

COST

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

COST Action TD1105

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New Sensing Technologies for Indoor and Outdoor Air Quality Control

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ELECTRODEPOSITED NANOSTRUCTURED MATERIALS FOR GAS SENSING



Nicola Cioffi, External Expert, nicola.cioffi@uniba.it

University of Bari / Italy

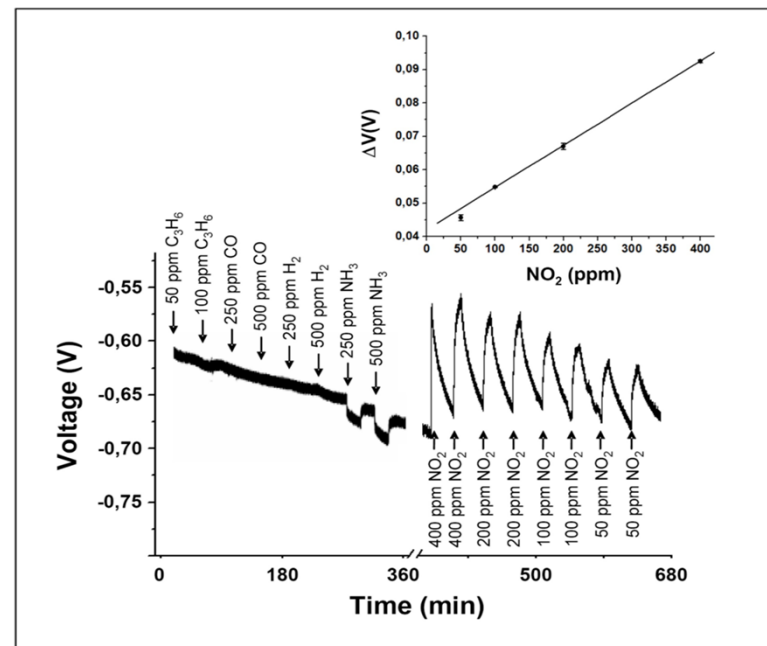
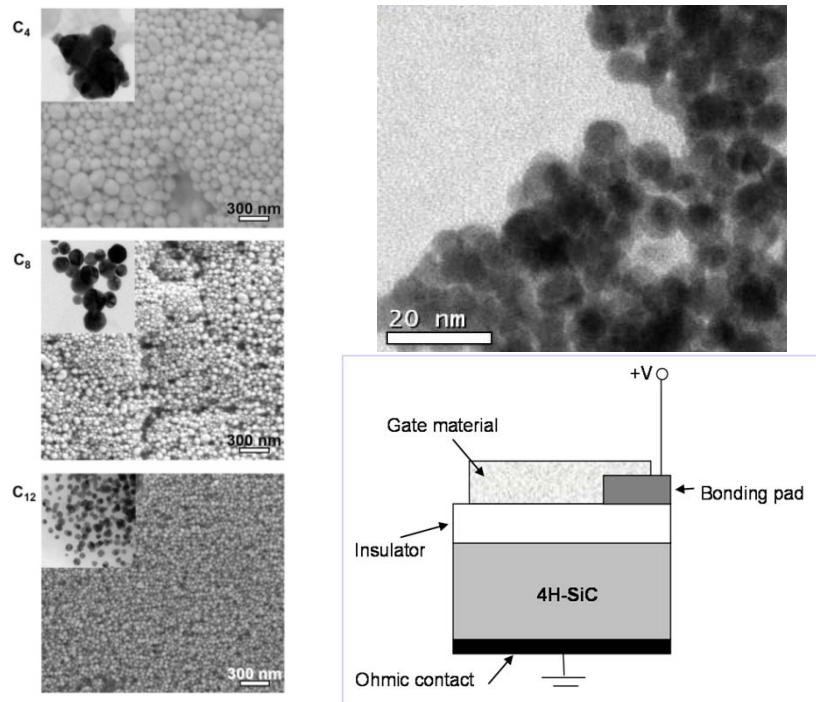
other authors: **E. Dilonardo, C. Di Franco, A. Afzal,
M. Alvisi, M. Penza, F. Palmisano, L. Torsi**

Outlook

- Background - Motivations
- Sacrificial Anode Electrosynthesis (SAE) of metal nanoparticles
- SAE electrodecoration of sol gel prepared Metal Oxides
- Electrodeposition of metal nanoparticles on carbon nanotubes

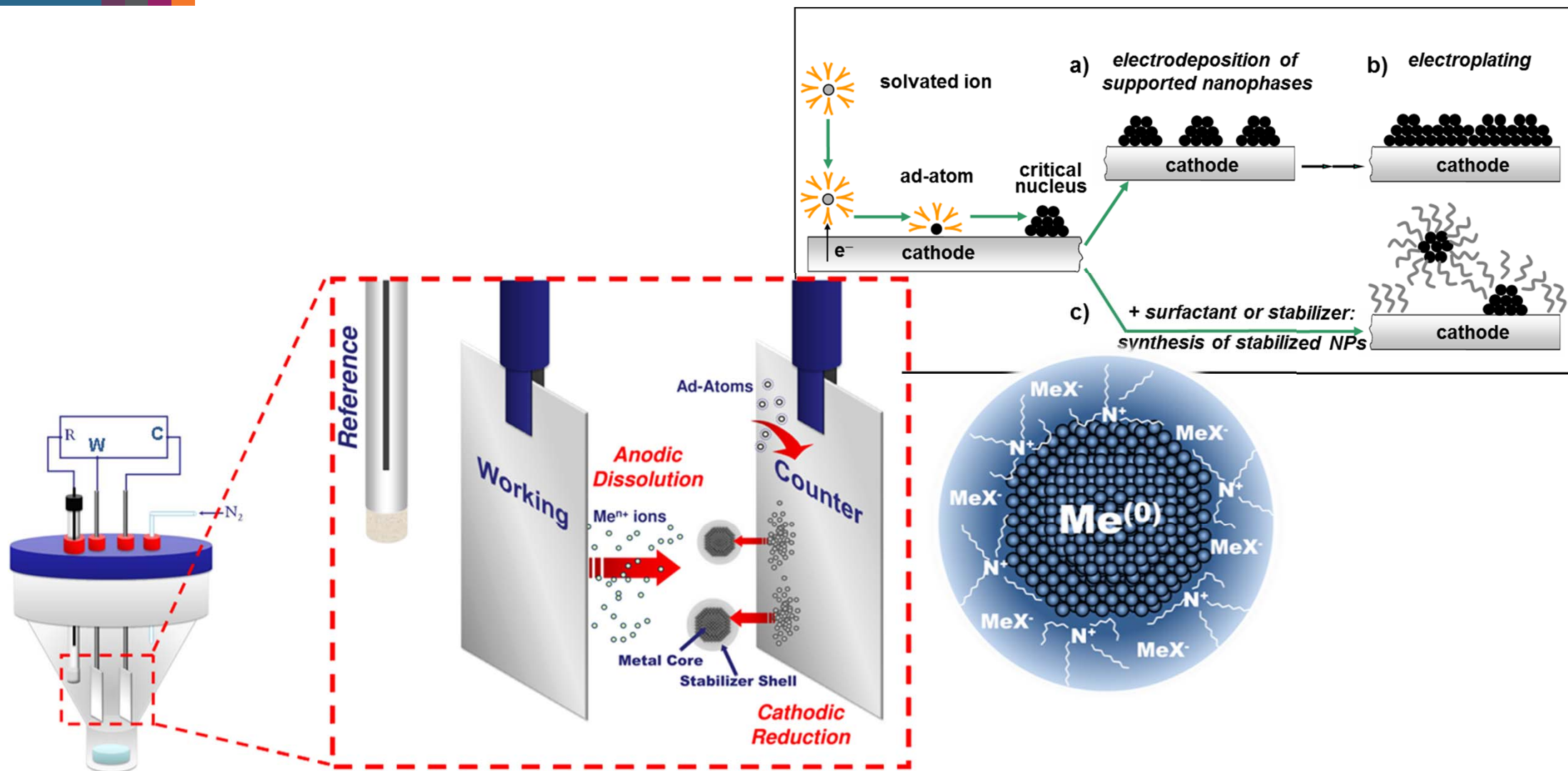
Background - Motivations

- Automotive Exhaust Gas Sensors (NO_x, HCs, CO, etc) based on catalytic metal nanoparticles supported on other nanomaterials (2 Natl. projects running on the topic)
- Previous experience on gold nanoparticle NO_x sensors



N. Cioffi, L. Colaianni, E. Ieva, R. Pilolli, N. Ditaranto, M.D. Angione, S. Cotrone, K. Buchholt, A. Lloyd Spetz, L. Sabbatini, L. Torsi, *Electrochimica Acta*, 56, 2011, 3713-3720

Sacrificial Anode Electrosynthesis



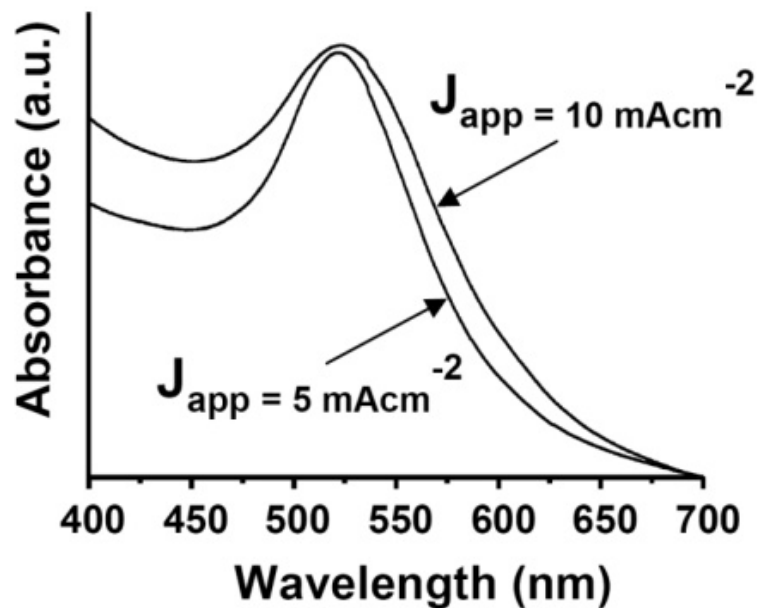
M. Reetz, W. Helbig. 1994. *J. Am. Chem. Soc.* 116, 7401.

