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COST Action TD1105

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New Trends and Challenges for Air Quality Control

University of Latvia - Faculty of Geography and Earth Sciences

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ELECTROCHEMICAL PROCESSES TO FUNCTIONALIZE NANOSTRUCTURED SENSITIVE LAYERS FOR NO_2 GAS SENSORS

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Motivation

❑ Environmental monitoring of pollutant gases

Pollulants/Analyte

- Reducing gases (CO, H_2, HCs, H_2S, NH_3)
- Oxidizing gases (O_2, O_3, NO_X,)

Chemical reaction at the interface:

- Oxidation/Reduction
- Chemisorption
- Ion exchange
- Adsortpion
- Acid-base
- Precipitation

Receptor: Sensitive layer

Transducer

Signal

- Electrochemical
- Photometric
- Magnetic
- Calorimetric

SENSING LAYER	SIZE	POWER	SELECTIVITY	SENSITIVITY	STABILITY
MOx	👍	👎	👎	👎	👍
CNTs	👍	👍	👎	👎	👎

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

Objectives

❑ Au Functionalization of Nanostructured Sensing Layer

✓Au NPs FUNCTIONALIZATION

SENSING LAYER	SIZE	POWER	SELECTIVITY	SENSITIVITY	STABILITY
Au@MOx	👍	👍	👍	👍	👍
Au/CNTs	👍	👍	👍	👍	👍

✓METHOD FOR FUNCTIONALIZATION

- ➢ Metal Sputtering
- ➢ Thermal Evaporation
- ➢ Electrochemical deposition

→

- ✓Tune of Metal Loading
- ✓NPs Aggregation
- ✓Material Degradation

Anal. Chem. 2010, 82, 250–257.
Carbon 2008, 46, 1966-1972.
Thin Solid Films 2011, 520, 959-965.

PROPOSED SOLUTION:

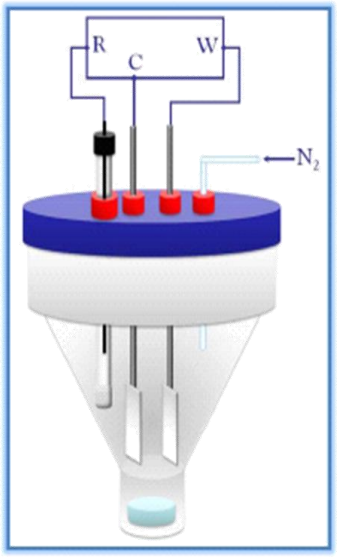
Electrochemical deposition of Au NPs directly on MWCNTs and MOx

- ✓ Tune Au loading
- ✓Prevent material degradation
- ✓Prevent Au NPs aggregation

Methods

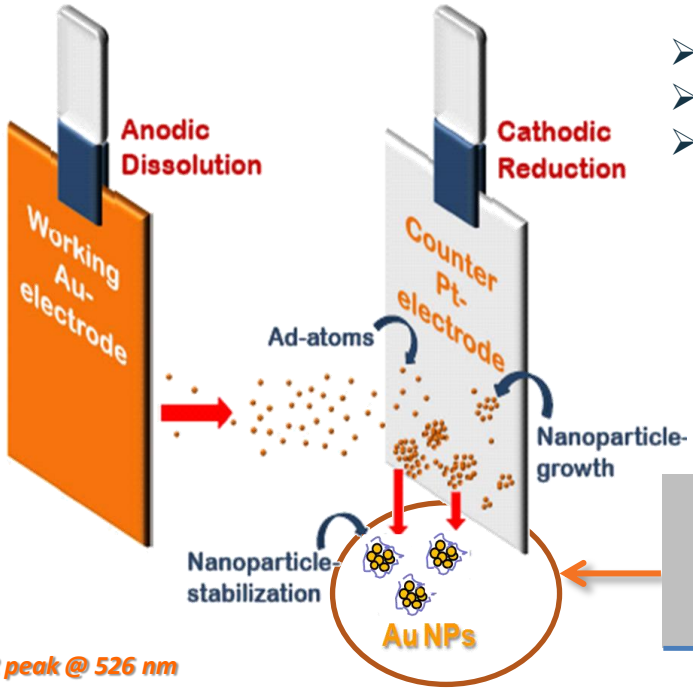
A. Electrochemical functionalization of MWCNTs by Au NPs

STEP 1 *Electrochemical synthesis of Au NPs by Sacrificial Anode Electrolysis (SAE)*



