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

COST Action TD1105

4th International Workshop *EuNetAir* on *Innovations and Challenges for Air Quality Control Sensors*

FFG - Austrian Research Promotion Agency - Austrian COST Association

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Metal-loaded Titania Nanostructures for Air Quality Sensors

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Function in the Action (MC, WG1&2, SIG II member)

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- Experimental and Results
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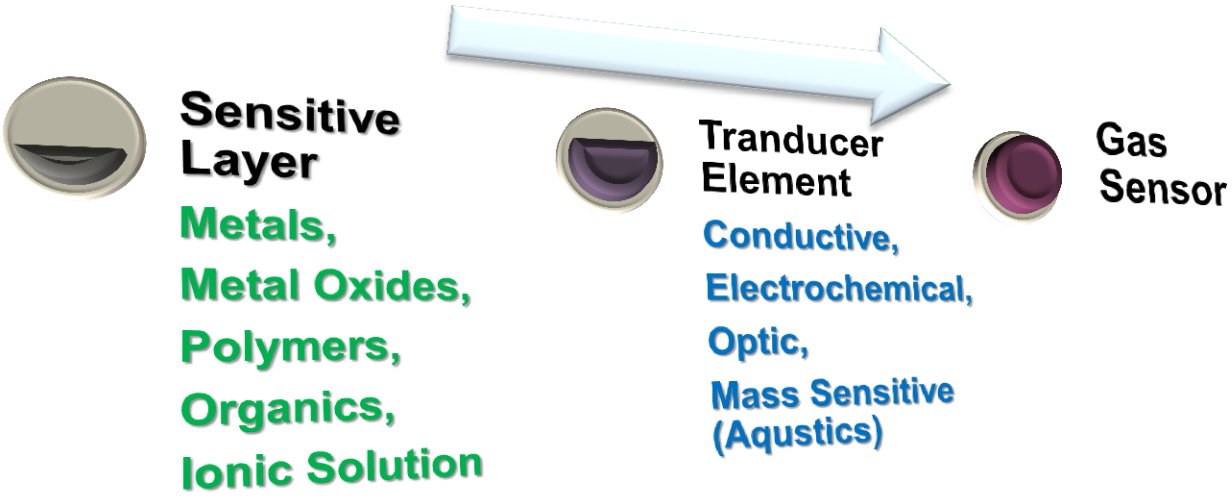
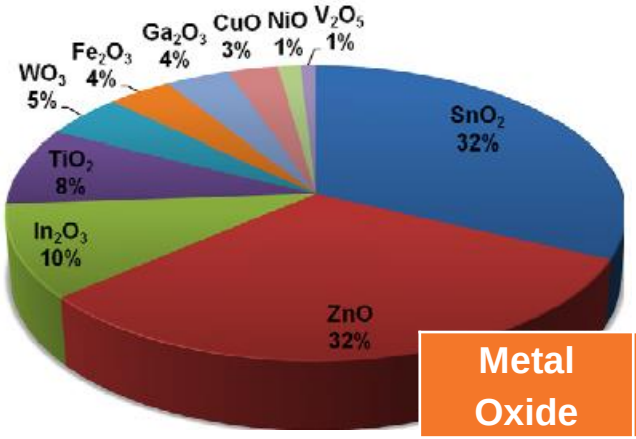
Gas Sensors



What	Why
Fast	Public Security
Robust	Personal Safety
Highly Sensitive & Selective	Industrial Process
Low-Cost*	Medical Diagnosis
Stable	

We Need?

METAL OXIDE MATERIALS FOR SENSING

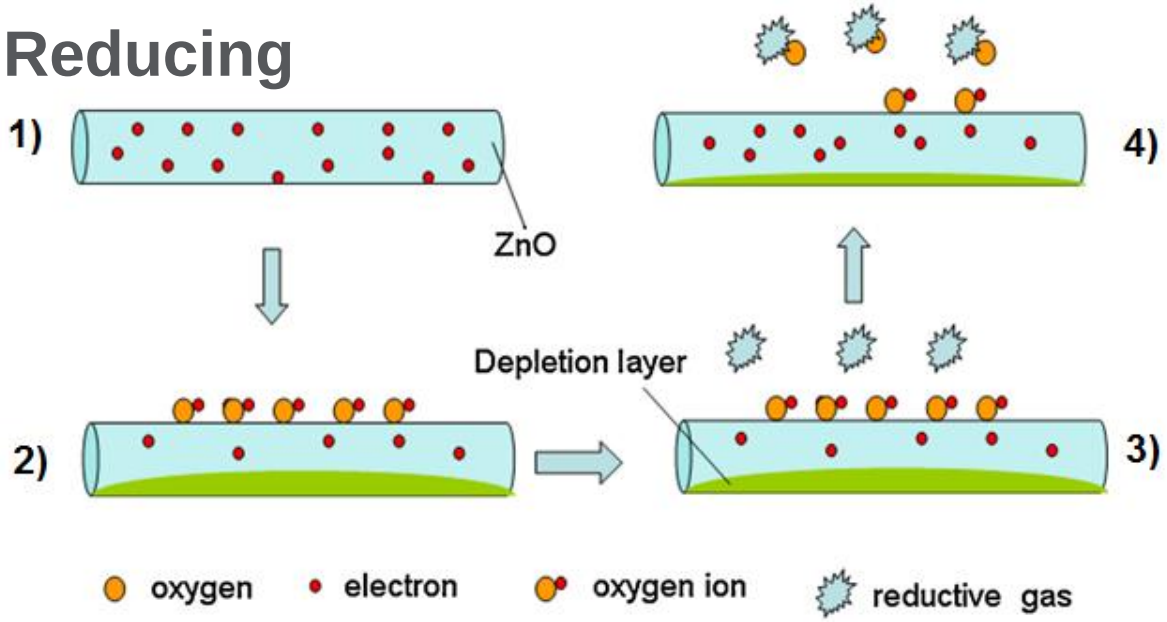


Metal Oxide	Test Gas	Temperature	Sensitivity (Concentration)	Response Time
SnO_2	NO_2	2 ppm (25 °C)	7 (100 ppm)	1 min
	H_2	1 ppm (200°C)	4 (1 ppm)	50s
	CO	100 ppm (25°C)	15 (500 ppm)	10 min
	H_2S	1 ppm (150°C)	6×10^6 (50 ppm)	10 s
In_2O_3	NO_2	0.5 ppm (25°C)	1×10^6 (100 ppm)	5 s
	H_2S	1 ppm (25°C)	1 (20 ppm)	48 s
ZnO	H_2	200 ppm (25°C)	0.04 (200 ppm)	30s
	CO	50 ppm (275°C)	3200 (400 ppm)	50 min
WO_3	H_2	100 ppm (25°C)	22 (1000 ppm)	40 s
CeO_2	CO	10 ppm (25°C)	2 (200 ppm)	10 s
Ga_2O_3	O_2	50 ppm (25°C)	20 (50 ppm)	1s

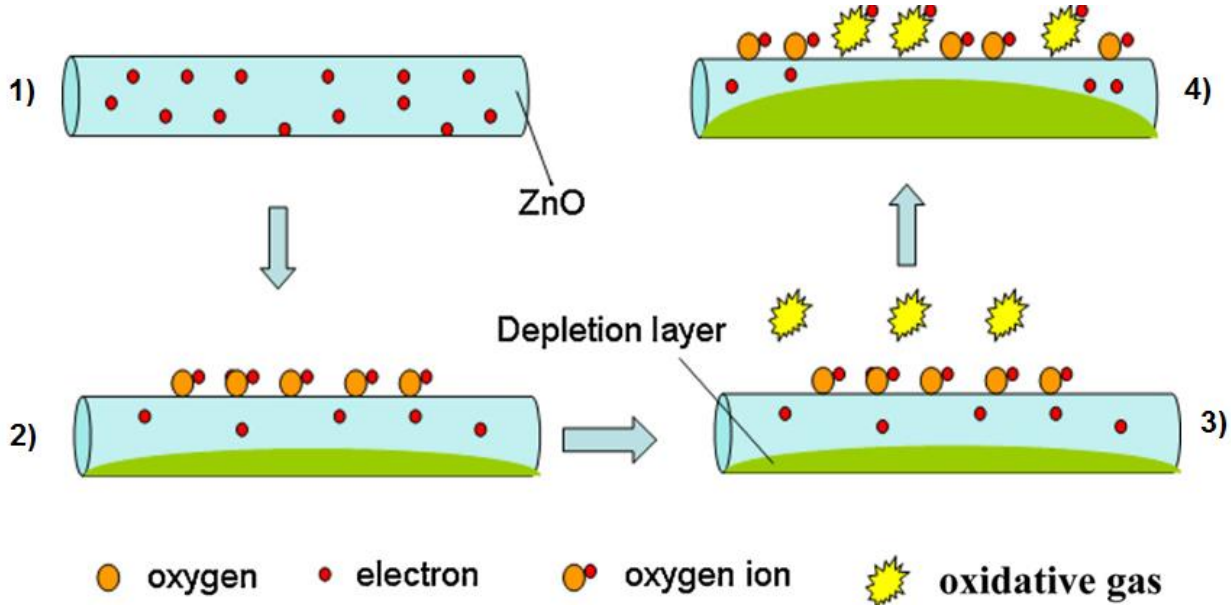
Choi K. J. and Jang H. W., One-Dimensional Oxide Nanostructures as Gas-Sensing Materials: Review and Issues, Sensors, 10, 4083-99,

