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Electrophoretic Gold Nanoparticles Depostion On Carbon Nanotubes For NO_2 Sensors

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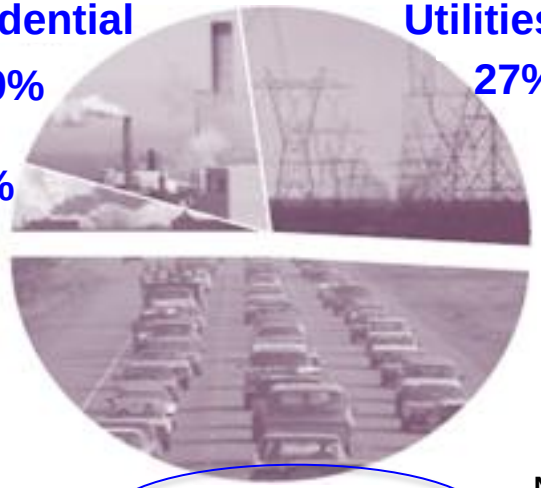
Source and Effects of NO_2: *Why NO_2 Monitoring?*



EURO 6 limits NOx emissions: 0.060 g/km
(entry into force in Sept. 2014)

Ground-level Ozone (Smog)- formed when NO_2 react in the presence of sunlight.

Acid Rain – NO_2 react with other substances in air to form acids

Visibility – NO_2 blocks light reducing visibility

Global Warming – NO_2 is a grrenhouse gas

Mobile- NO_2 transported long distances on prevailing winds

NO_2

Respiratory problems: inflammation of the lining of the lungs, and it can reduce immunity to lung infections.

Particles – NO_2 reacts to form acid vapor and particles

NO_2 useful detection limits*: 10 ppb
(EPA- U. S. Environmental Protection Agency March 2013)

Strict emission standards and the increasing awareness have induced the growth of sensor market.

LIMITATIONS: *Current gas sensors address only a minimal set of sensing needs.*

- Sensitivity/Detection Limit
- Selectivity
- Kinetic response
- Temperature range
- Stability and Reproducibility
- Life Time

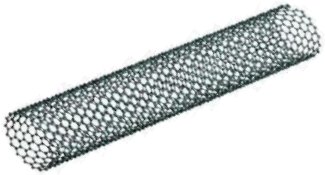
Material Selection for Gas Sensing: *CNTs*

Advantages and Disadvantages of Existing Gas Sensors

SENSOR	SIZE	POWER	SELECTIVITY	SENSITIVITY	STABILITY
Analytical equipment	☹	☹	☺	☺	☺
Electrochemical sensors	☺	☺	☹	☺	☺
Catalytic bead sensors	☺	☹	☹	☹	☺
Metal oxide semiconductors	☺	☹	☹	☹	☺
Conductive polymer sensors	☺	☺	☹	☺	☹

✓CARBON NANOTUBE as *sensing material*

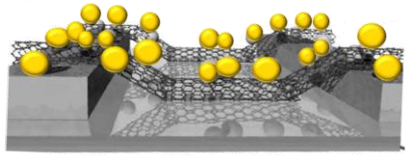
☺ Nanostructured material: high surface area
☺ High adsorption capacity
☺ Large change in electrical properties
☺ High selective
☺ Stable physically and chemically



✓FUNCTIONALIZATION WITH METAL NPs TO IMPROVE GAS SENSING PROPERTIES

FUNCTIONALIZED CNTs (p-type): MODEL OF CATALYTICALY-INDUCED CHARGE TRANSFER

Interaction with gas molecules results in an electronic charge transfer between the molecule and the CNT-NP sensor, which affects the position of the Fermi energy and, hence, the conductivity of the detection unit.