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

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

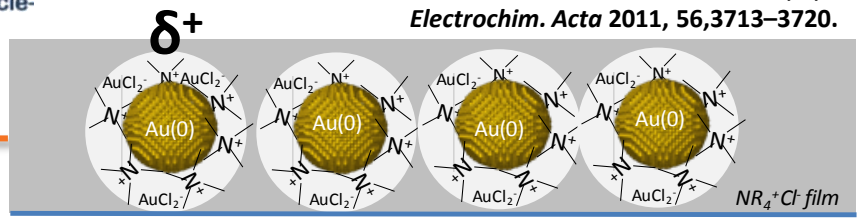


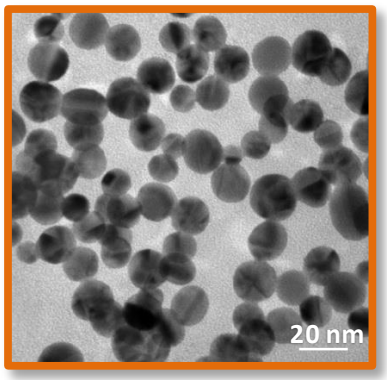
Au NP SPR peak @ 526 nm

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

Core/shell nanomaterial	Working potential (V)	Mean current density (mA/cm^2)	[Au] (mol/l)	λ_{max} (nm)
Au-NPs/TOAC	1.00	1.5	0.2	**526**

Sens. Lett. 2006, 6, 1-8.
Electrochim. Acta 2011, 56,3713–3720.





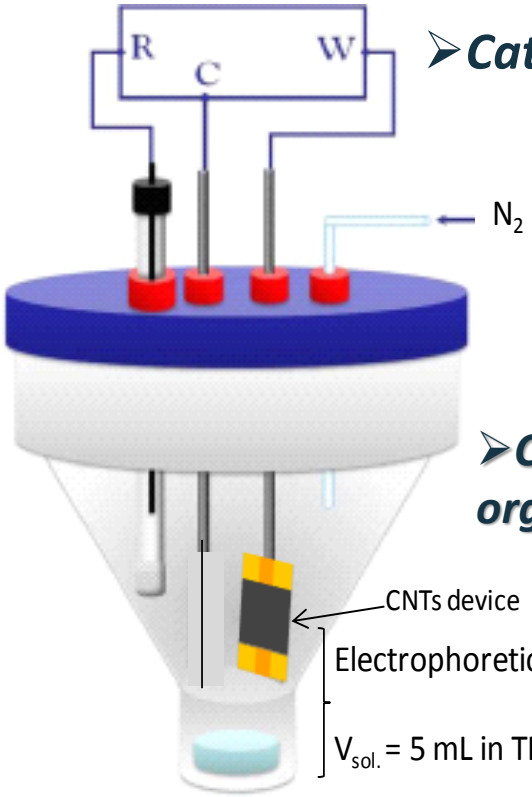
J. Am.Chem. Soc. 1994,116, 7401.
Science 1995, 267, 367.

✓ *Stabilized spherical Au NPs with diameter of 12 nm*

Methods

A. Electrochemical functionalization of MWCNTs by Au NPs

STEP 2 *Electrophoretic deposition of Au NPs on MWCNT-based gas sensors*



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

Process parameters:

$t_{deposition}$: 90 s → $i = 6.3\ 10^{-4}$ A

$t_{deposition}$: 300 s → $i = 3.4\ 10^{-4}$ A

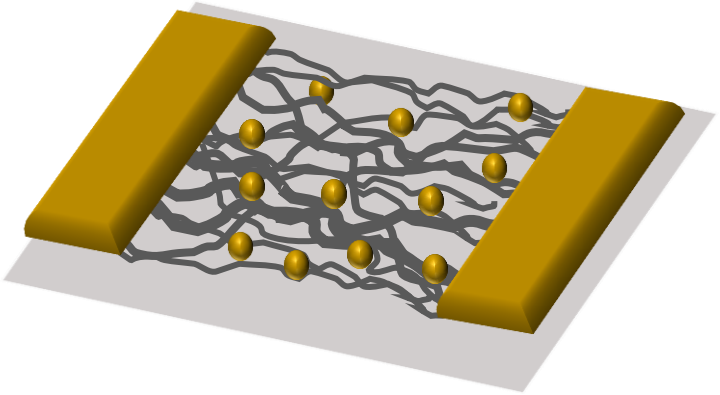
$t_{deposition}$: 600 s → $i = 3.4\ 10^{-4}$ A

Electrophoretic solution:[Au NPs]= 10 mM

[TOAC] = 5 mM

$V_{sol.}$ = 5 mL in THF/ACN = 3/1

➢ *Clean of the hybrid AuNPs/CNTs film by drops of ACN solution to remove the organic shell from Au NPs.*

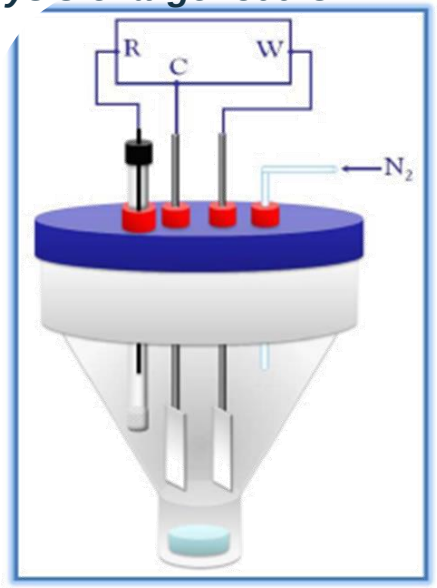


Methods

B. Electrochemical functionalization of MOx by Au NPs

Sacrificial Anode Electrolysis (SAE) has been proposed to obtained stabilized gold Au NPs directly deposited on the surface of MOx nanostructured powders.