Sensing Mechanism

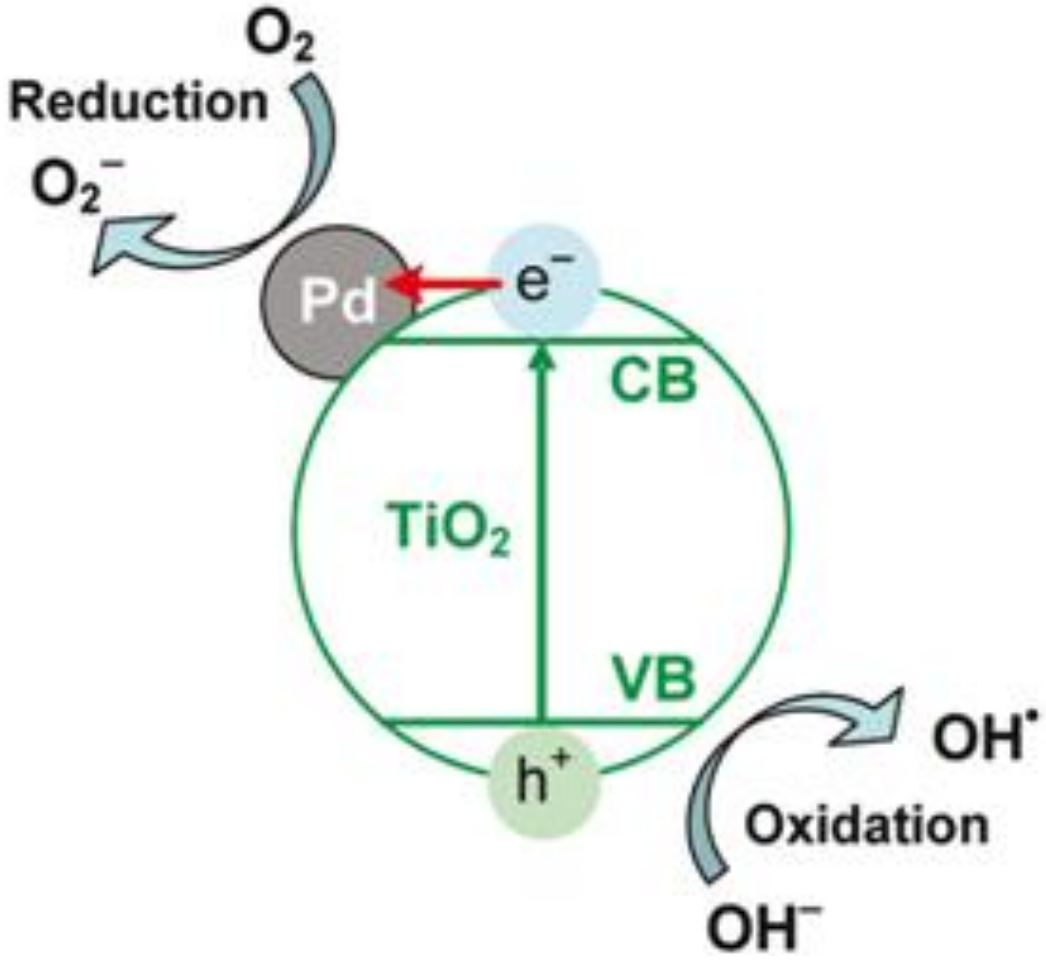
Reducing

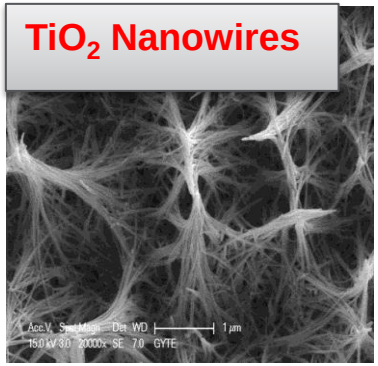


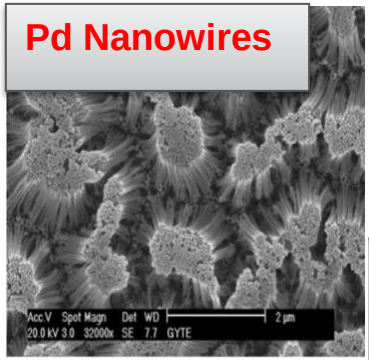
Oxidizing

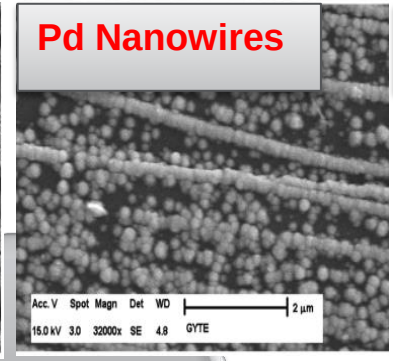


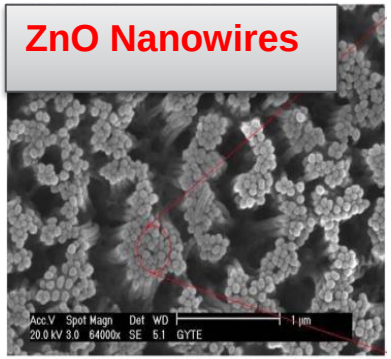
Sensitization

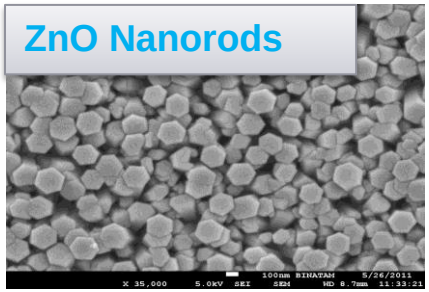


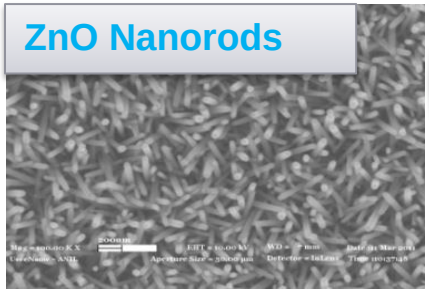

TiO_2 Nanowires


Pd Nanowires


Pd Nanowires


ZnO Nanowires


ZnO Nanorods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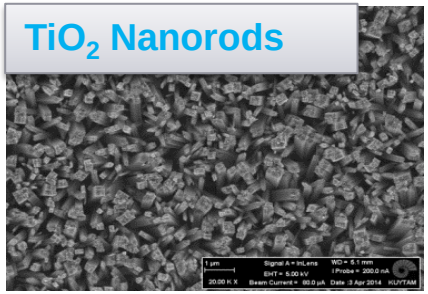
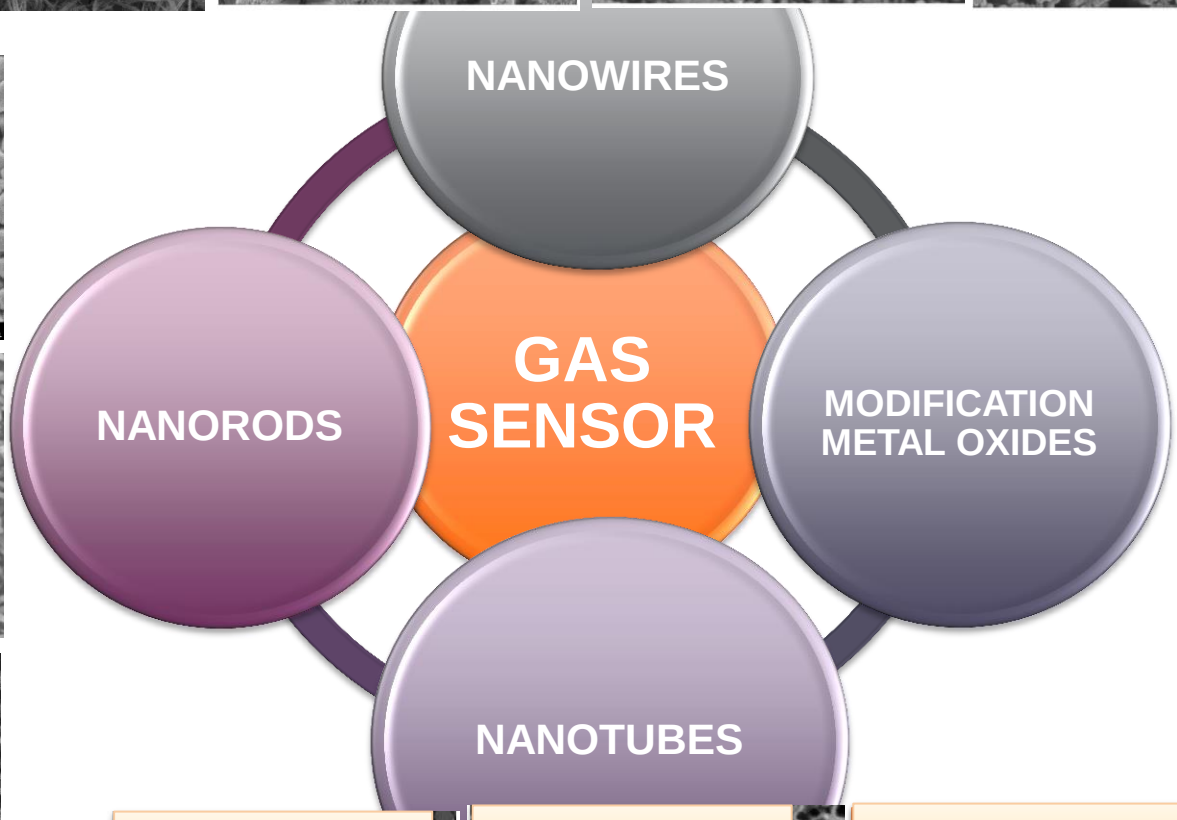
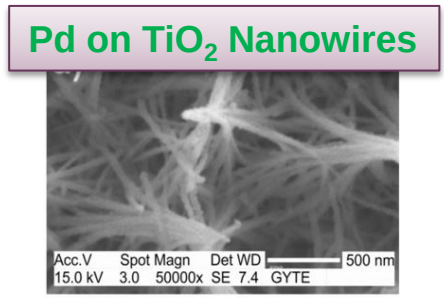
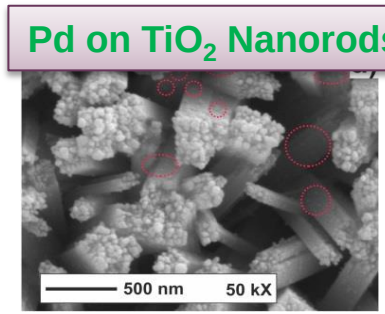
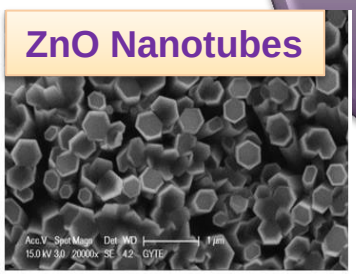
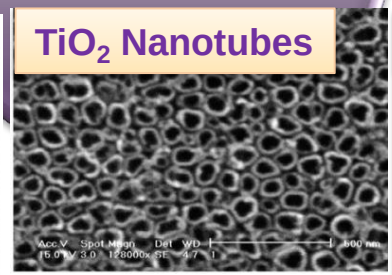

TiO_2 Nanorods

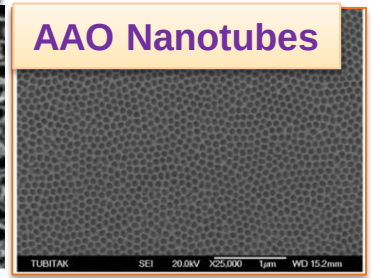

NANOWIRES
NANORODS
GAS SENSOR
MODIFICATION METAL OXIDES
NANOTUBES


Pd on TiO_2 Nanowires


Pd on TiO_2 Nanorods


ZnO Nanotubes

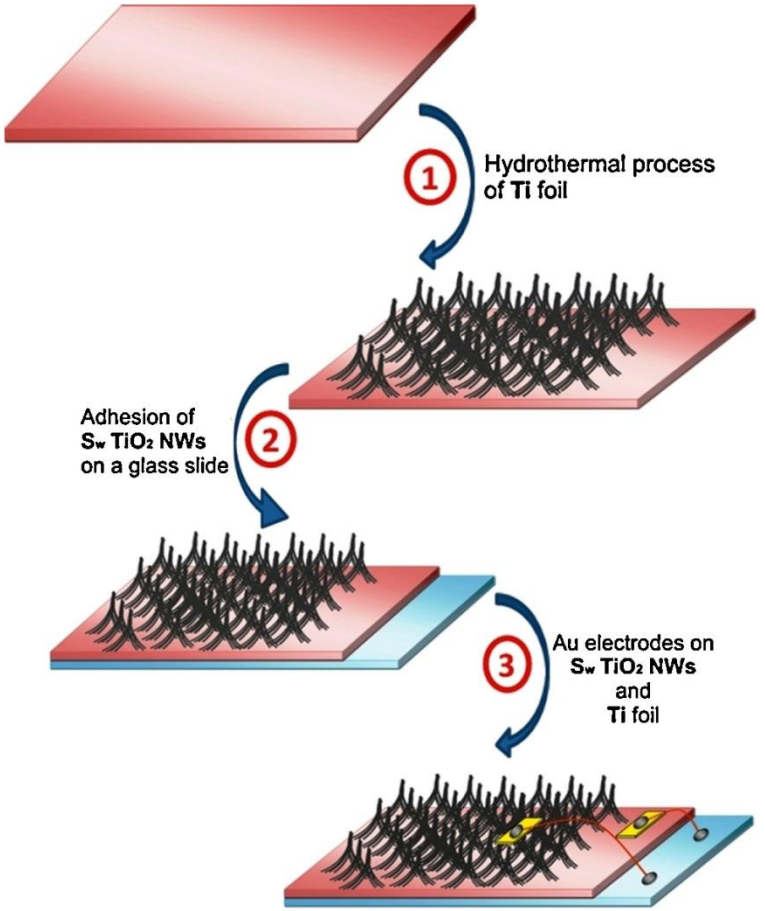

TiO_2 Nanotubes


AAO Nanotubes

Fabrication of TiO_2 Spider- web Nanowires

by hydrothermal method

1M NaOH
220 °C
4 hours



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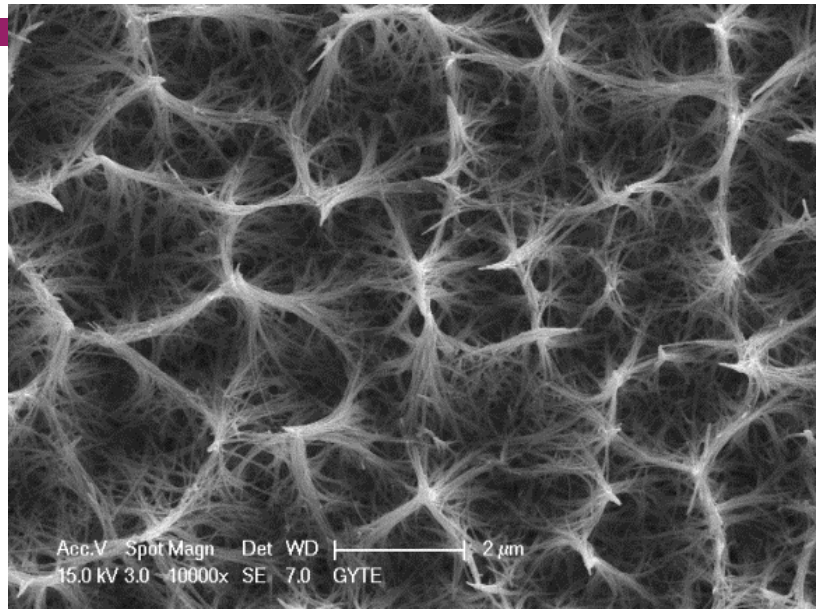

