High-Temperature Nano-Derived Micro-H_2 and -H_2S Sensors

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Objectives

- Develop micro-scale, chemical sensors composed of nano-derived, metal-oxide materials which display stable performance within high-temperature environments (>500°C).
- Short term– Develop high-temperature H_2 and H_2S sensor using low cost, easily reproducible methods with 3D porous nanomaterials.
- Long term – Develop high-temperature micro-sensor arrays to detect gases such as NO_x, SO_x, H_2S, H_2, HCs.
- Collaboration with NexTech Materials, Ltd. (Lewis Center, OH).

Proposed Work Plan

<u>Task 2.0 Synthesis and Characterization of Nano-Composite Electrodes.</u> Doped-tin oxide, ceria, zirconate (perovskite and pyrochlore), and molybdate/tungstate nanomaterials will be synthesized using hydrothermal and/or glycine-nitrate processes and characterized.

<u>Task 3.0 Lost-Mold Microcasting of the Selective Electrode Structure.</u> Develop microcasting methods for patterning microscale, chemically selective pads on alumina wafers.

<u>Task 4.0 Fabrication of Micro-Sensors and Arrays.</u> Fabricate functional hydrogen micro-sensors and micro-sensor arrays. In addition, stable IDEs for high-temperature applications must be developed.

<u>Task 5.0 Micro-Sensor and Sensor Array Testing.</u> Micro-sensors will be first characterized for baseline resistance using external furnace heat at temperatures ranging from 600°C to 1000°C. Key tests include:

- *Sensitivity and selectivity*
- *Humidity sensitivity (0-10% H_2O)*
- *O_2 requirements (0.1-20%)*
- *CO cross-sensitivity (ppm-% CO)*
- *Temperature sensitivity (500-1000°C)*

Proposed Work Schedule

Schedule of tasks and milestones

Task/*Milestone*	Quarter after Project Initiation											
	1	2	3	4	5	6	7	8	9	10	11	12
Task 1. Project Management and Planning (Q1-Q12)												
Subtask 1.1: Kick-Off Meeting and Sensor Design at WVU.	━	━										
→ *MS: Sensor and Array Established*		▲										
Subtask 1.2: Project Meetings and Reporting	━	━	━	━	━	━	━	━	━	━	━	━
→ *DL: Quarterly Reports*	●	●	●	●	●	●	●	●	●	●	●	●
→ *DL: Annual Progress Reports*				●				●				
→ *DL: Final Technical Report*												●
Task 2. Synthesis and Characterization of Nano-Composite Electrodes. (Q1-Q7)												
Subtask 2.1: Synthesis of Zirconate Electrode Compositions	━	━	━	━	━	━	━					
→ *MS: Process for synthesizing ABO_3 and $A_2B_2O_7$ nano-powder established*				▲								
Subtask 2.2: Composite Selective Electrodes	━	━	━	━	━							
→ *DL: NexTech nano-catalyst delivered to WVU for stability testing*			●									
Subtask 2.3: Electrode Characterization			━	━	━	━	━					
→ *MS: Stability of H_2 and H_2S nano-composites electrodes defined to 1200℃*						▲						
Task 3. Lost-Mold Microcasting of the Selective Electrode Structure. (Q5-Q11)												

Task/*Milestone*	Quarter after Project Initiation											
	1	2	3	4	5	6	7	8	9	10	11	12
Task 3. Lost-Mold Microcasting of the Selective Electrode Structure. (Q5-Q11)												
Subtask 3.1: Micro-Mold Fabrication												
→ *MS: Microcasting process defined*						▲						
→ *DL: Micro-molds delivered to NexTech for commercial microcasting demonstration*					●	●	●	●				
Subtask 3.2: Lost-Mold Microcasting and Sintering of Micro-Selective Electrode												
Subtask 3.3: Selective Electrode (SE) Characterization.												
Task 4. Fabrication of Micro-Sensors and Arrays (Q6-Q12)												
Subtask 4.1: Pt Interconnect and Counter-Electrode (CE) Deposition												
Subtask 4.2: Selective Electrode (SE) Deposition/Sintering												
→ *MS: Micro-sensor fabricated*								▲				
Subtask 4.3: H_2-H_2S Micro-Sensor Array Fabrication												
→ *MS: Micro-sensor array fabricated*									▲			
Task 5. Micro-Sensor and Sensor Array Testing (Q8-Q12)												
Subtask 5.1: Testing of H_2 micro-sensors												
→ *MS: Micro-sensor specification targets achieved*											▲	
→ *DL: Delivery of sensors to NexTech for testing*							●	●	●	●	●	
Subtask 5.2: Testing of H_2S micro-sensors and H_2-H_2S array												
→ *MS: Micro-sensor array specification targets achieved*												▲