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



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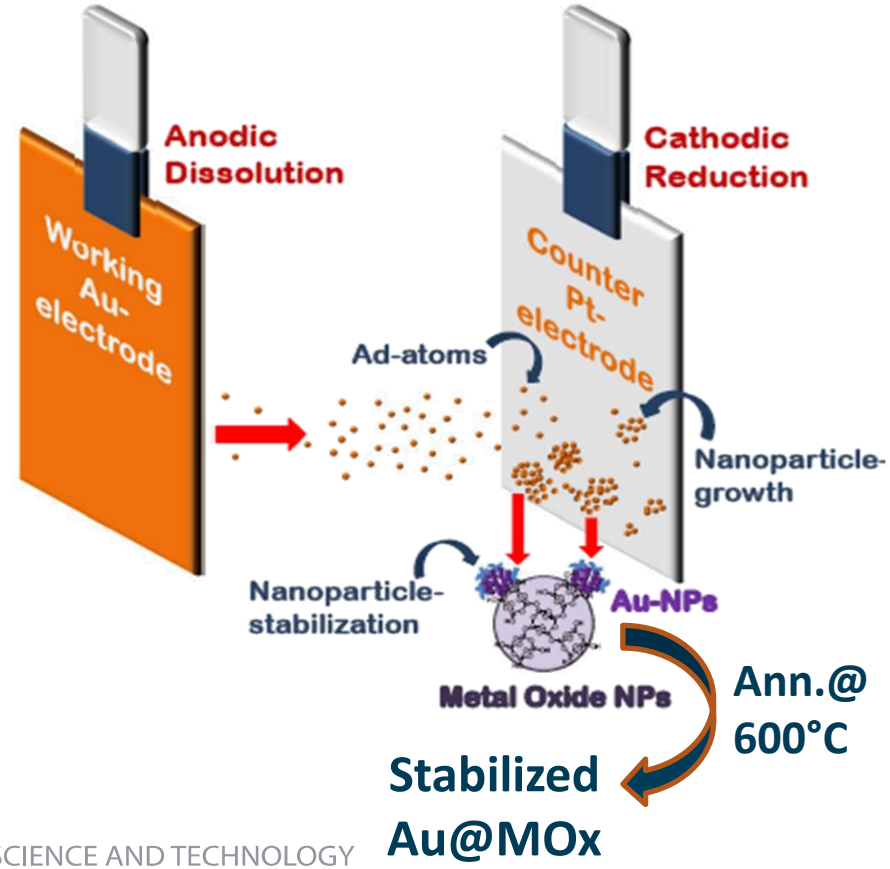
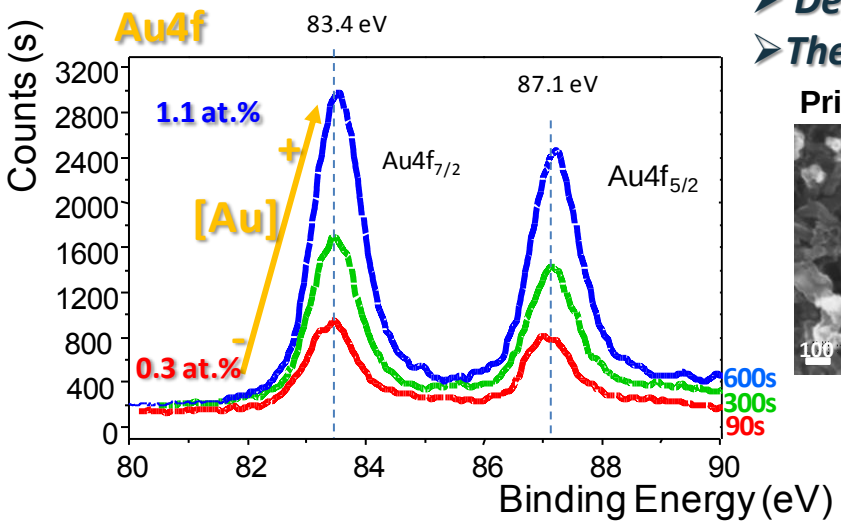
$M^{n+} + n\,e^- \rightarrow M_{(nanoparticles)}$