N. Cioffi, L. Torsi, L. Sabbatini, P. G. Zambonin, T. Bleve-Zacheo. 2000. *J. Electroanal. Chem.* 488, 42.

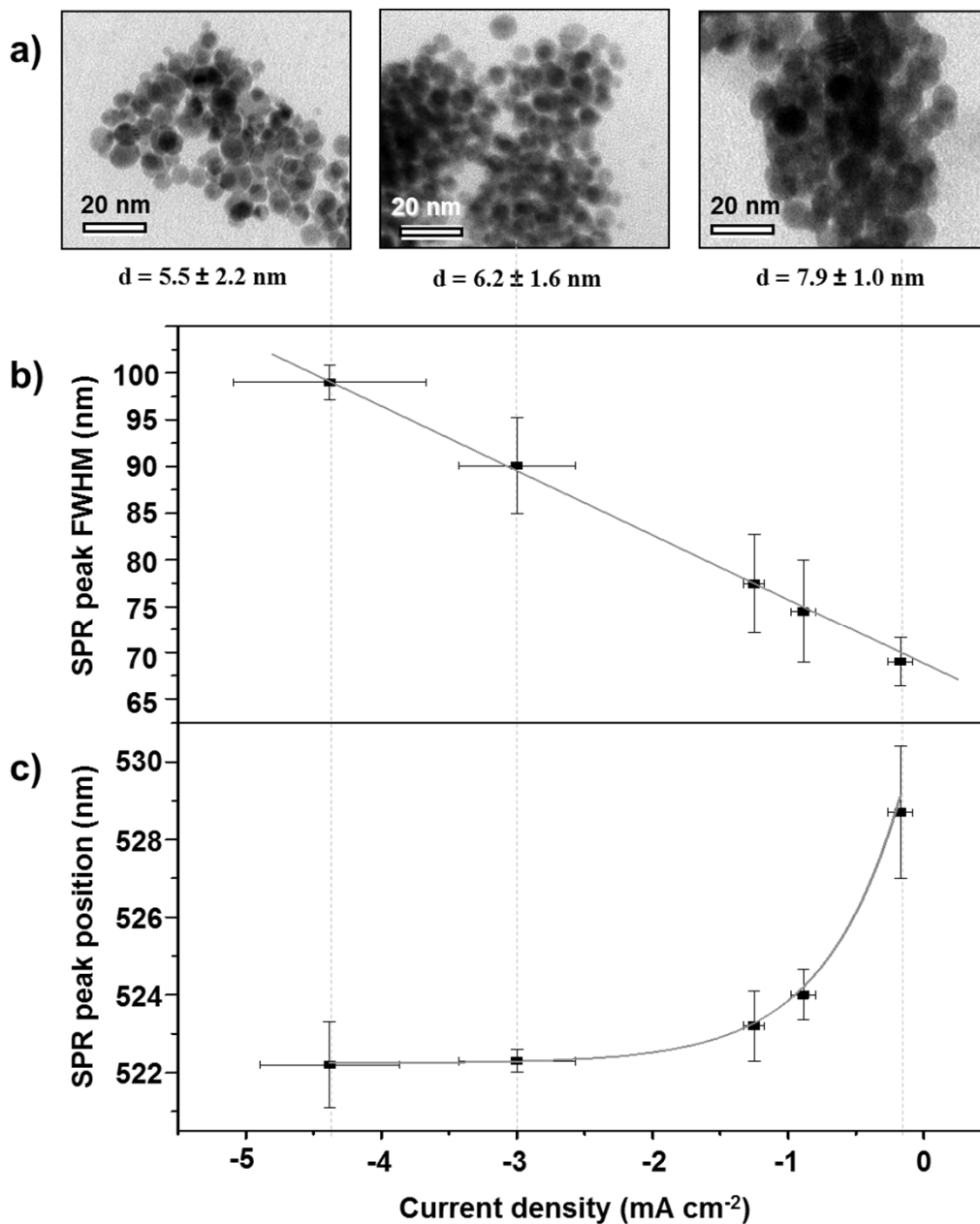
N. Cioffi, N. Ditaranto, L. Sabbatini, L. Torsi, P.G. Zambonin, *European Patent Application number: EP 2123797A1*, 25.11.2009

N. Cioffi, N. Ditaranto, L. Sabbatini, G. Tantillo, L. Torsi, P.G. Zambonin, *European Patent Application number: EP 2157211A1*, 24.02.2010 .

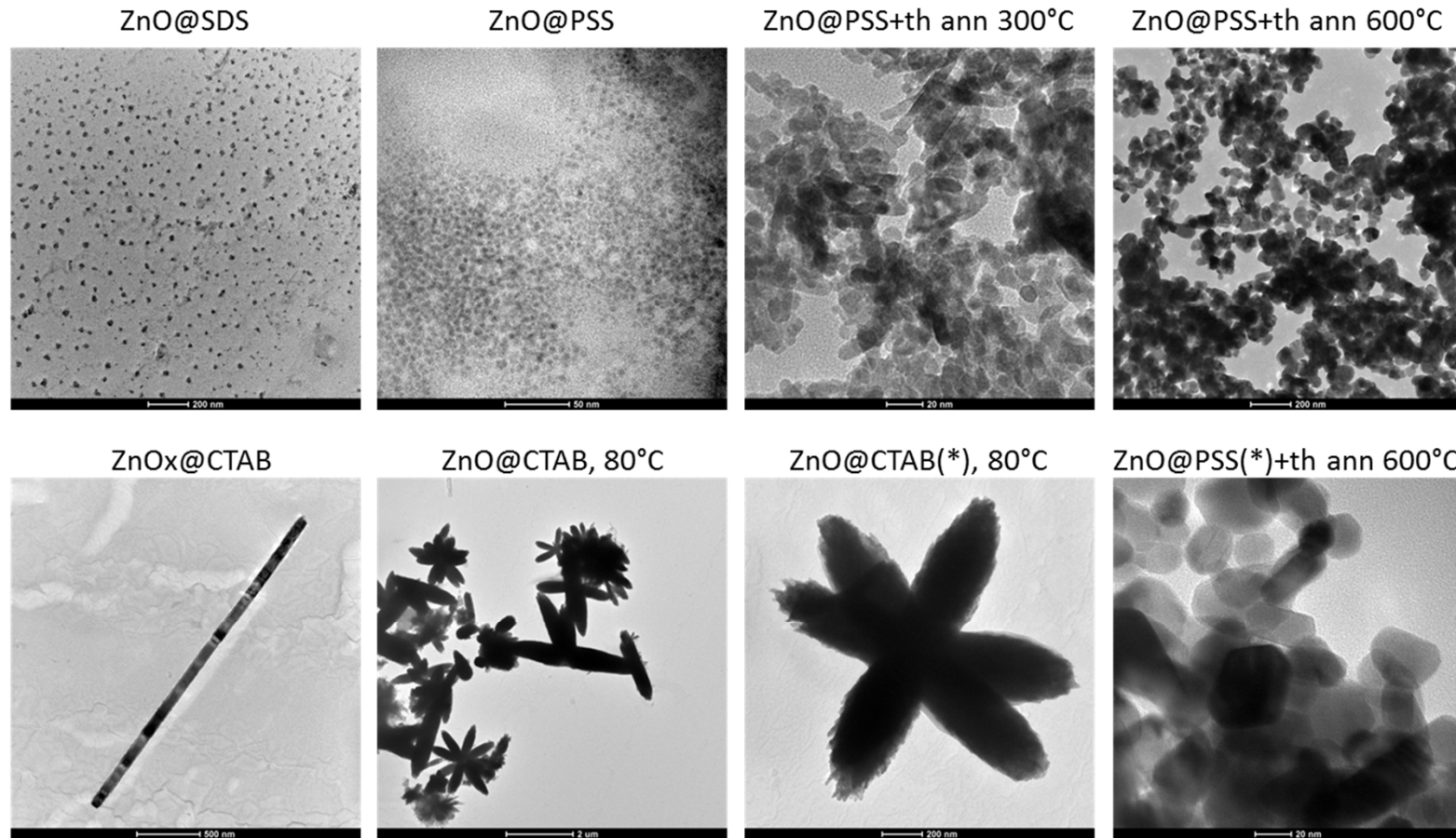
Sacrificial Anode Electrosynthesis



“Electrochemical synthesis of colloidal gold nanoparticles” E. Ieva, N. Cioffi, in *Nanomaterials: New Research Developments*, E.I. Pertsov Ed., Nova Science Publishers 2008,



Sacrificial Anode Electrosynthesis



*R.A. Picca, D. Hötger, M.C. Sportelli

SAE electrodecoration of Metal Oxides

PLAN OF WORK:

To electrodecorate sol gel prepared metal oxides (MO_x) by means of catalytic metal nanoparticles (<10nm)

“Au – Metal Oxide Composite Nanoparticles”