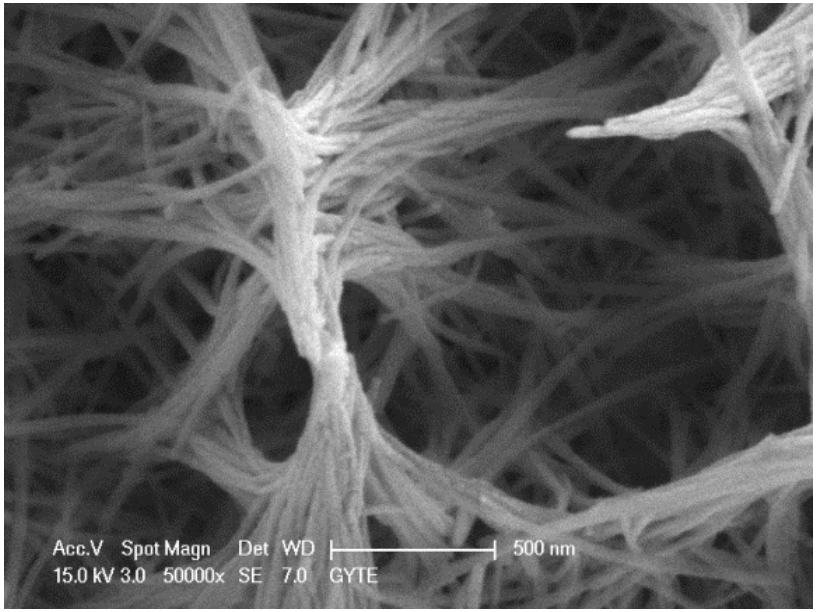

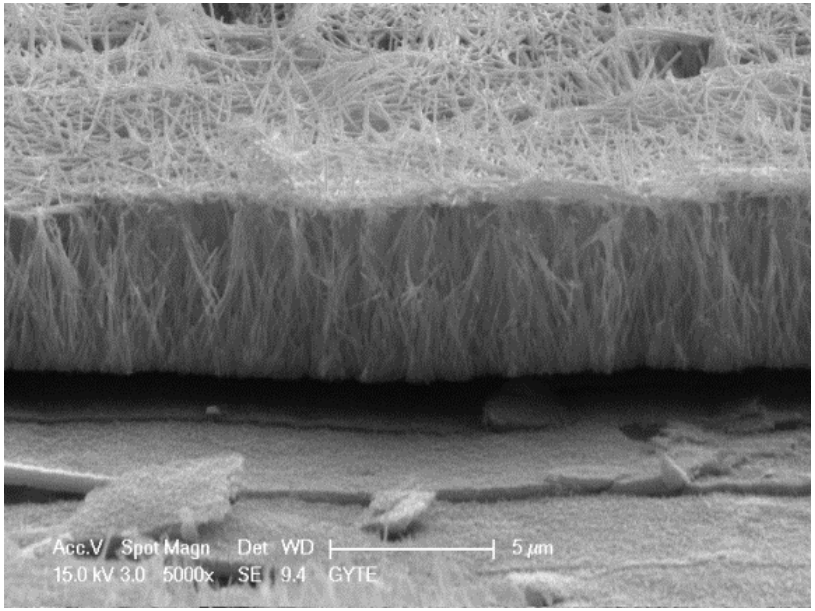

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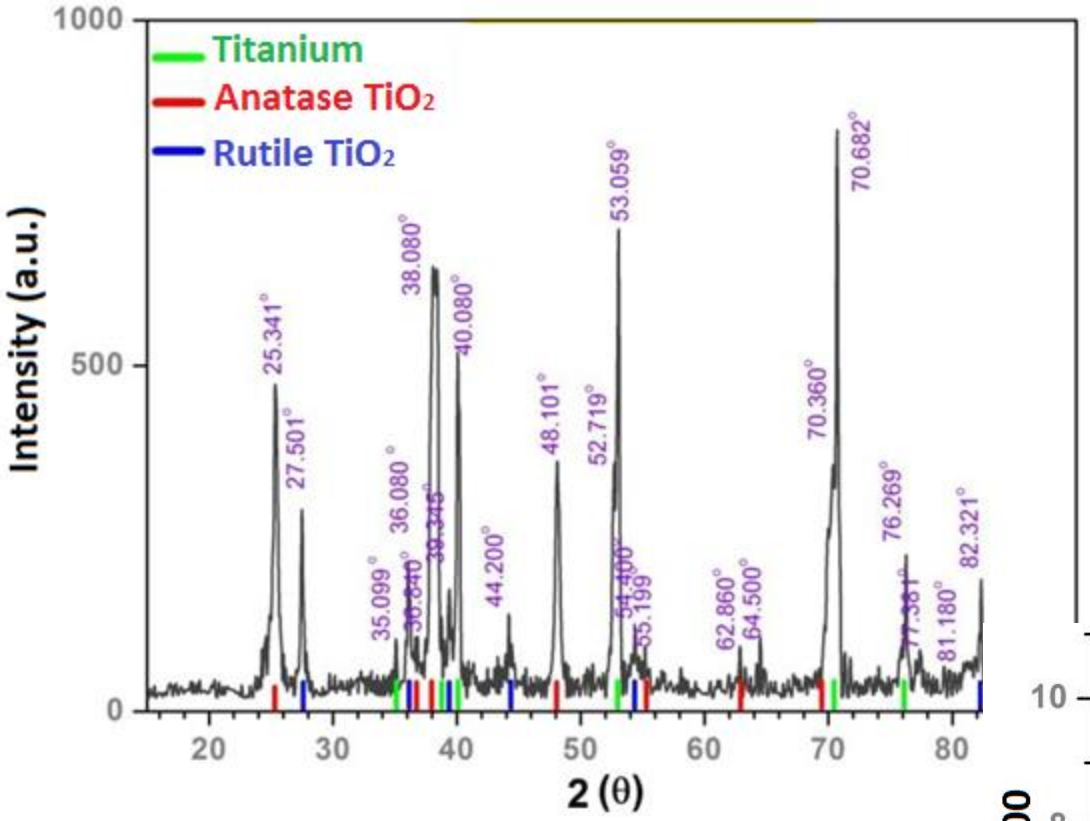