Proposed Milestones

- Sensor and Sensor Array design established – **Q2**
- Process for synthesizing nanomaterials established – **Q4**
- Stability of H_2 and H_2S nano-composites electrodes defined– **Q8**
- Micro-casting process defined – **Q6**
- Micro-sensors fabricated – **Q8**
- Micro-sensor array fabricated – **Q9**
- Micro-sensor specification targets achieved – **Q11**
- Micro-sensor array specification targets achieved – **Q12**

Closure of testing labs in January at WVU due to aged ventilation. Remodeling expected to be completed in August.

Proposed Deliverables

1) **Quarterly and annual progress reports to DOE**

2) **Subtask 2.2-** industrial partner delivers nanomaterials to WVU for stability testing ***(Q3)***

3) **Subtask 3.1-** Micro-molds delivered to industrial partner for commercial microcasting demonstration ***(Q5-8)***

4) **Subtask 5.1-** Delivery of micro-sensors to industrial partner for testing ***(delivery start of each quarter Q7-Q11)***

5) **Subtask 5.2-** Delivery of arrays to industrial partner after testing- ***delayed due to testing.***

Presentations of this Work

1. "High temperature nano-derived hydrogen sensors," Christina Wildfire, Engin Ciftyurek, Katarzyna Sabolsky, Edward M. Sabolsky, European Ceramics Society (ECerS) XII conference in Stockholm, Sweden, June 19-23 2011, Nanomaterials Symposium; **INVITED PRESENTATION**

2. "Performance and Stability of High-Temperature Nano-Derived Hydrogen Sensors," Edward M. Sabolsky, Christina Wildfire, Engin Ciftyurek, Katarzyna Sabolsky, 220th Electrochemical Society Meeting, Boston, MA, Oct. 9-14, 2012; **PRESENTATION**

3. "High-Temperature Nanomaterials for Electrochemical Micro-Sensors," Edward M. Sabolsky, Christina Wildfire, Engin Ciftyurek, Energy Materials and Applications (EMA) 2012 Conference in Orlando, FL, January 18-20, 2012, S1: New Frontiers in Electronic Ceramic Structures, Advanced Electronic Material Devices and Circuit Integration; **PRESENTATION**

4. "Nano-Derived, Micro-Chemical Sensors for High-Temperature Applications," Edward M. Sabolsky, Christina Wildfire, Engin Ciftyurek, Katarzyna Sabolsky, 221st Electrochemical Society Meeting in Seattle, WA, May 6-10, 2012; **INVITED PRESENTATION**

5. "High-Temperature Nano-Derived Chemical Micro-Sensors," Edward M. Sabolsky, Christina Wildfire, Engin Ciftyurek, Katarzyna Sabolsky, 10th International Symposium on Ceramic Materials and Components for Energy and Environmental Applications (CMCEE) 2012 in Dresden, Germany, May 20-23, 2012; **PRESENTATION**

Presentations of this Work

6) "Nano-Derived, Micro-Chemical Sensors for High-Temperature Applications," E. M. Sabolsky, C. Wildfire, E. Ciftyurek, K. Sabolsky, 221st Electrochemical Society Meeting in Seattle, WA, May 6-10, 2012; **INVITED PRESENTATION**.

7) "High-Temperature Compatible Electrodes with Various Microstructural Architectures," E. Çiftyürek, K. Sabolsky, and E.M. Sabolsky, 221st Electrochemical Society Meeting in Seattle, WA, May 6-10, 2012; **PRESENTATION**.

8) "Degradation of Platinum Thin Films Electrodes for High-Temperature MEMS Applications", E. Çiftyürek, K. Sabolsky and E. M. Sabolsky, WV Academia Science 2012 Charleston, West Virginia, USA. **PRESENTATION**.

9) "High-Temperature Nano-Derived Sensors for Online Monitoring of SO_2 Emissions", E. Çiftyürek, C. Wildfire, and E. M. Sabolsky, Materials Science & Technology 2012, Pittsburgh, Pennsylvania, USA. **PRESENTATION**.

