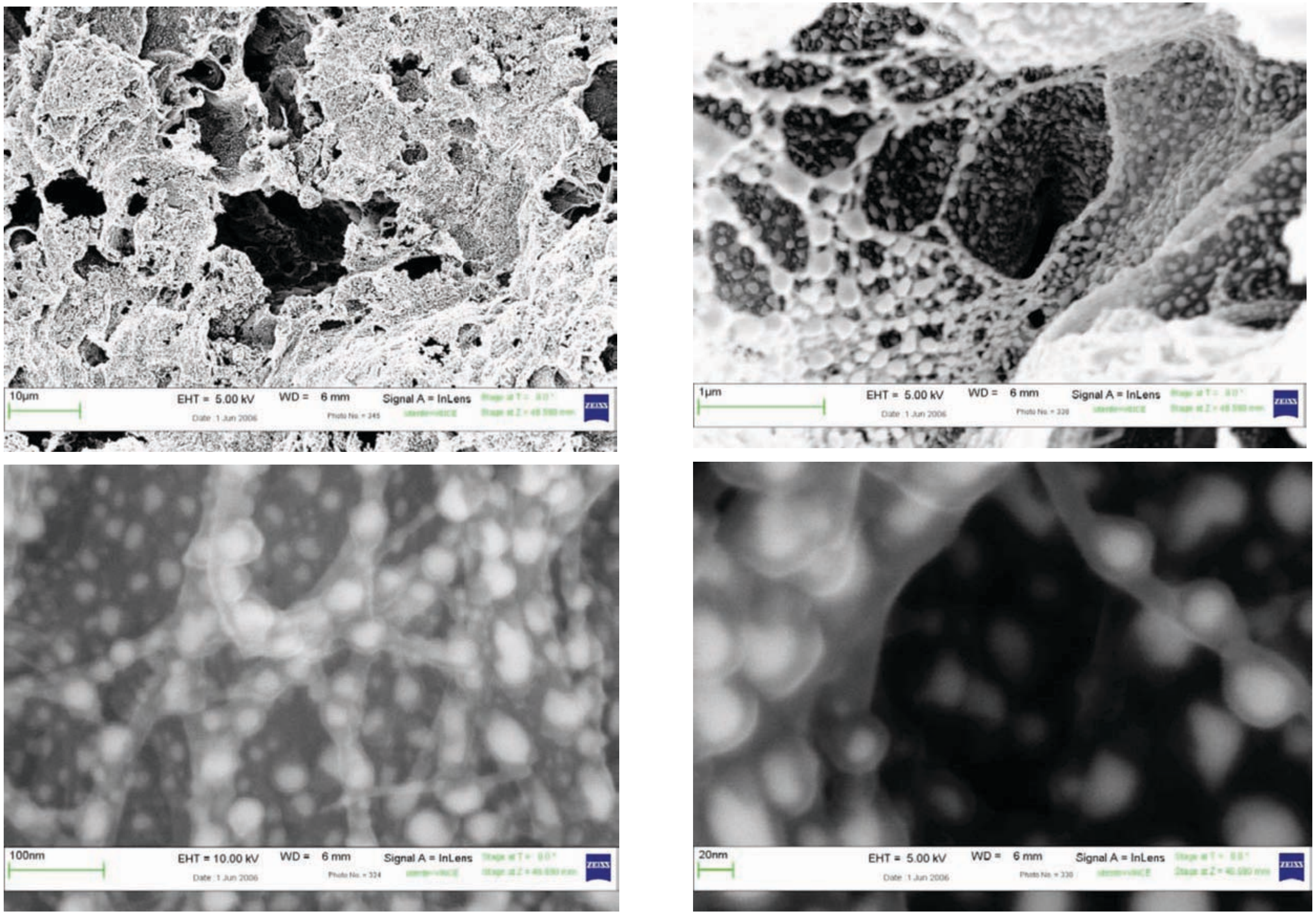


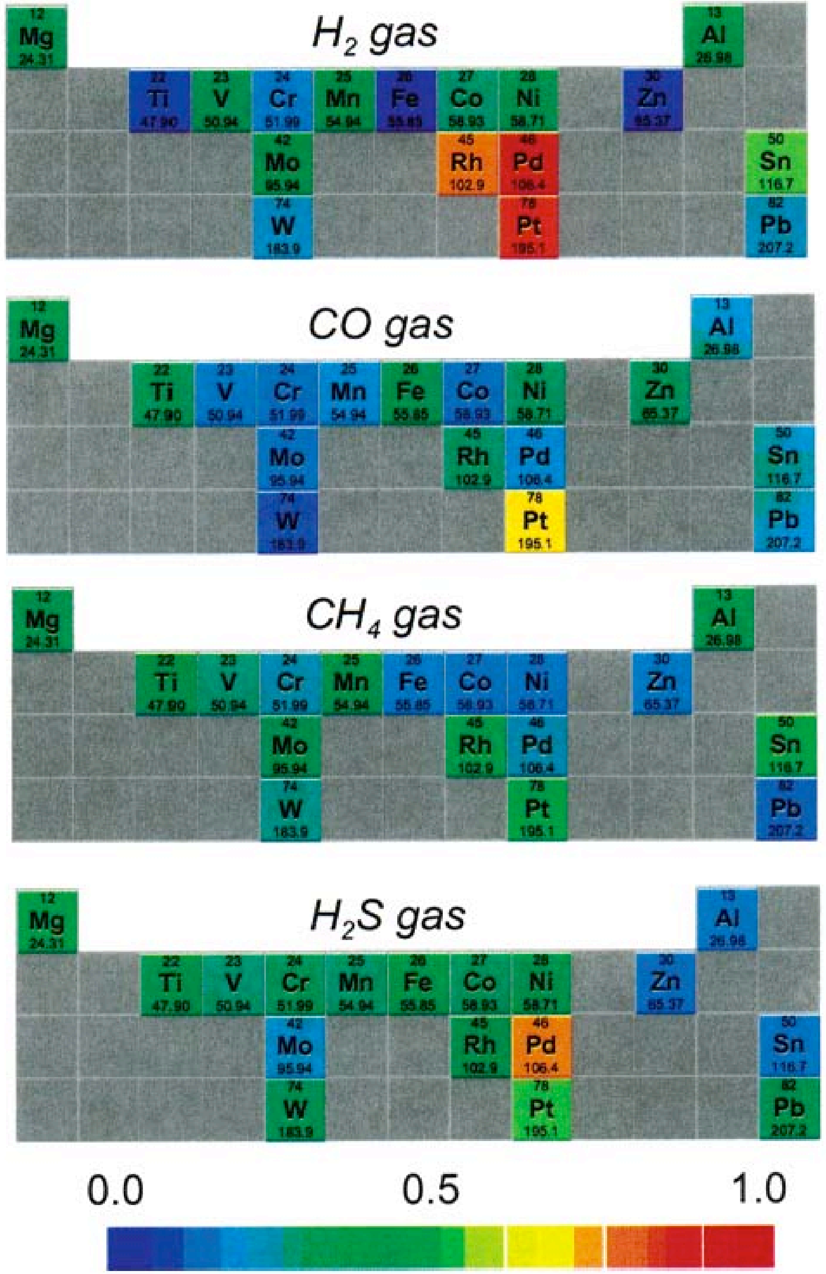
At room temperature pure “clean” CNTs are refractory to any gas adsorption (NO_2, SO_2, NO, H_2O, CO, O_2, H_2,…)