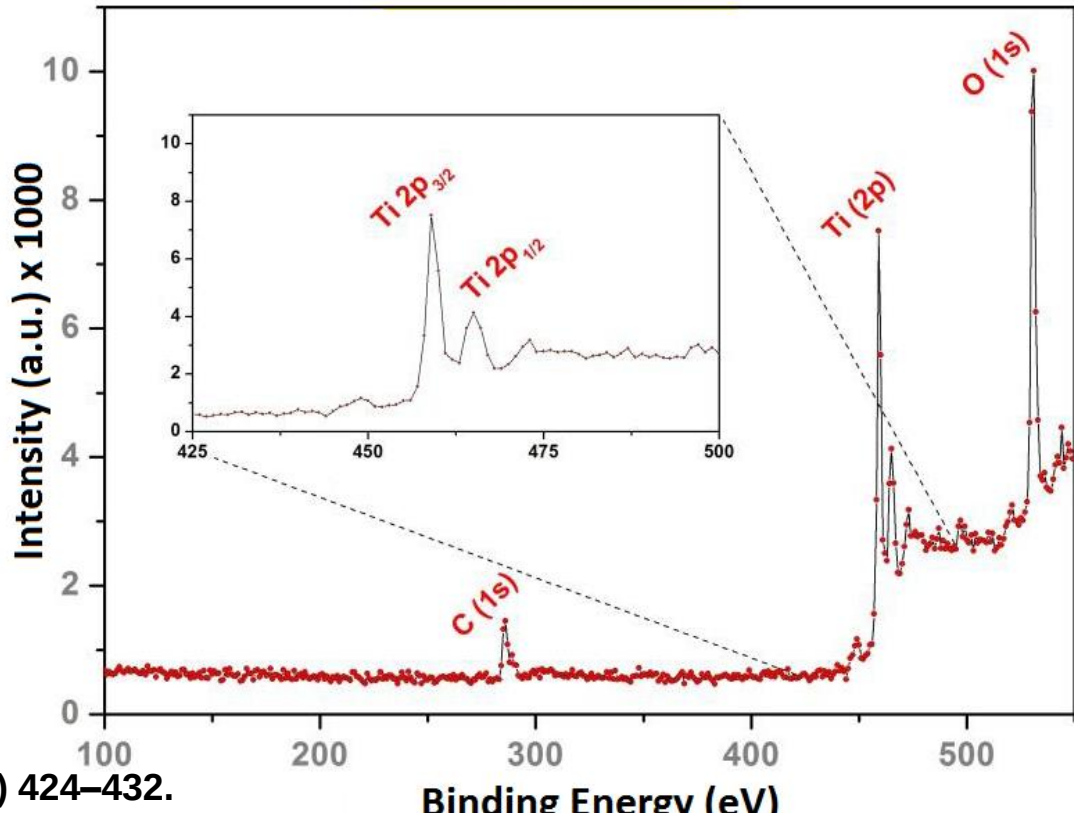

cost
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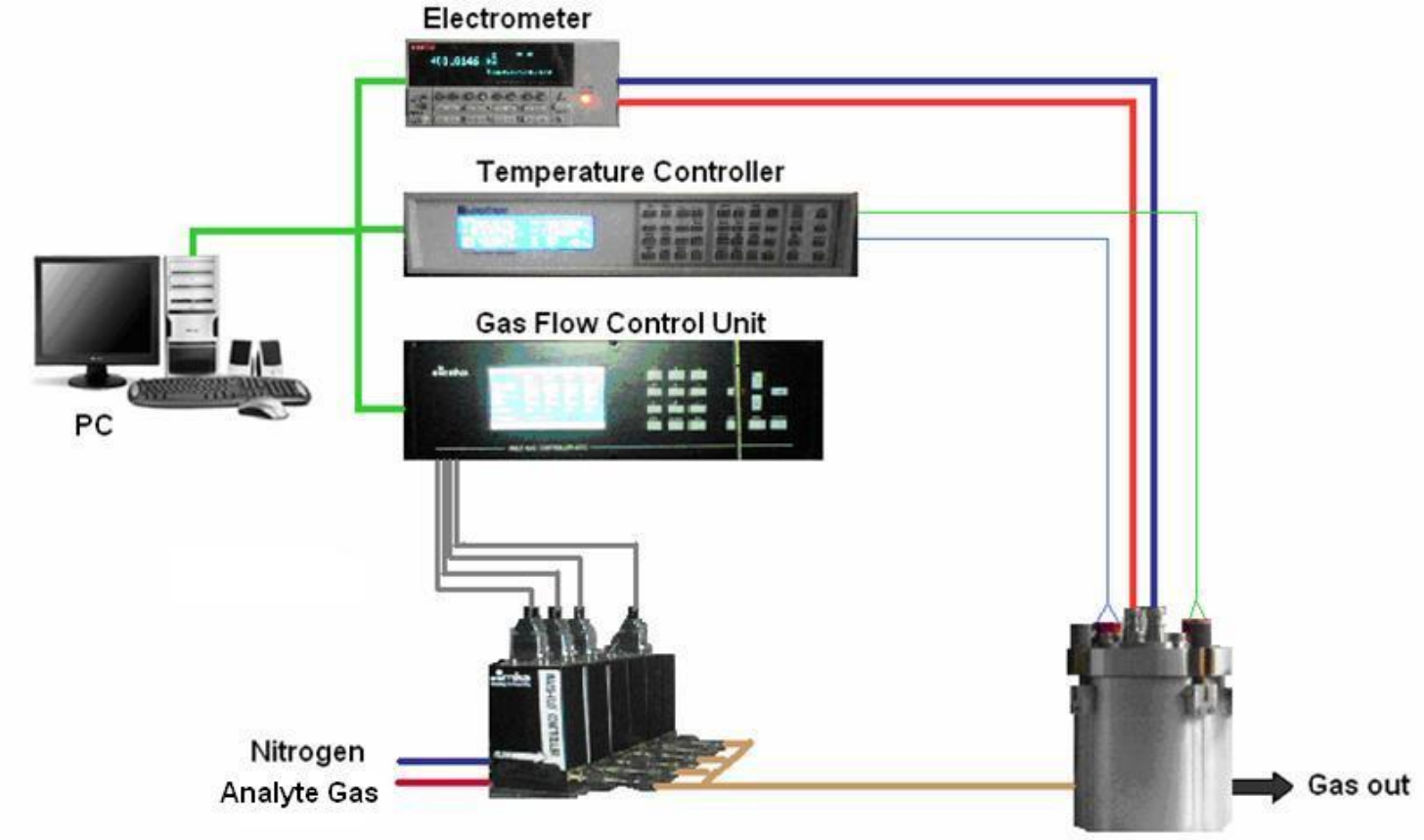
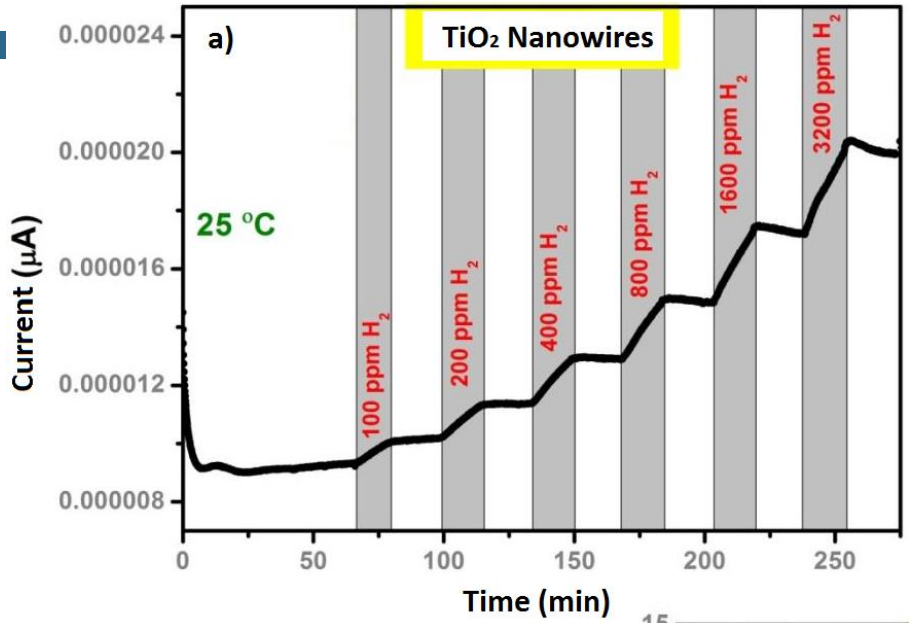
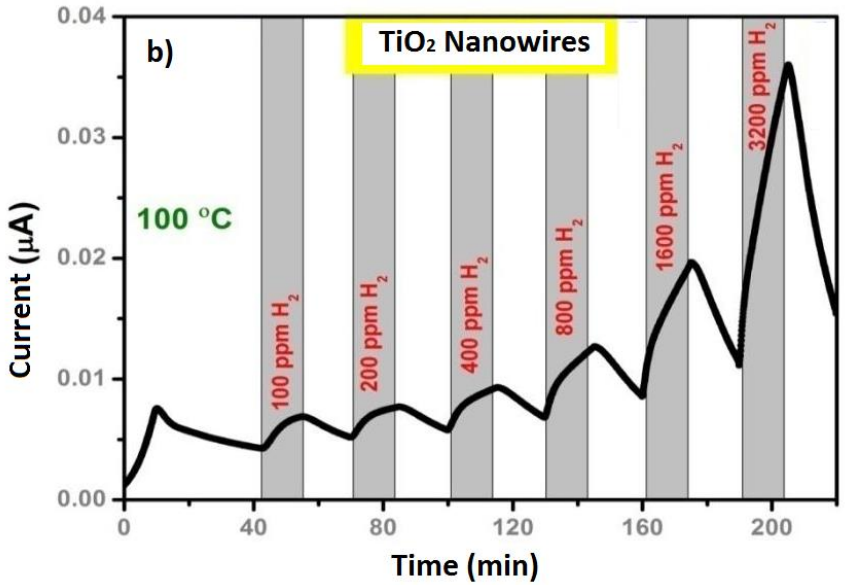
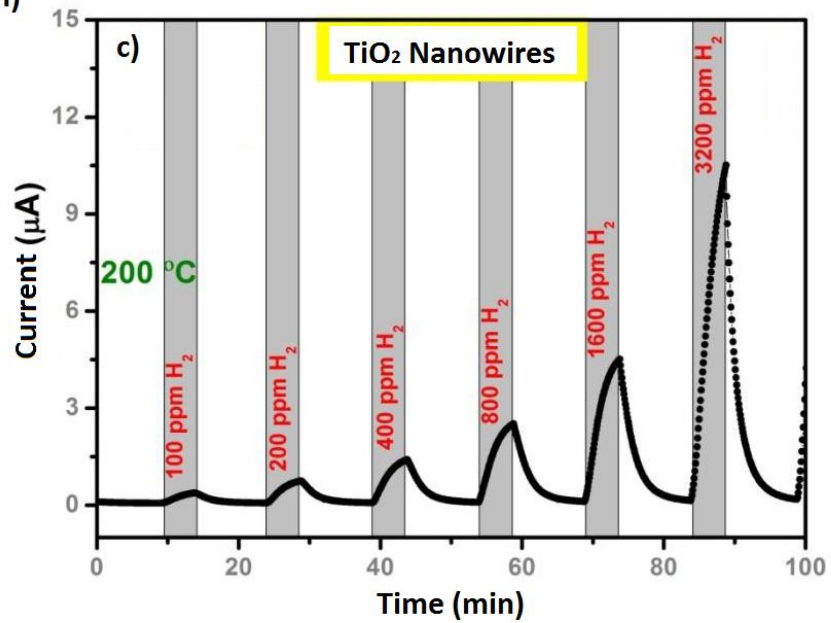
GAS SENSING MEASUREMENTS









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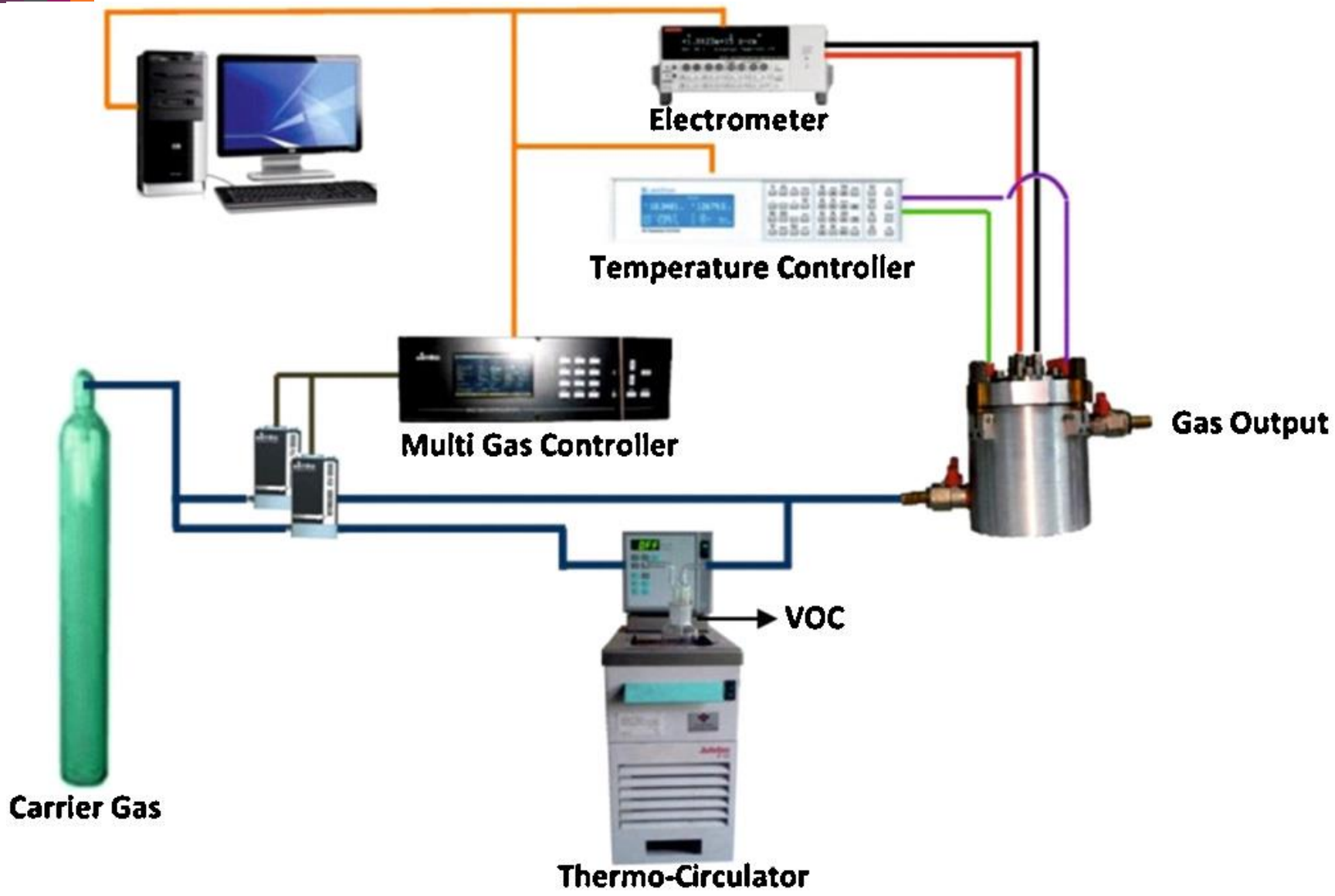
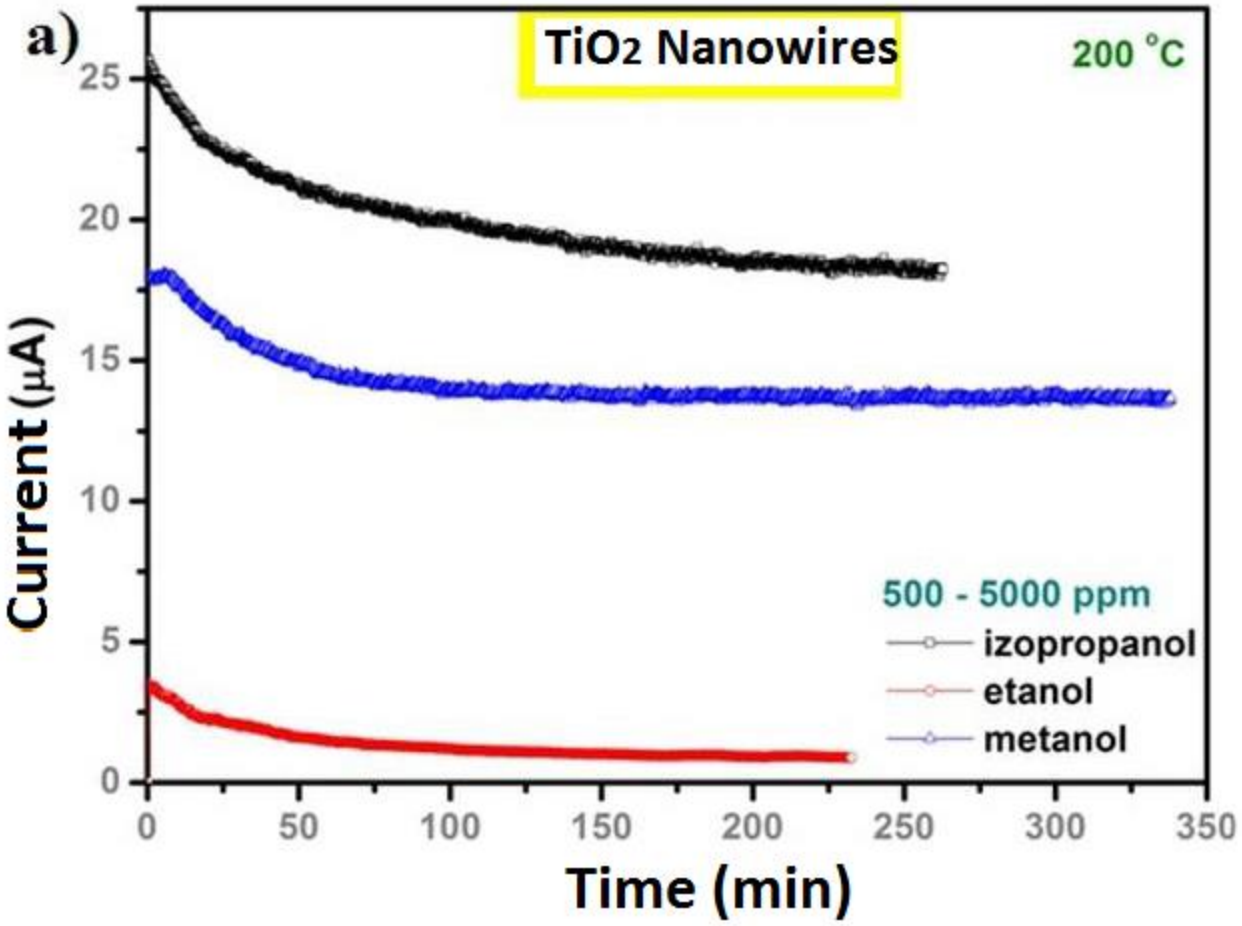
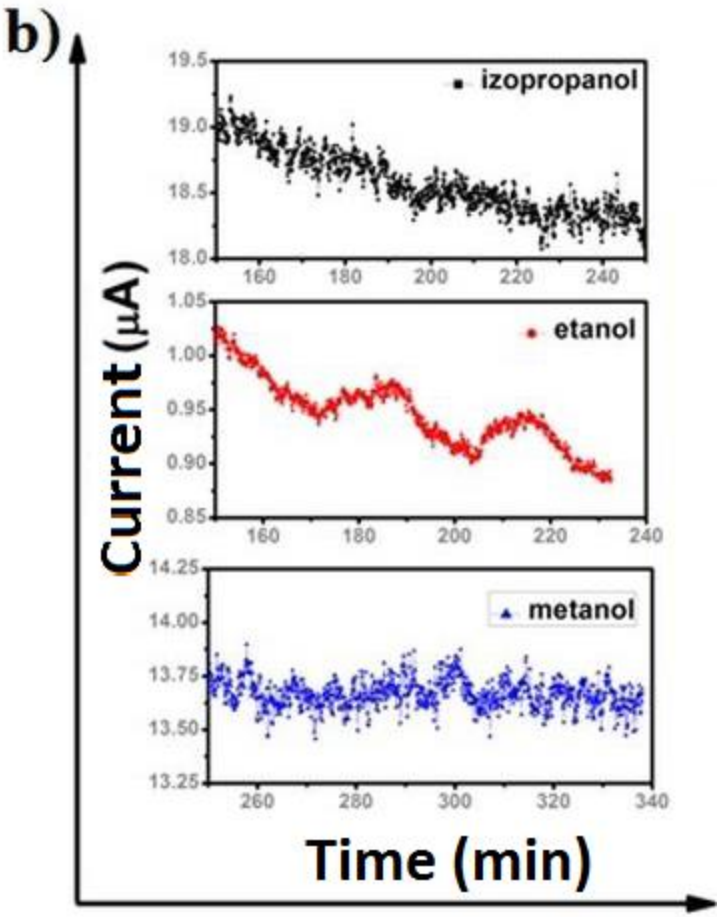