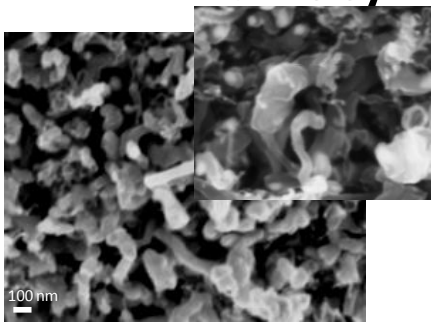


Electron acceptor gases (NO_2, O_2) → -Resistance ↓ -Conductivity ↑

Electron donating gases (NH_3, CO) → -Resistance ↑ -Conductivity ↓

Experimental Set-Up

▪CNTs synthesis



CNTs GROWTH By CVD TECHNOLOGY

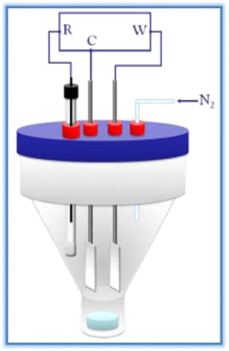
Substrate: film cobalt (Co) nanoclusters, 6 nm thick

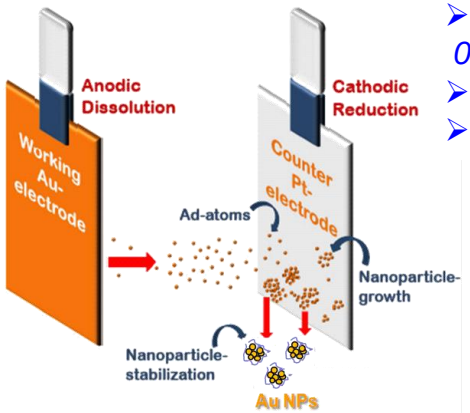
1st step: H_2 plasma pretreatment @ 550°C

2nd step: $H_2 + C_2H_4$ @ 550°C

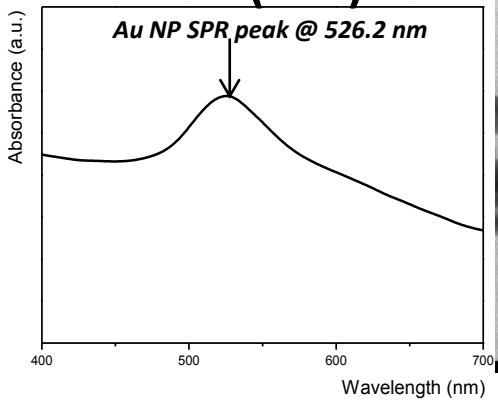
M. Penza et al., Sens. Actuators B 144 (2010) 387-394

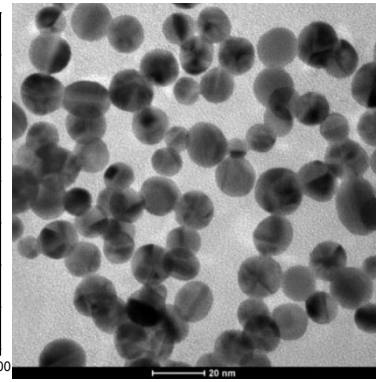
▪Au-NPs electrochemical synthesis Sacrificial Anode Electrolysis (SAE)





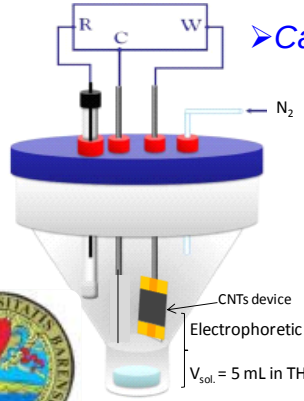
- *Electrolytic solution : 0.05 M TOAC in THF/ACN=3:1*
- *Electrolysis potential: 1 V*
- *Electrolysis charge: 300 C*





Stabilized spherical Au NPs with diameter of 12 nm

▪Electrophoretic deposition of Au NPs on CNTs-based gas sensor device



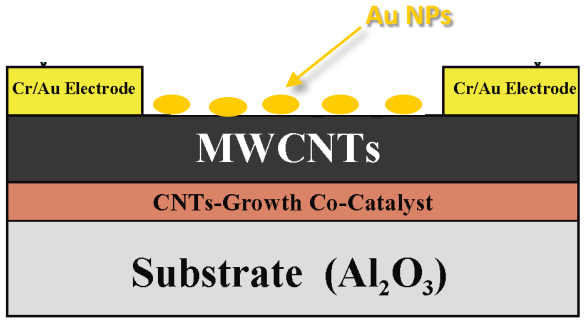
- *Cathodic process E(V) = -0.5 V (ocp: -0.3 V)*