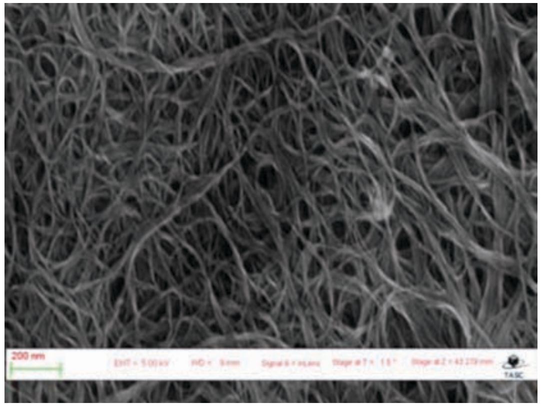
R. Larciprete, L. Petaccia, S. Lizzit and A. Goldoni, J. Phys. Chem. C 111, (2007)

Nanotubes as Support for Catalytic Nanoparticles: Rh/SWCNTs

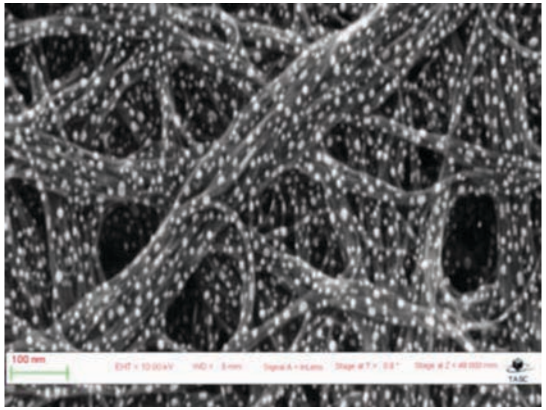
R. Larciprete, L. Petaccia, S. Lizzit and A. Goldoni, Appl. Phys. Lett. **88**, 243111 (2006)