Electrometer
Temperature Controller
Multi Gas Controller
Gas Output
VOC
Carrier Gas
Thermo-Circulator

VOC Sensing





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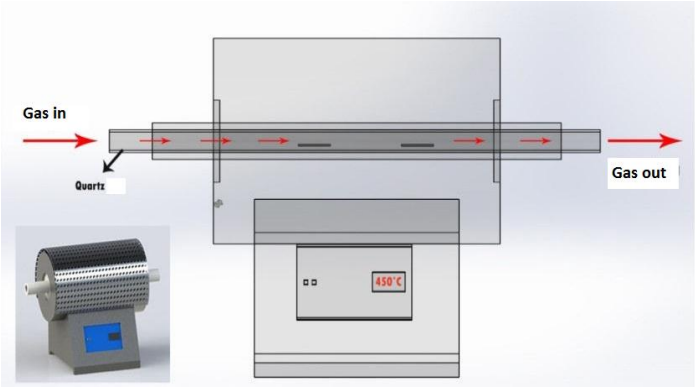
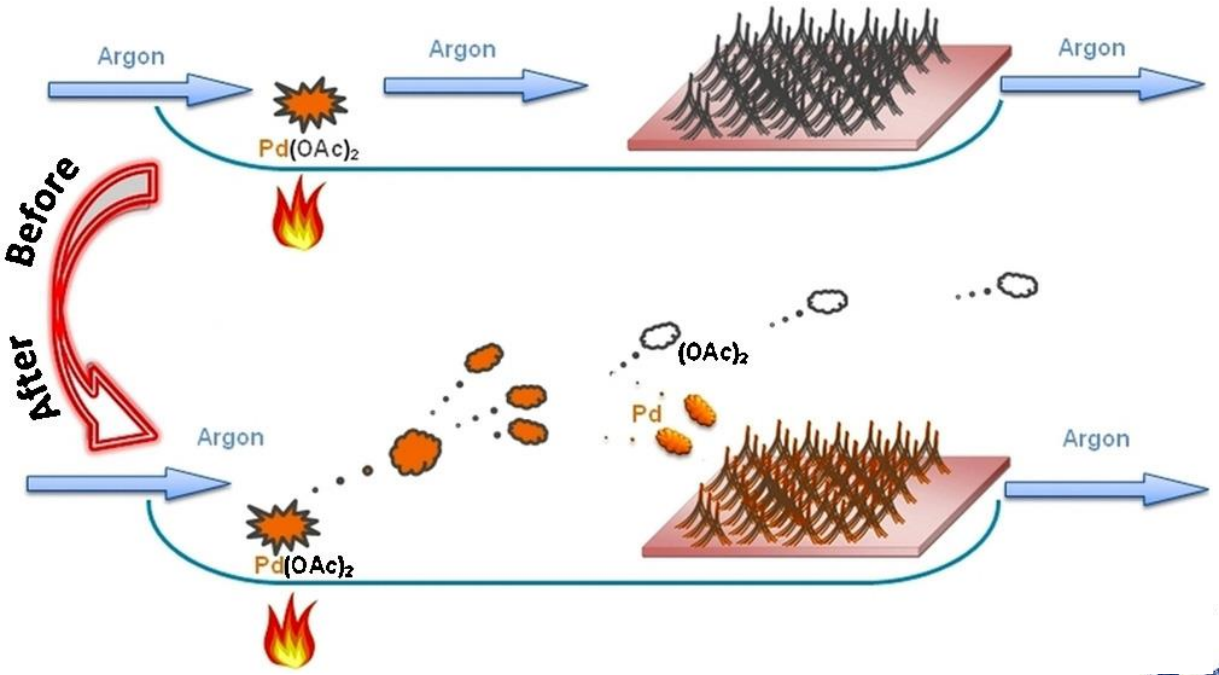
Fabrication of Pd-TiO_2 Spider- web Nanowires





Pd Acetate Powder

<u>Thermal. process:</u>
450 °C
1 hour
Ar media

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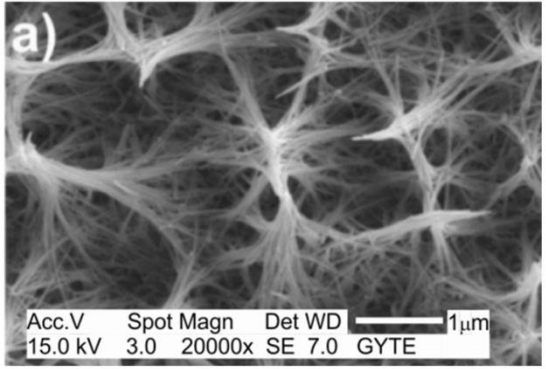
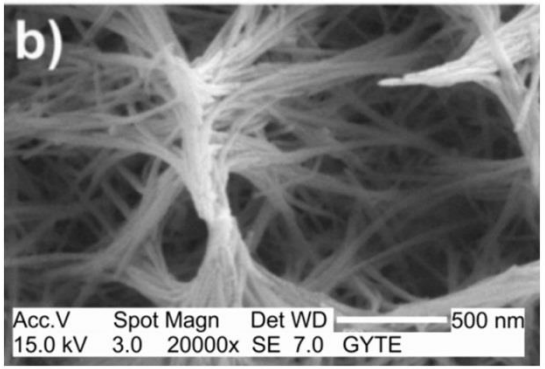
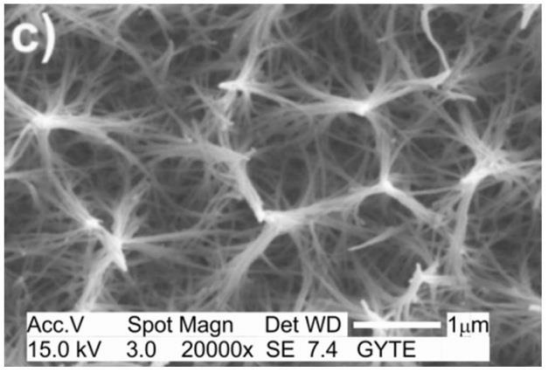
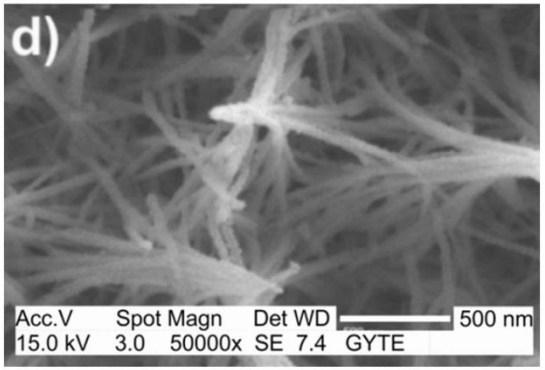
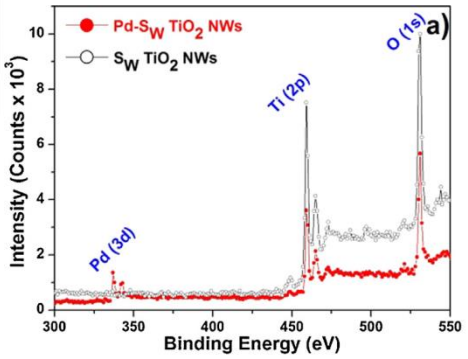
GEBZE TECHNICAL UNIVERSITY

