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

COST Action TD1105

WGs and MC Meeting at ISTANBUL, 3-5 December 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016

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

Electrophoretic Au NPs Deposition on Carbon Nanotube Networked Layers for Gas Sensors

Elena Dilonardo, External Expert, elena.dilonardo@uniba.it

Università degli studi di Bari Aldo Moro, Bari/ Italy

other authors: **M. Penza**, **M. Alvisi**, **C. Di Franco**, **D. Suriano**, **R. Rossi**, **F. Palmisano**, **L. Torsi**, **N. Cioffi**

Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile

COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

Background - Motivation

- **Involved in 2 National Projects** concerning the synthesis of Automotive Exhaust Gas Sensors based on catalytic metal nanopartciles supported on nanostructured materials for monitoring NOx, HCs.
- **Background:** Electrochemical Synthesis of colloidal metal nanoparticles; Sol-gel synthesis of nanostructured metal oxides (MOx); Electrochemical modification of nanostrucutrued nanostrucutred materials by metal nanoparticles.

Current research activities

ELECTROCHEMICAL FUNCTIONALIZATION OF CNT-BASED GAS SENSORS BY METAL NPs TO IMPROVE GAS SENSING PROPERTIES

Research collaboration with the sensor laboratory of Dr Michele Penza and the thin film laboratory of Dr Marco Alvisi @ENEA in Brindisi

ENEA
AGENZIA NAZIONALE PER LE NUOVE TECNOLOGIE, L'ENERGIA E LO SVILUPPO ECONOMICO SOSTENIBILE

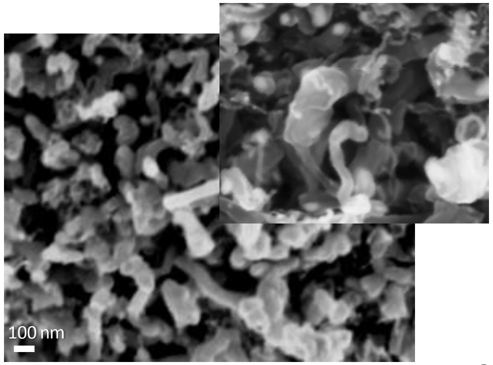
- ❑ **CNT-based chemoresistive gas sensors**
- ❑ **Gas sensing set-up**

Università degli Studi di Bari Aldo Moro

- ❑ **Direct functionalization of CNT-based chemoresistive gas sensors by electrophoretic Au NPs deposition**
- ❑ **Chemical and morphological characterization of gas sensors**

Experimental set-up

▪CNTs GROWTH By CVD TECHNOLOGY @ENEA THIN FILM LABORATORY



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

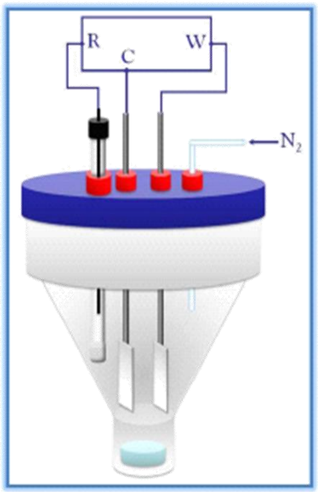
1st step: H_2 plasma pretreatment @ 550°C

2nd step: $H_2 + C_2H_4$ @ 550°C

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

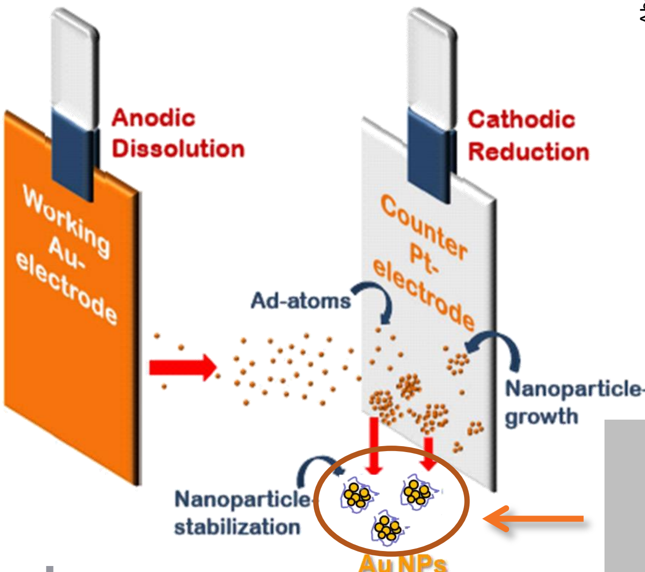
▪Au-NPs electrochemical synthesis Sacrificial Anode Electrolysis (SAE) @UNIBA