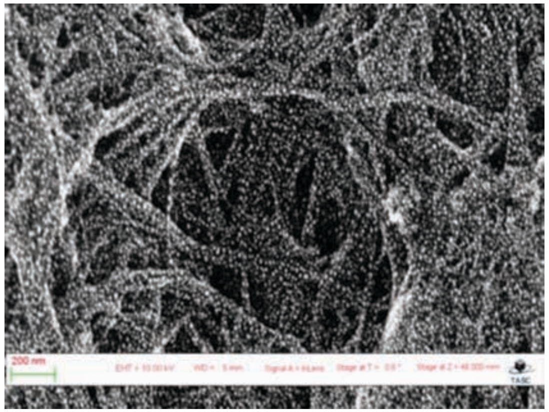




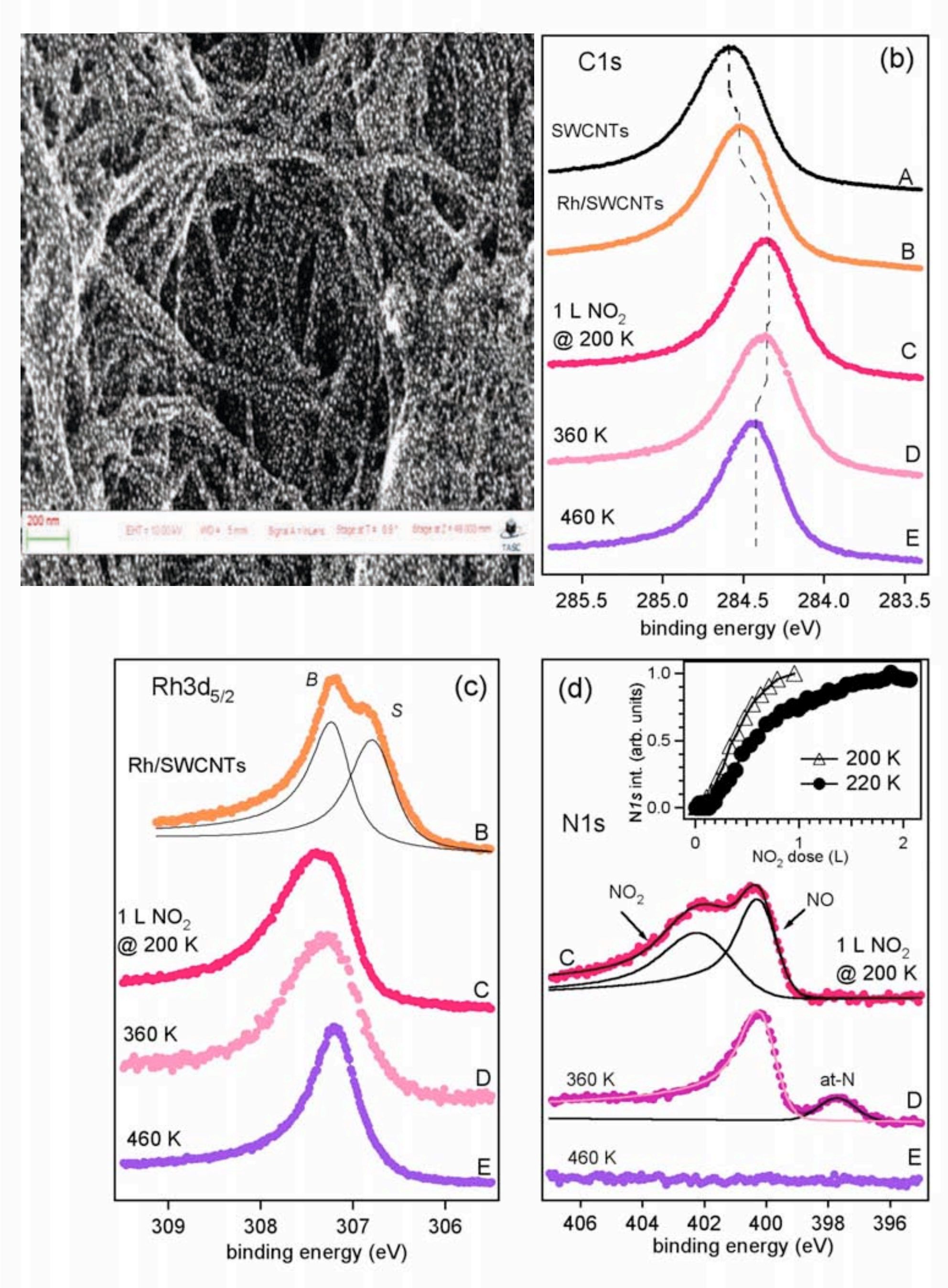
Clean



Pd



Rh



Coating CNTs with metals

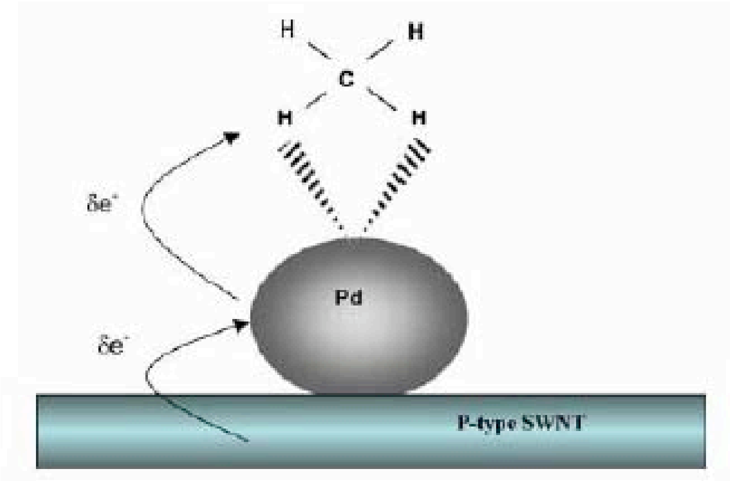
The NO_2 molecules interact with Rh only, no direct interaction with carbon atoms.

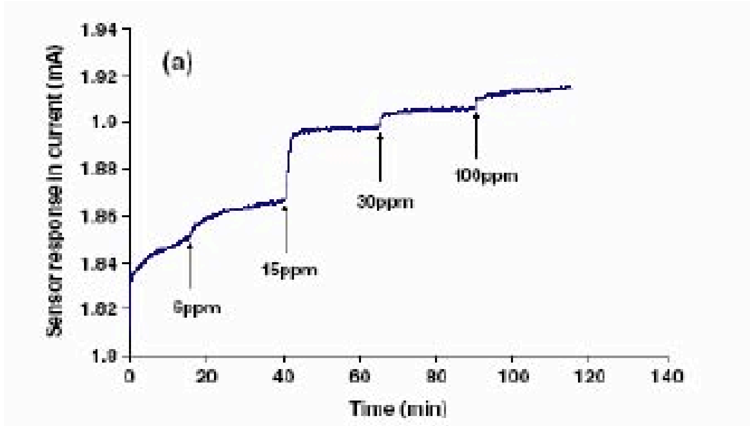
The C 1s core level does not change shape, simply shifts

Change of the barrier height at the CNT/Rh contact due to the NO_2 interaction with Rh

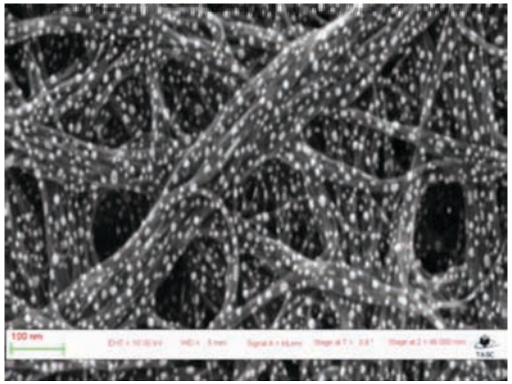
R. Larciprete, L. Petaccia, S. Lizzit and A. Goldoni, J. Phys. Chem. C 111, (2007)

- Covered CNTs with Pd nanoparticles
- Resistance changes as methane attaches
- Sensitivity 6 ppm
- Improvements in sensitivity, size, and power consumption





