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

COST Action TD1105

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Year 3: 1 July 2014 - 30 June 2015 (***Ongoing Action***)

Functionalised Carbon Nanotube Sensors for Detecting Benzene at Trace Levels

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Sub-WG Leader: Carbon nanomaterials

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Outline

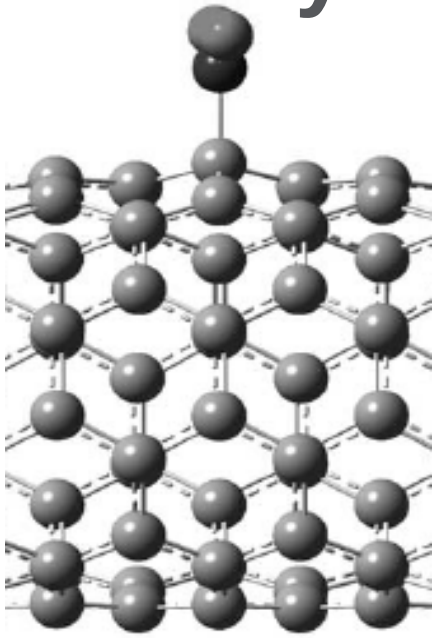
- Detecting benzene: What for?
- Carbon nanotube gas sensors: Some advantages and … many issues.
- Strategies for increased sensitivity and selectivity
  - Decoration of CNTs with metal NPs
  - Functionalisation with macro-molecules: towards molecular recognition?
- Conclusions and outlook

Detecting benzene: what for?

- Benzene is known to be carcinogenic.
  - Environmental monitoring.
  - Workspace exposure.
    - Road construction and repair
    - Petrol stations
    - Petrochemical industry
    - Land reclamation
    - …

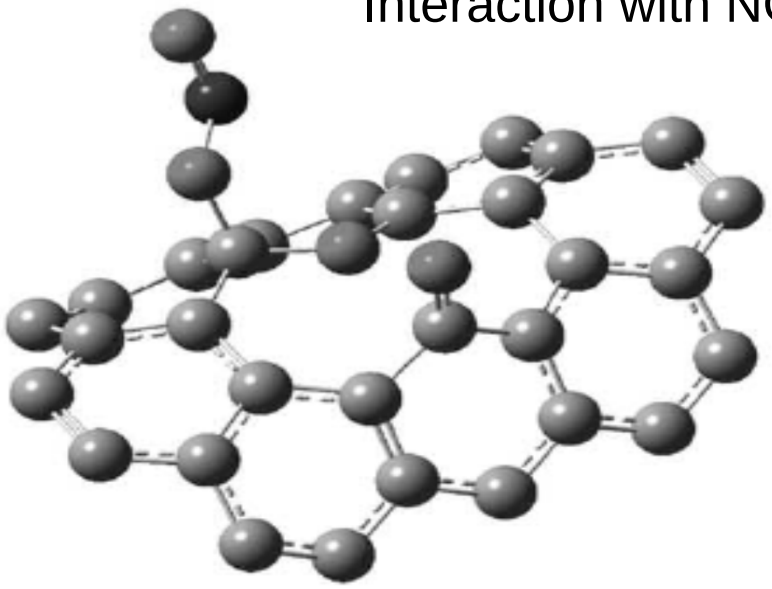
A safe exposure level to benzene may not exist!

Carbon nanotube gas sensors: Some advantages and … many issues



E_i = 21.4 kcal/mol

Interaction with NO_2



Ei = 48.3 kcal/mol

- High surface area for interaction
- Surface chemistry can be tailored: defects, grafting of functional groups, substitutional doping, …
- Room temperature operation possible

R.Ionescu, E.H. Espinosa, E. Llobet et al., Sensors and Actuators B 113 (2006) 36–46

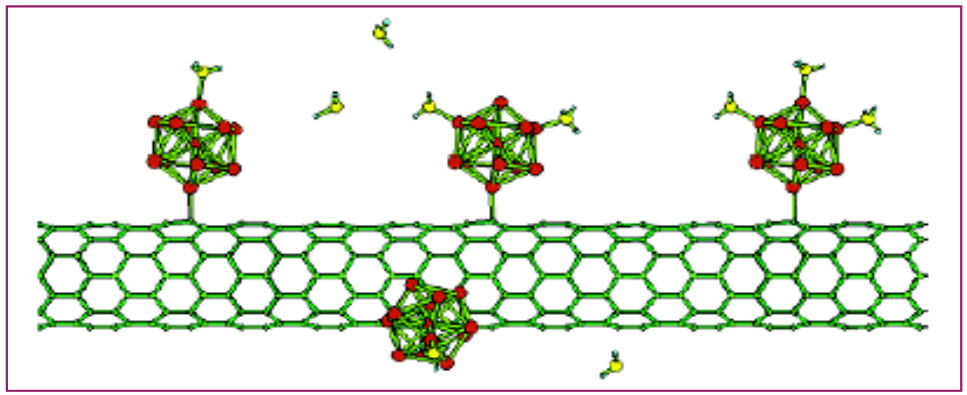
Carbon nanotube gas sensors: Some advantages and … many issues

- Transfer of CNTs to substrate, residues from solvents, contamination from patterning, electrode to CNT contacts have a deep influence in gas sensing properties (exogenous sensitivity, lack of reproducibility…)
- Procedures to reach better dispersion of CNTs make these more hydrophilic and this promotes moisture cross-sensitivity.
- Often room-temperature response does not mean room temperature recovery.
- Carbon nanotubes show response to a wide spectrum of volatile compounds (NOx, NH3, alcohols,…): Lack of selectivity.

Strategies for increased sensitivity and selectivity

A new road to chemical sensors: cluster surfaces serve as reactive sites for gas adsorption

New in 2005!



Q. Zhao, M. Buongiorno Nardelli, W. Lu and J. Bernholc Nano Letters 5 (2005) 847-851

Key concept:

Use of relatively small clusters that donate or accept a significant amount of charge upon adsorption of a target molecule

Electron transport in the nanotube is affected

Resistive gas sensors made possible

Strategies for increased sensitivity and selectivity

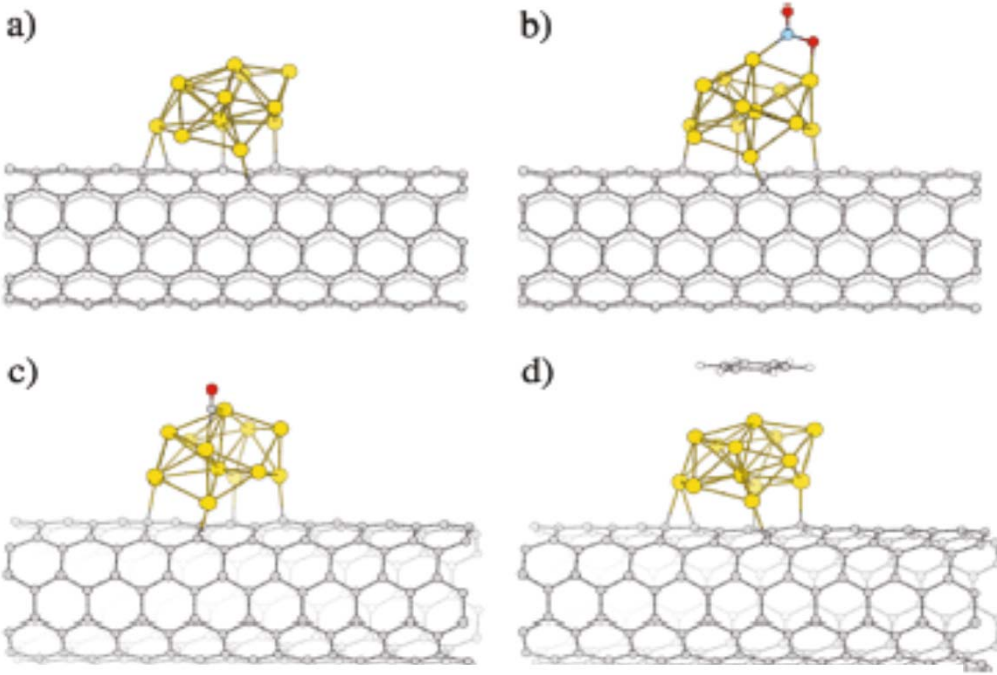
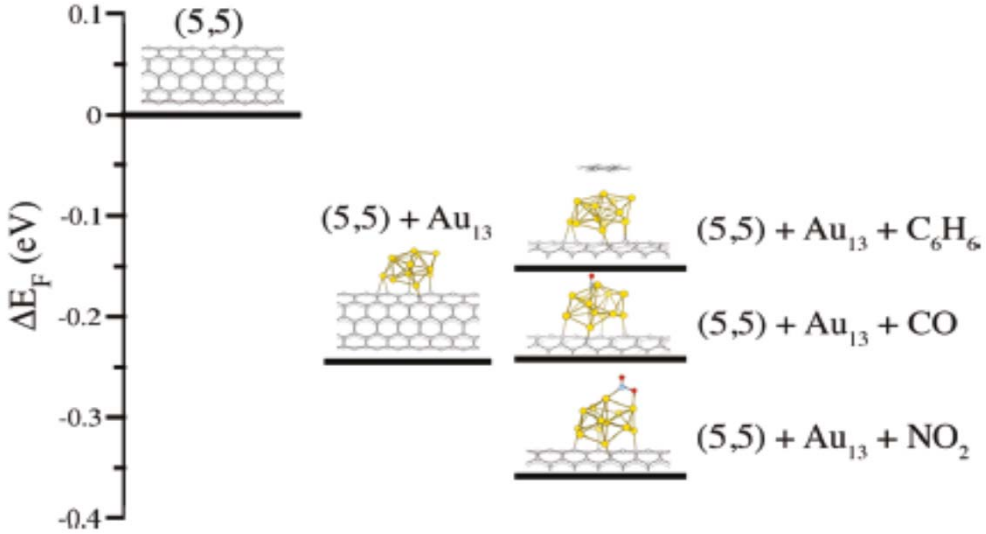


TABLE 1. Computed Binding Energies (E_B, eV), Charge Transfer (Δq, $|e|$), Au_{13}–SWNT Bond Length (d_{Au}, Å), and Molecule–Au_{13} Bond Length (d_{gas}, Å)

	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.