Au-ZnO

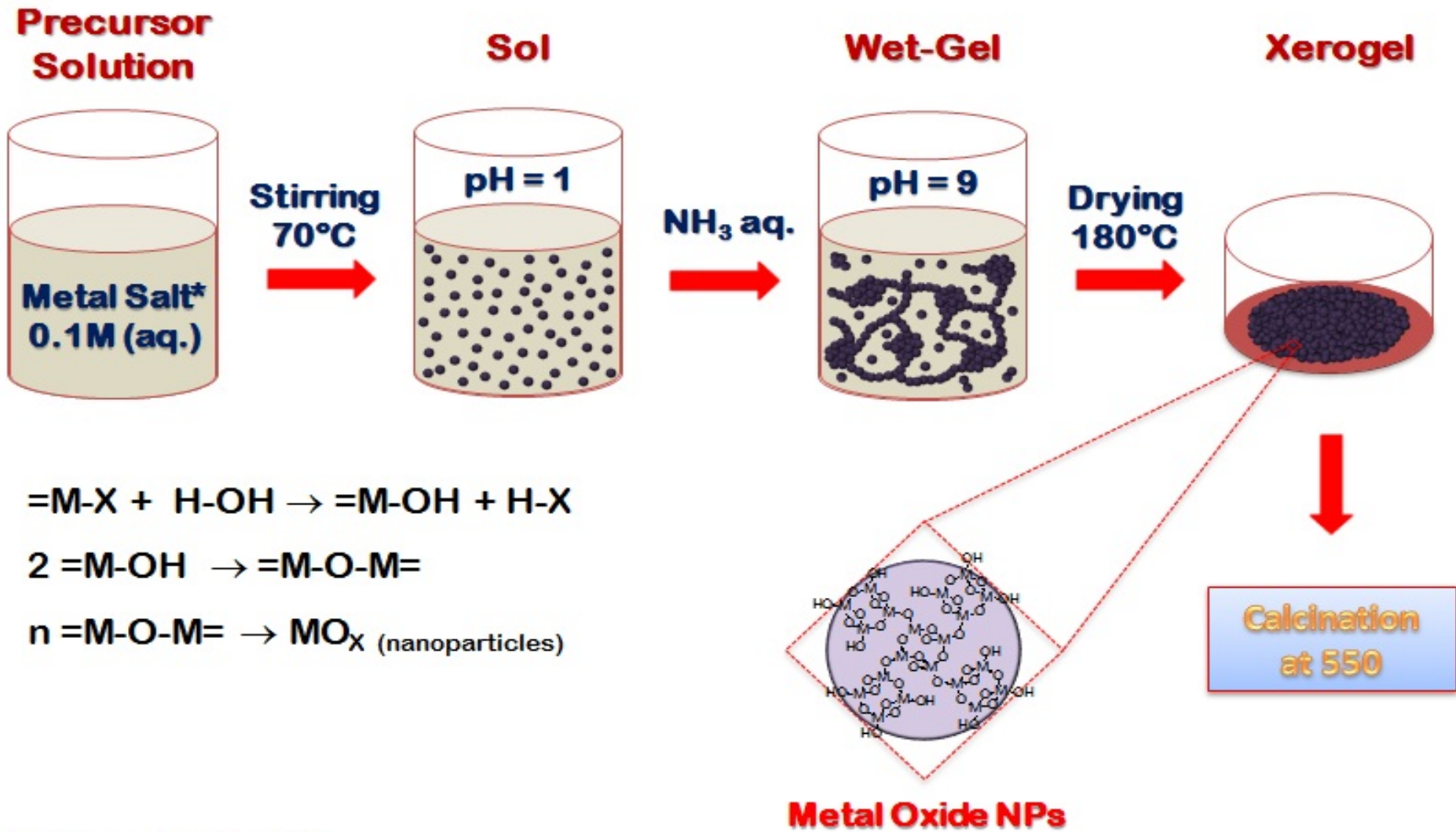
Au-ZrO₂

Au-In₂O₃

Au-ZrO₂-In₂O₃ (ZrInO_x with different Zr:In ratios)

etc..

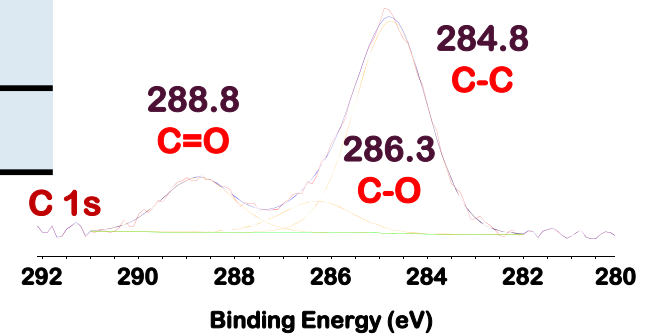
I step. MO_x syntheses: Sol-Gel Method



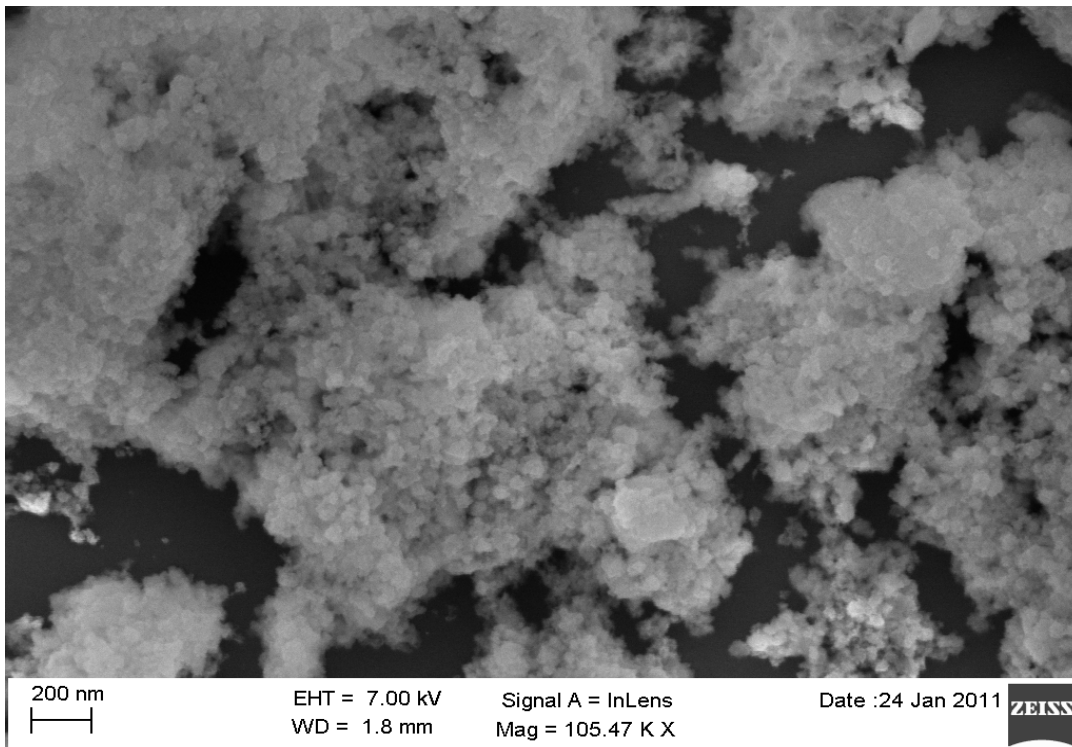
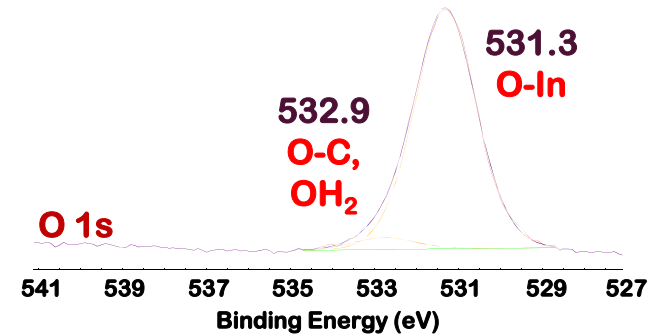
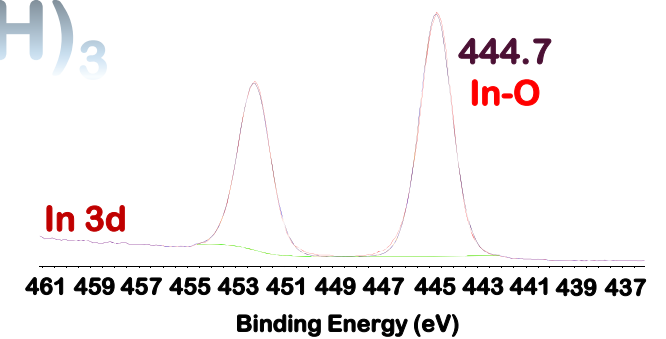
* InCl₃ and/or ZrOCl₂

In₂O₃: As-prepared

% C	% In	% <u>O</u> -In	% <u>O</u> -C, <u>OH</u> ₂ , etc	O/In
18.3±0.1	19.9±0.4	57.5±1.4	3.8±1.4	2.9