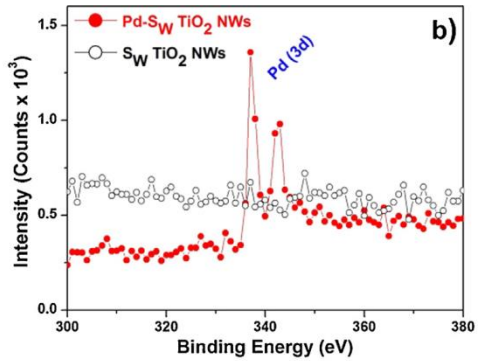


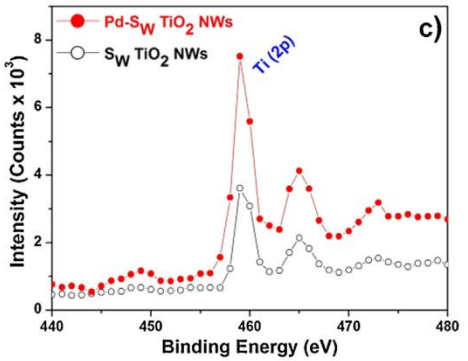


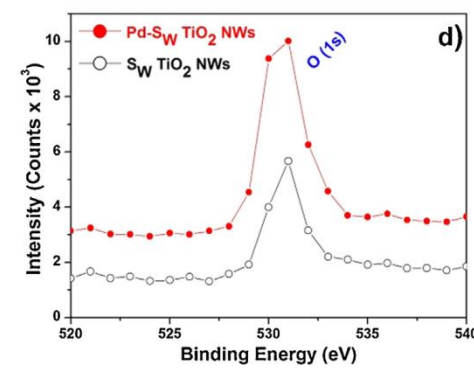












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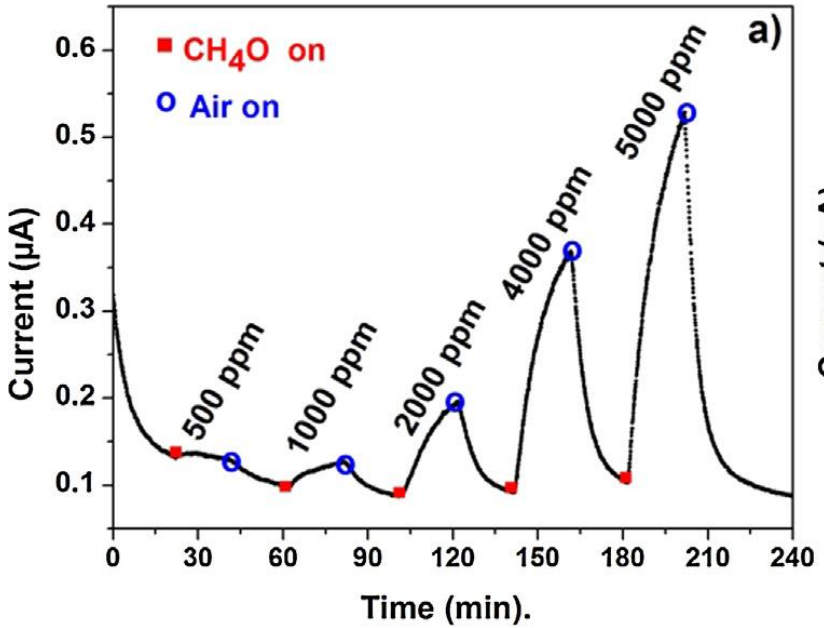
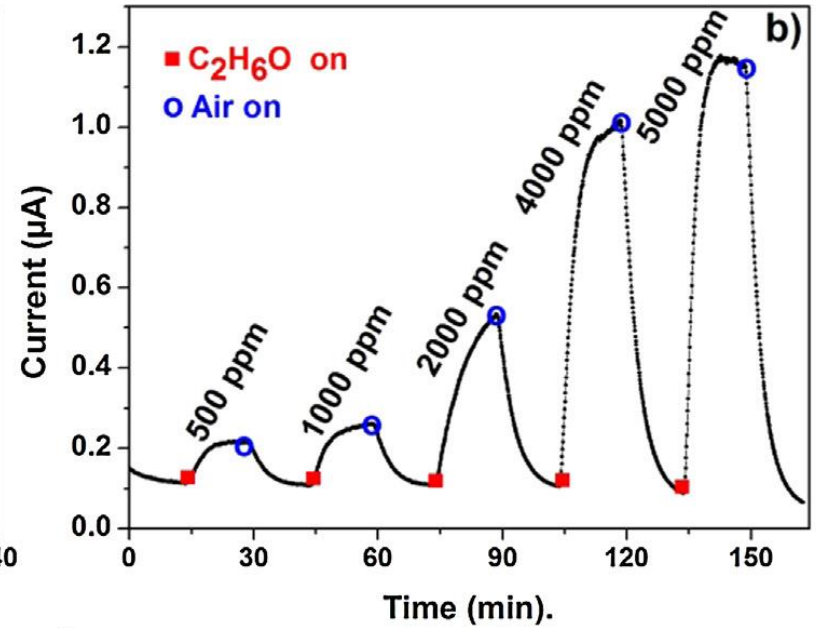
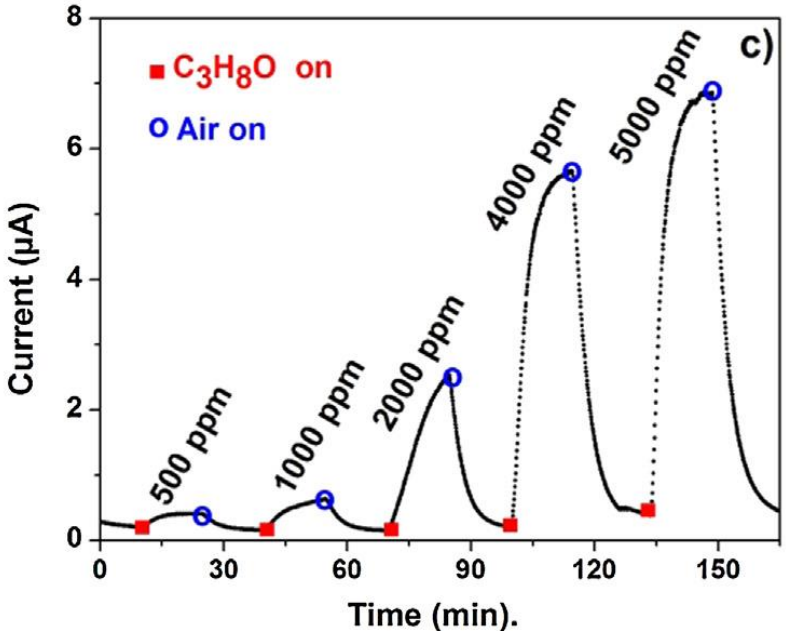
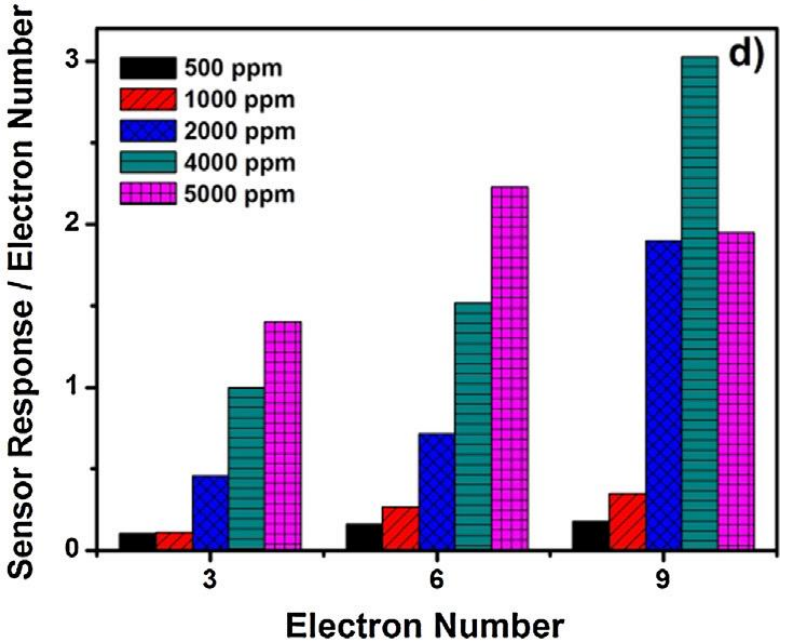
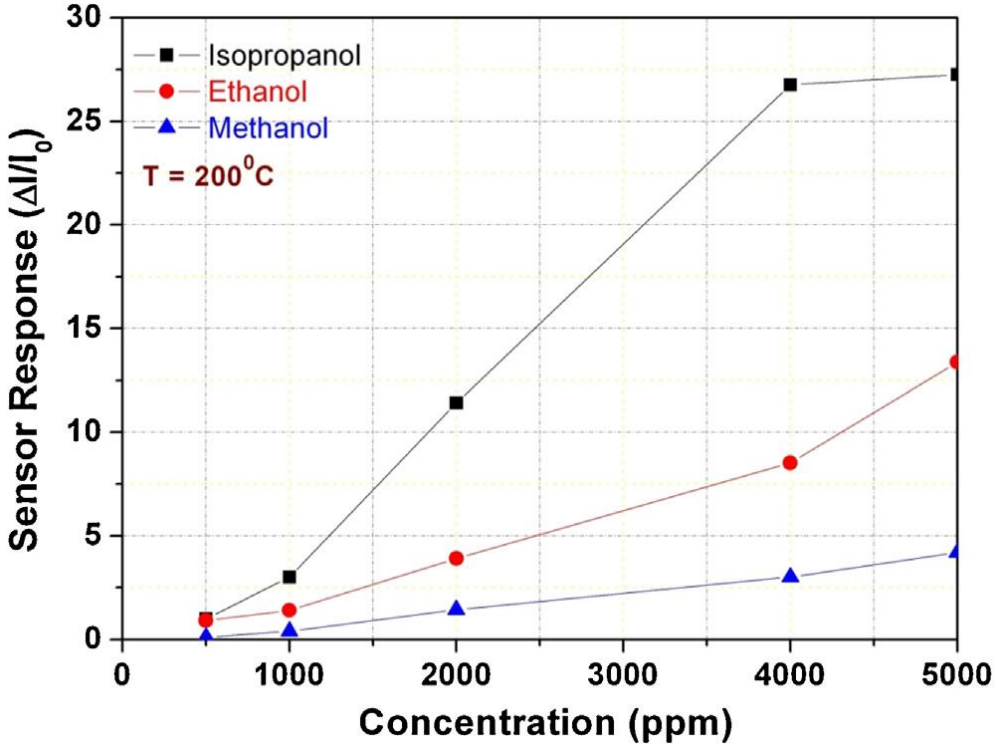
VOC Sensing

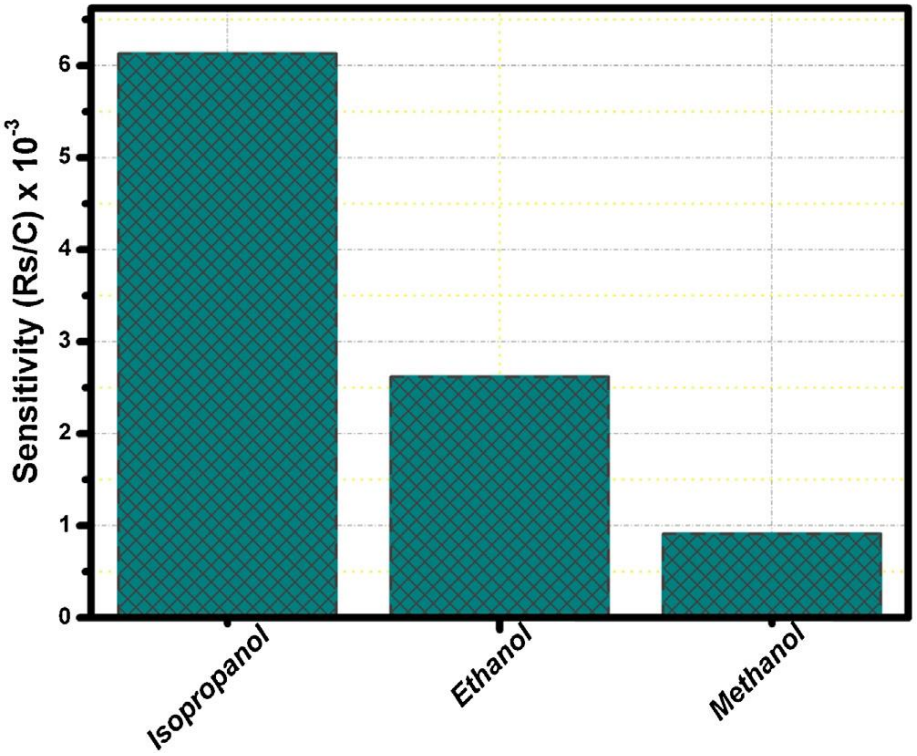

a)
■ CH_4O on
o Air on
500 ppm
1000 ppm
2000 ppm
4000 ppm
5000 ppm
Current (μA)
Time (min).


b)
■ C_2H_6O on
o Air on
500 ppm
1000 ppm
2000 ppm
4000 ppm
5000 ppm
Current (μA)
Time (min).


c)
■ C_3H_8O on
o Air on
500 ppm
1000 ppm
2000 ppm
4000 ppm
5000 ppm
Current (μA)
Time (min).


d)
500 ppm
1000 ppm
2000 ppm
4000 ppm
5000 ppm
Sensor Response / Electron Number
Electron Number





$$CH_3OH + 3O^-(ads) \rightleftarrows CO_2(g) + 2H_2O(g) + 3e^-$$

$$CH_3CH_2OH + 6O^-(ads) \rightleftarrows 2CO_2(g) + 3H_2O(g) + 6e^-$$

$$(CH_3)_2CHOH + 9O^-(ads) \rightleftarrows 3CO_2(g) + 4H_2O(g) + 9e^-$$

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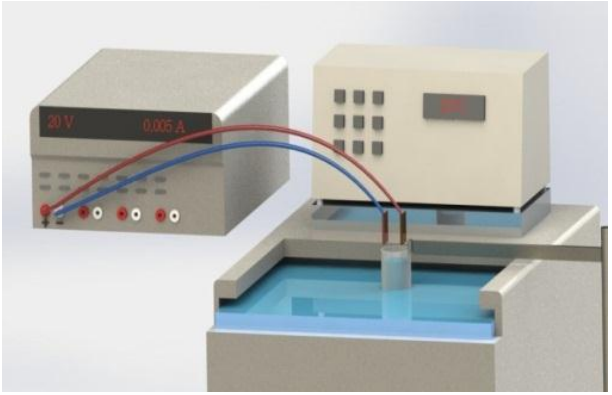
Fabrication of Co-TiO_2 nanowires