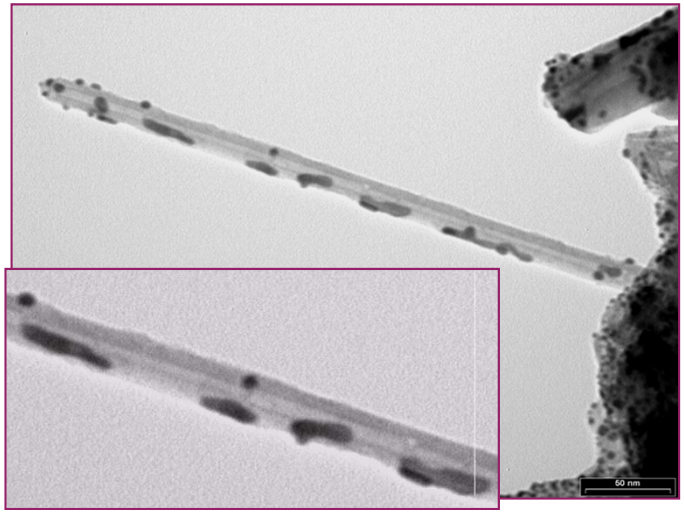


Pristine or Au NP decorated CNT are not suitable for detecting a-VOCs

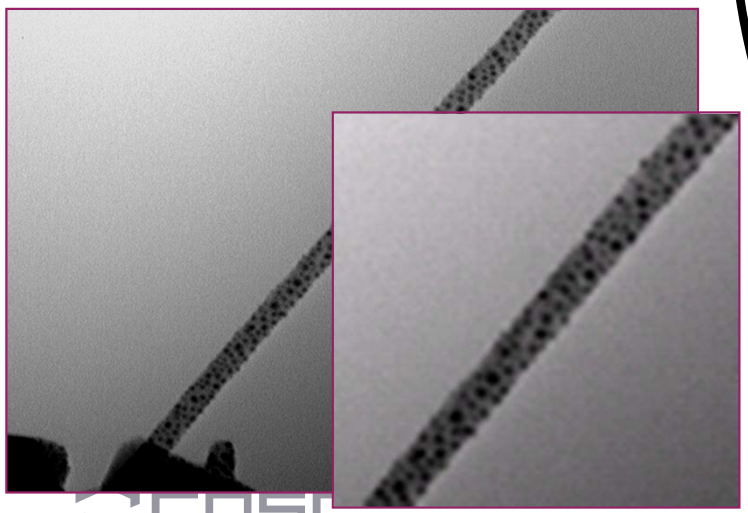
R. Leghrib, E. Llobet et al., *ACS Nano*, 5 (2011) 4592-4599