In(OH)₃

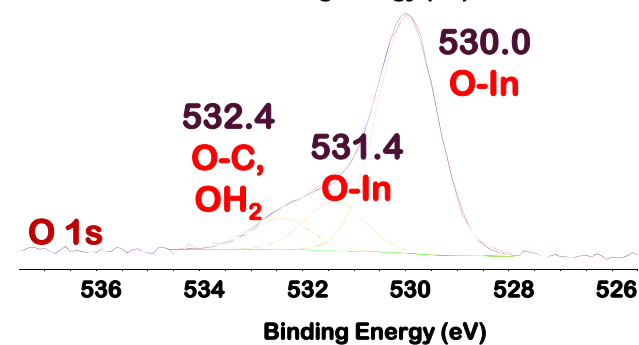
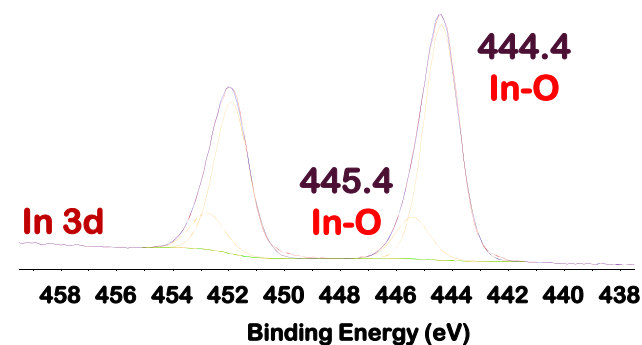
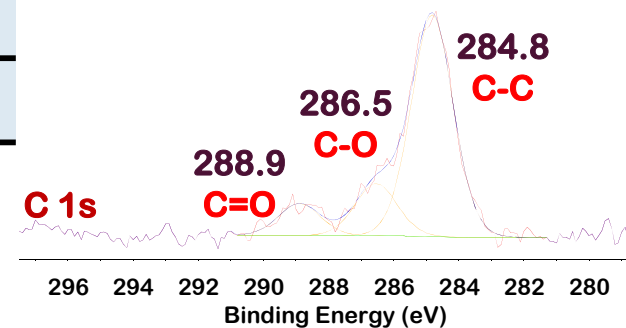
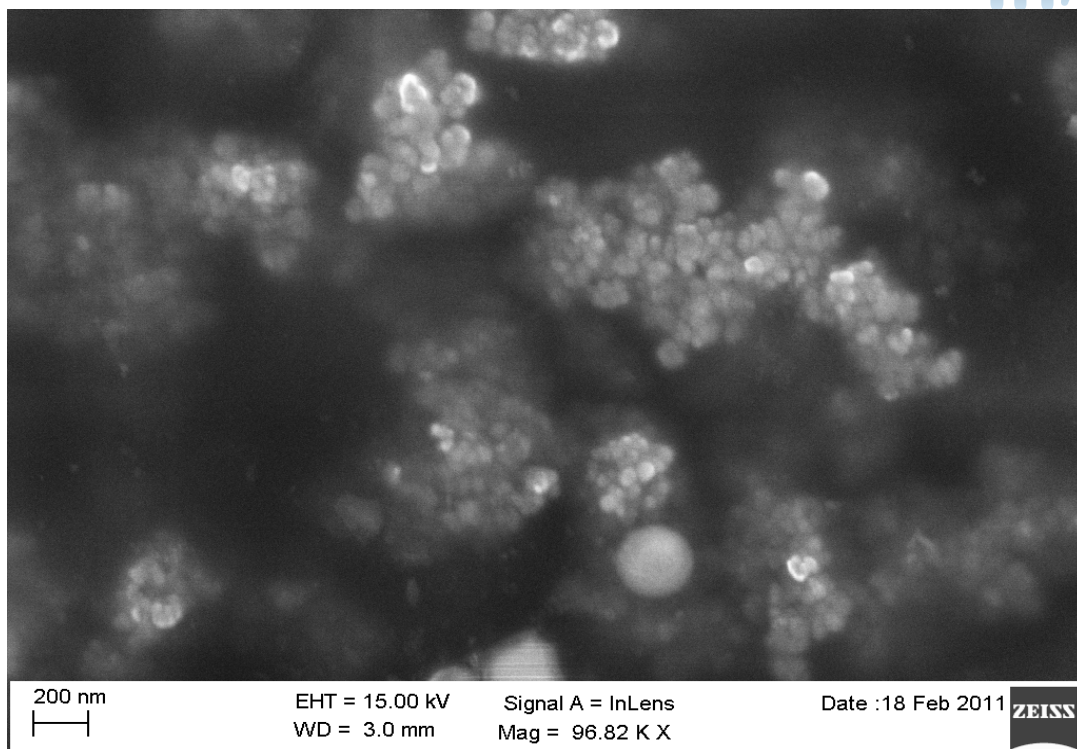


In₂O₃: Calcined

% C	% In	% <u>O</u> -In	% <u>O</u> -C, OH ₂ , etc.	O/In
17.6±0.3	33.8±0.4	44.1±1.4	4.1±0.6	1.3