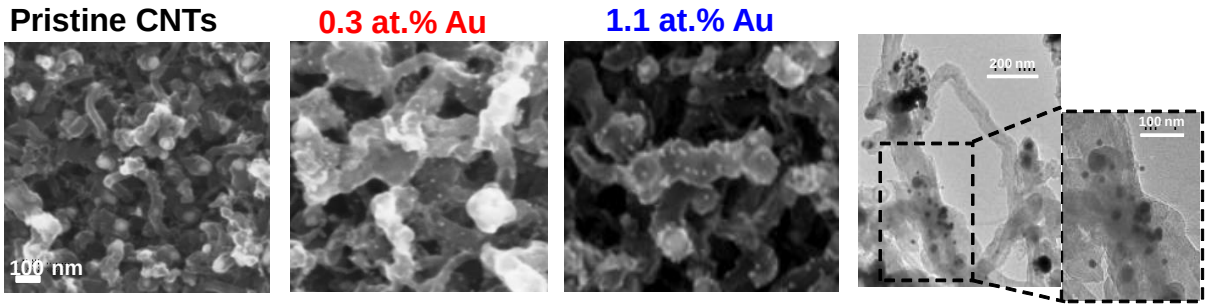


Characterization

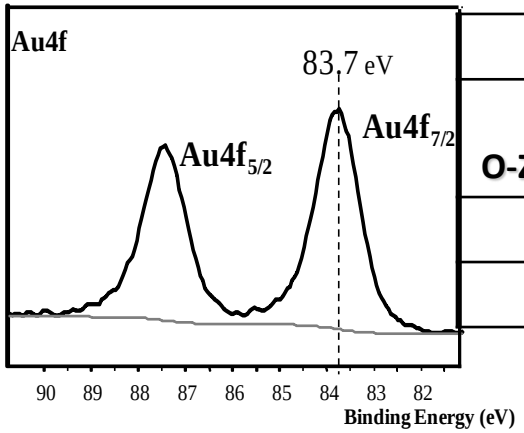
A. Au NPs/CNTs



- *Deposition of Au NPs on CNTs : Au NPs decorate CNTs.*
- *The content of deposited Au NPs increases increasing the process time.*