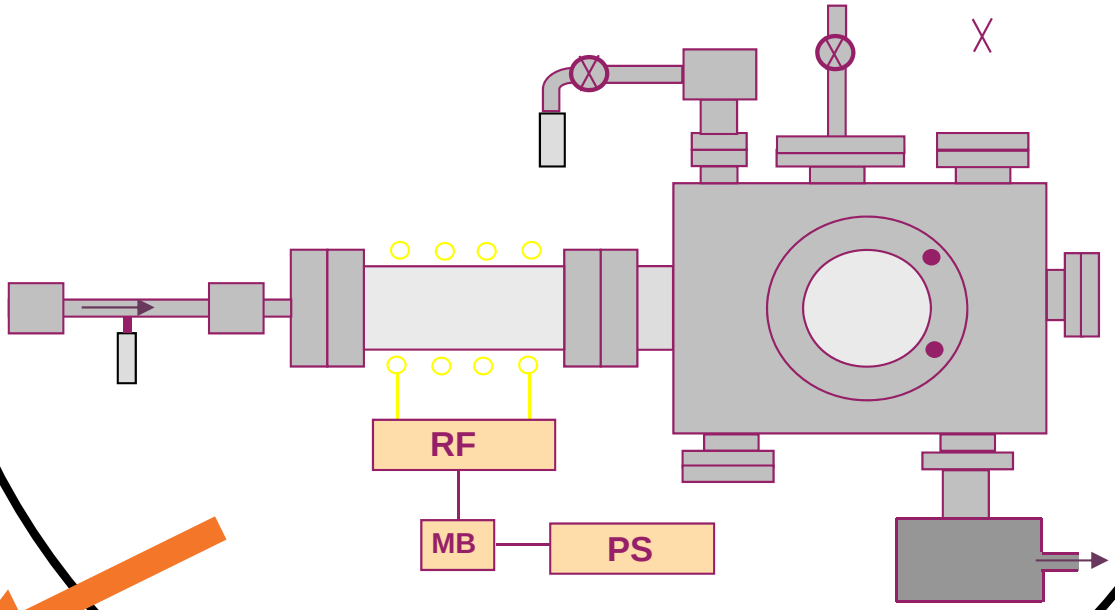
Decoration of CNTs with metal NPs

as grown MWCNTs



O_2

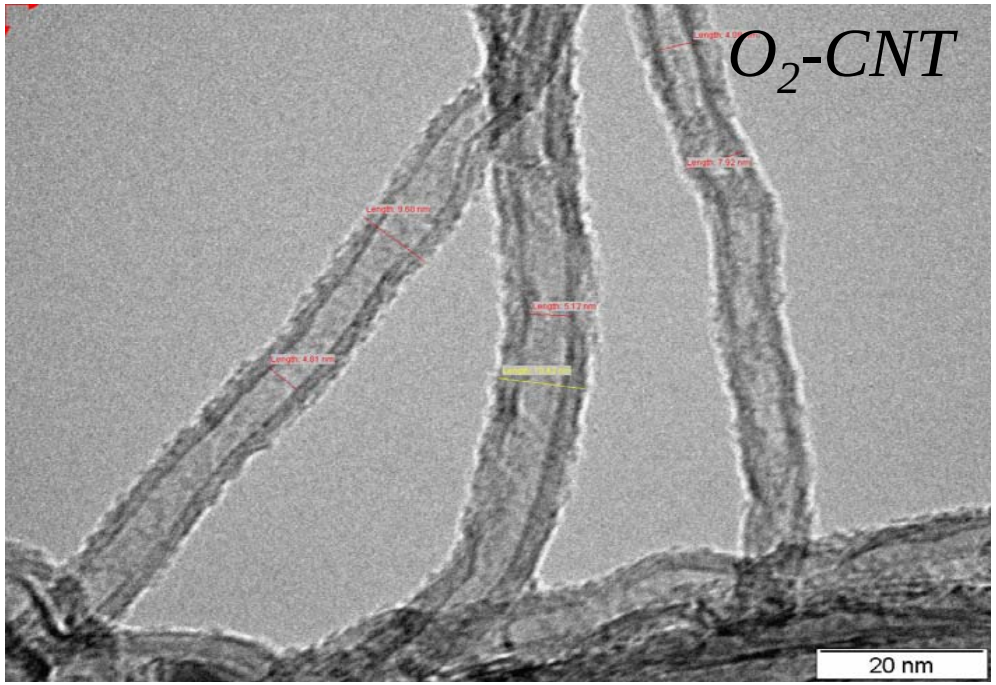


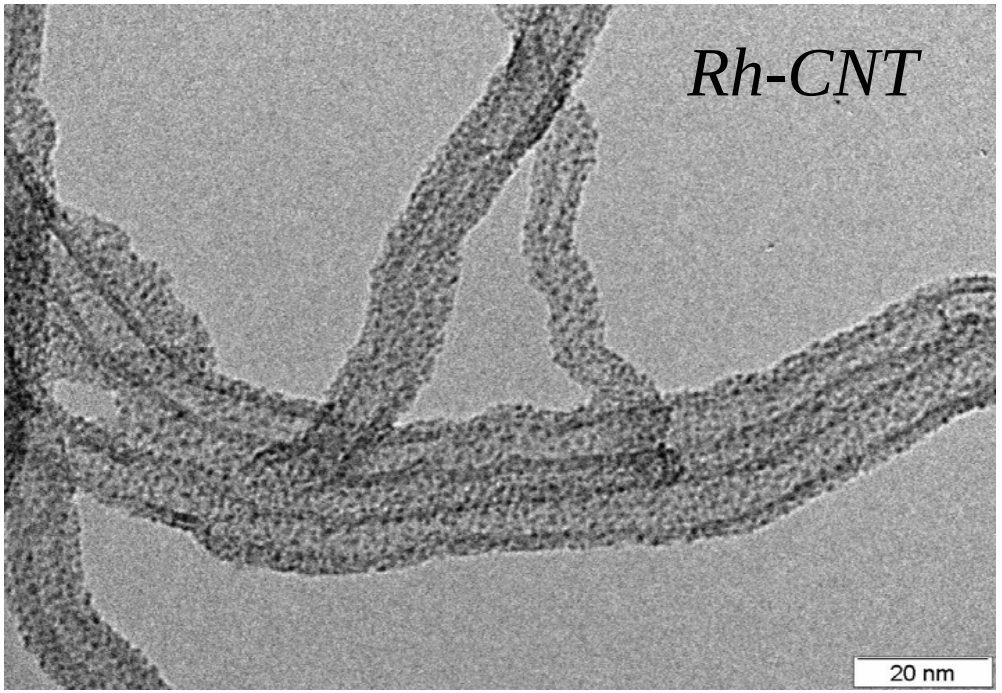


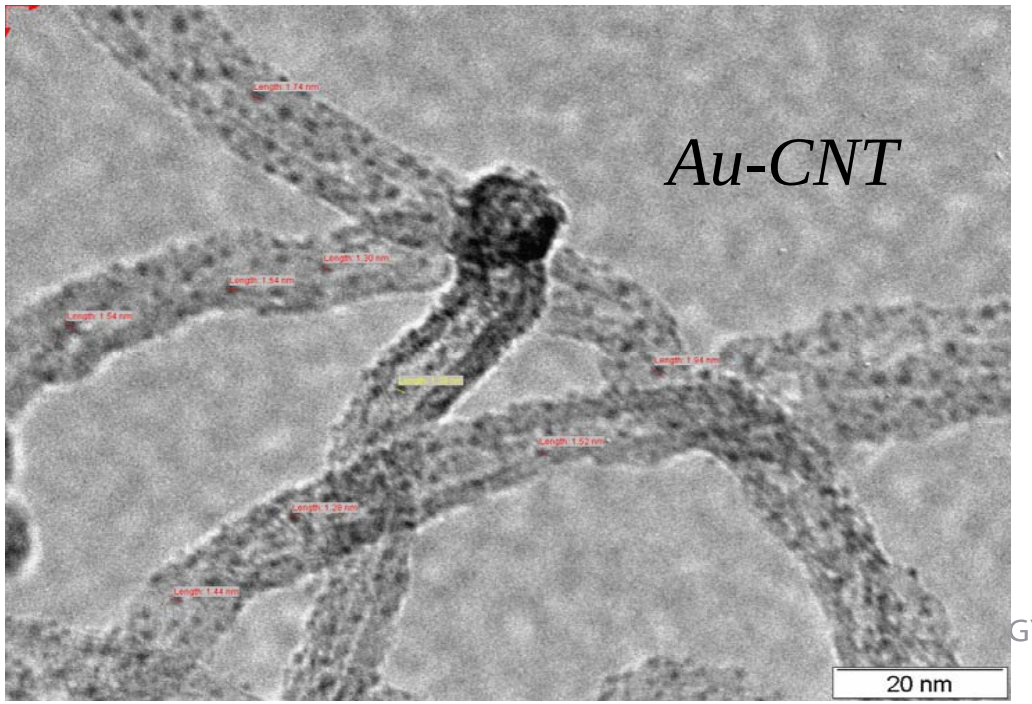
Plasma treatment and evaporation or sputtering

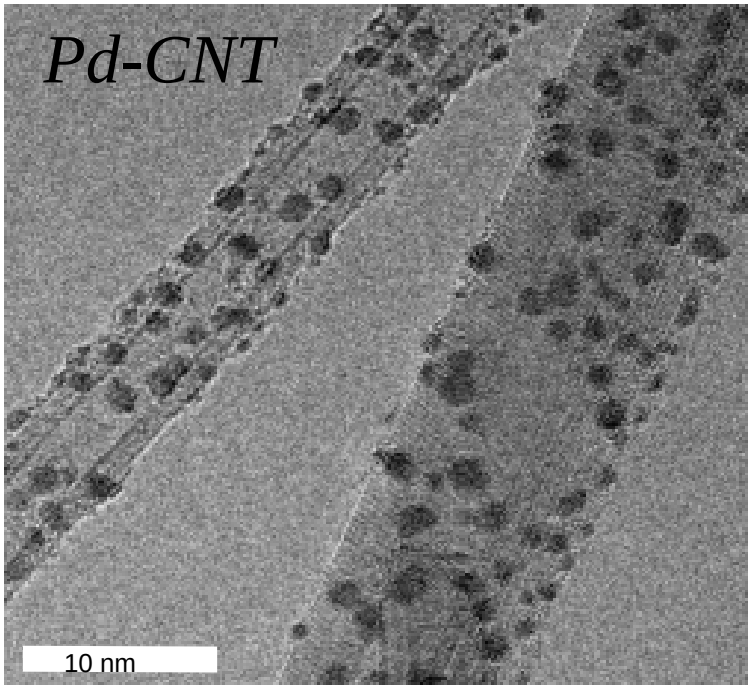
R. Leghrib, E. Llobet, et al.,
Nanotechnology 20 (2009) 375501

Decoration of CNTs with metal NPs









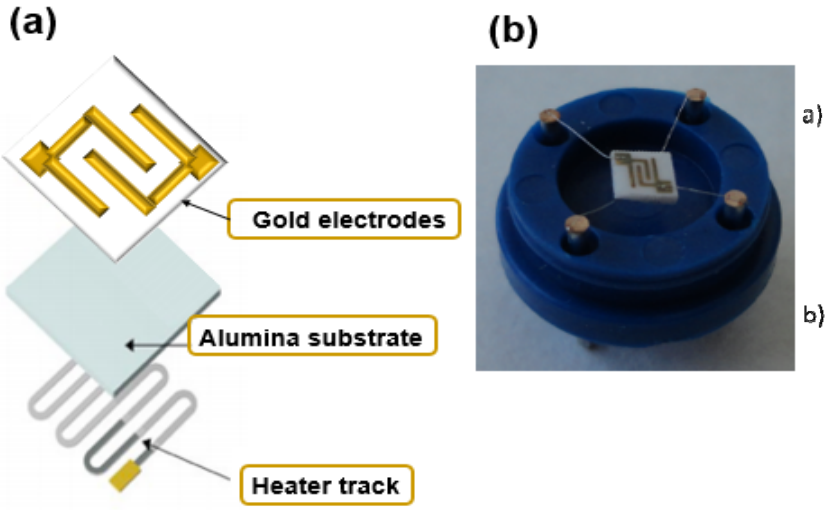
and Pt, Ni or Fe

Coating of CNTs

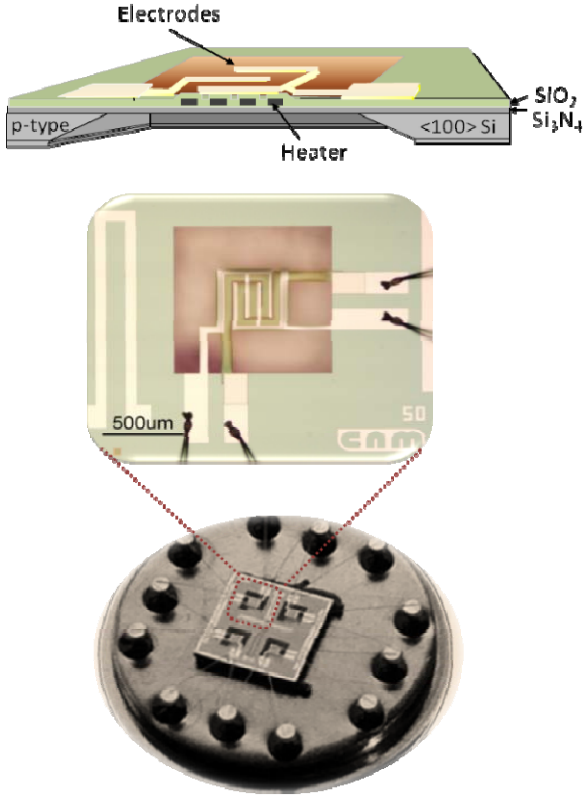
Air-brushing of CNTs dispersed on a suitable solvent onto a heated substrate. Film resistance monitored for reproducibility