In₂O₃



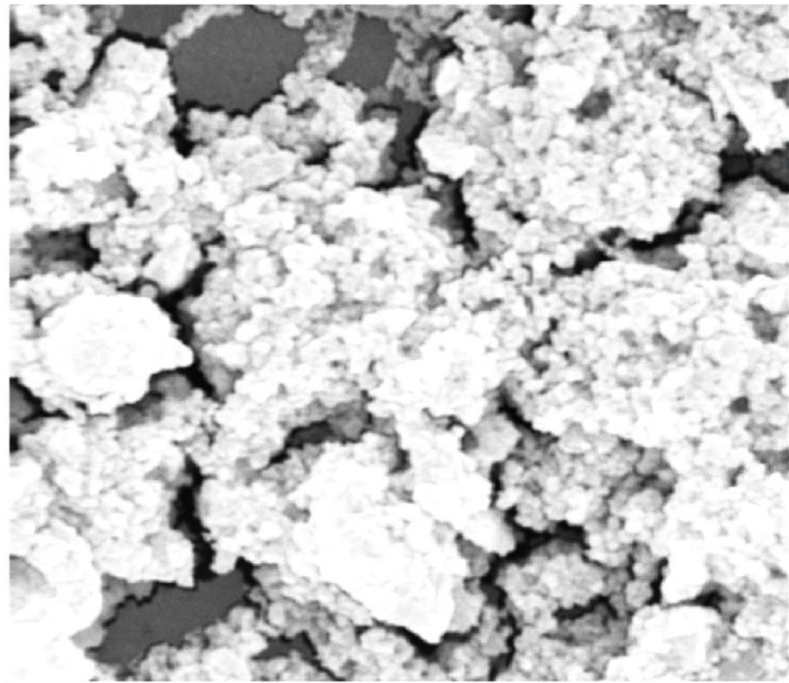
ZrO₂: As-prepared & Calcined

% C	% Zr	% <u>O</u> -Zr	% <u>O</u> -C, etc.
33.1±1.0	14.5±0.3	46.9±1.2	5.5±1.2

O/Zr
3.2

% C	% Zr	% <u>O</u> -Zr	% <u>O</u> -C, etc.
20.2±0.3	25.3±0.3	49.7±1.2	4.8±1.0

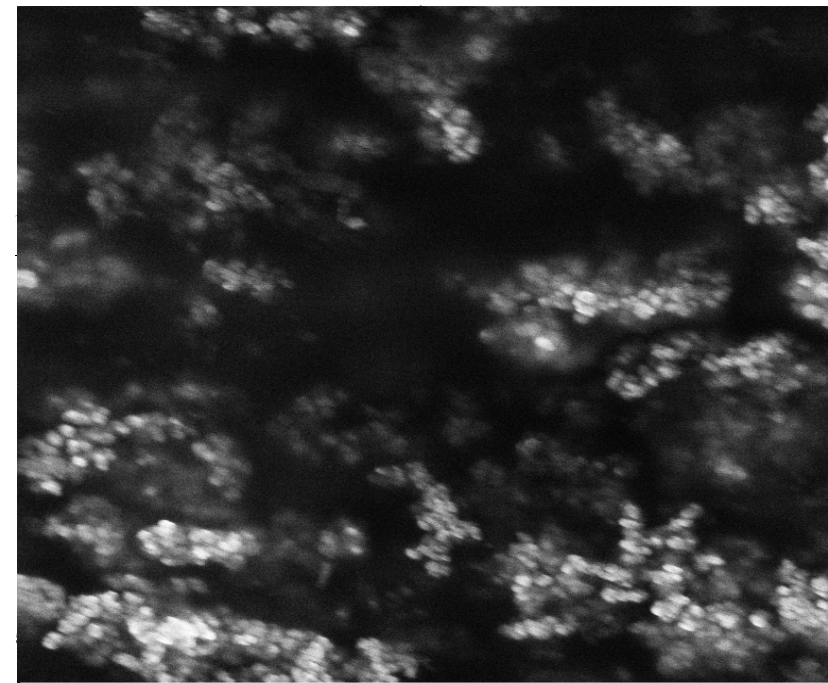
O/Zr
2.0



ZrO₂/Zr(OH)₄



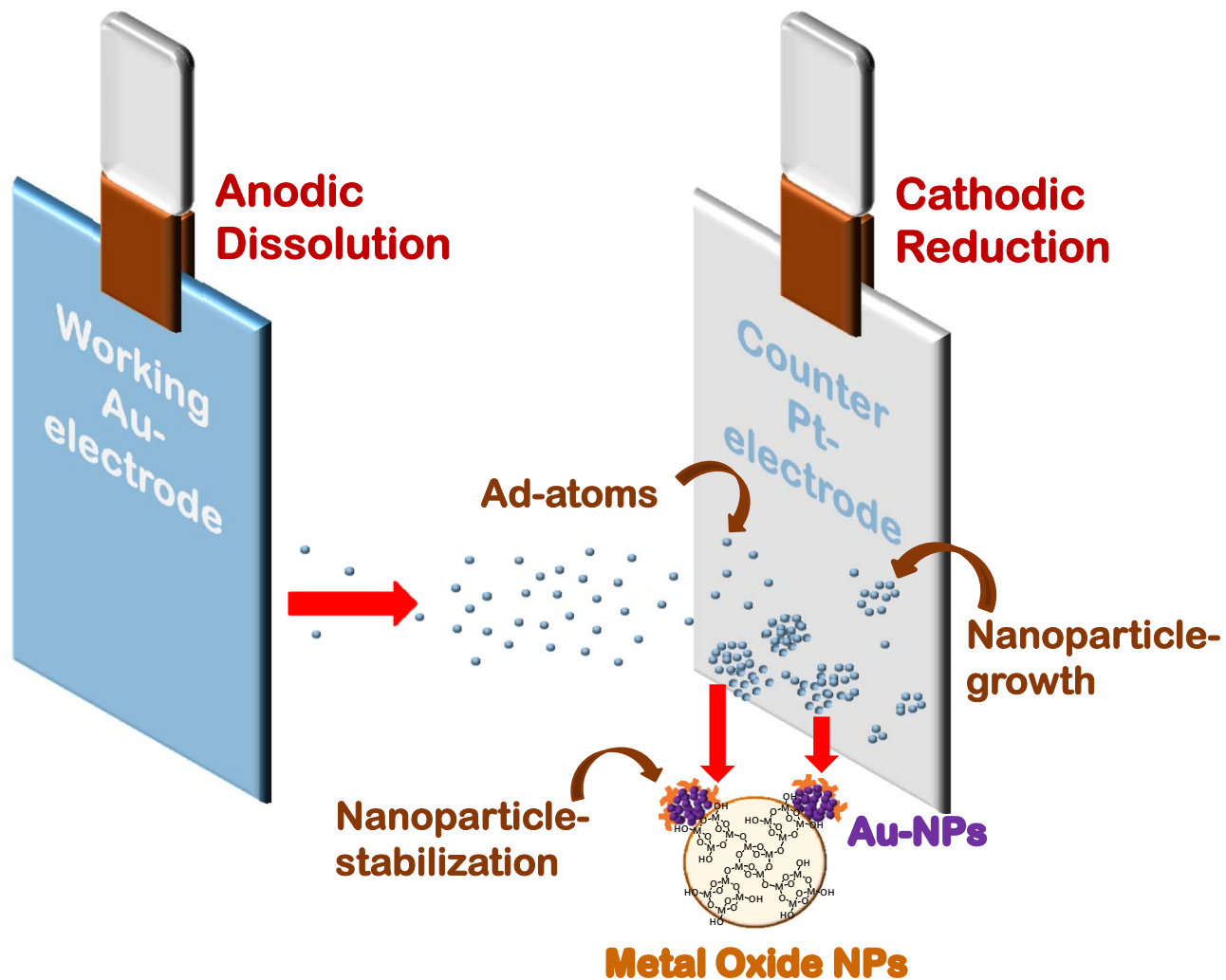
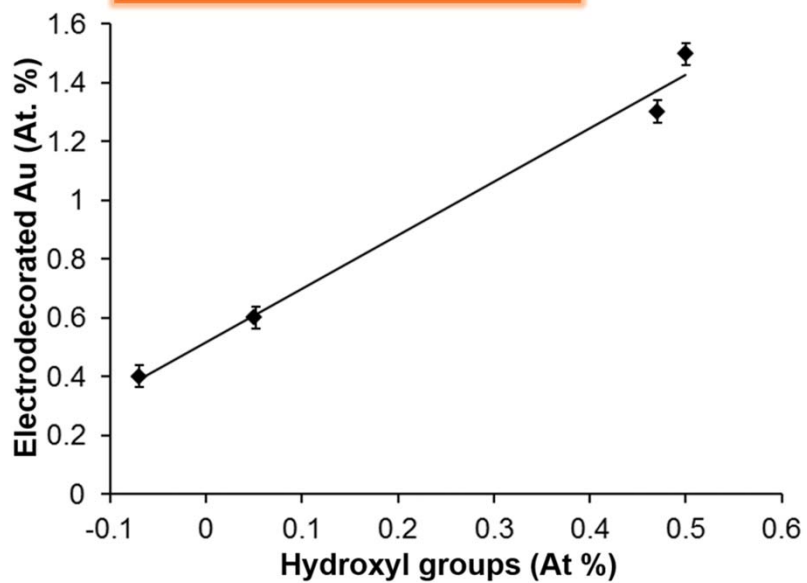
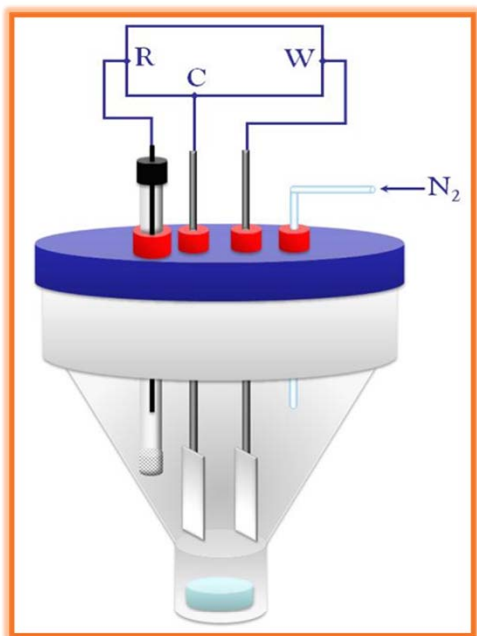
ZrO₂



1 μm EHT = 10.00 kV Signal A = InLens
WD = 2.1 mm Mag = 41.23 K X

1 μm EHT = 7.00 kV Signal A = InLens
WD = 2.6 mm Mag = 48.34 K X

II step. Au-NPs Electrosynthesis onto the MOx particles

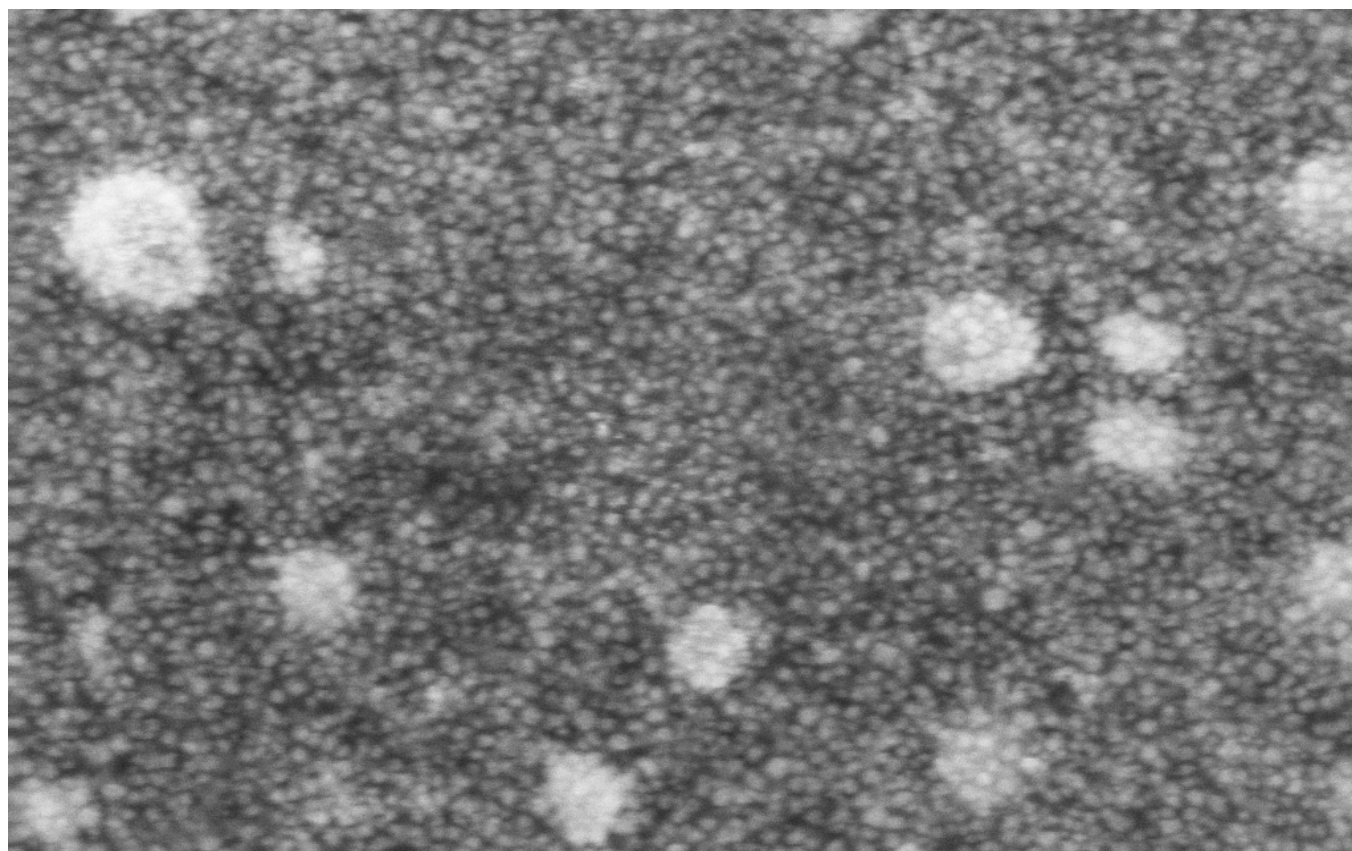


N Cioffi et al (2007) Curr Nanosci 3, 121-27

“Design of novel indium oxide supported gold nanocatalysts and their application in homocoupling of arylboronic acids” A. Monopoli, A. Afzal, C. Di Franco, N. Ditaranto, N. Cioffi, P. Cotugno, A. Nacci, L. Torsi Journal of Molecular Catalysis A: Chemical , in press,