Process parameters:

$t_{deposition}$: 90 s — *i = 6.3 10⁻⁴ A Q = 5.598 10⁻² C*

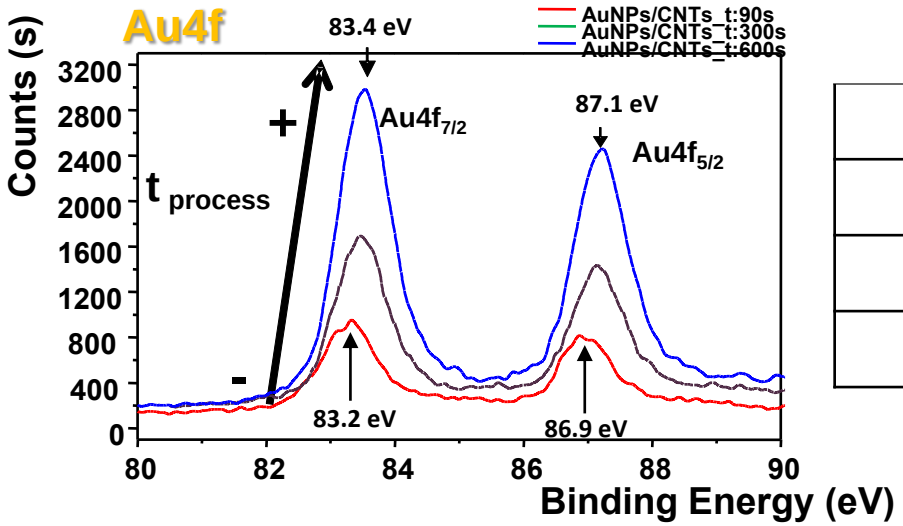
$t_{deposition}$: 300 s — *i = 3.4 10⁻⁴ A Q = 9.869 10⁻² C*

$t_{deposition}$: 600 s — *i = 3.4 10⁻⁴ A Q = 2.069 10⁻¹ C*



Characterization

▪Surface Chemical Analysis

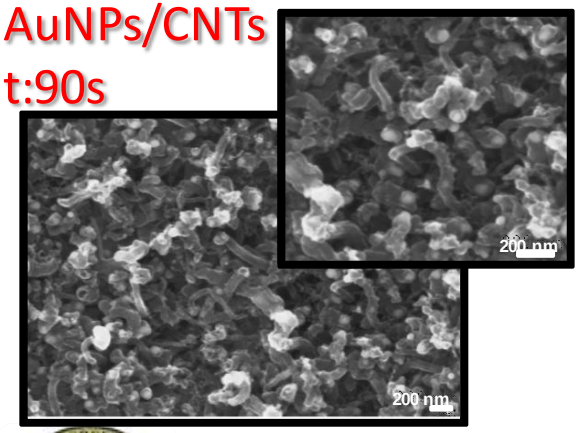


	C1s(%)	Au4f (%)	O1s(%)
CNTs as received	95.0 ± 0.5	/	5.0 ± 0.5
Au NPs/CNTs t:90s	94.4 ± 0.5	0.3 ± 0.2	5.3 ± 0.5
Au NPs/CNTs t:300s	92.0 ± 0.5	0.5 ± 0.2	7.5± 0.5
Au NPs/CNTs t:600s	91.2± 0.5	1.1 ± 0.2	7.8± 0.5