Resistive sensor transducers

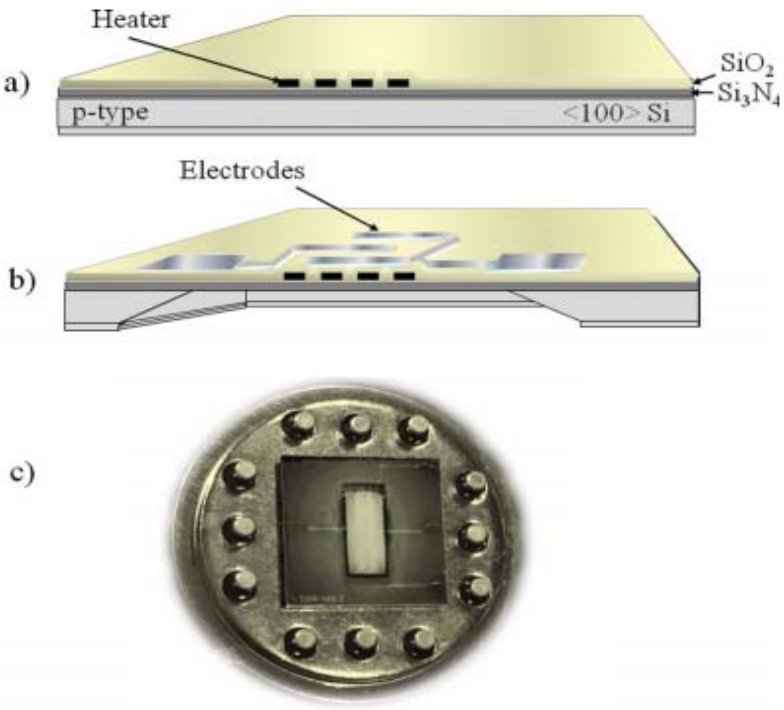
Ceramic



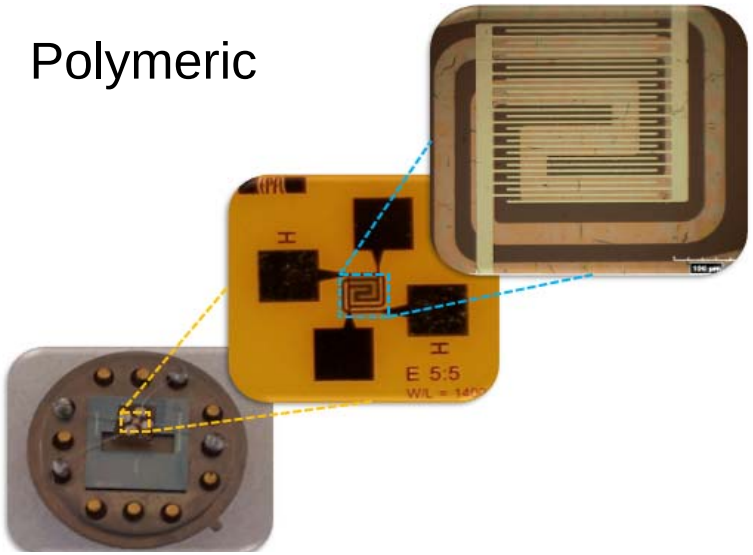
Si-MEMS 1



Si-MEMS 2



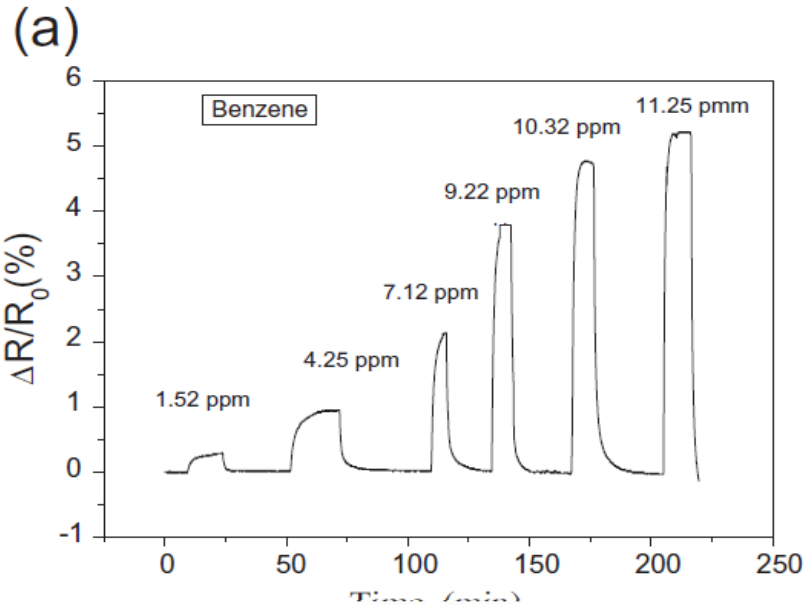
Polymeric

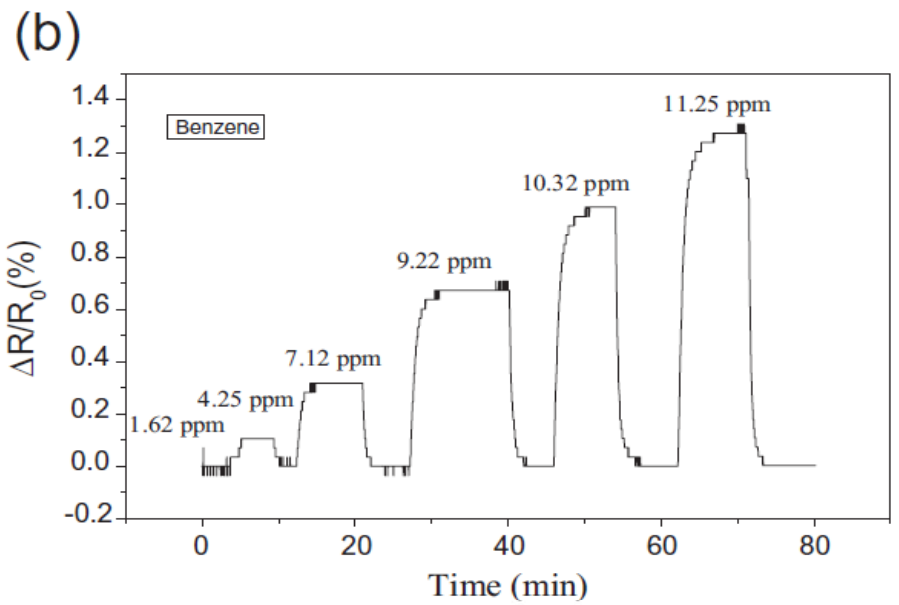


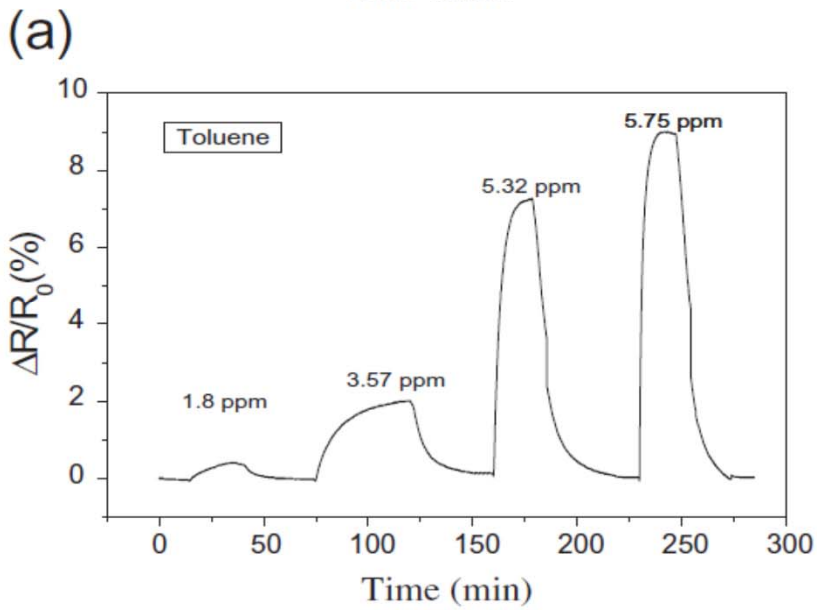
Array of metal decorated CNTs

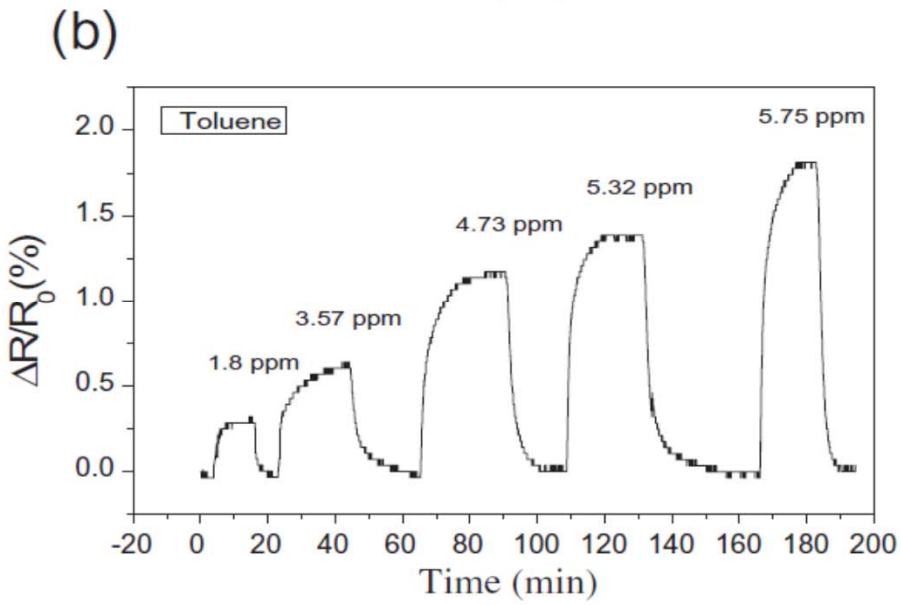
P. Clément, E. Llobet, et al. Sensors and Actuators B 182 (2013) 344– 350