Au-In₂O₃: As-prepared

% C	% In	% <u>O</u> -In	% <u>O</u> -C, <u>O</u> -H ₂ , etc	% Au
37.3±0.9	14.5±0.1	43.1±2.0	6.0±2.0	1.4±0.1



100 nm



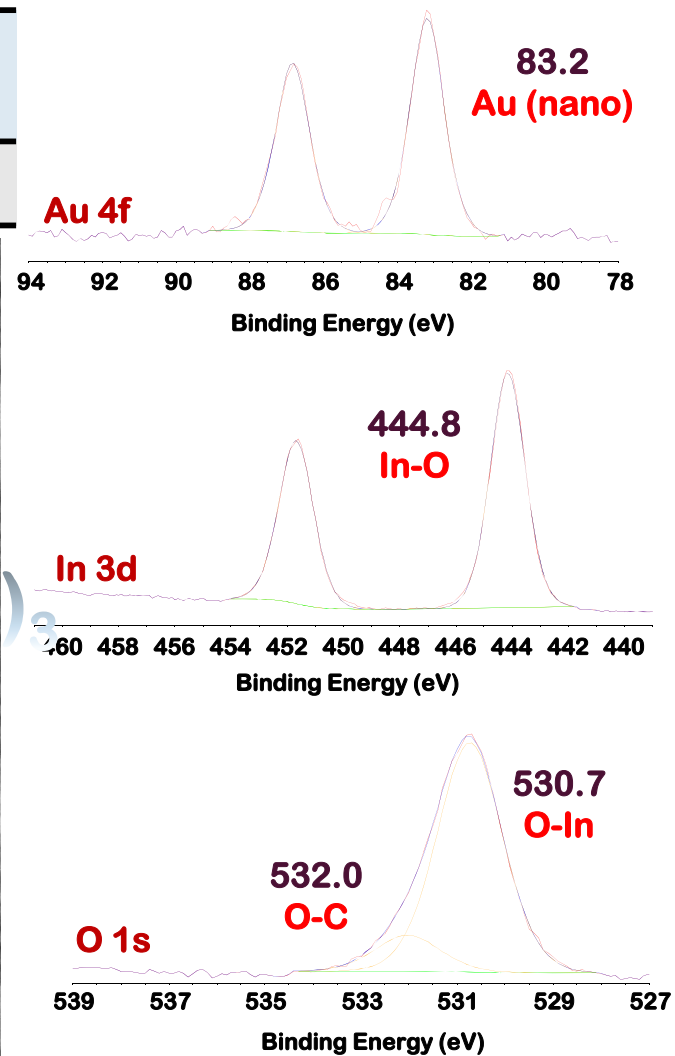
EHT = 5.00 kV

WD = 1.4 mm

Signal A = InLens

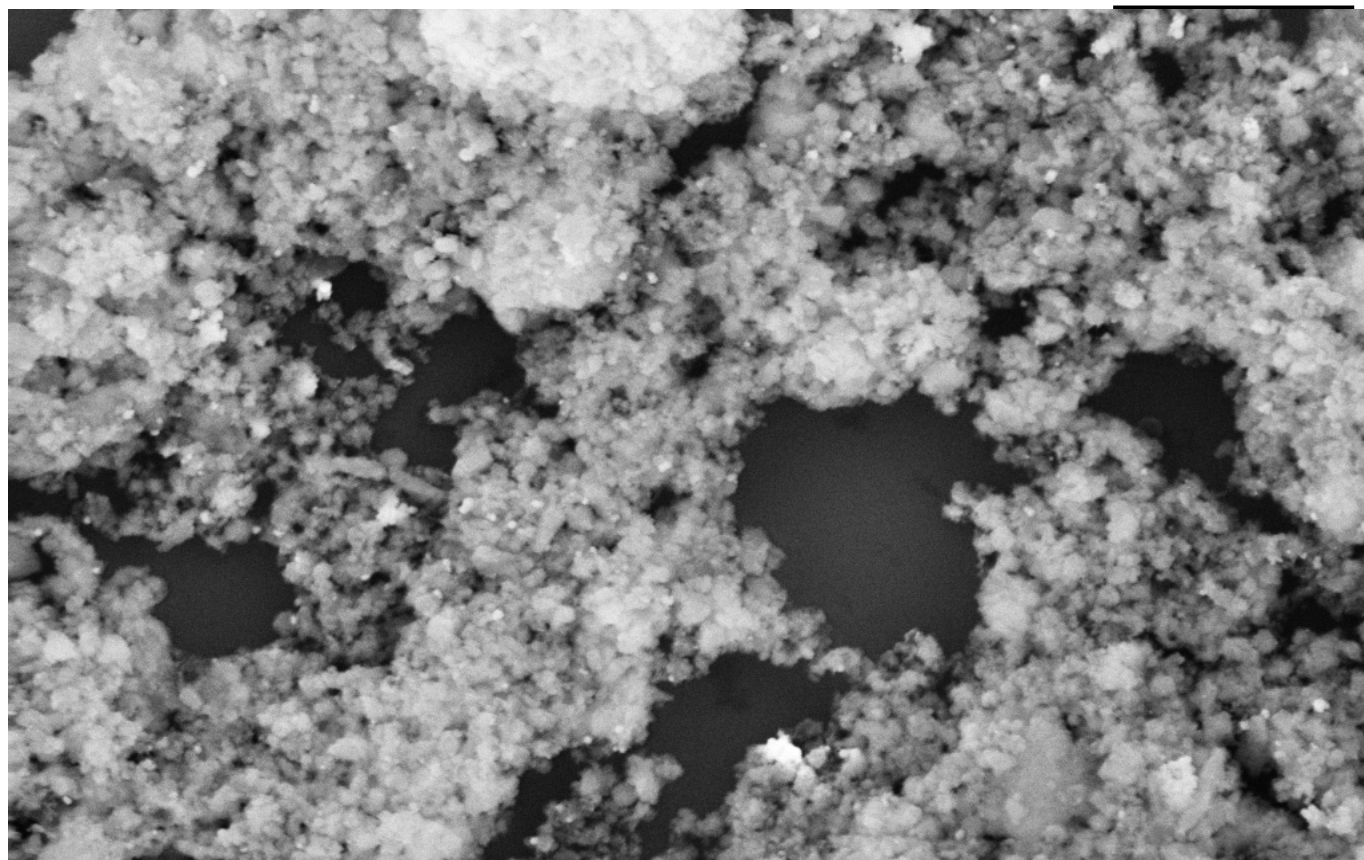
Mag = 124.12 K X

Date : 1 Dec 2010



Au/In₂O₃: Calcined at 550°C

% C	% In	% <u>O</u> -In	% <u>O</u> -C, <u>O</u> -H ₂ , etc	% Au
19.5±1.3	30.5±0.3	42.9±1.4	5.6±0.1	1.5±0.2



200 nm



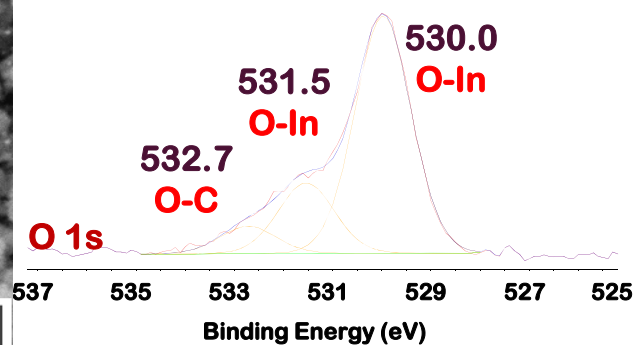
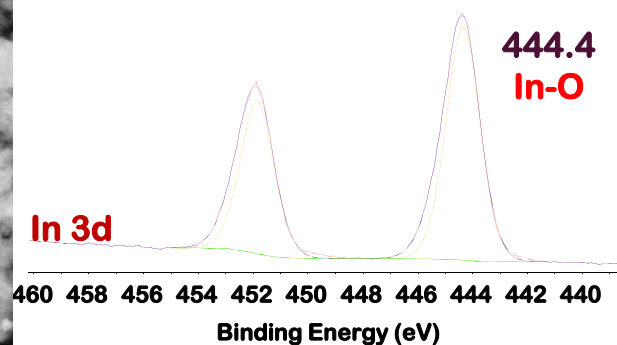
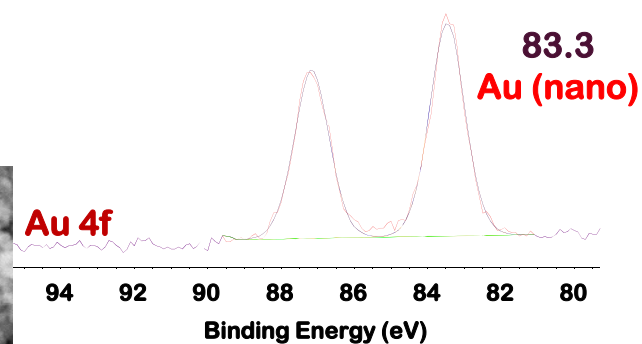
EHT = 10.00 kV