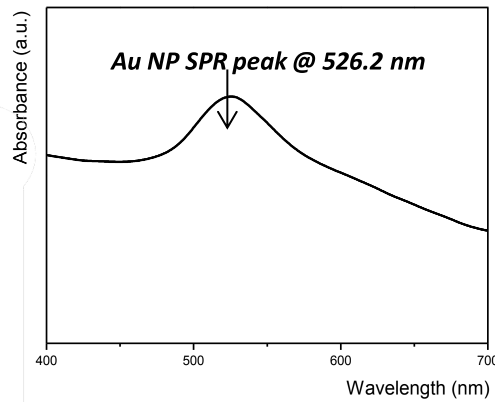
- *Electrolytic solution :*
  0.05 M TOAC in THF/ACN=3:1
- *Electrolysis potential: 1 V*
- *Electrolysis charge: 300 C*

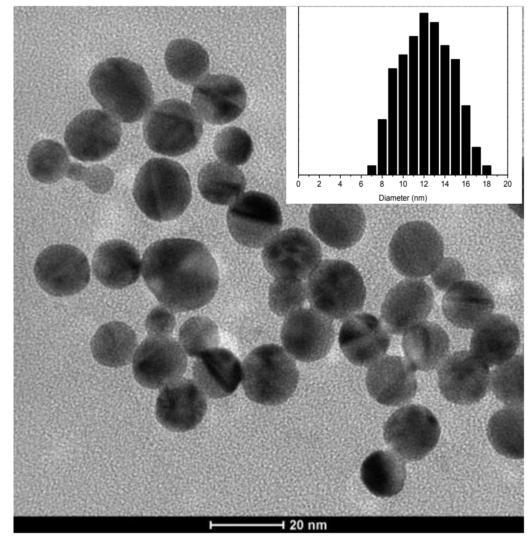


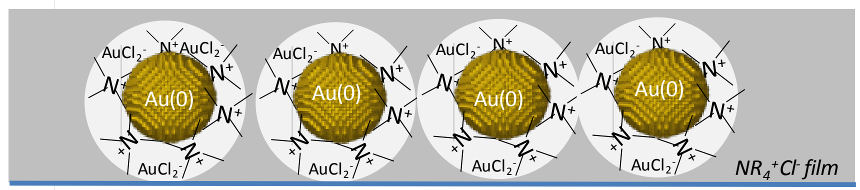
$M_{(bulk)} \rightarrow M^{n+} + n\,e^-$