10) "High-Temperature Nano-derived Sensor Development for Detection of H_2S and SO_2 Emissions." E. Çiftyürek, K. Sabolsky, and E. M. Sabolsky, Materials Science & Technology 2013, Quebec, Canada. **TO BE PRESENTED**.

Publications of this Work

1) E. Çiftyürek, K. Sabolsky, and E. M. Sabolsky, “Platinum Thin Film Electrodes for High-Temperature Chemical Sensor Applications.”, Published in Sensors and Actuators B: Chemical, ISSN 0925-4005, 10.1016/j.snb.2013.02.058.

2) E.M. Sabolsky, C. Wildfire, E. Çiftyürek, and K. Sabolsky, “Nano-Derived, Micro-Chemical Sensors for High-Temperature Applications”, Published in ECS Transactions, 45 (3) 495-506 (2012).

3) C. Y. Wildfire, E. Çiftyürek, K. Sabolsky, and E. M. Sabolsky, “Investigation of Doped-Gadolinium Zirconate Nanomaterials for High-Temperature Hydrogen Sensor Application”, Accepted to Sensors and Actuators B: Chemical, March 2013.

4) C. Y.Wildfire, E. Çiftyürek, K. Sabolsky, and E. M. Sabolsky, “Development and Testing of High Temperature Hydrogen Micro-Sensors.”, Submitted to Sensor Letters, in June 2013.

5) E. Çiftyürek, K. Sabolsky, and E. M. Sabolsky “Functionally Gradient Zr-Pt Composite Thin Films for Stable High-Temperature Electrodes”, To be submitted to Journal of Microelectromechanical systems, in June 2013.

6) C. Wildfire, E. Çiftyürek, K. Sabolsky, and E. M. Sabolsky, “High Temperature Semiconducting Hydrogen Sensors Based on Lanthanum Stannate Materials”, To be submitted to Sensors and Actuators B: Chemical, in August 2013.

3 more publications currently being prepared for H_2S and SO_2 sensing.

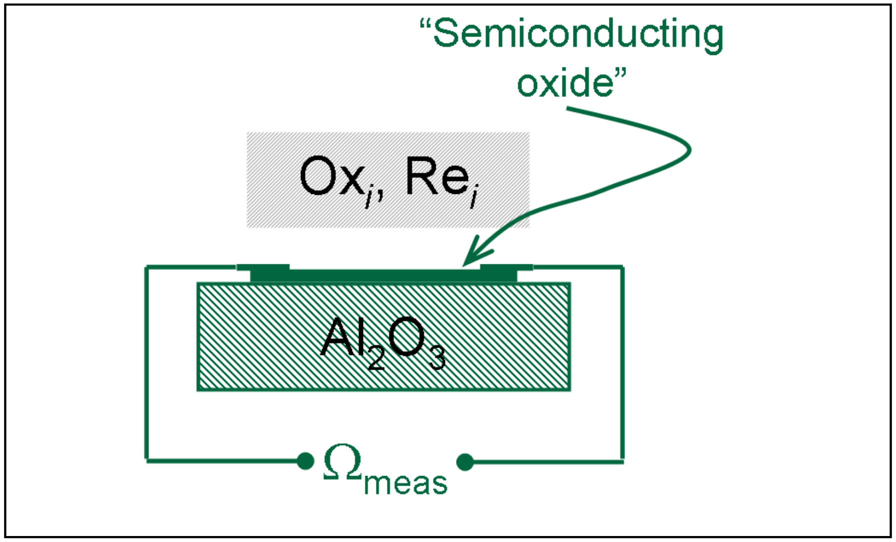
Background

Background– Sensor Requirements

Regardless of Sensor Type:

a) Chemically stable
b) Reversible
c) Fast
d) Highly sensitive
e) Durable
f) Simple operation
g) Small size (portability, reduction in cost, rapid response)