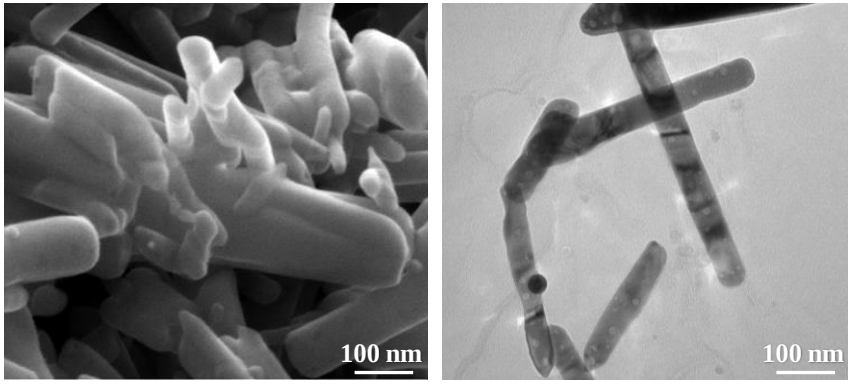
B. Au@ZnO



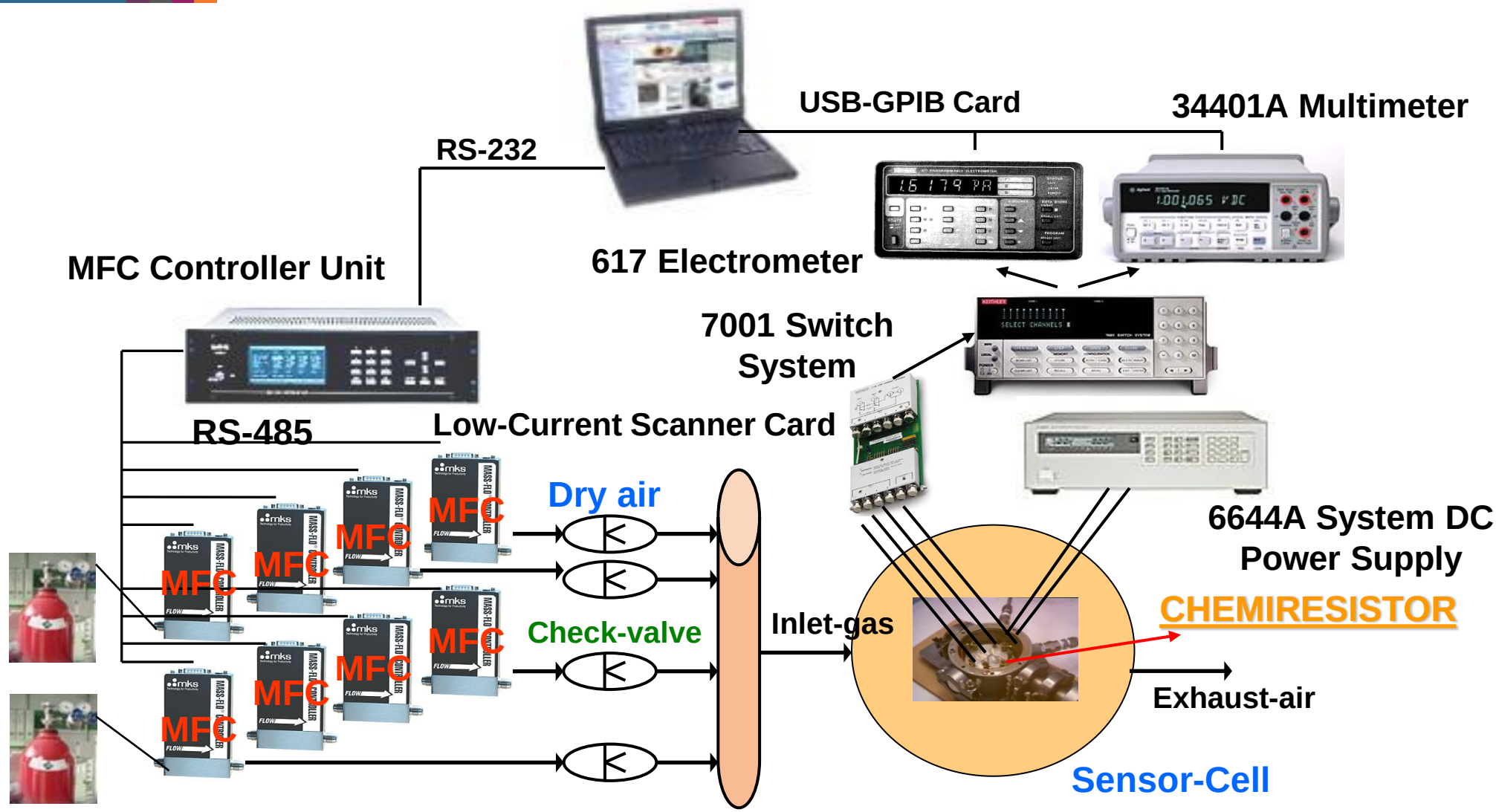
C1s	14.0% ± 0.5 %
O1s	46.0% ± 0.5%
O-Zn(530.5 eV ± 2 eV)	37.5% ± 0.5%
Zn2p	38.5% ± 0.5%
Au4f	1.5 ± 0.2%