Y. Lu, J. Li, J. Han, H. T. Ng, C. Binder, C. Partridge, and M. Meyyappan, *Chem. Phys. Lett.*, **391**, 344 (2004).

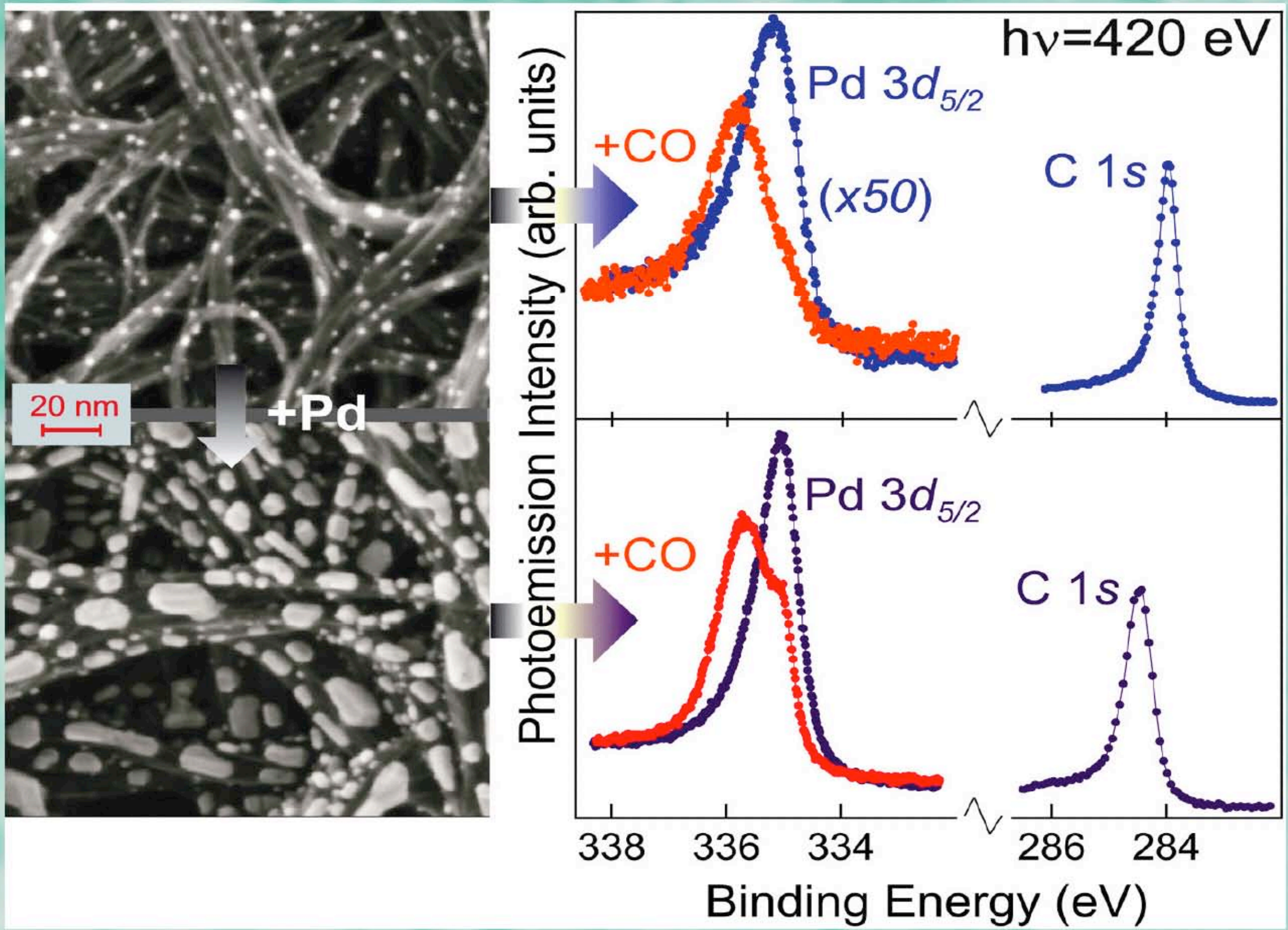


Similar behavior with H_2

Response time 5 s, recovery time 30 s - 300 s

R. Larciprete, L. Petaccia, S. Lizzit and A. Goldoni, unpublished (2012)

Reactivity of Pd clusters anchored to DWCNTs: adsorption of CO

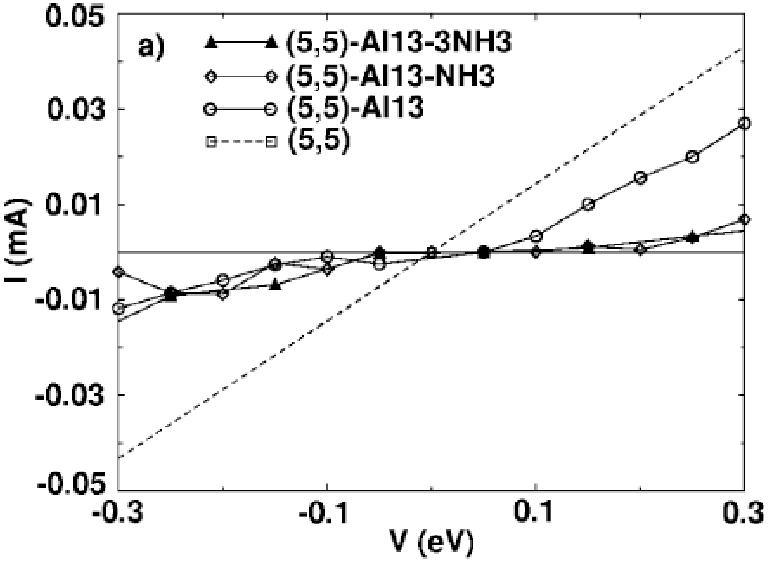


No CO adsorption occurs on the bare nanotubes. CO binds to the Pd nano-clusters. The C1s BE shift induced by CO is mediated by the Pd clusters.

R. Larciprete, L. Petaccia, S. Lizzit and A. Goldoni, unpublished (2012)

Theory: Al nanoclusters on SWCNTs

Theoretical calculations suggest a similar behavior with Al clusters and NH_3



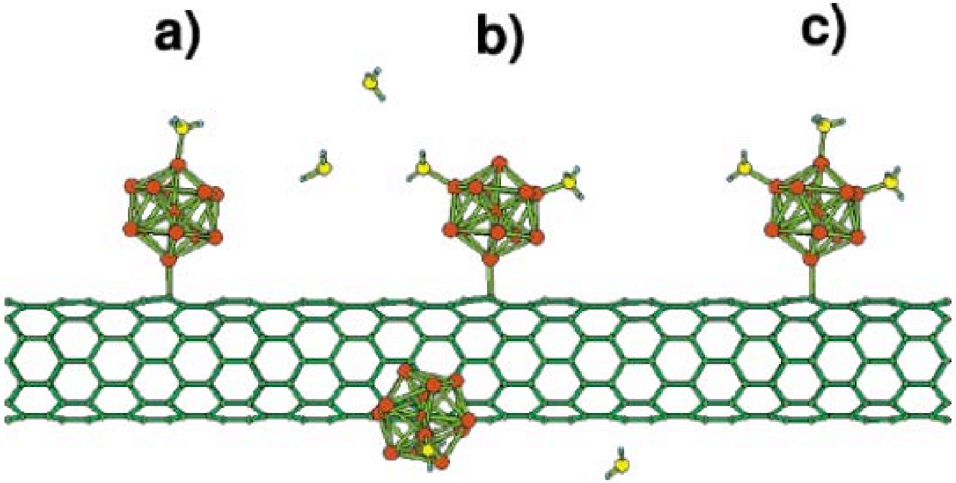
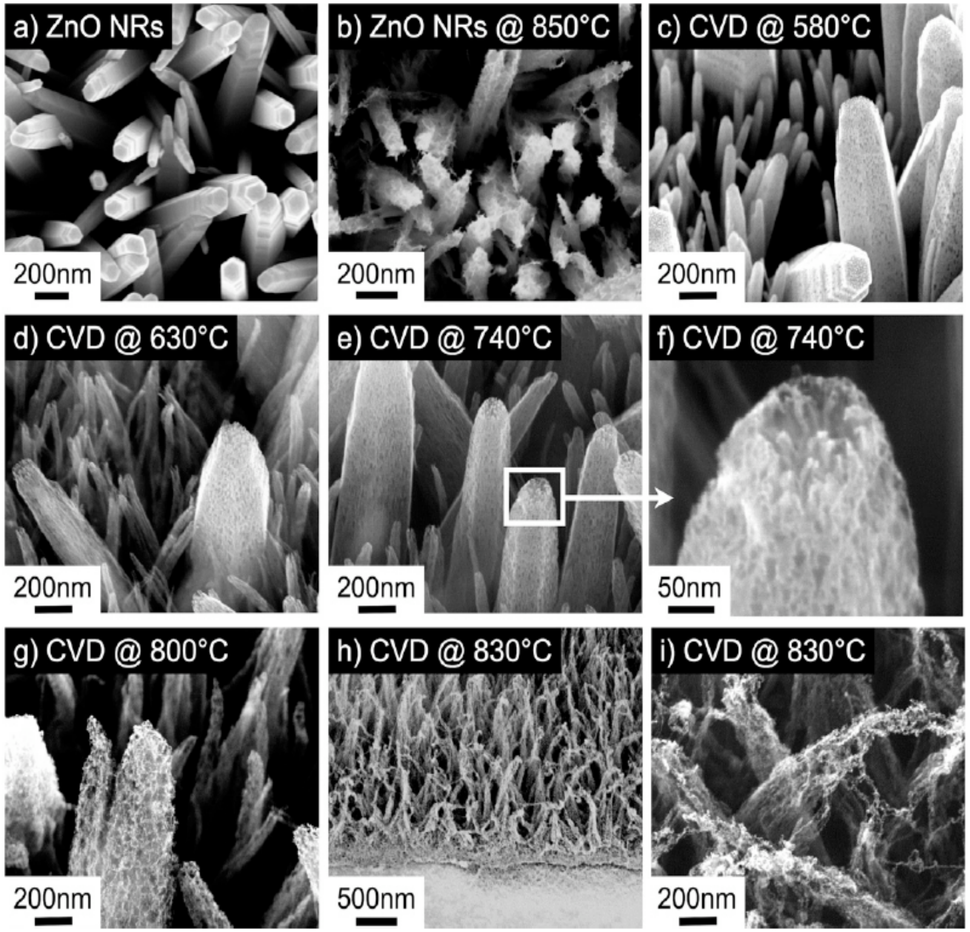


Figure 1. Illustration of carbon nanotube−metal cluster assembly for molecule sensing with metal clusters as the reactive sites. See text.