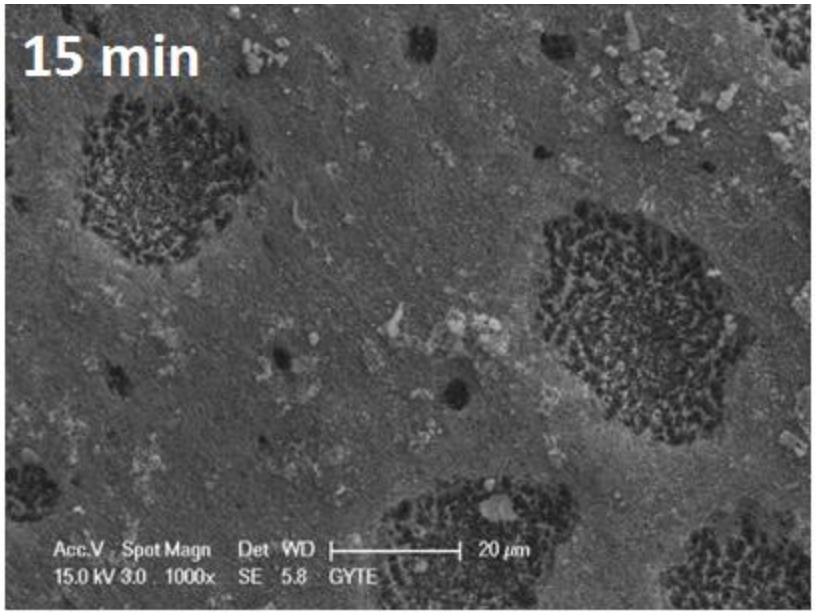
Solution:
1 M NaOH

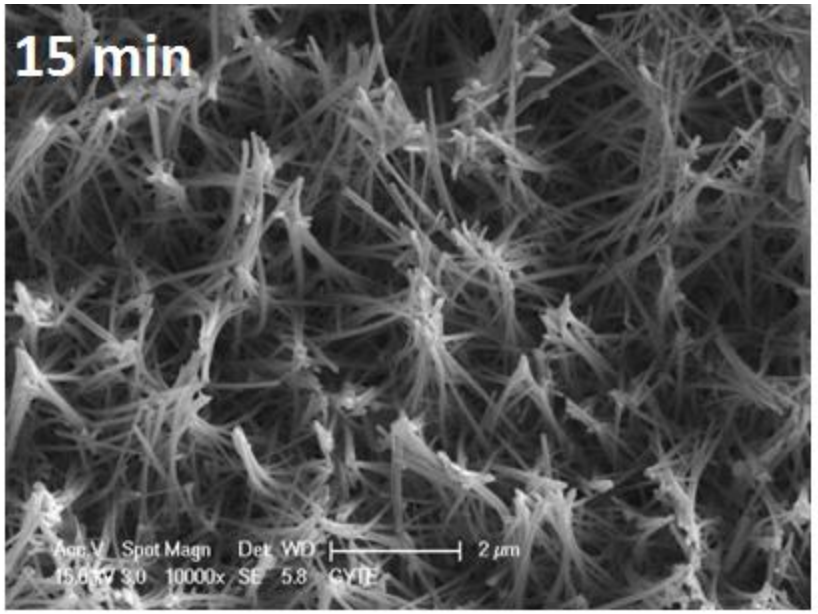
Hydrot. process:
220 °C
4 hours

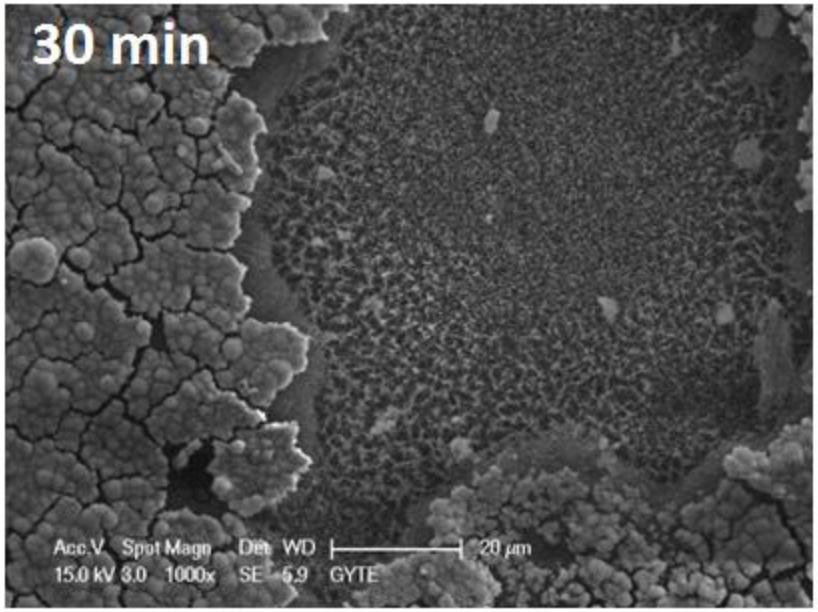


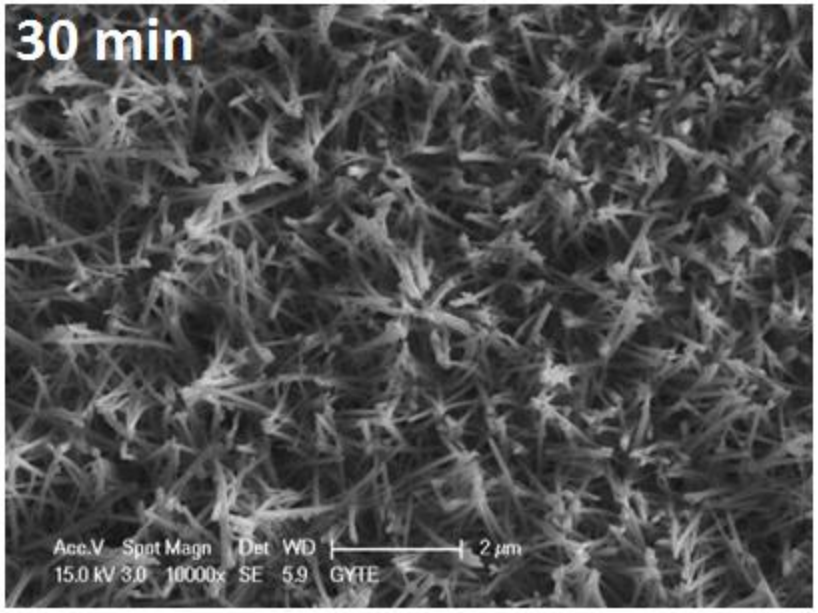
Solution:
0.001 M CoAcetate

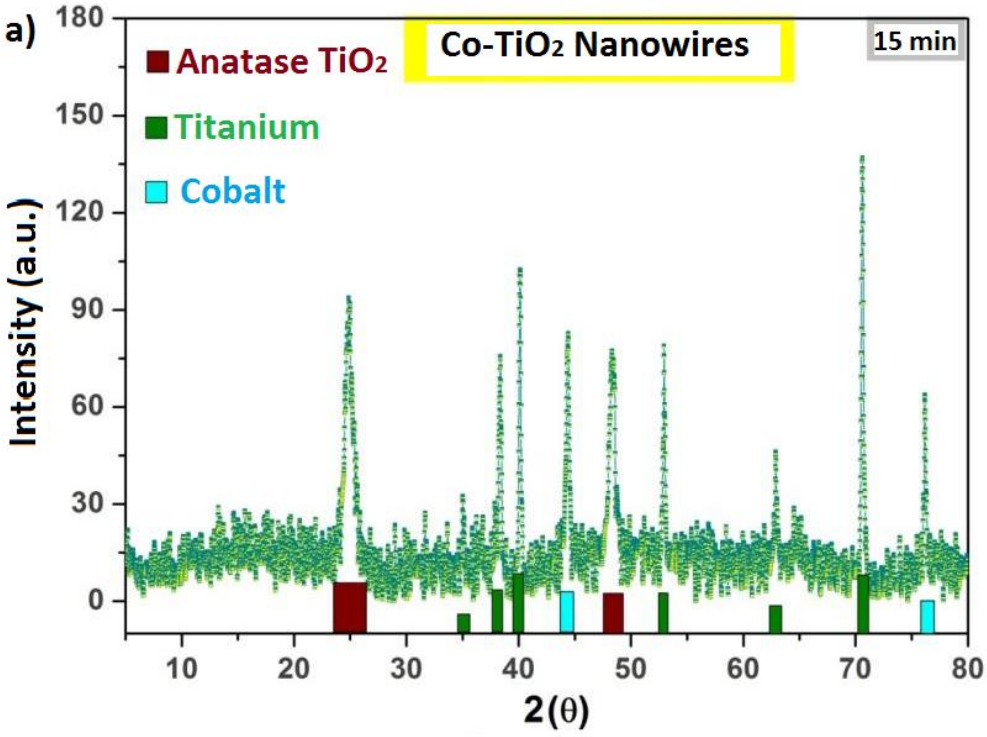
Cathodization. process:
20 °C
10 V
15, 30 mins

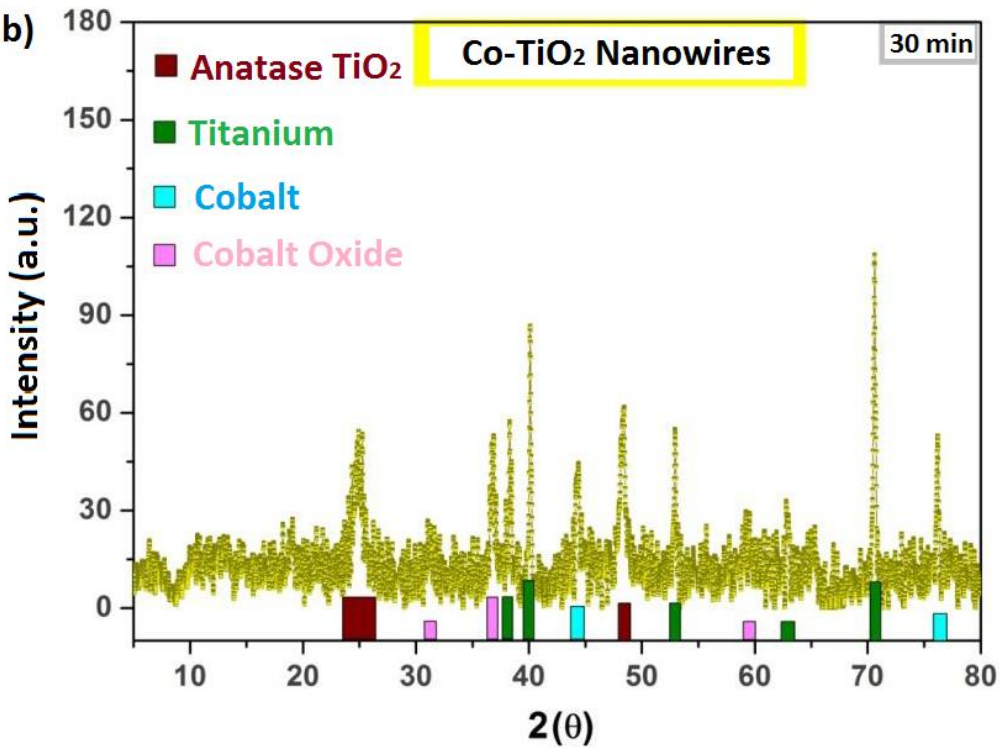

15 min
Acc.V Spot Magn Det WD 20 µm
15.0 kV 3.0 1000x SE 5.8 GYTE

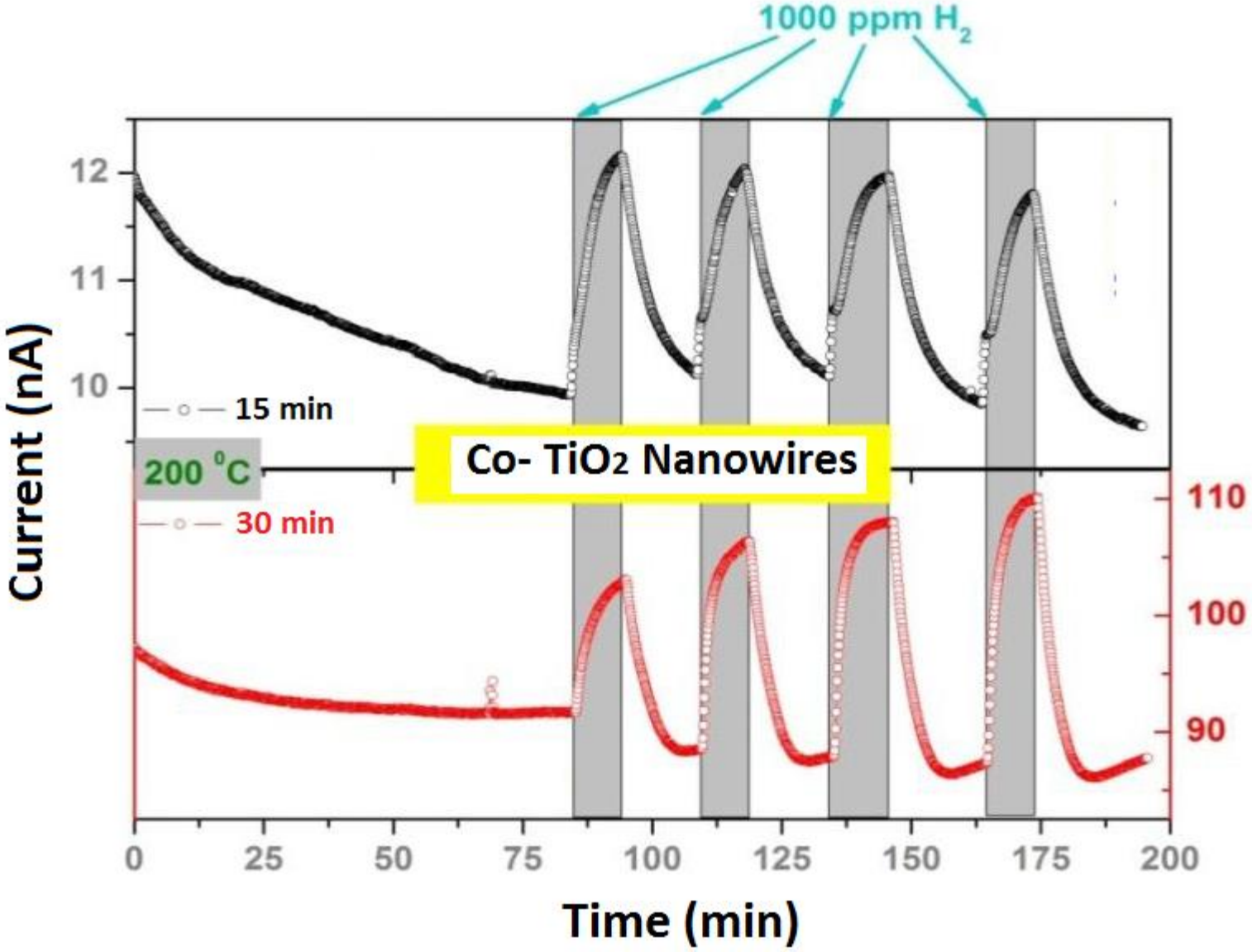

15 min
Acc.V Spot Magn Det WD 2 µm
15.0 kV 3.0 10000x SE 5.8 GYTE


30 min
Acc.V Spot Magn Det WD 20 µm
15.0 kV 3.0 1000x SE 5.9 GYTE


30 min
Acc.V Spot Magn Det WD 2 µm
15.0 kV 3.0 10000x SE 5.9 GYTE


a)
Co-TiO2 Nanowires
15 min
Anatase TiO2
Titanium
Cobalt
Intensity (a.u.)
2(θ)
0
30
60
90
120
150
180
10
20
30
40
50
60
70
80


b)
Co-TiO2 Nanowires
30 min
Anatase TiO2
Titanium
Cobalt
Cobalt Oxide
Intensity (a.u.)
2(θ)
0
30
60
90
120
150
180
10
20
30
40
50
60
70
80