$M^{n+} + n\,e^- \rightarrow M_{(nanoparticles)}$









N. Cioffi et al., Electrochimica Acta 56 (2011) 3713–3720

Experimental set-up

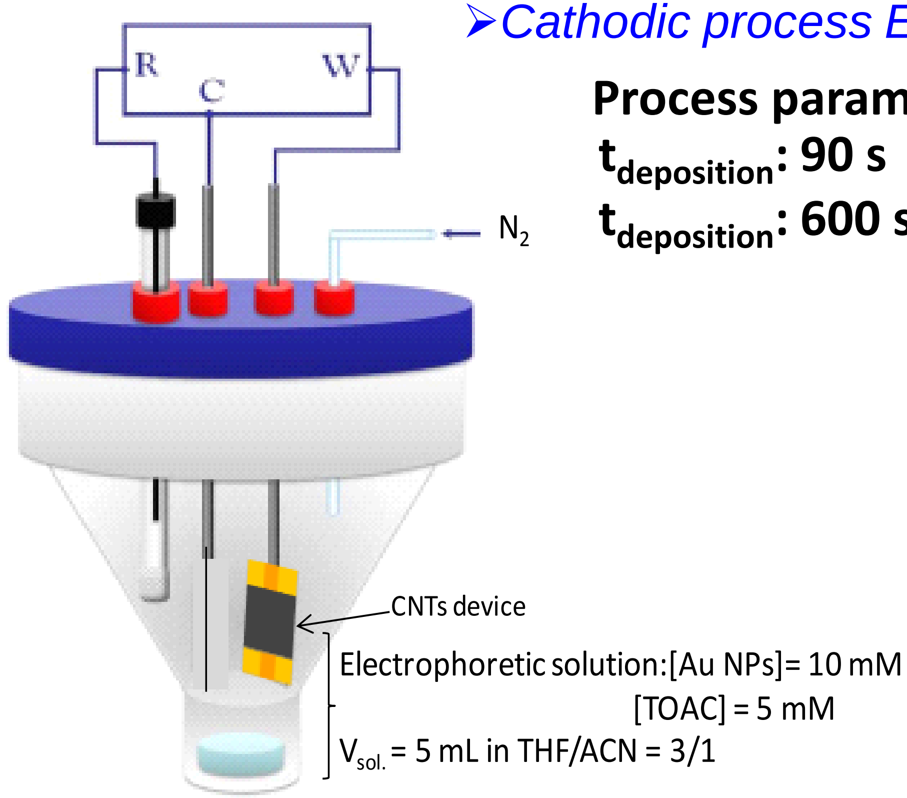
- **Electrophoretic deposition of Au NPs on CNTs-based gas sensor device @ UNIBA**

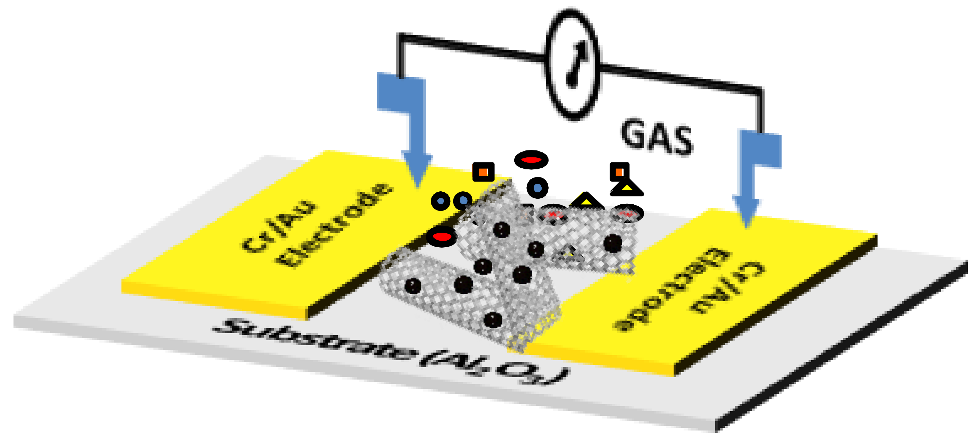
  - *Cathodic process E(V) = -0.5 V (ocp: -0.3 V)*

Process parameters:

$t_{deposition}$: 90 s ➔ ***$i = 6.3\ 10^{-4}$ A $Q = 5.598\ 10^{-2}$ C***

$t_{deposition}$: 600 s ➔ ***$i = 3.4\ 10^{-4}$ A $Q = 2.069\ 10^{-1}$ C***

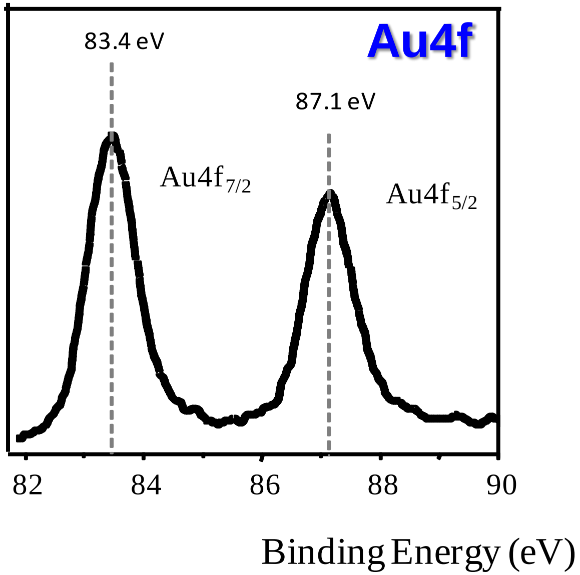




E. Dilonardo et al.., J. Sens. Sens. Syst. 3 1–8 2014.

Characterization

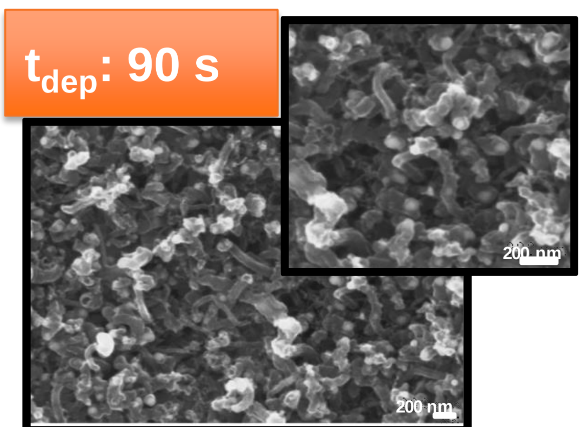
▪Surface Chemical Analysis by XPS @UNIBA

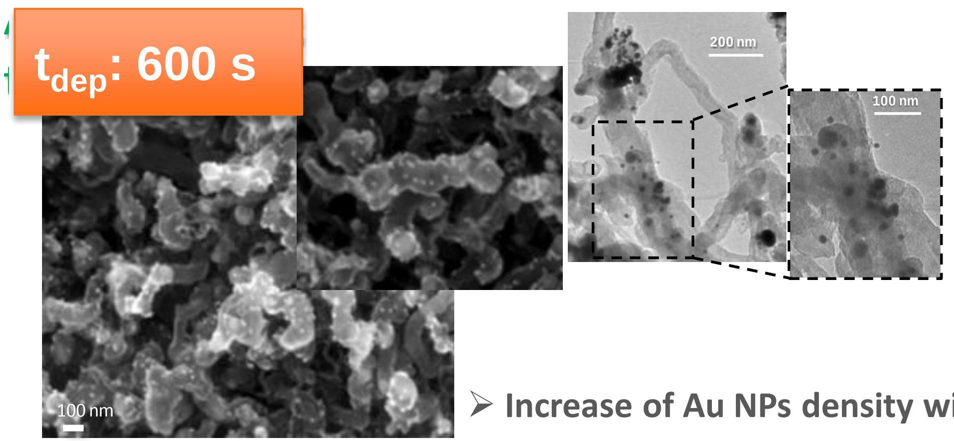


SAMPLE	C (%)	Au (%)	O (%)
CNTs as received	95.0 ± 0.5	/	5.0 ± 0.5
Au NPs/CNTs t:90s	94.4 ± 0.5	0.3 ± 0.2	5.3 ± 0.5
Au NPs/CNTs t:600s	91.2± 0.5	1.1 ± 0.2	7.8± 0.5

- Successful electrophoretic decoration of CNT by Au NPs.
- Nano size of gold particles: Au4f$_{7/2}$@ 83.4 eV (initial state size effects).
- Fine tuning of Au content by deposition time: increasing of Au loading with the deposition time.

▪Morphological and Structural analyses @UNIBA





- Increase of Au NPs density with the deposition time.