Q. Zhao et al., NanoLetters 5, 847 (2005)

Table 3. Summary of sensing performance of metal functionalized CNT sensors. (Note: N/S = Not-stated.)

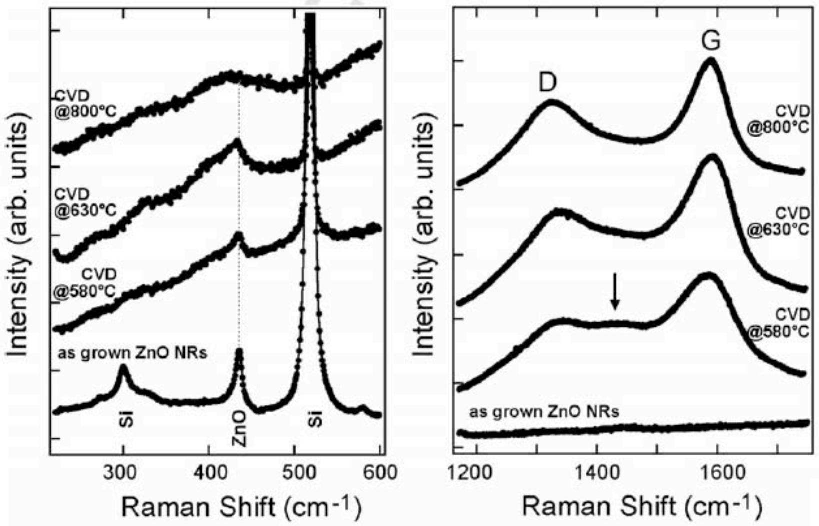
Metal	CNT type	Sensor configuration	Targeted gas/vapor	Functionalization method	Detection limit	Response time (s)	Reversibility	Ref
Pd	Single SWNT	ChemFET	H_2	Electron-beam evaporation	<40 ppm	5–10 (for half resistance change)	Reversible	Kong *et al* [70]
Pd	SWNTs	Chemiresistor	CH_4	Sputter-coating	6 ppm	120–240	Reversible (UV)	Lu *et al* [71]
Pd	SWNTs	Chemiresistor	H_2	(1) Chemical functionalization, (2) Sputter-coating	1000 ppm	N/S	Reversible	Sayago *et al* [72]
Pd	SWNTs	Chemiresistor	H_2	(1) Thermal evaporation (2) Sputtered coating	~10 ppm	<600	Reversible	Oakley *et al* [73]
Au, Pt	MWNTs	Chemiresistor	NO_2, NH_3	Sputter-coating	100 ppb (NO_2), 5 ppm (NH_3)	<600	Reversible (150 °C)	Penza *et al* [77]
Au	SWNTs	Chemiresistor	NO_2	Drop-coating monolayer Au clusters	4.6 ppb	N/S	Reversible (UV)	Young *et al* [74]
Pt, Pd	MWNTs	Chemiresistor	H_2, NO_2, H_2O	Chemical functionalization	N/S	600–1800	Reversible	Kumar *et al* [75]
Pd	SWNTs	Chemiresistor	H_2	Electrochemical functionalization	100 ppm	600	Reversible	Mubeen *et al* [76]
Pt, Pd, Sn, Rh	SWNTs	ChemFET	H_2, CH_4, CO, H_2S	(1) Electrochemical functionalization (2) Electron-beam evaporation	N/S	600	Reversible	Star *et al* [78]
Pd	SWNTs	Chemiresistor	H_2	Electrochemical functionalization	100 ppm	3–60 (for 36.8% resistance change)	Reversible	Sun and Wang [80]



Hybrid carbon Nanostructures:

CNs/ZnO grown by CVD

At high temperature the ZnO almost disappears and only carbon remains



P. Mbuyisa, S. P. Bhardwaj, F. Rigoni, E. Carlino, S. Pagliara, L. Sangaletti, A. Goldoni, M. Ndwandwe, C. Cepek, Carbon (2012)

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY
EuNetAir
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

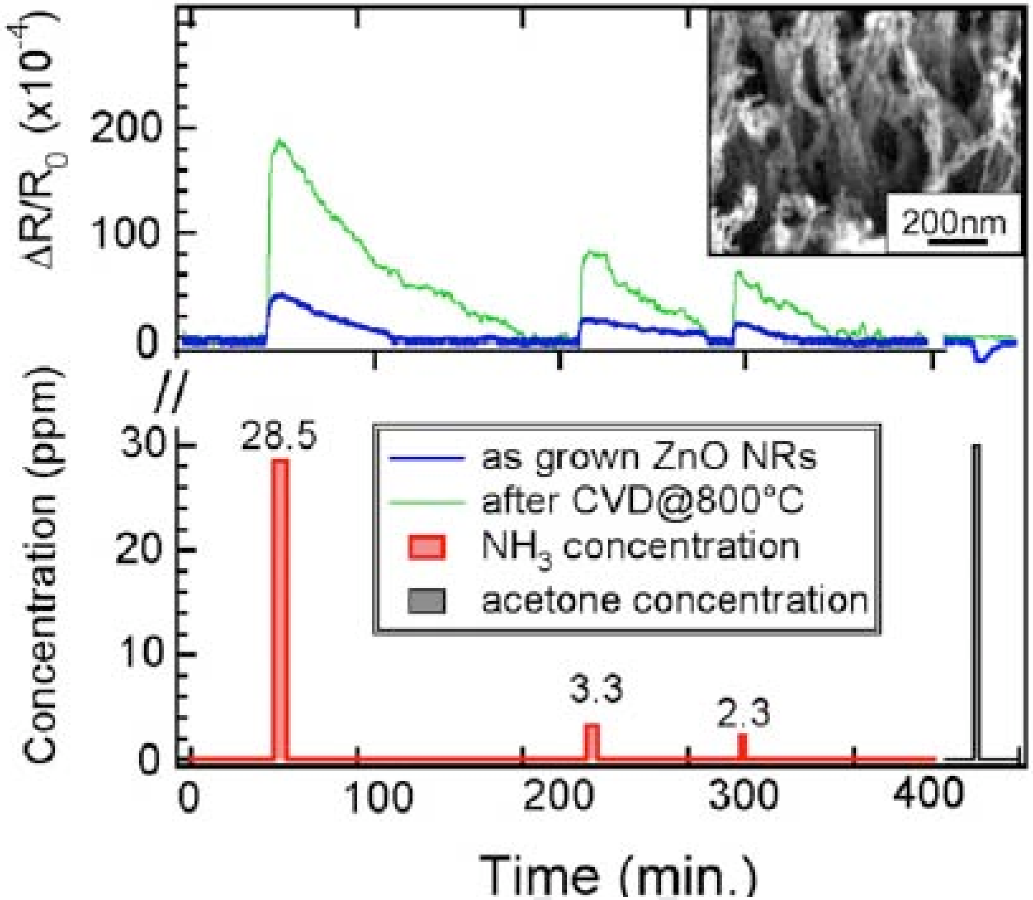


Table I – $\Delta R/R_0$ measured at 25.5 °C (±0.5 °C) with a relative humidity R.H. = 31% ± 1%.