O-Zn/Zn=1.0

Stoichiometric ratio

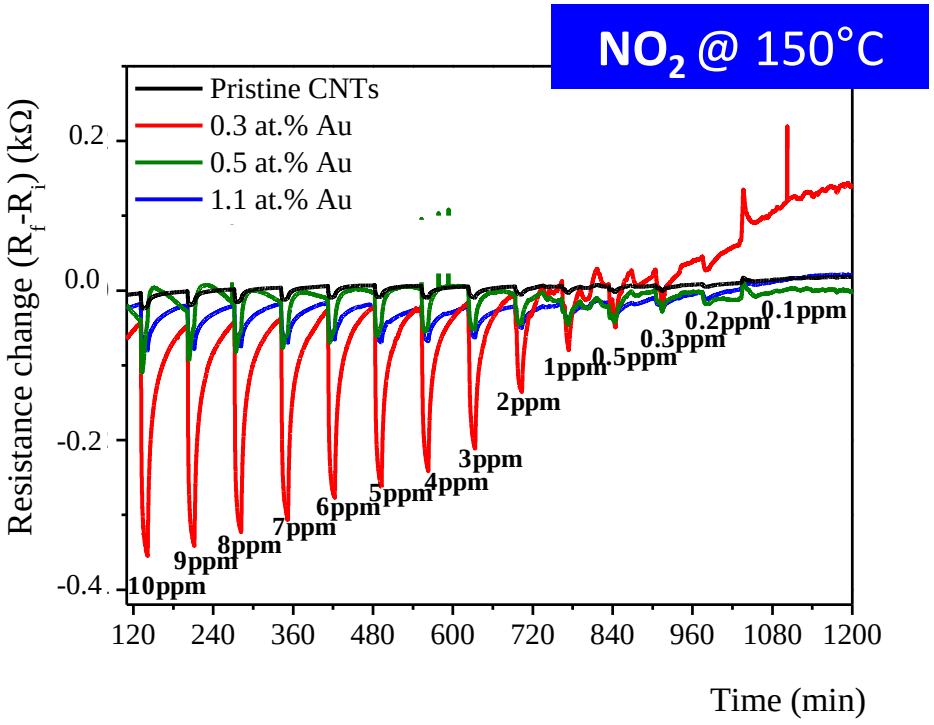


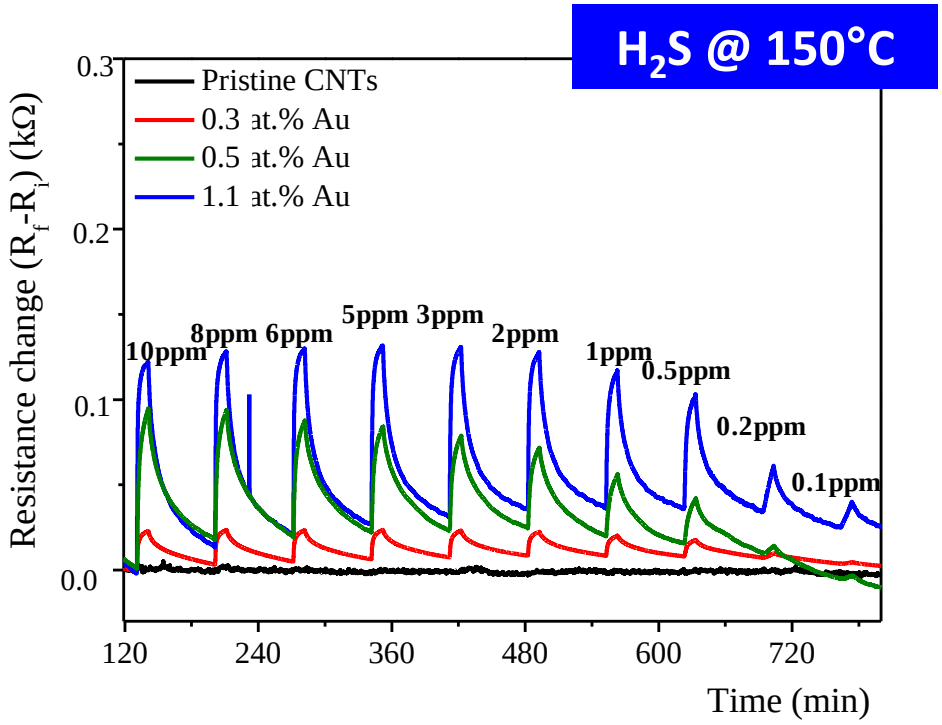
GAS SENSING TESTS



GAS SENSING TESTS

A. Au NPs/CNTs





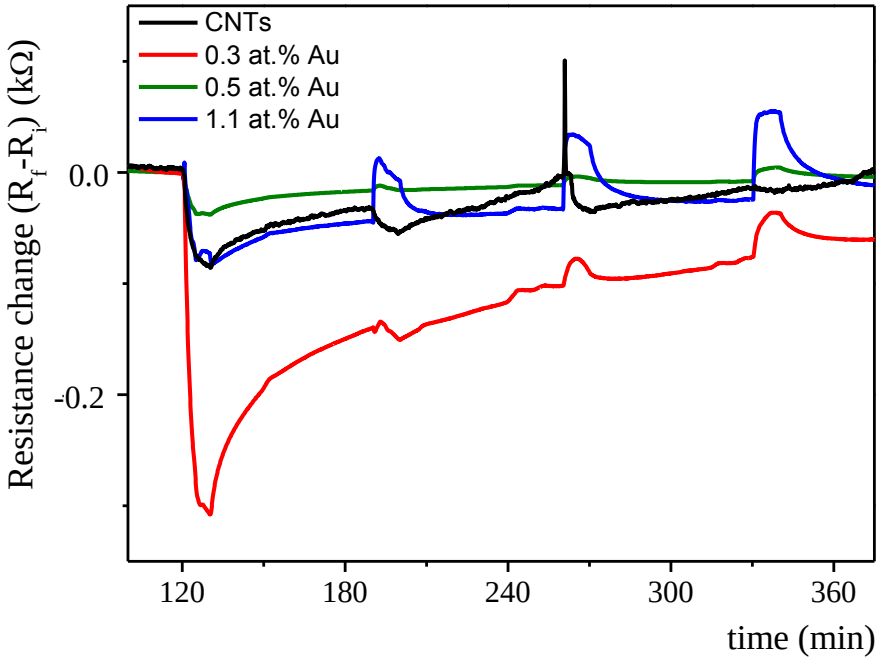
	CNTs	0.3% Au	0.5% Au	1.1% Au
Mean S_{H2S} (%*ppm^{-1}) @ T= 150°C	0	0.2	0.6	1.0
Mean S_{NO2} (%*ppm^{-1}) @ T= 150°C	0.5	1.0	0.8	0.6