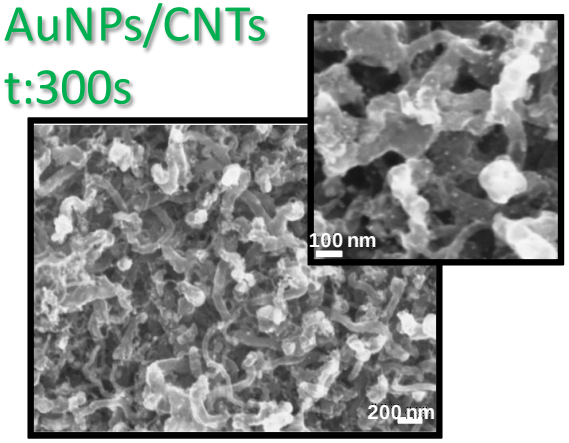
- **Deposition of Au NPs on CNTs : Au NPs decorate CNTs.**
- **The content of deposited Au NPs increases increasing the process time.**
- **Shift of Au4f B.E. to higher eV increasing the deposition process time (*increase of NPs cluster dimension)***

▪Morphology

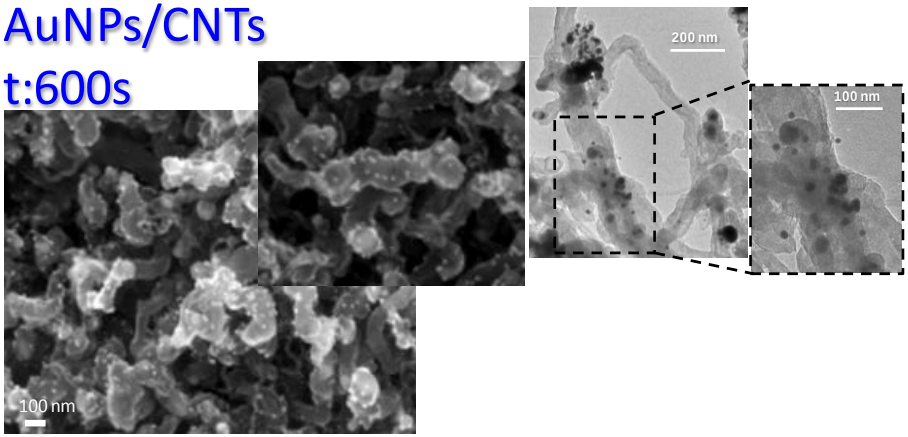
AuNPs/CNTs t:90s



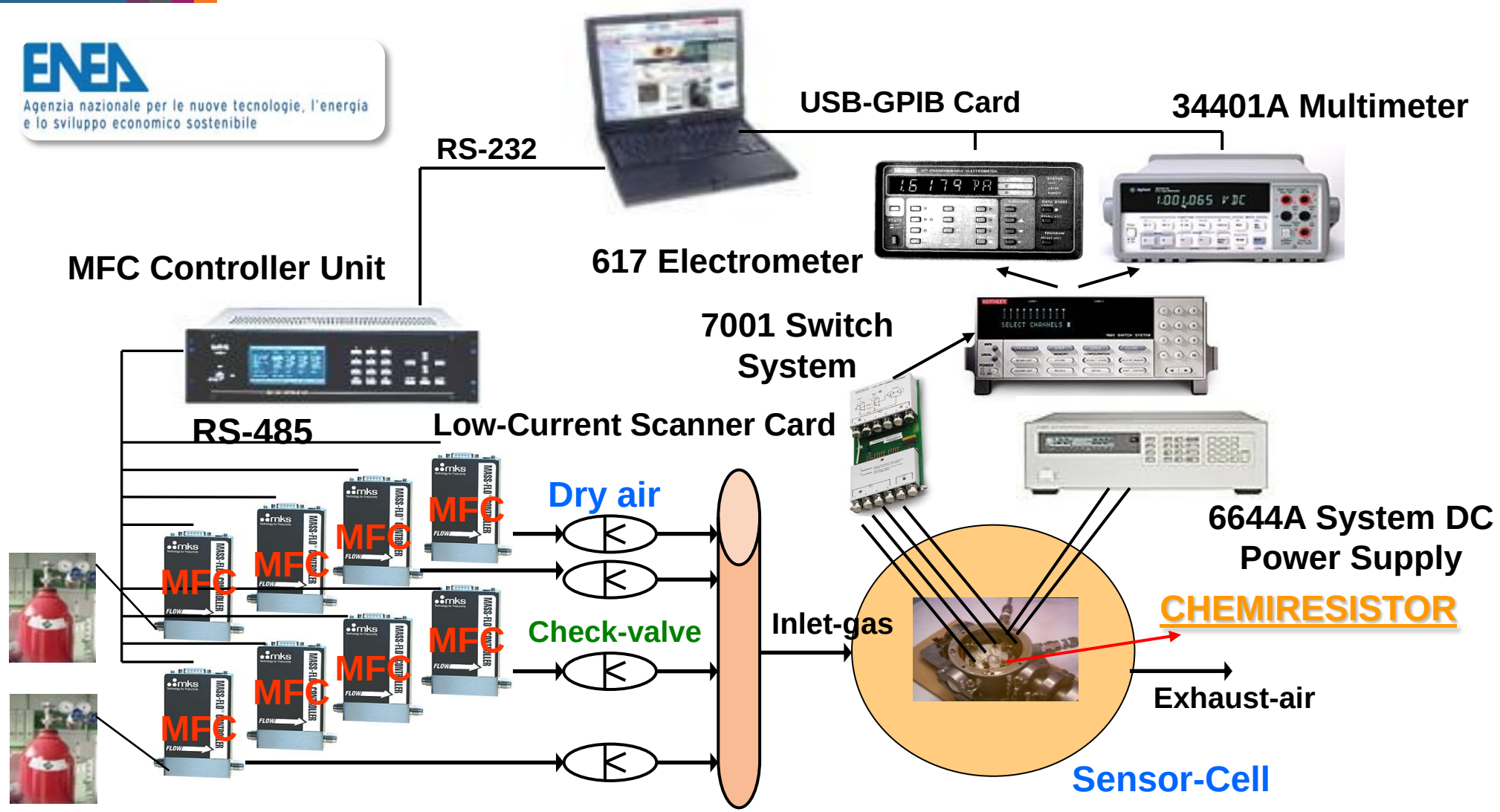
AuNPs/CNTs t:300s