CARBON 78 (2014) 510–520



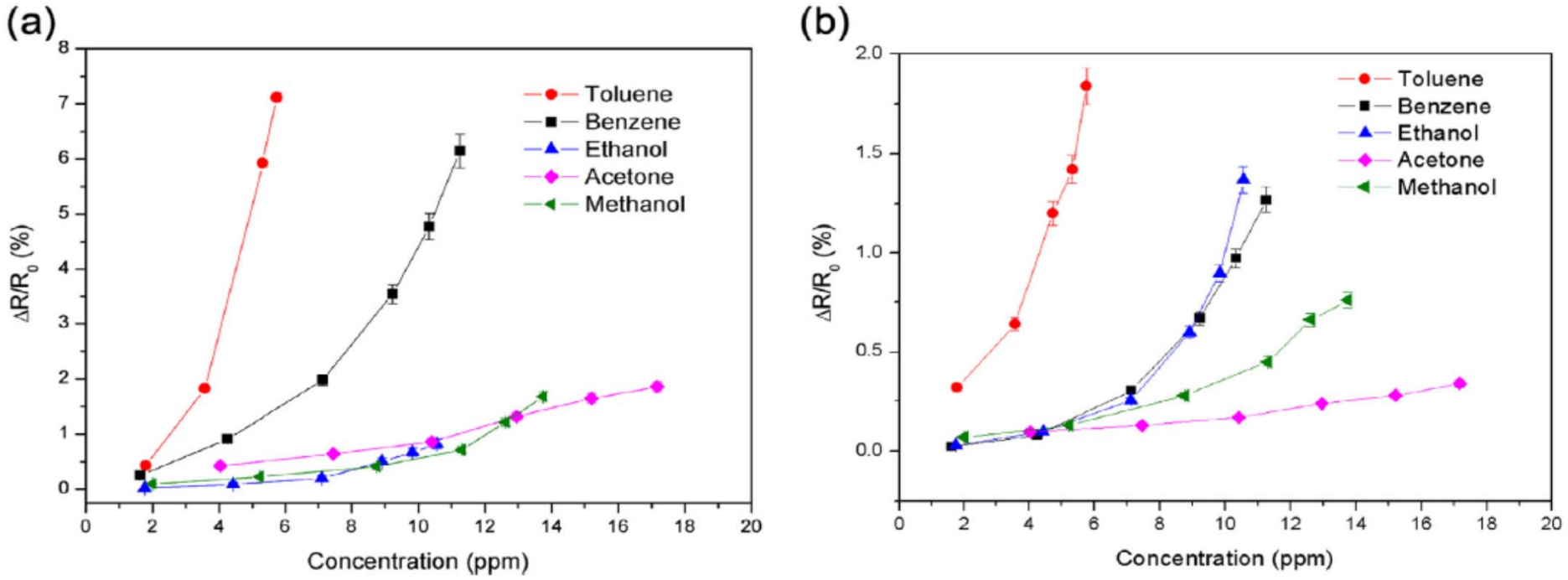




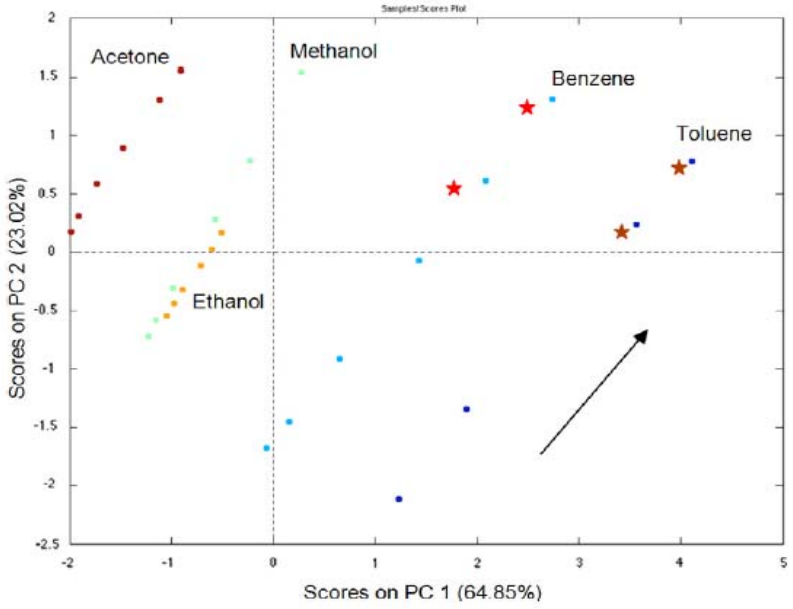


Responses of (a) MWCNTs and (b) Fe decorated MWCNTs to increasing concentrations of benzene (top) or toluene (bottom).

Array of metal decorated CNTs



Calibration curves for (a) oxygen plasma treated CNTs and (b) FeO-CNT sensors.

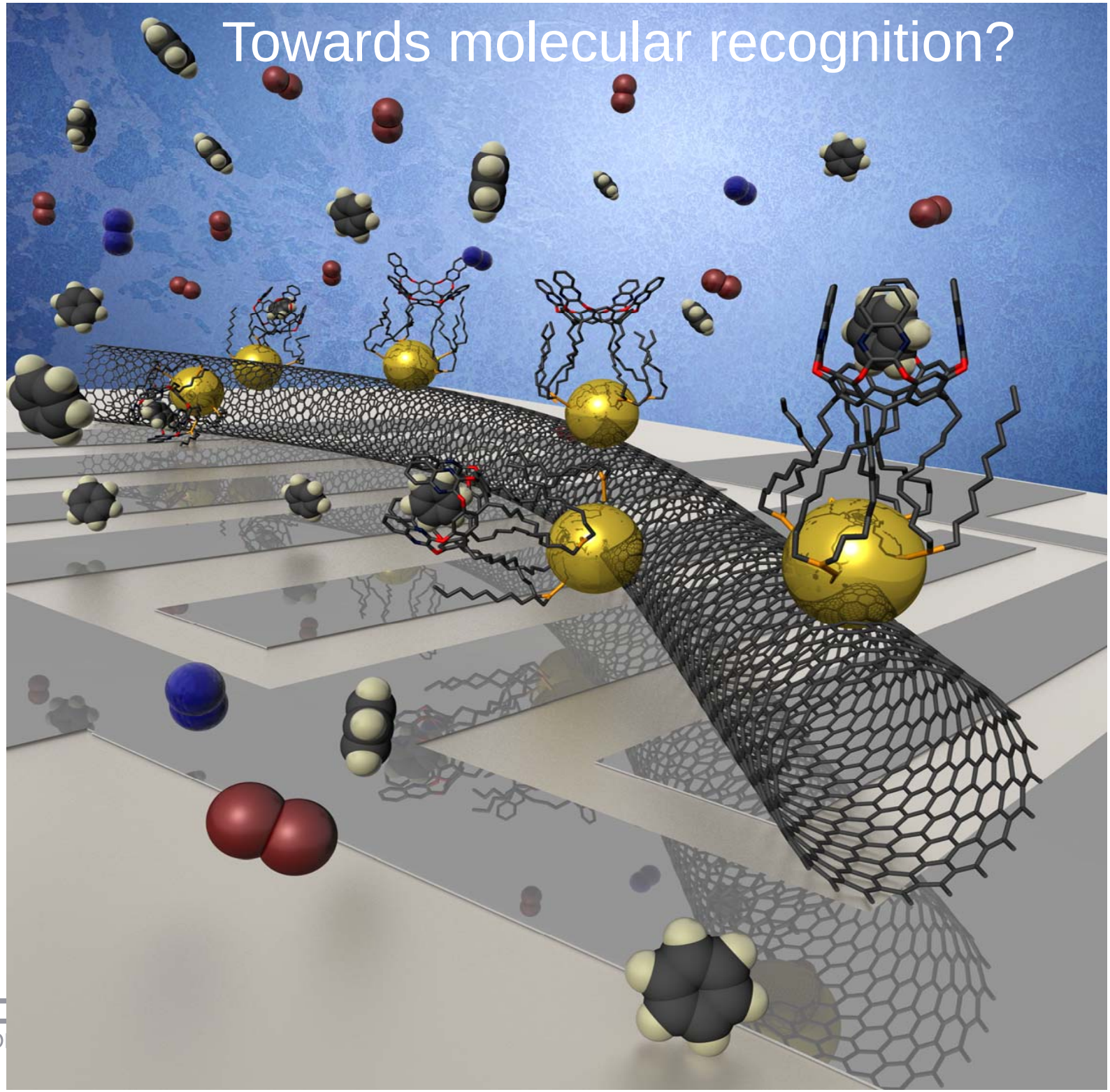


PCA using the responses and response times of a 2-element sensor array. Stars are the scores for (toluene + ethanol, and benzene + ethanol) mixtures.