1000 ppm H_2
12
11
10
Current (nA)
15 min
200 °C
30 min
Co- TiO_2 Nanowires
110
100
90
0
25
50
75
100
125
150
175
200
Time (min)

Fabrication of Ni-TiO_2 nanowires

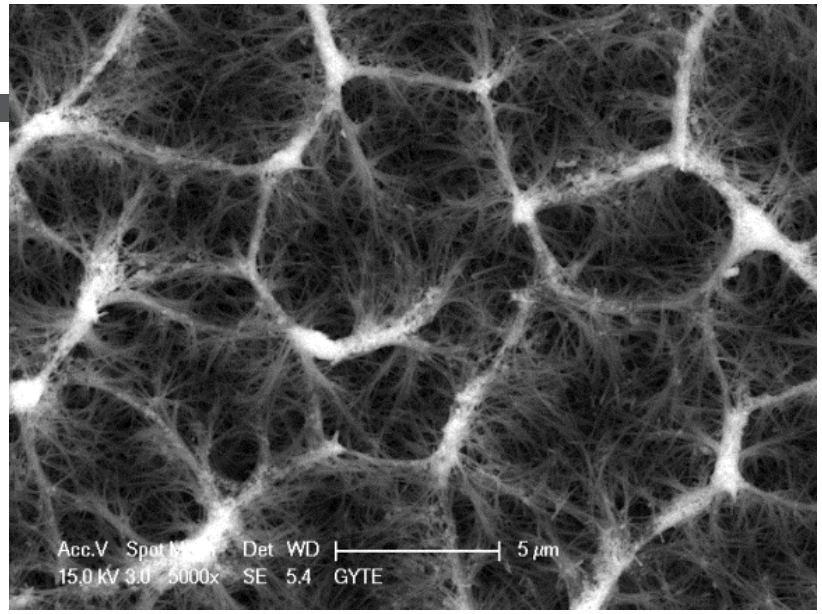
Solution:

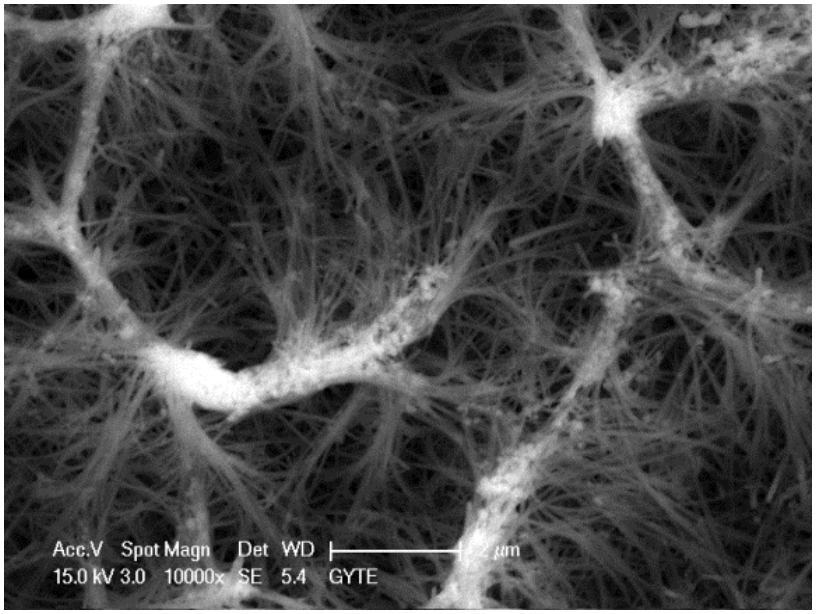
1 M NaOH + Ni Formate (1 %)

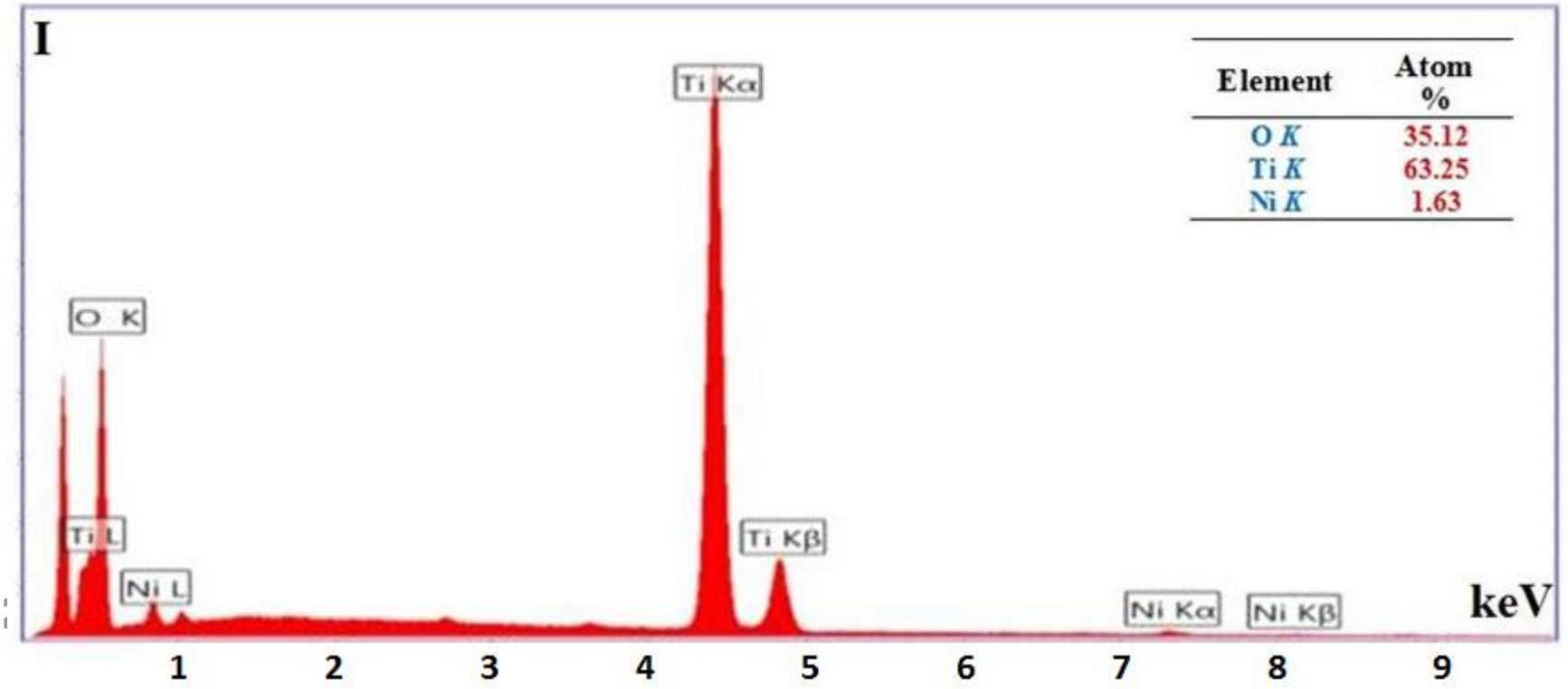
Hydrot. process:

220 °C

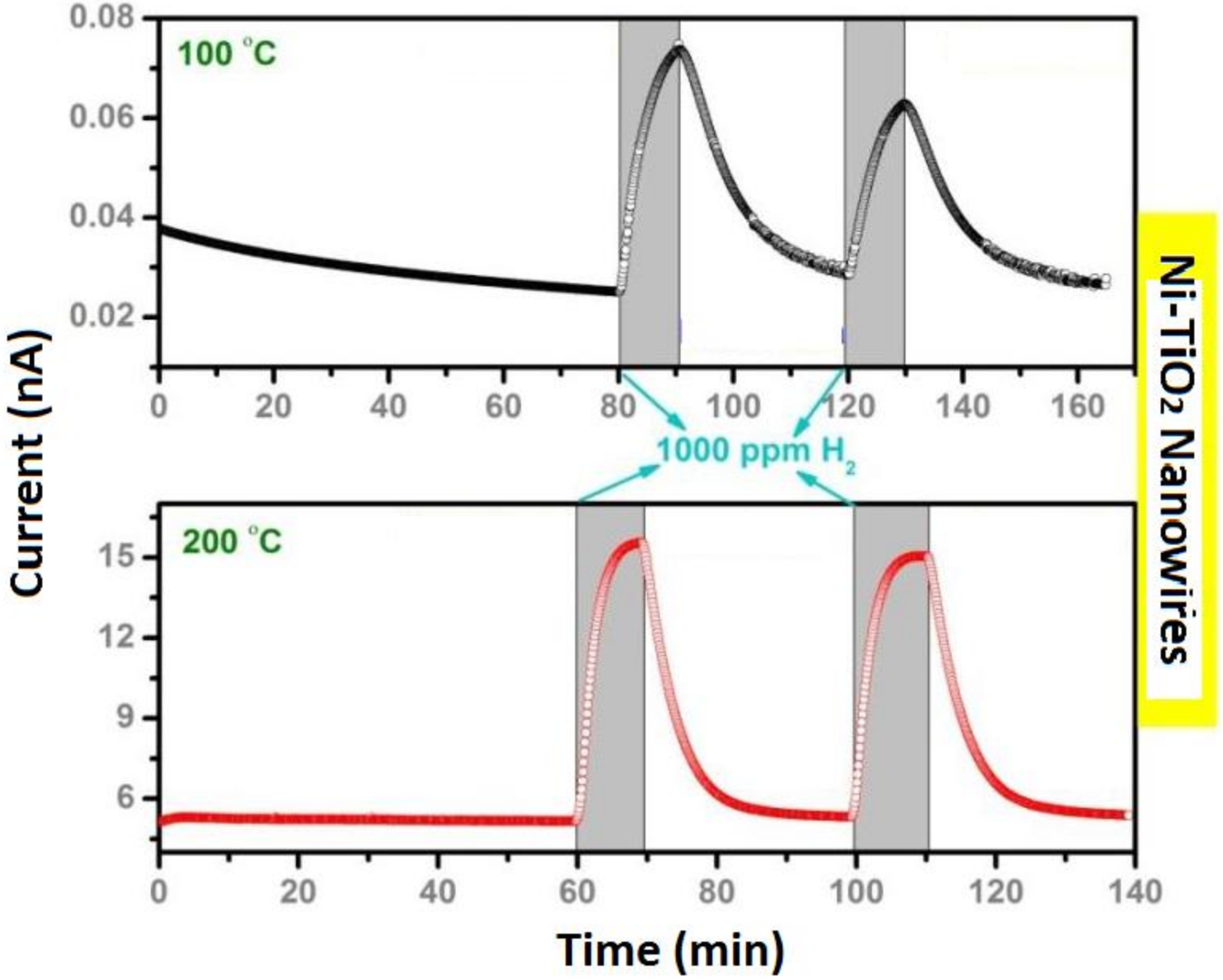
4 hours







Element	Atom %
O *K*	35.12
Ti *K*	63.25
Ni *K*	1.63


100 °C
0.08
0.06
0.04
0.02
0
20
40
60
80
100
120
140
160
1000 ppm H_2
200 °C
15
12
9
6
0
20
40
60
80
100
120
140
Current (nA)
Time (min)
Ni-TiO_2 Nanowires

Summarizing of the results for Metal loaded TiO_2 NWs

Gases / Nanostructures	H_2	EtOH	MetOH	IsOH	CCl_4	$CHCl_3$
TiO_2 NWs	27	0.05	X	X	X	X
Co-TiO_2 NWs	0.2	0.05	X	X	X	X
Ni-TiO_2 NWs	1.8	0.24	X	X	X	X
Pd-TiO_2 NWs	86.7	12.06	4.2	17.45	X	X

NWs: Nanowires
X: No response

CONCLUSIONS

- TiO_2 nanowires on Ti foil were fabricated by hydrothermal method.
- Co, Ni and Pd were loaded on TiO_2 nanowires by cathodization, hydrothermal and CVD methods, respectively.
- TiO_2 nanowires were more selective for H_2 than the other structures.
- Pd loaded TiO_2 nanowires were more sensitive against measured gases than Ni and Co loaded TiO_2 nanowires.

??? THANK YOU ???

Acknowledgements
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