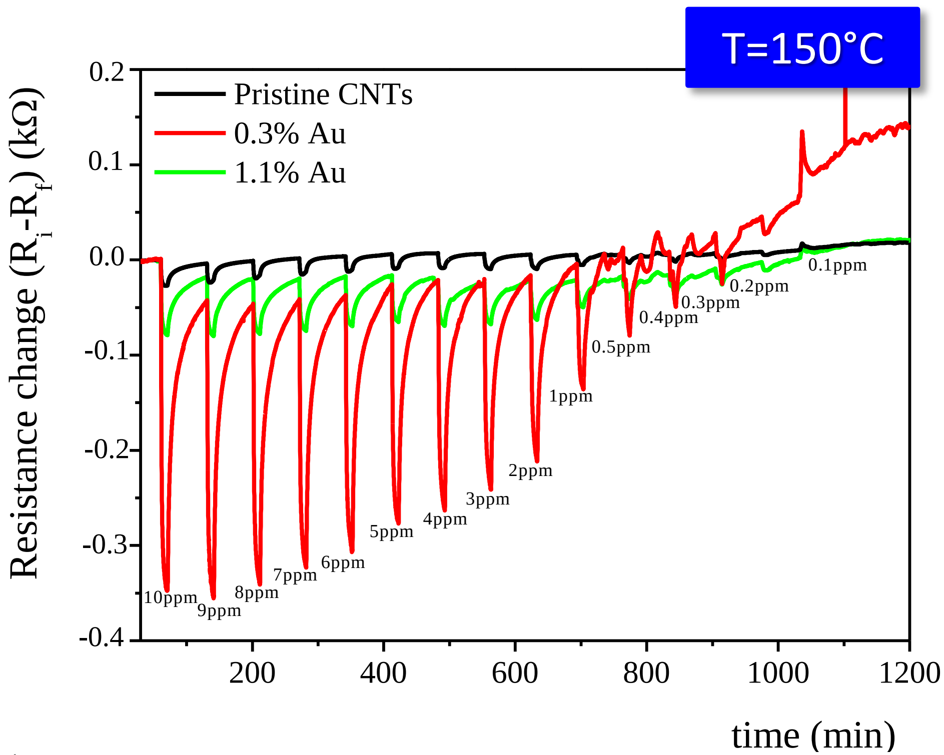
Characterization

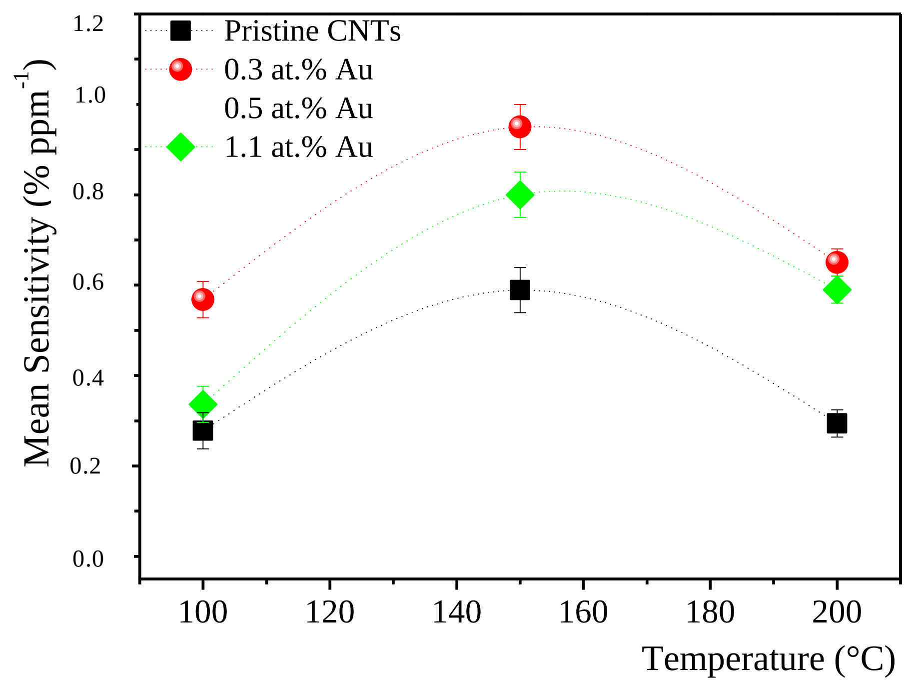
▪**Gas Sensing Measurements @ENEA**

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]*





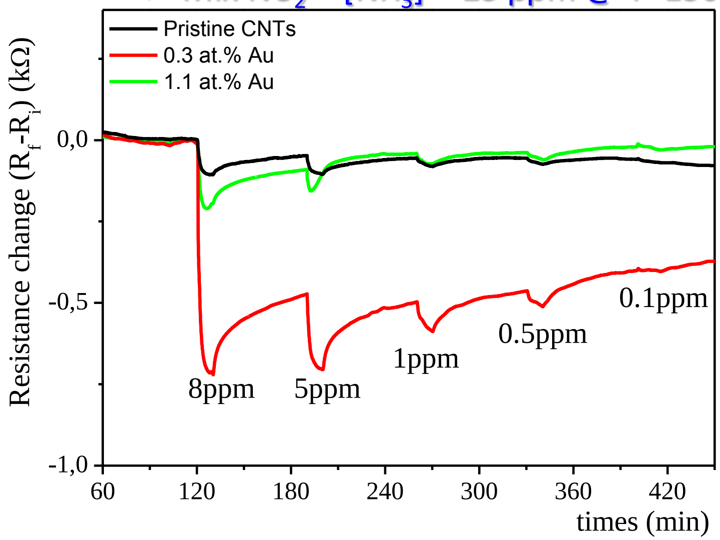
✓NO_2 MEAN SESNITIVITY IS HIGHER FOR Au NPs DECORATED CNTs AT ALL INVESTIGATED T