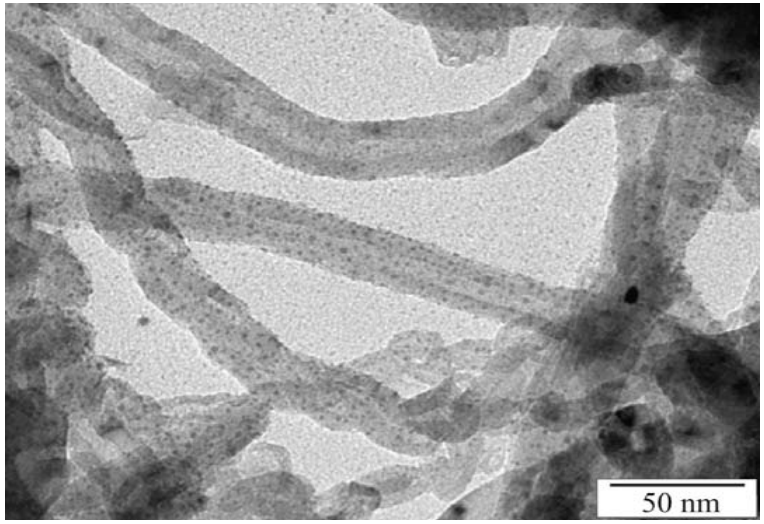
P. Clément, E. Llobet, et al. Sensors and Actuators B 182 (2013) 344– 350

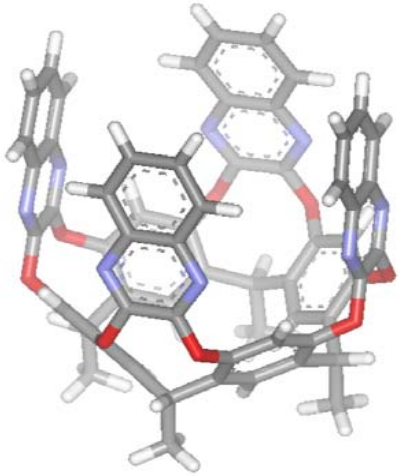
CARBON 78 (2014) 510–520

Towards molecular recognition?