WD = 2.9 mm

Signal A = InLens

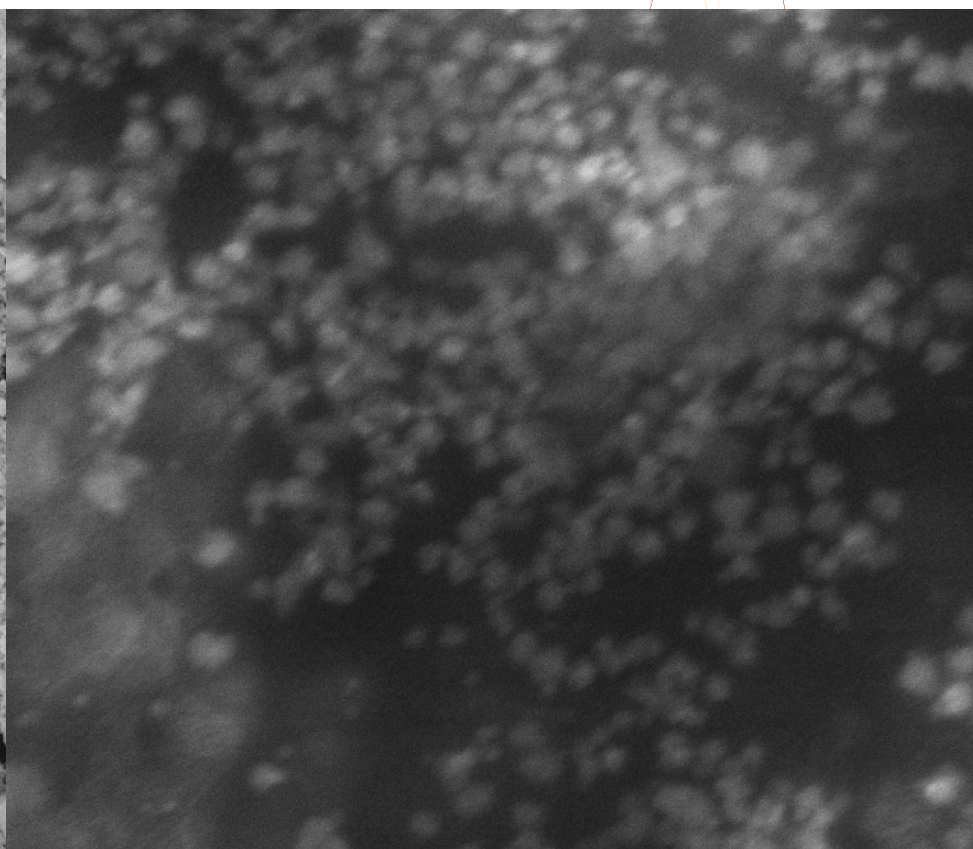
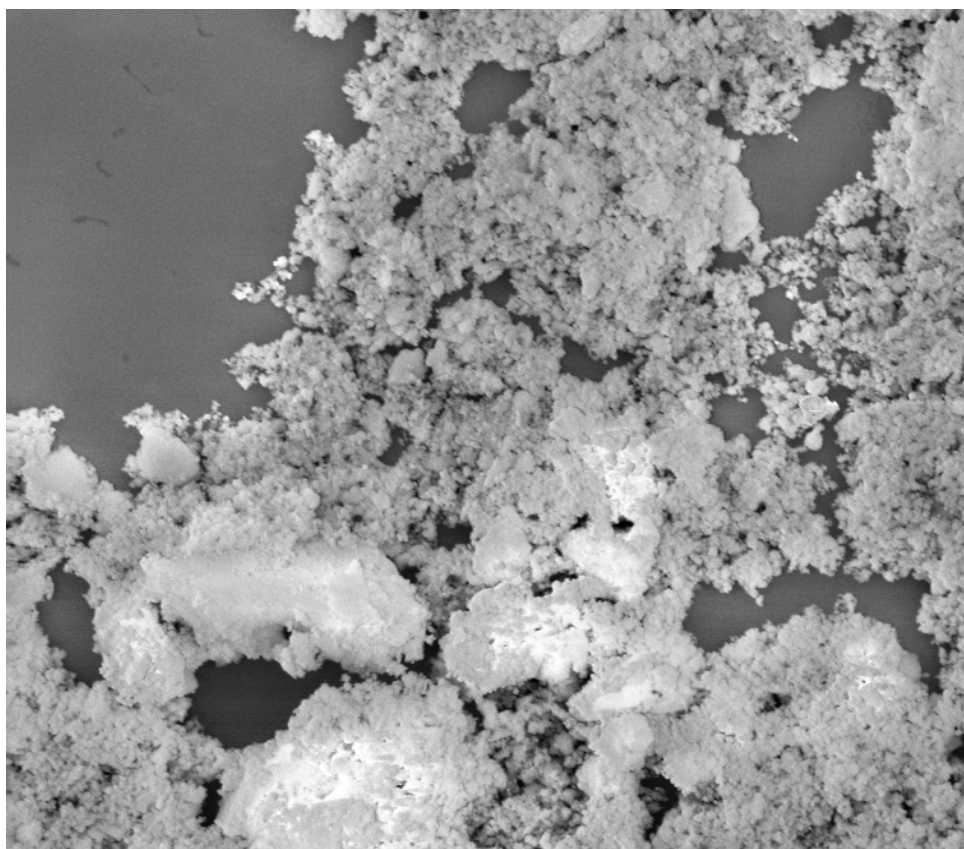
Mag = 61.86 K X

Date : 3 Feb 2011



ZrInO_x: Mixed Metal Oxides (MMO_x) – As-prepared

% Zr	% In	% <u>O</u> -M	O/M
7.8±0.2	7.9±0.1	46.7±0.8	3.0

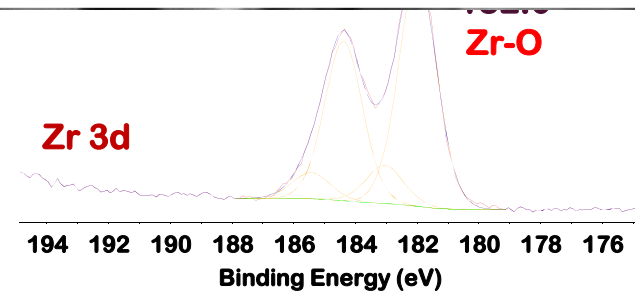
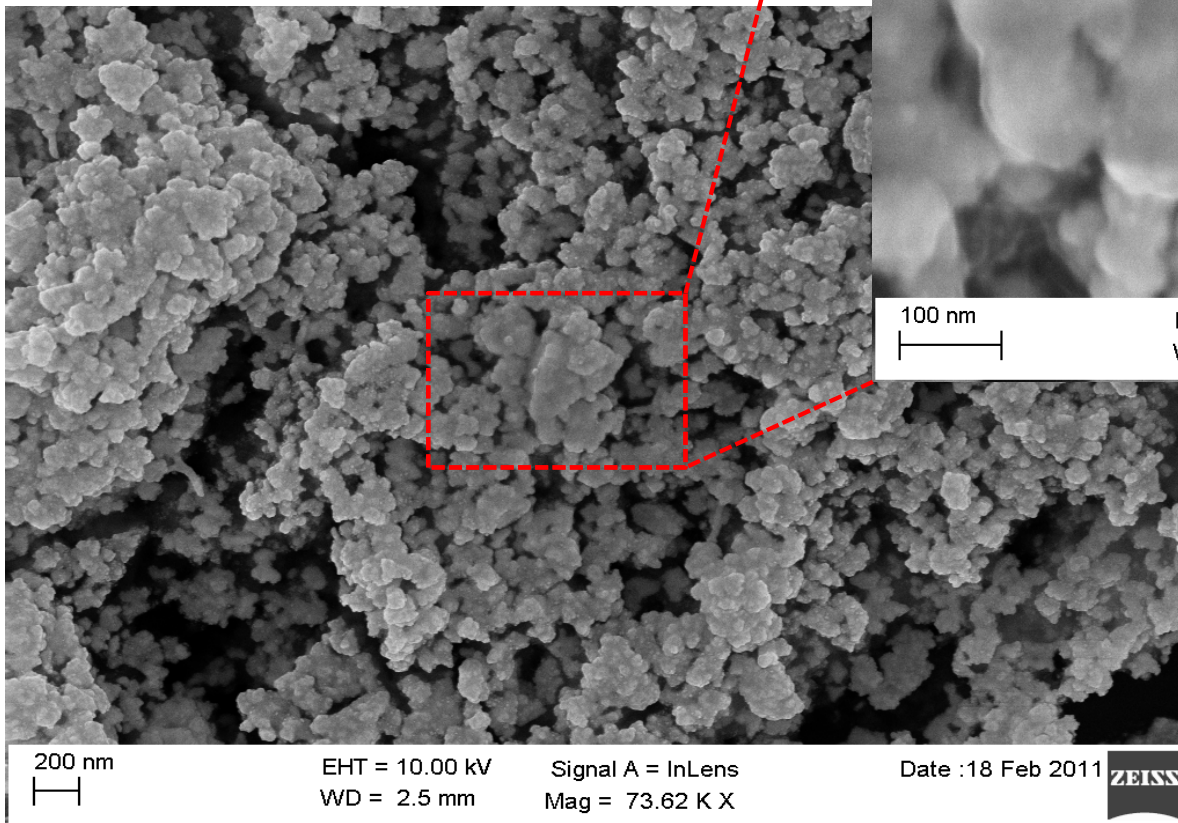
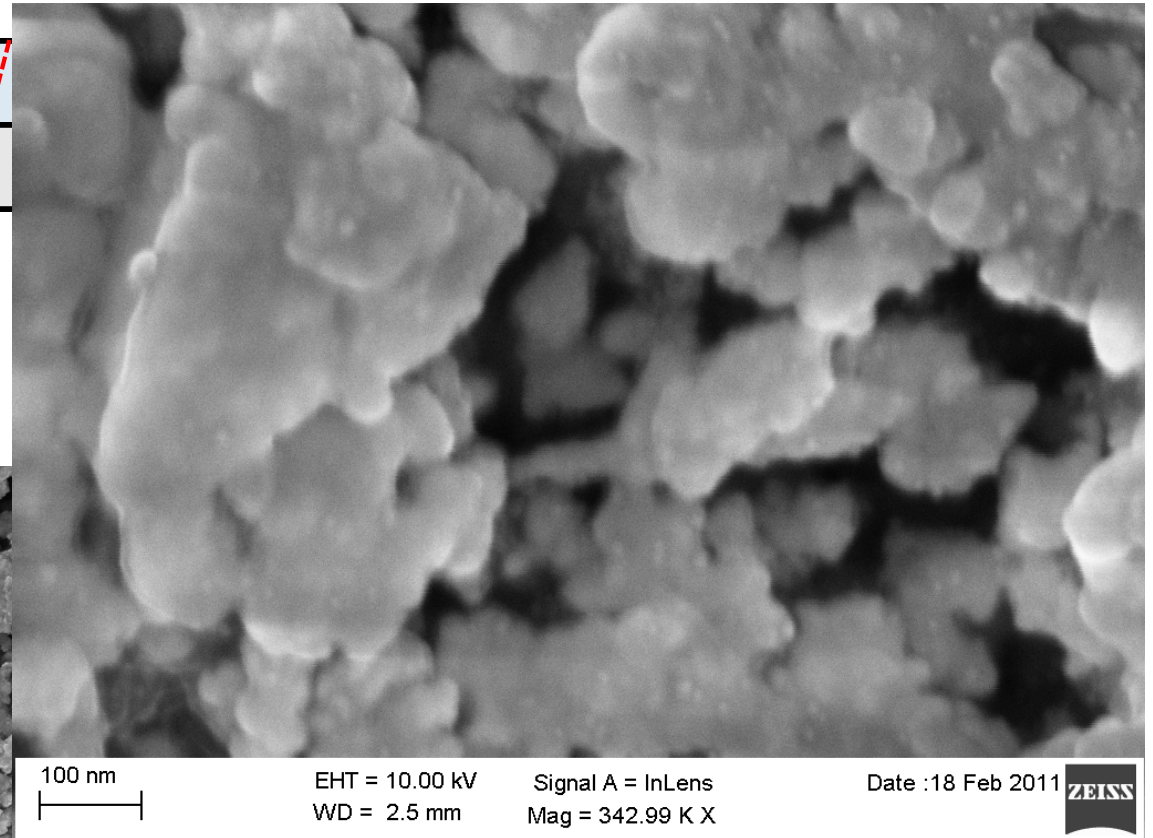