AuNPs/CNTs t:600s



GAS SENSING FUNCTIONAL TESTS



M. Penza et al., Sens. Actuators B 135 (2008) 289-297

NO_2 GAS SENSING

Gas: **NO_2** - Carrier Gas: Air

$t_{exposure}$: 10 min – $t_{recovery}$: 60 min (in Air)

- *NO_2 concentration effect [range: 10-0.1 ppm]*
- *$T_{process}$ effect [range 100-200°C]*

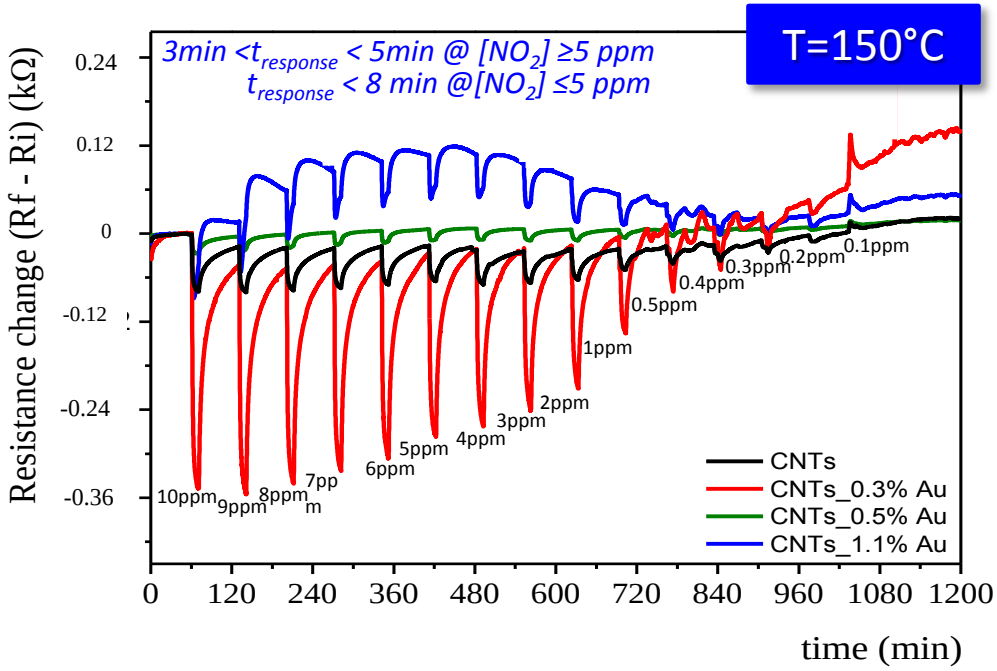
$$S_m = \frac{1}{n}\sum_{i=1}^{n}\frac{(\Delta R / R)_i}{c_i}(\% / ppm)$$