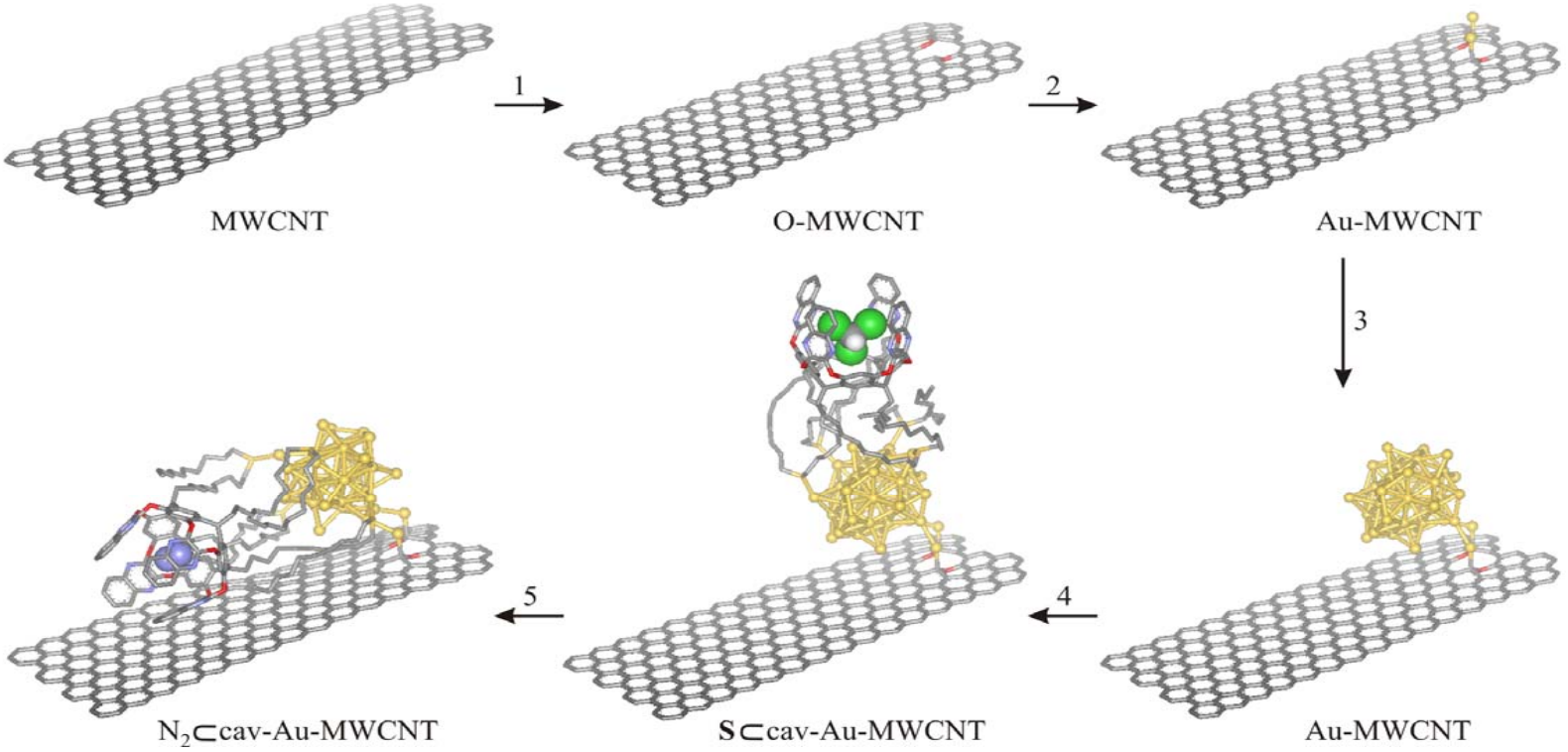


Functionalisation with macromolecules



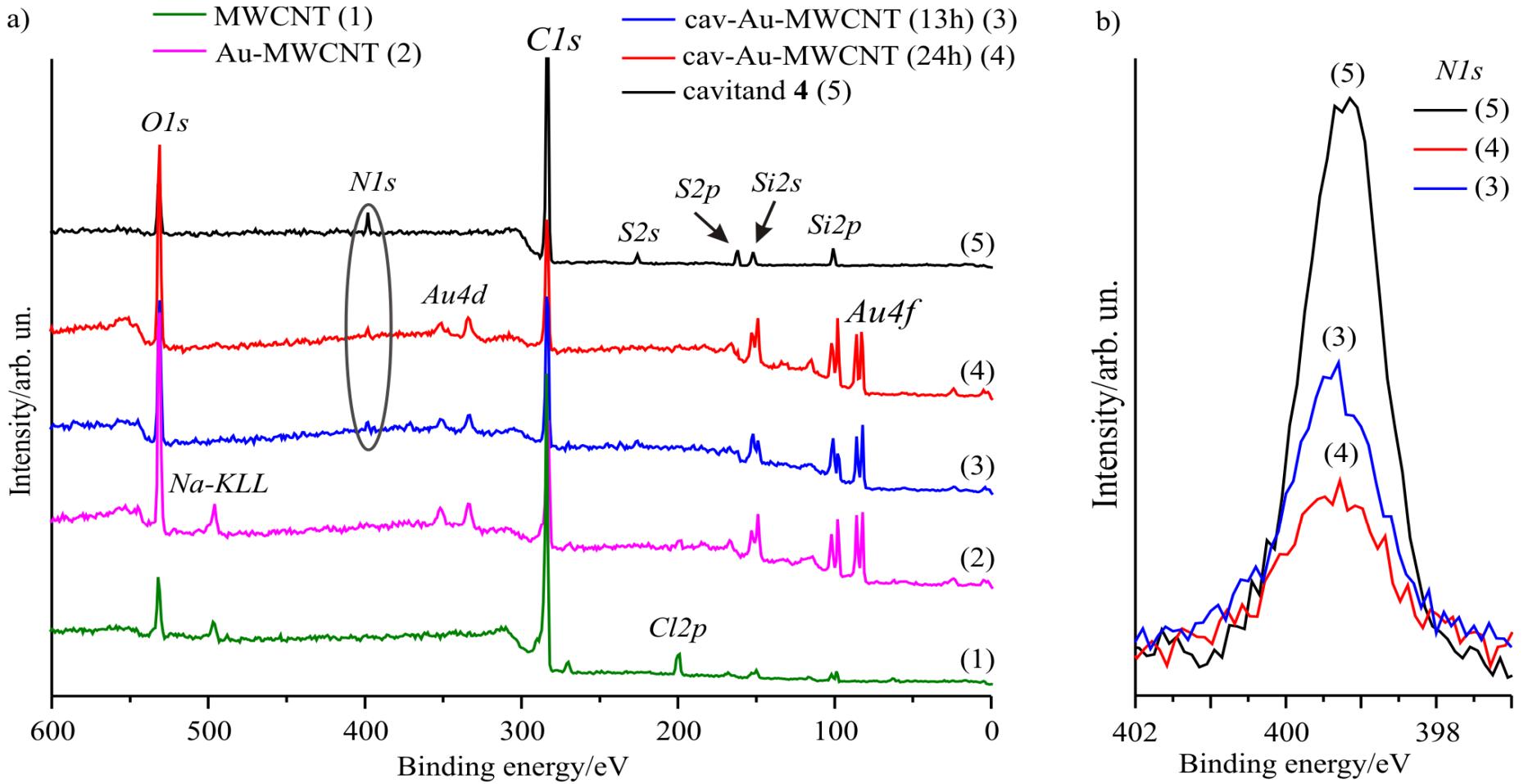


SAM of a quinoxaline-walled thioether-legged cavitand



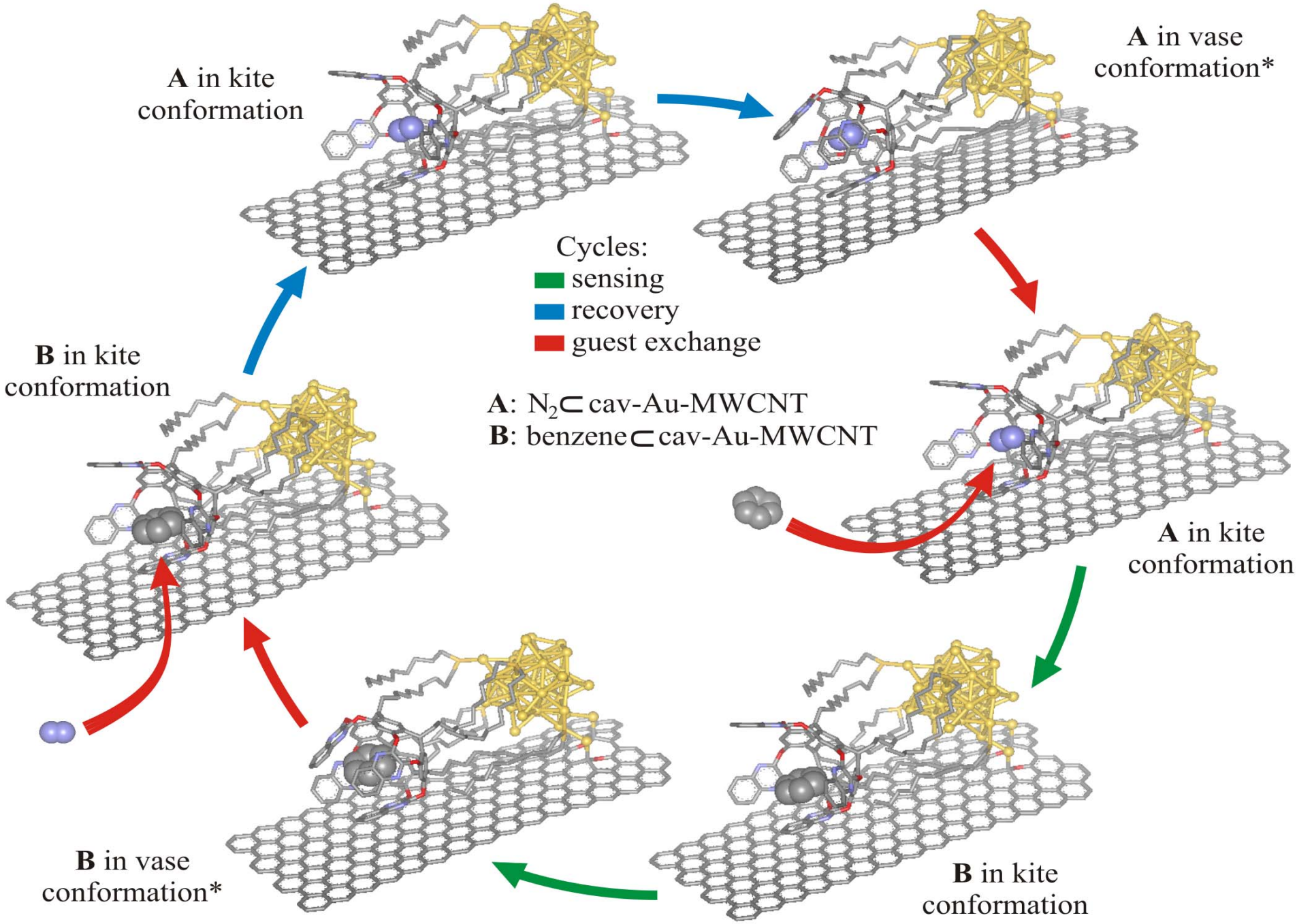
P. Clément, E.J. Parra…, E. Llobet. Advanced Functional Materials 2015. DOI: 10.1002/adfm.201501234
Patent filled 2014

Cavitand functionalised carbon nanotubes

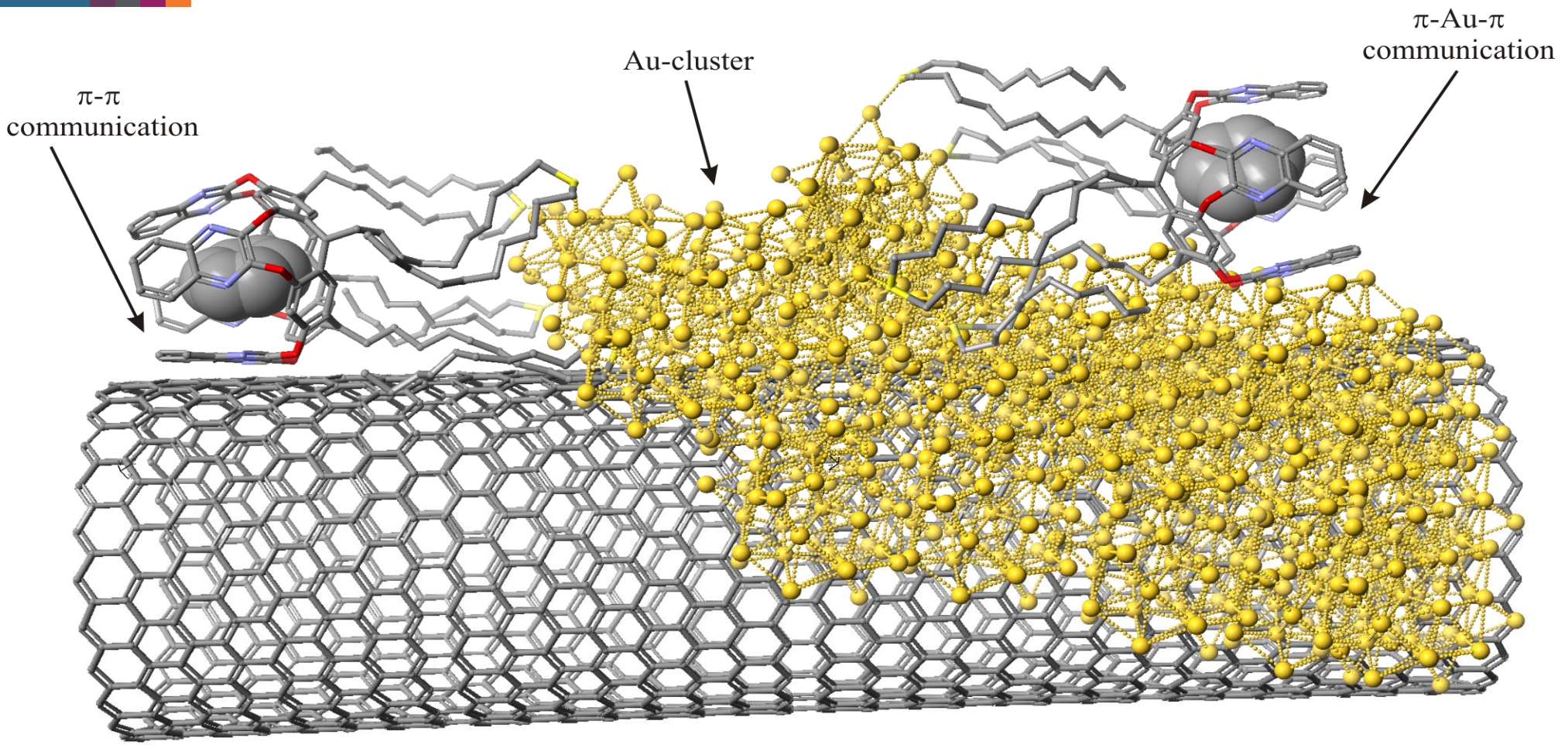


a) Survey spectra acquired for each step of the MWCNTs modification (1-4) and for the cavitand (5). b) a zoom-in of N1s core level spectra are plotted as acquired from cavitand (5) and cav-Au-MWCNT samples (3 and 4).