(NH3) (ppm)	$\Delta R/R_0$ uncoated ZnO	$\Delta R/R_0$ ZnO/CND	$(\Delta R/R_0)_{CND+ZnO}/(\Delta R/R_0)_{ZnO}$
28.5	0.0040	0.0190	4.75
3.3	0.0020	0.0090	4.50
2.3	0.0015	0.0065	4.33

CONCLUSIONS

Many experimental evidences demonstrate the high sensitivity of CNTs to several molecular species in gas phase, both organic and inorganic.

Clean purified CNTs behave like HOPG: they are refractory to any gas adsorption/interaction

Coatings and/or functionalization are the goals to obtain very sensitive sensors

Experimental problem: it is important to develop efficient ways to distinguish among the different gaseous molecules in a mixture

A prototype device

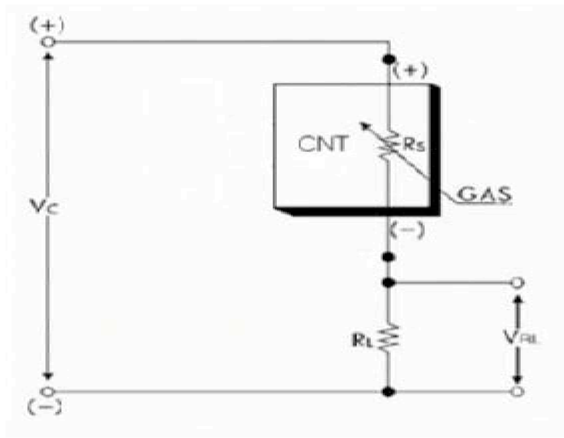
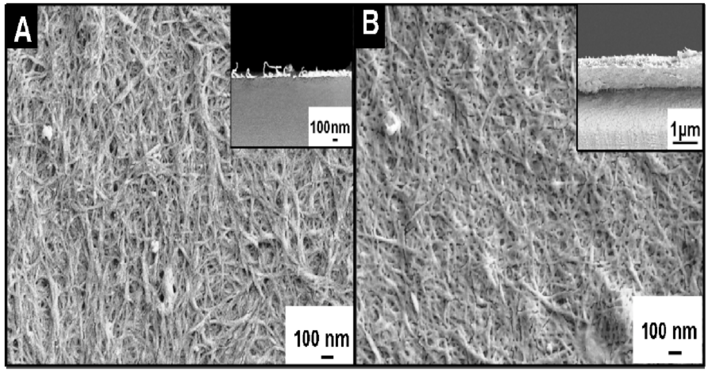
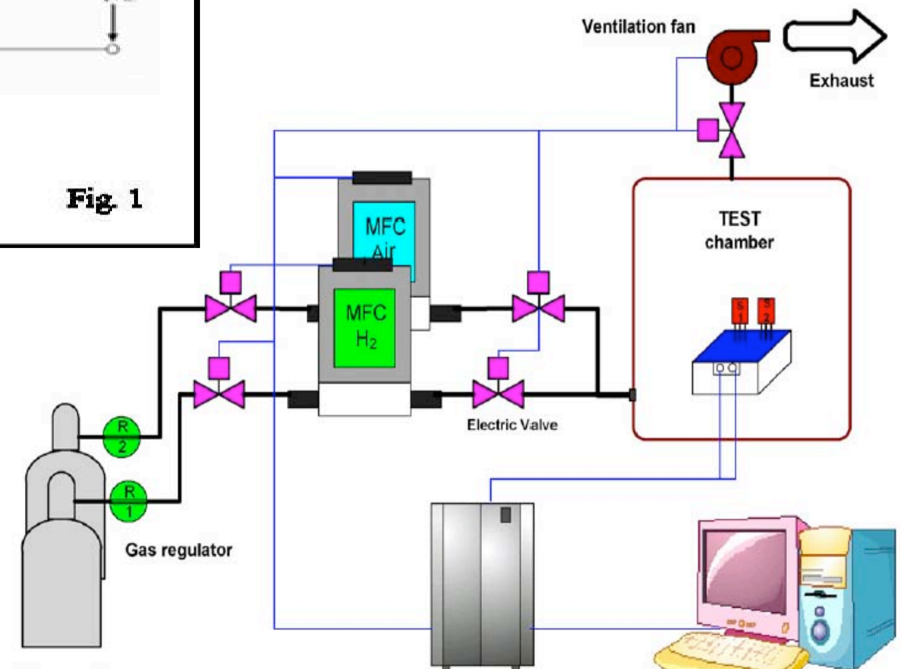
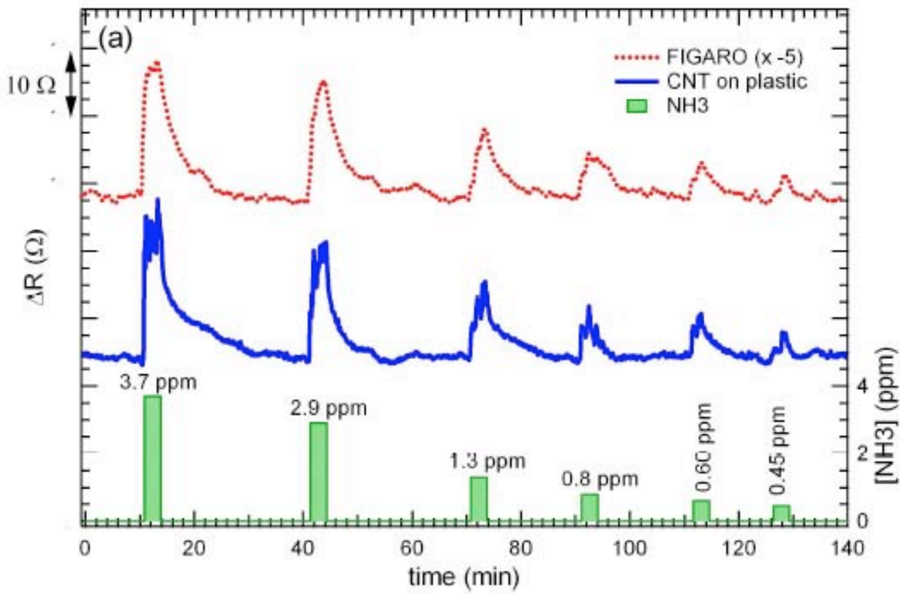