2 μm
EHT = 5.00 kV
WD = 2.9 mm
Signal A = InLens
Mag = 22.56 K X

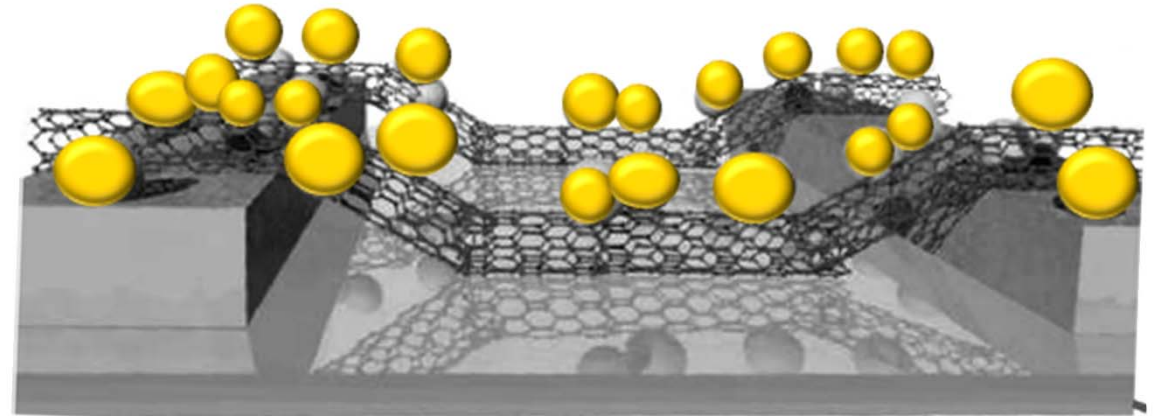
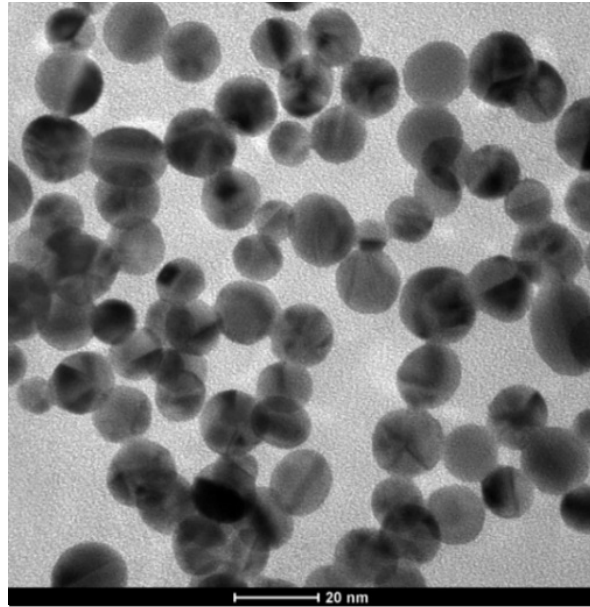
200 nm
EHT = 10.00 kV
WD = 2.9 mm
Signal A = InLens
Mag = 271.93 K X

ZrInO_x and Au/ZrInO_x: Calcined

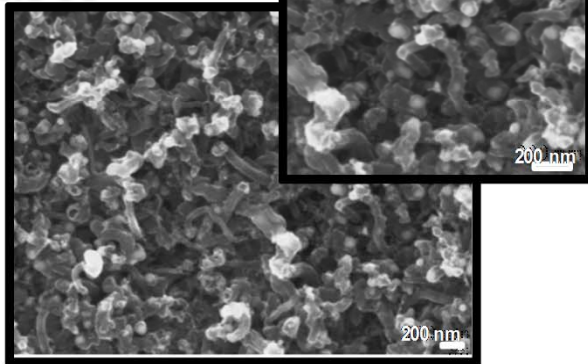
% Zr	% In	% <u>O</u> -M
11.7±0.1	11.4±0.1	46.9±0.6
% Au (nano)	% Au (Au ₂ O ₃)	
1.1	0.1	



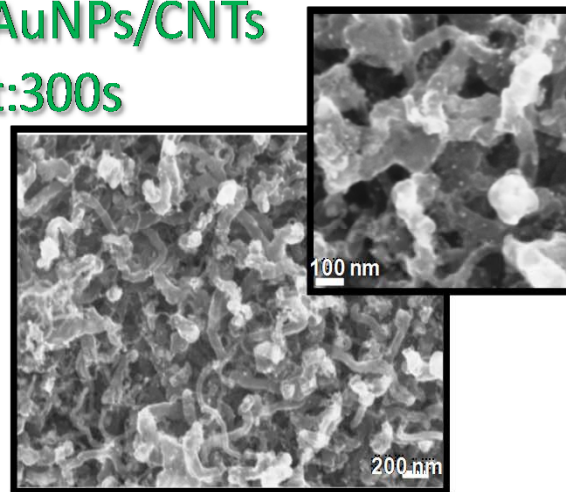
Electro(phoretic) deposition of AuNPs on CNTs(*)



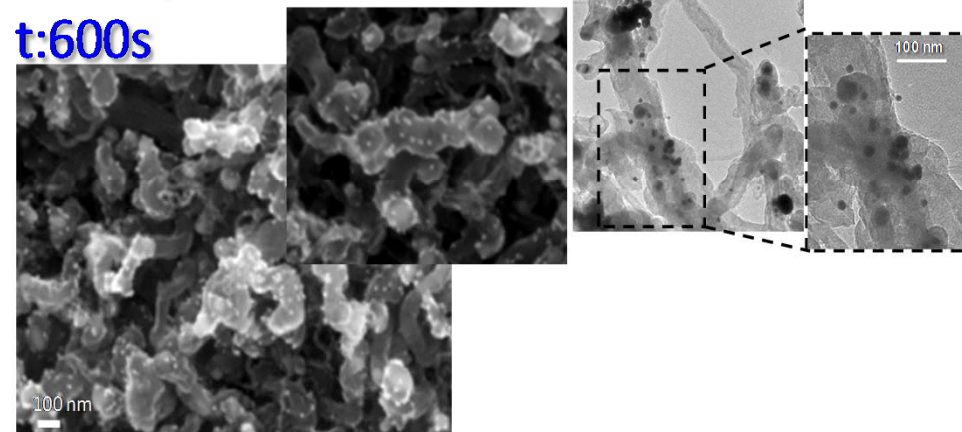
AuNPs/CNTs
t:90s



AuNPs/CNTs
t:300s



AuNPs/CNTs
t:600s



(*) for details pls see poster presentation by Elena Dilonardo, session #7

CONCLUSIONS

- **Electrochemical methods for the size & shape controlled preparation of catalytic metal nanocolloids**
- ***in situ* electrodecoration of metal hydroxides and oxides by Au NPs**
- **Post synthesis electrophoretic deposition of AuNPs on CNTs**
- ***Work is in progress...on sensors fabrication & testing***

Acknowledgements

Financial support by

- M.I.U.R., Programma Operativo Nazionale “Ricerca e Competitività” (R&C) 2007-2013 PON02_00576_3333604: “INNOVHEAD: Tecnologie innovative per riduzione emissioni, consumi e costi operativi di motori Heavy Duty” 2012-2015
- M.I.U.R., Programma Operativo Nazionale “Ricerca e Competitività” (R&C) 2007-2013 PON01_02238 “EURO6. “Elettronica di controllo, sistema d’iniezione, strategie di combustione, sensoristica e tecnologie di processo innovativi per motori diesel a basse emissioni inquinanti” 2011-2015

Thank you!