Cavitand functionalised carbon nanotubes



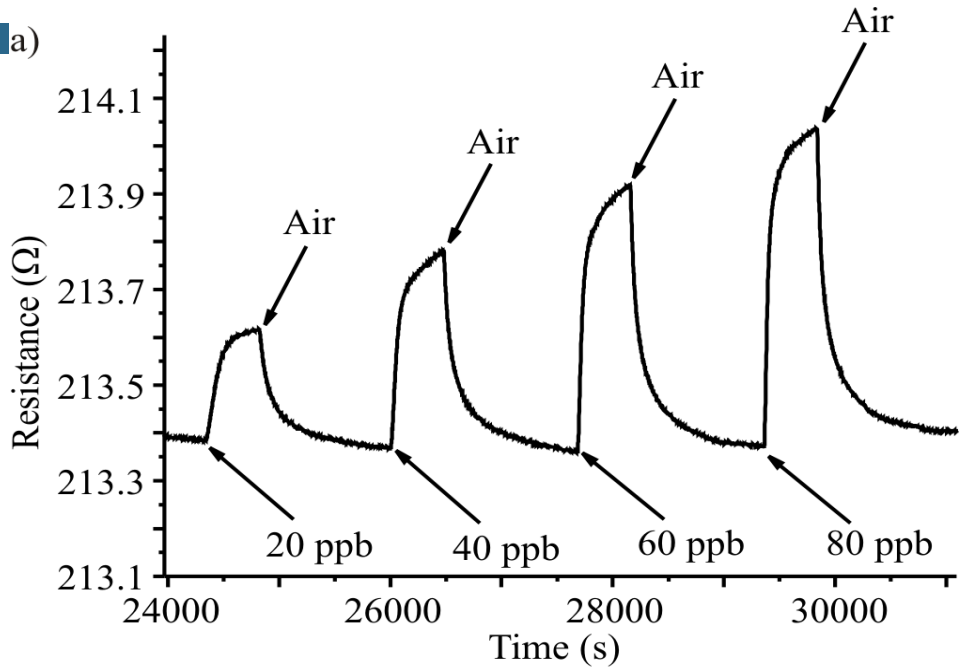
Cavitand functionalised carbon nanotubes

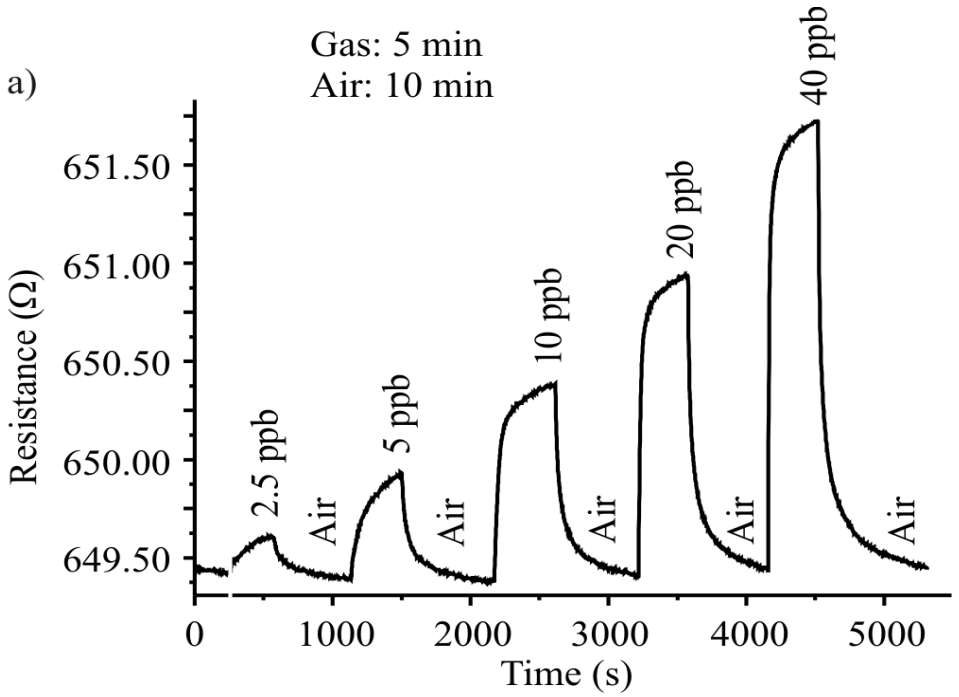


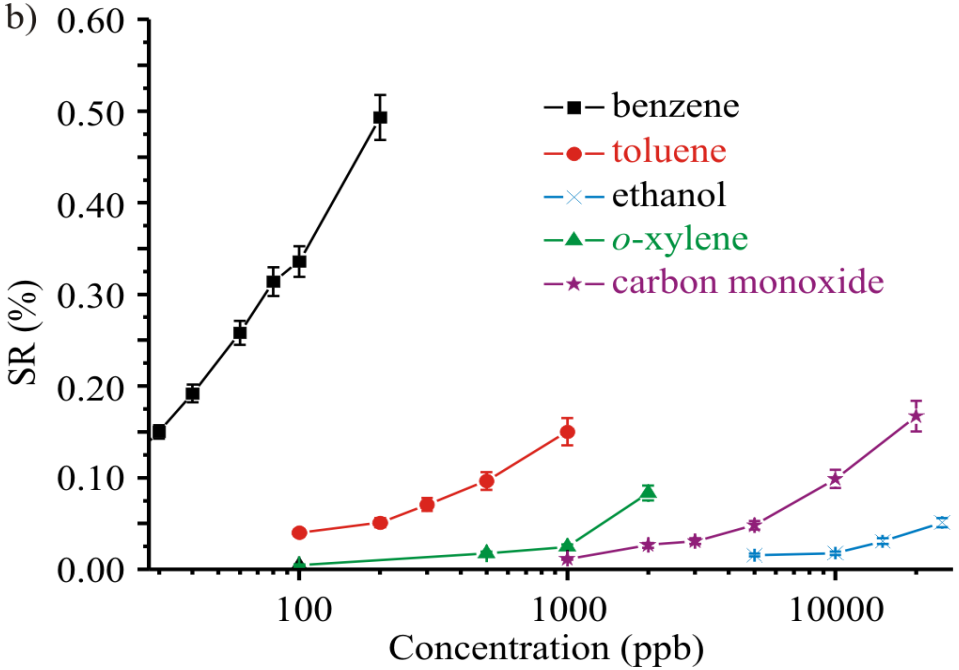
Representation of two proposed types of communication between the cavitand and the Au-MWCNT.

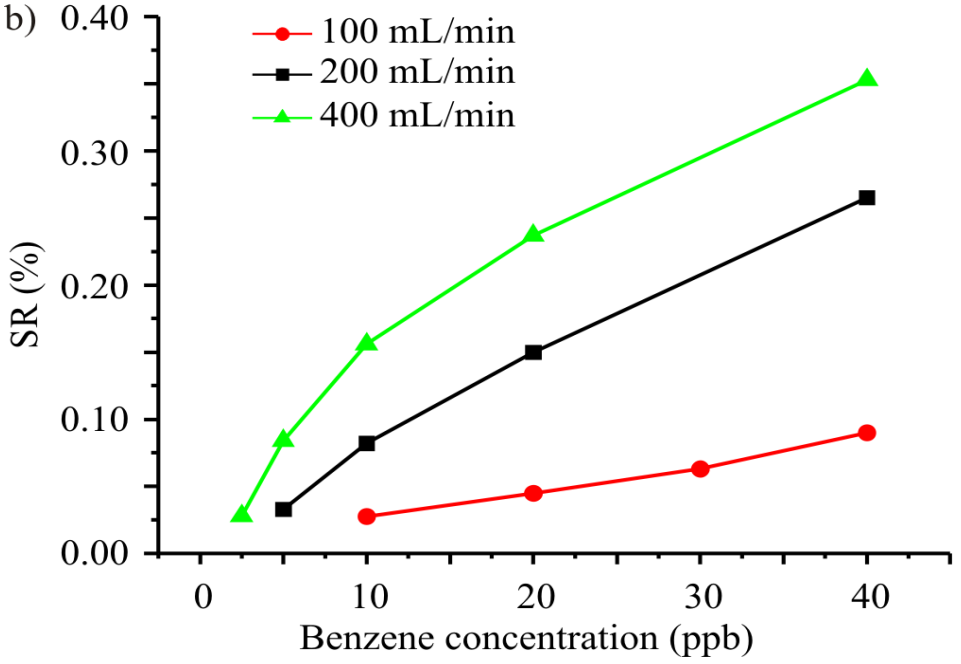
P. Clément, E.J. Parra…, E. Llobet. Advanced Functional Materials 2015. DOI: 10.1002/adfm.201501234
Patent filled 2014

Detection results









P. Clément, E.J. Parra…, E. Llobet. Advanced Functional Materials 2015. DOI: 10.1002/adfm.201501234
Patent filled 2014

Conclusions and outlook

• CNTs enable the detection of a-VOCs with sensors that can be fully operated at room temperature.

• The decoration of CNT sidewalls with metal nanoparticles helps tuning sensitivity to target species.

• However, a significant overlapping sensitivity remains present.

• Functionalisation with SAMs of macromolecules helps dramatically increasing sensitivity and promotes selectivity.

• Fighting humidity cross-sensitivity remains an open issue.

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