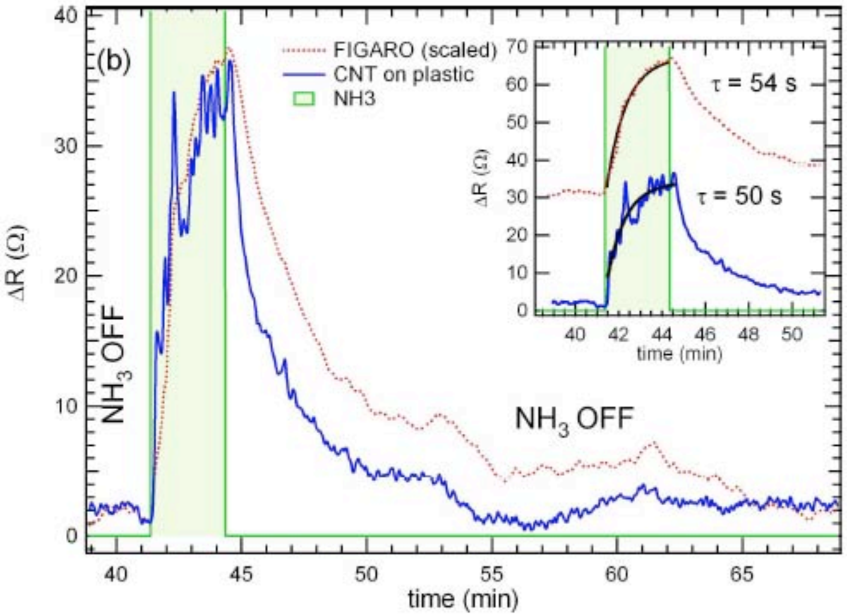
Fig. 1

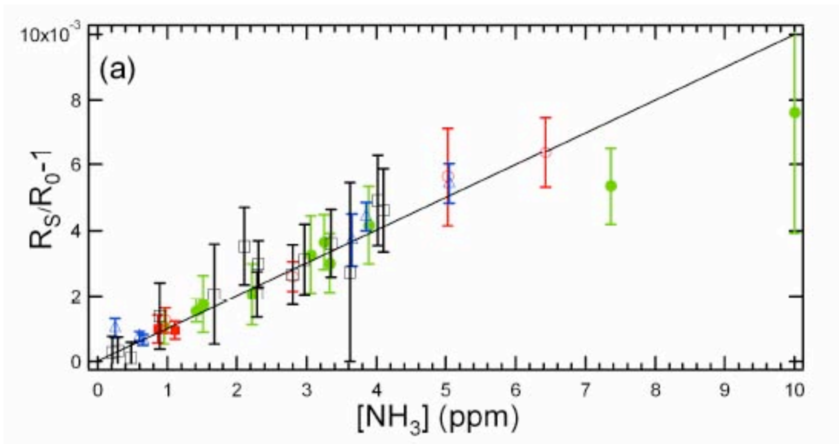


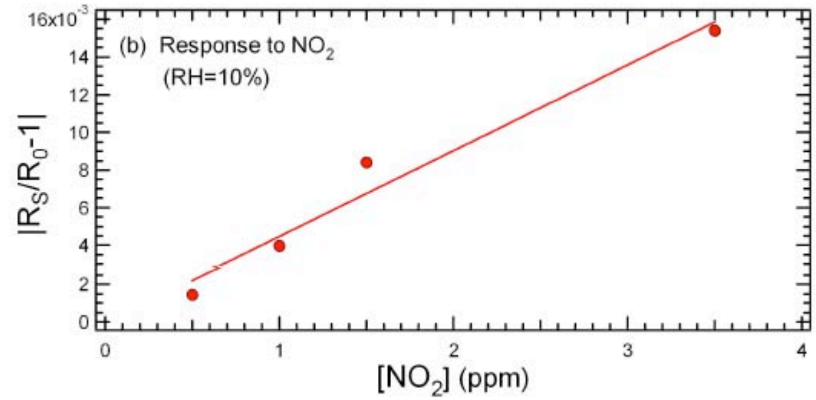
InkJet printed CNTs on PET compared with a commercial device FIGARO TGS 2602









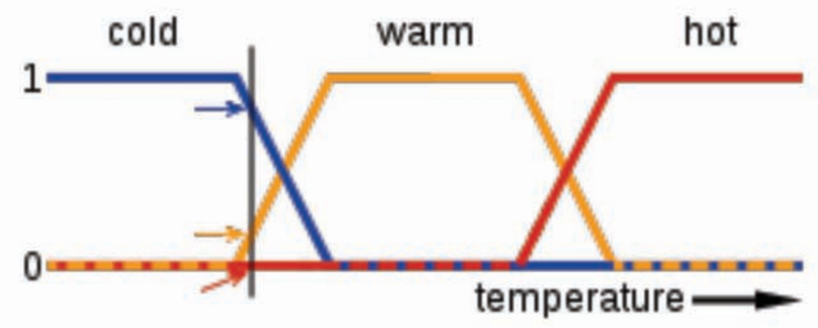


Fit with one exponential curve to obtain the response time τ

In which way we can recognize a mixture of gasses?