Background-High-Temp Solid State Sensors

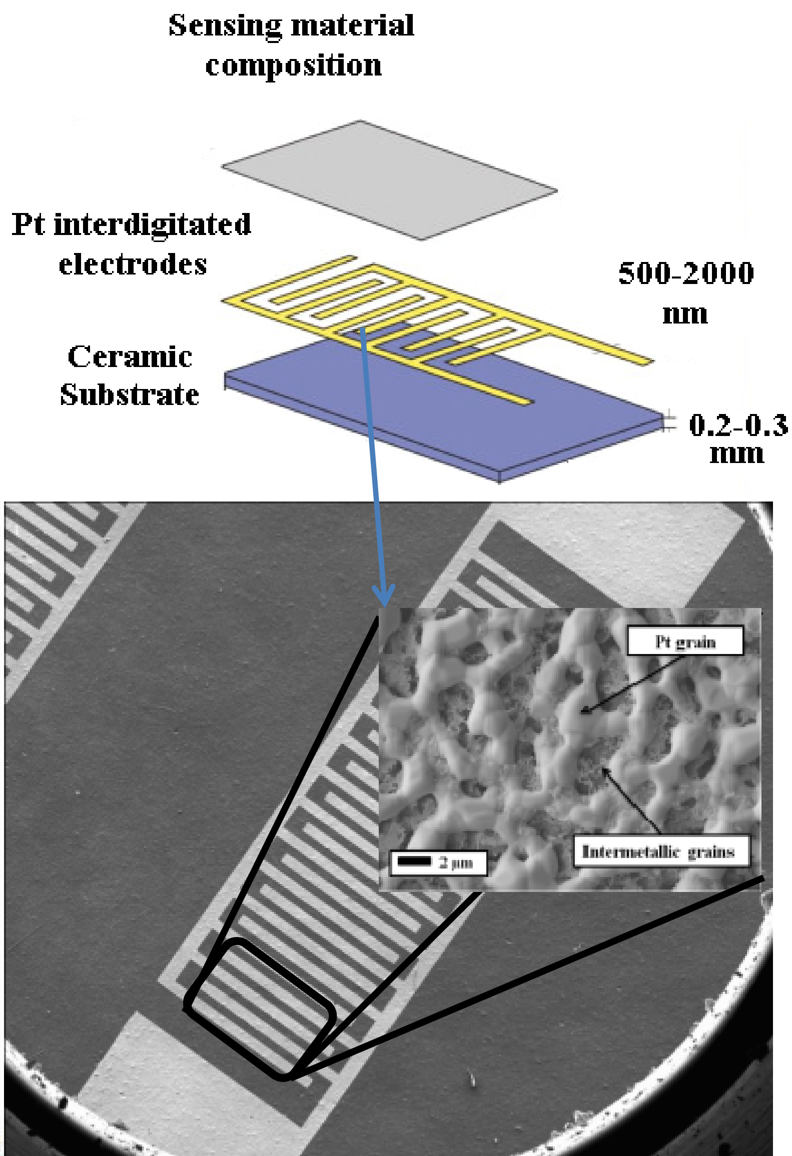


*T. Armstrong presentation, 20th Annual Fossil Energy Conference (2006).

Chemiresistive- (Resistive-type)

- Absorption / interaction with surface alters resistivity.
- Typical operating T ≤ ~600°C (band gap and stability limited).
- Simple design allows for micro-chemical sensor arrays.
- Selectivity problem due to sensitivity mechanism.

Background- Chemiresistive Sensors



1. Adsorption of chemical species on metal-oxide surface causes redox reaction (change in current carriers).

2. Affects depletion area thickness resulting in a change in the resistance.

3. Metal-oxide semiconductor's (MOS) shape, size, composition, and surface characteristics controls the selectivity and sensitivity.

4. Nanomaterials provide ultra-high surface area and will enhance interaction with chemical species.

Presented in Previous Reviews (2010-2012)

1) Hydrothermal processes for synthesis of ionic and mixed-conducting *zirconate, stannate, and titanate pyrochlores* (3-10 nm).

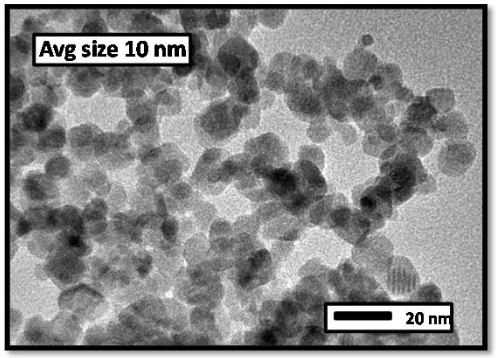
2) Resistor-type, macro-sensors of composite nanomaterials sense 500-4000 ppm H_2 (in air) at 600-1000°C.