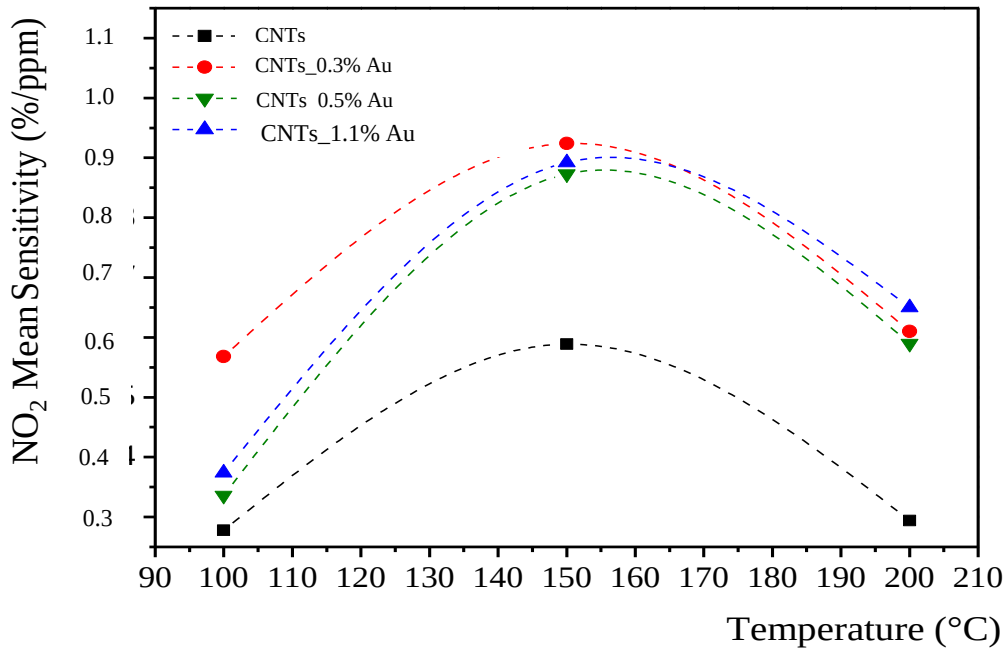
S_m = average sensitivity

$\Delta R / R_i$ = sensor response

c_i = gas concentration

n = number of exposures





✓NO_2 MEAN SESNITIVITY IS HIGHER FOR Au NPs DECORATED CNTs AT ALL INVESTIGATED T

✓AuNPs DECORATED CNTs ARE STABLE IN THE INVESTIGATED RANGE OF T

✓MAXIMUM NO_2 MEAN SENSISTIVITY @ T= 150°C

INTERFERING GASES

❑ **SO_2** (10-0.5ppm) @ T =150°C

VERY LOW RESPONSE: **$\Delta R/R_i$ (%) < 0.5 %**

❑ **CO** (1000 – 25 ppm) @ T =150°C

VERY LOW RESPONSE: **$\Delta R/R_i$ (%) < 0.2 %**

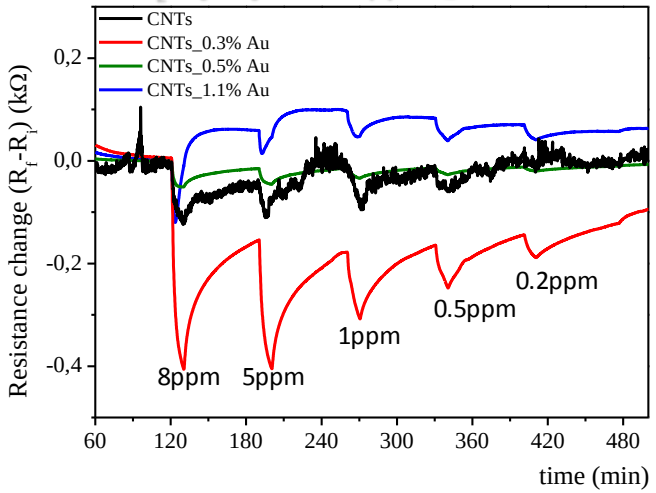
❑ **CH_4** (7000-300ppm) @ T =150°C

VERY LOW RESPONSE: **$\Delta R/R_i$ (%) < 0.5 %**

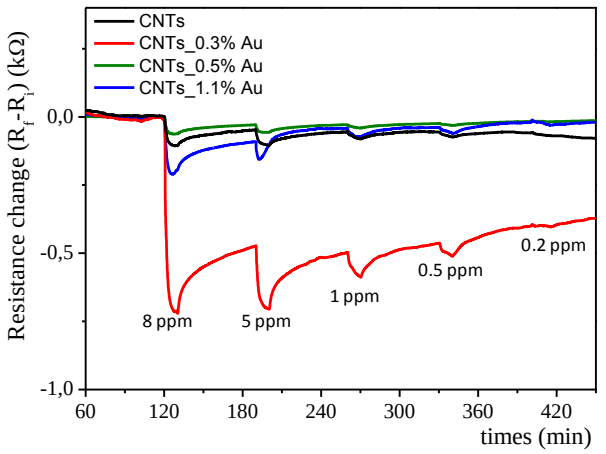
❑ **NH_3** (1000-5ppm) @ T =150°C

VERY LOW RESPONSE: **$\Delta R/R_i$ (%) < 0.5 %**

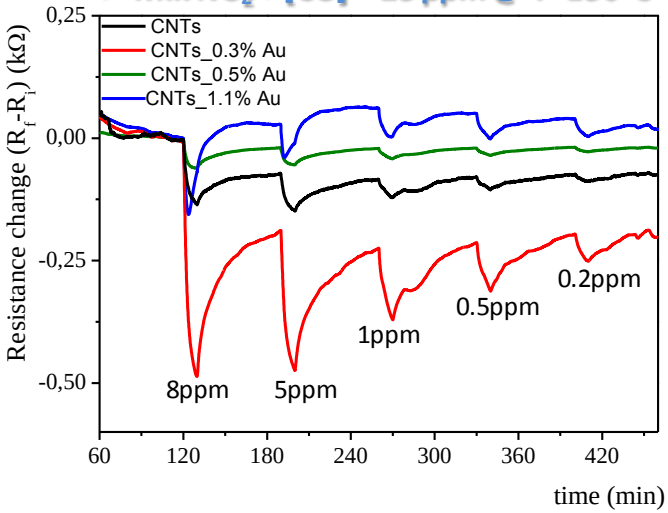
➢ Mix NO_2 + [CO] = 1000 ppm @ T=150°C



➢ Mix NO_2 + [NH_3] = 25 ppm @ T=150°C



➢ Mix NO_2 + [CO] = 25 ppm @ T=150°C



✓ High sensitivity for NO_2 also in contemporary presence of intering gases

HIGH SELECTIVITY FOR NO_2

CONCLUSION

✓A tunable loading of Au NPs with uniform dimension is efficiently deposited directly on the surface of CNTs-based sensor device by electrophoretic process.

✓Au NPs functionalized CNTs-based gas sensor have an higher thermal stability than un-functionalized one.

✓Au NPs functionalized CNTs-based gas sensor have an higher NO_2 sensitivity and selectivity than un-functionalized one, revealing [NO_2] in sub-ppm range.

FUTURE PROSPECTIVES

✓Investigation of other interfering gases.

✓Optimization of electrophoretic deposition conditions.

✓Electrophoretic functionalization of CNTs-based gas sensor devices with other metals and/or metal oxides nanoparticles.


THANK YOU !