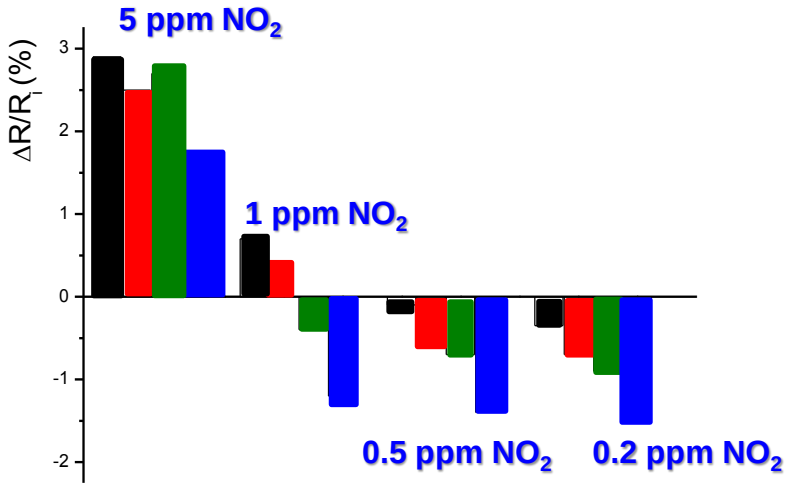
- ✓ High selectivity for NO_2 at low Au content
- ✓ High selectivity for H_2S at high Au content

GAS SENSING TESTS

A. Au NPs/CNTs

- **Binary Mixture: NO_2 + [H_2S] = 1 ppm @ T=150°C**



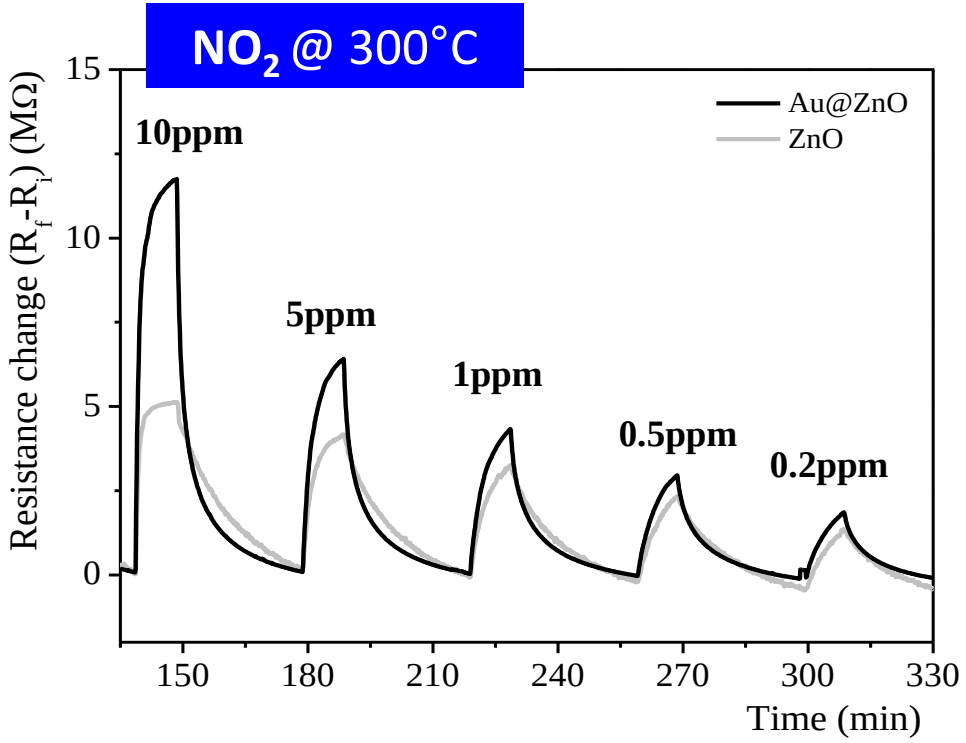


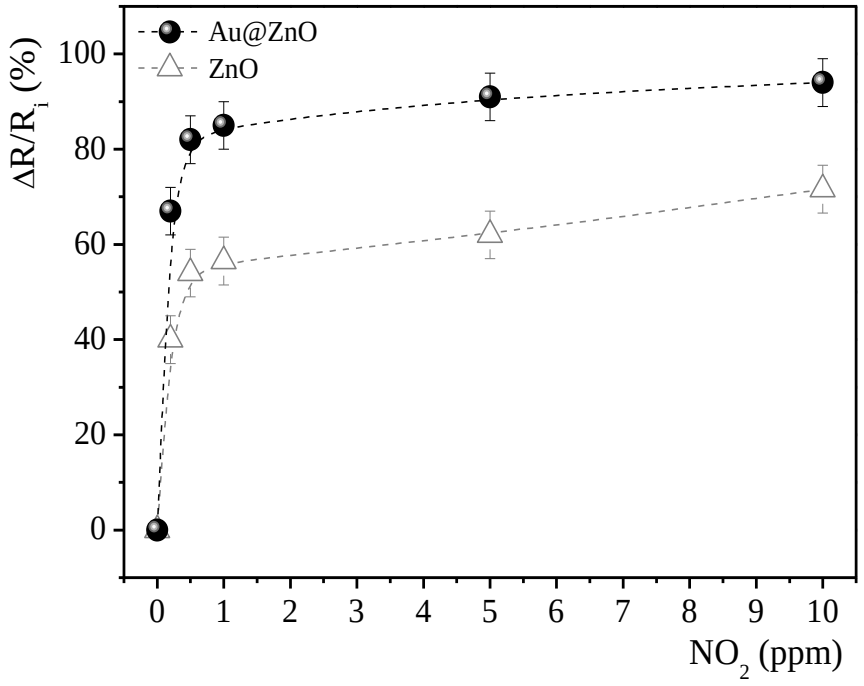
- ***The sensitivity to H_2S increases increasing the Au content onto CNTs surface.***
- ***Control of the selectivity by tuning the Au content onto CNTs surface.***