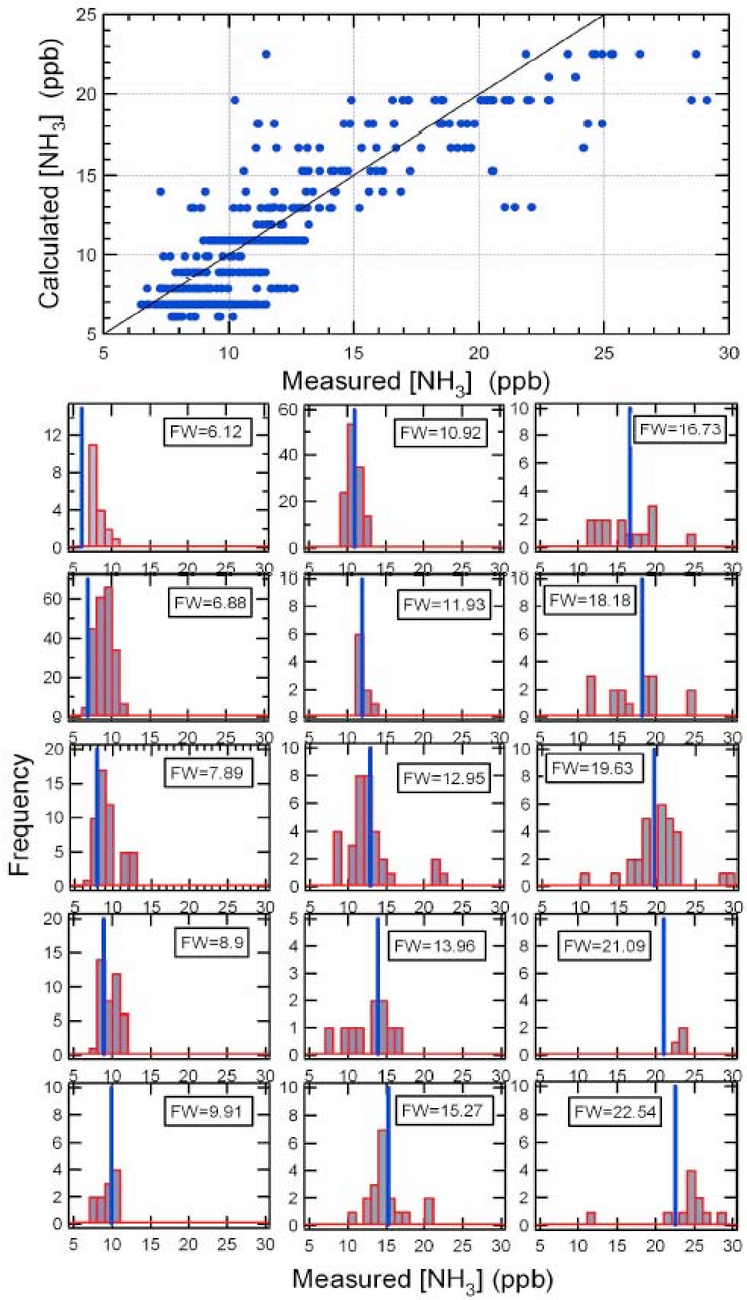
FUZZY LOGIC

The *fuzzy logic* is a fuzziness of the binary logic (1 & 0, black & white, cold & hot etc…): the reality, depending on continuous variables, is not simply black and white, cold and hot, but it is generally blurred. This logic is not imprecise or ambiguous but may gives more clear answers to normal life questions. It forms the basis of the kind of computer programming designed to allow computers to mimic human intelligence.



Each definitions make a fuzzy set that can be true (1) or false (0) or something in between depending on a continuous variable (see the example with the variable T). These are the basis of the "expert program" that given a value of the variable (T) extracts parameters (the three arrows) to feed the "inverse fuzzy program (or de-fuzzy)". The de-fuzzy indeed extract a range of values of the quantity we want to control (or determine) . The center of mass (or the maximum or the minimum) is the "correct" value.

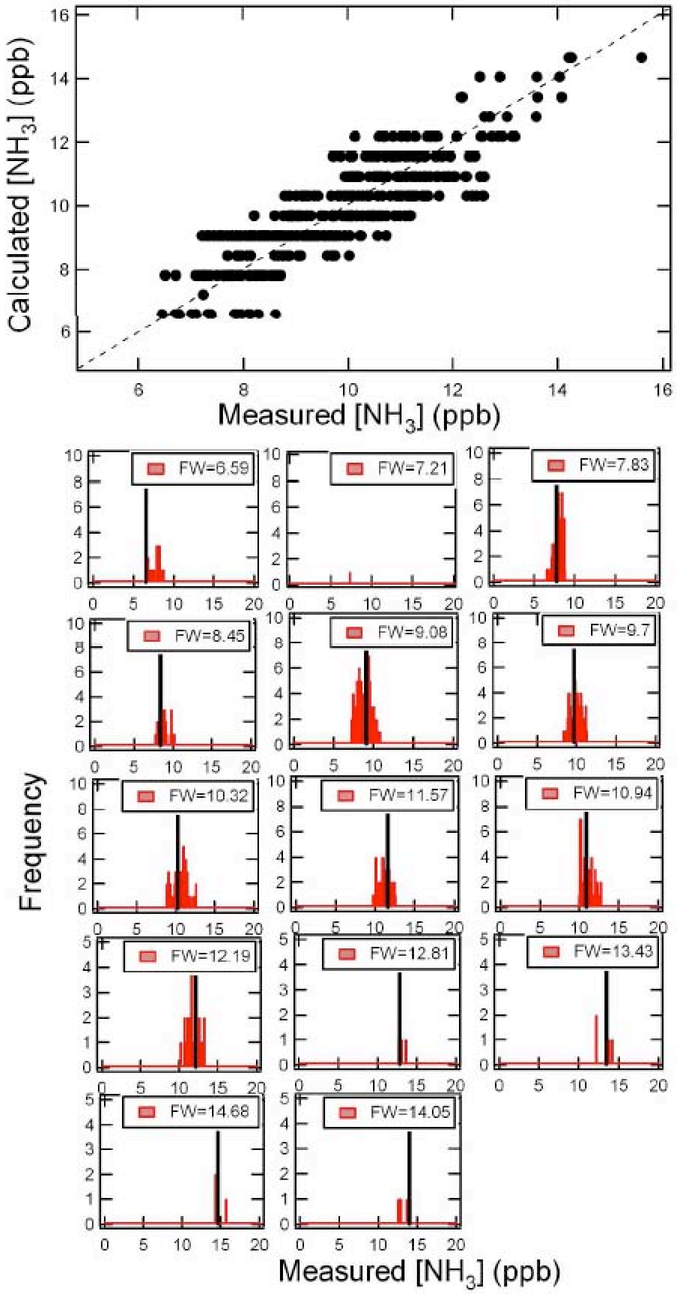
Using the retroactivity, the "expert program" may learn from the previous results (experience) obtained by the de-fuzzy program, becoming better.



MEASURED | TRUE

$[NH_3]_{FW}$ [ppb]	Number of measured data	$[NH_3]_{AVE}$ [ppb]	Δ [ppb]	σ [ppb]	Δ between consecutive FW values [ppb]
6.12	18	8.32	2.2	0.73	
6.88	218	8.93	2.05	1.08	0.76
7.89	50	9.17	1.28	1.56	1.01
8.9	41	9.68	0.78	1.09	1.01
9.91	11	9.18	0.73	1.09	1.01
10.92	129	10.79	0.13	0.91	1.01
11.93	9	11.83	0.10	0.61	1.01
12.95	29	11.89	1.06	1.72	1.02
13.96	8	12.46	1.5	3.33	1.01
15.27	19	14.90	0.37	2.45	1.31
16.73	15	16.14	0.59	3.67	1.46
18.18	16	17.19	0.99	4.1	1.45
19.63	28	20.04	0.41	3.67	1.45
21.09	3	23.50	2.41	0.62	1.46
22.54	11	23.75	1.21	4.40	1.45

Mixed gases (air, NH3, NO2, O_3)



MEASURED — **TRUE**

$[NH_3]_{FW}$ [ppb]	Number of measured data	$[NH_3]_{AVE}$ [ppb]	Δ [ppb]	σ [ppb]	Difference between consecutive FW values [ppb]
6.59	17	7.56	0.97	0.65	
7.21	1	7.26	0.05	-	0.62
7.83	60	7.98	0.15	0.50	0.62
8.45	22	8.82	0.37	0.67	0.62
9.08	91	8.72	0.36	0.85	0.63
9.7	58	9.86	0.16	0.75	0.62
10.32	61	10.56	0.24	0.96	0.62
10.94	56	10.97	0.03	0.78	0.62
11.57	42	11.01	0.56	0.71	0.63
12.19	25	11.69	0.50	0.87	0.62
12.81	4	12.98	0.17	0.45	0.62
13.43	4	13.01	0.42	0.99	0.62
14.05	5	13.27	0.79	0.69	0.62
14.68	3	14.69	0.01	0.78	0.63

Mixed gases (air, NH_3, NO_2, NO, O_3)