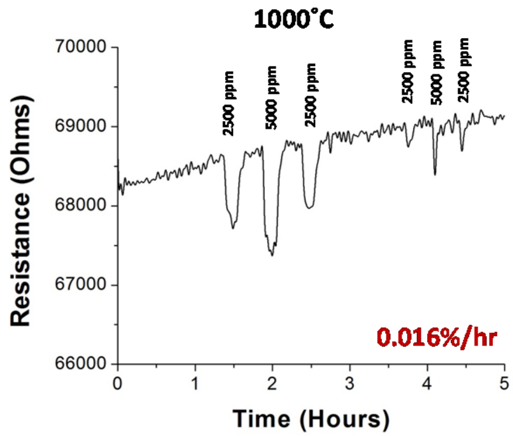
3) Nano-zirconate and SnO_2/zirconate nano-composites displayed enhanced stability.
   - From 0.792%/hr to 0.016%/hr (0.014 sensitivity for 500 ppm at 1000°C)

4) Initiated work on Pt-based micro-IDEs that are stable to 1200°C.

5) Initiated development of micro-casting and Dip Pen Nanolithography (DPN) processes for fabricating micro-sensor arrays.

$Gd_{1.8}Y_{0.2}Zr_2O_7$





Challenges Current Work Addresses:

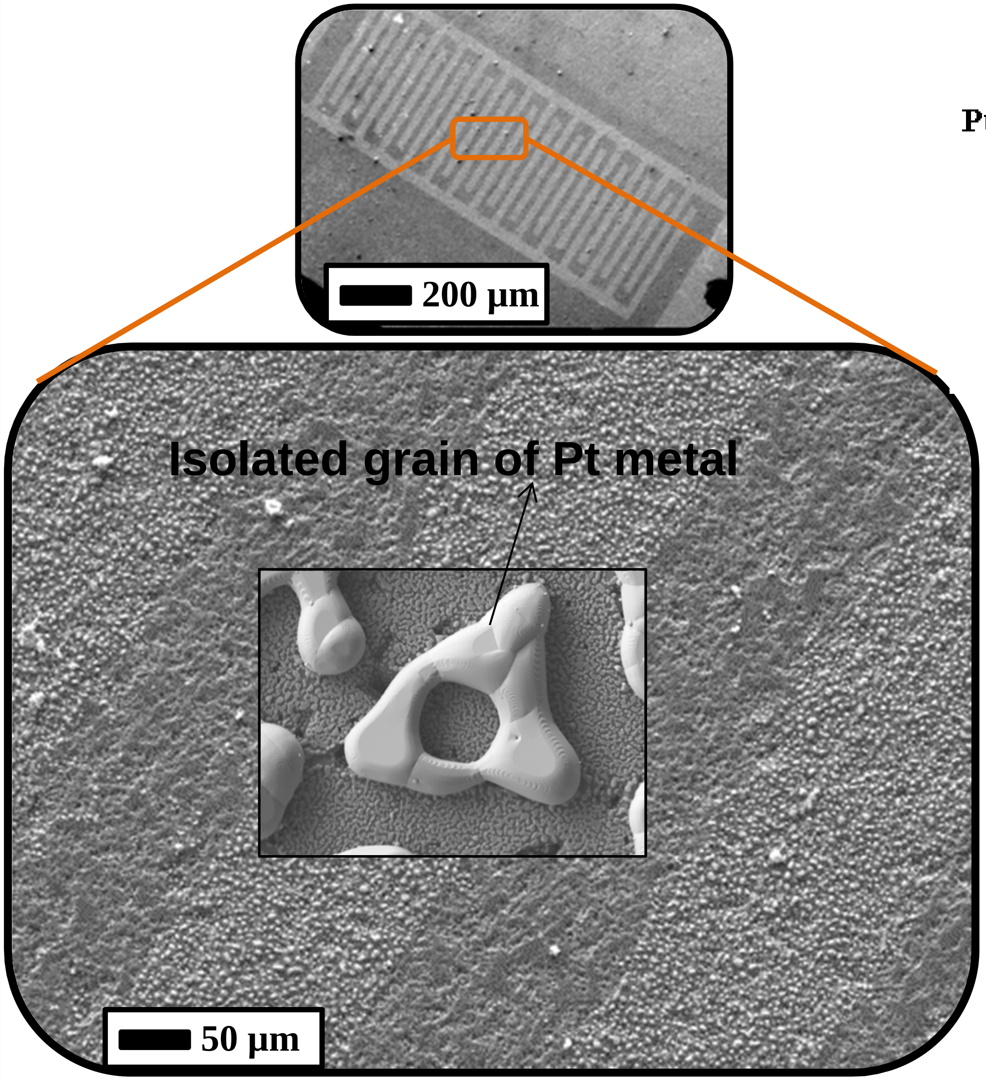
1) *High-temperature stable micro-electrodes.*
   a. *Develop stable, DC sputtered micro-electrodes for specific sensing mechanism.*
   b. *Method for depositing and patterning potential complex microstructures and refractory metals.*