GAS SENSING TESTS

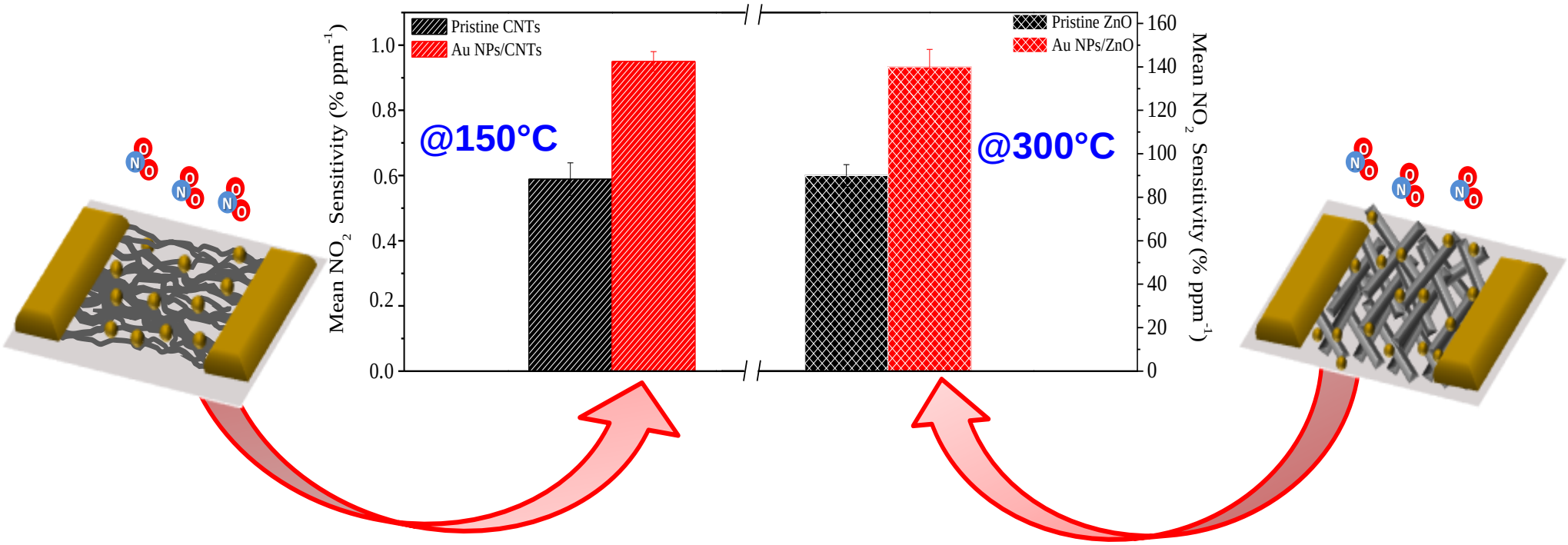
B. Au@ZnO

➢ ***Drop-casting of annealed hybrid Au@ZnO powder, dispersed in ACN solution, as sensitive layer in chemoreisitve gas sensor***





NO_2 SENSING


Pristine CNTs
Au NPs/CNTs
Pristine ZnO
Au NPs/ZnO
@150°C
@300°C
Mean NO2 Sensitivity (% ppm-1)
Mean NO2 Sensitivity (% ppm-1)
0.0
0.2
0.4
0.6
0.8
1.0
0
20
40
60
80
100
120
140
160

CONCLUSIONS

✓A tunable loading of Au NPs with uniform dimension is efficiently deposited directly on the surface of CNTs and ZnO-based gas sensors device by electrochemical processes.

✓Au NPs functionalized CNTs and ZnO-based gas sensor have an higher sensitivity towards NO2 gas compared to pristine ones, revealing [NO_2] in sub-ppm range.

✓The Au loading on CNTs-based gas sensor influences the sensitivity and selectivity: a low Au loading improves the NO_2 gas sensing; a high Au loading improves H_2S gas sensing.

FUTURE PROSPECTIVES

✓ Functionalization of CNTs and ZnO-based gas sensors with other metal or metal oxides nanoparticles.

✓ Gas sensing measurements to detect other toxic and polluting gases.

THANK YOU FOR YOUR ATTENTION