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

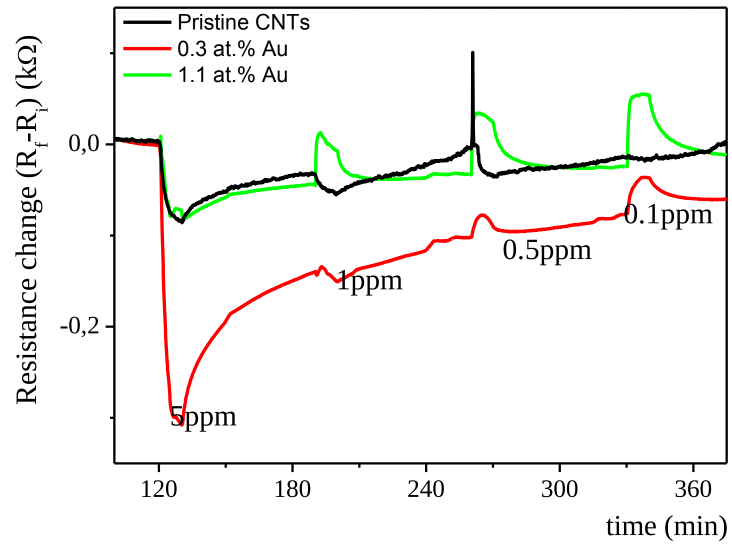
✓MAXIMUM NO_2 MEAN SENSISTIVITY @ T= 150°C

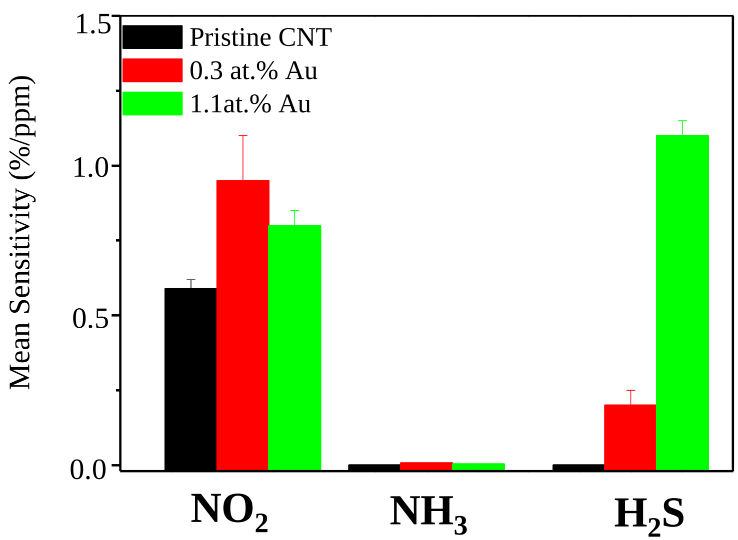
▪INTERFERING GASES

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



➤ Mix NO_2 + $[H_2S]$ = 1 ppm @ T=150°C





✓ High selectivity for NO_2 at low Au content

✓ High selectivity for H_2S at high Au content

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.

✓Functionalized CNTs-based gas sensor with low Au content reveals an higher NO_2 sensitivity and selectivity, also for [NO_2] in sub-ppm range.

FUTURE PROSPECTIVES

✓Investigation of the gas sensing mechanism of Au-functionalized CNTs towards NO_2 and H_2S.

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

Acknowledgments

The authors thank the Ministry of University and Scientific Research (MIUR) of Italy, for funding *INNOVHEAD - Tecnologie innovative per riduzione emissioni, consumi e costi operativi di motori Heavy Duty* - PON 2007-13 (N. contract PON-02_00576-3333604).


THANK YOU
FOR YOUR
ATTENTION!!!
FORZA BARI
#amalabari