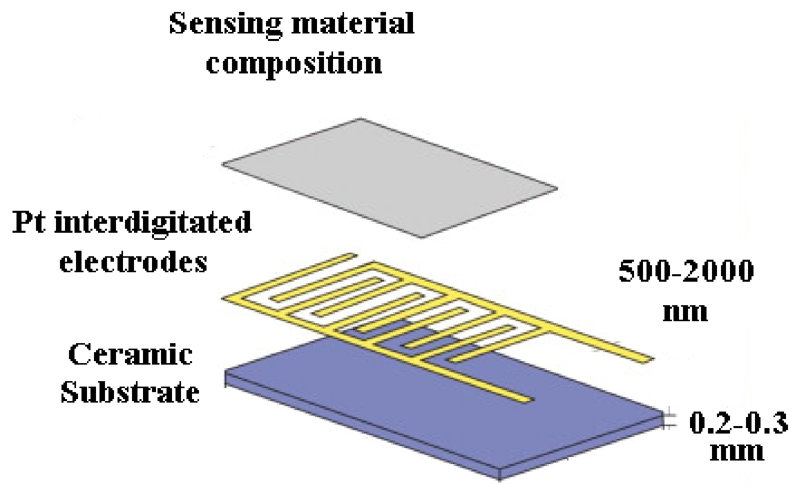
2) *High-temperature, stable, nanomaterials for sensing (H_2S, SO_2).*
   a. *Selective to species of interest.*
   b. *React with other gas species in environment.*
   c. *Morphological stability at high temperature due to sintering and coarsening mechanisms (Driving Force $\approx 1/D^n$).*

3) *Method to micro-pattern particulate nanomaterials.*

High-Temperature Stable Electrodes (Inter-Digitized Electrodes, IDEs)

IDE Limitations



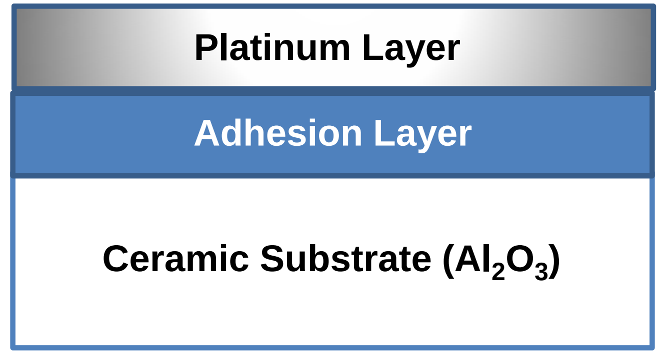


Current sensor technology is limited to operate at low temperature due to

- Sensing material composition
- Processing
- **Incapable electrodes**

Breaks Apart !!!

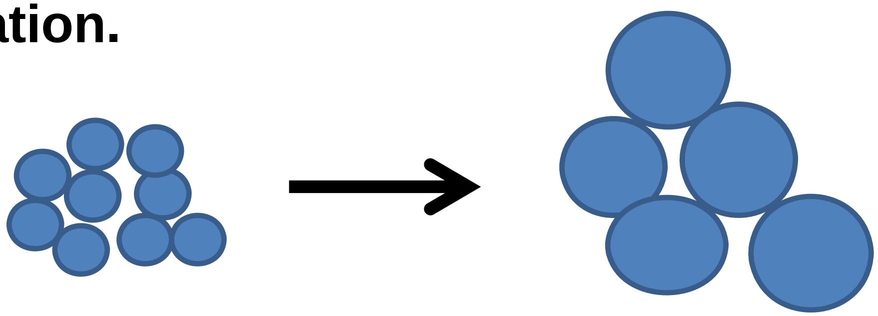
Strategy to Stabilize IDEs



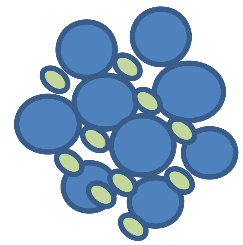
•Using intermediate layer i.e. adhesion layer. → **Surface tension**

Combat

•Using second phase precipitation. → **Coarsening**



Coarsening/Sintering



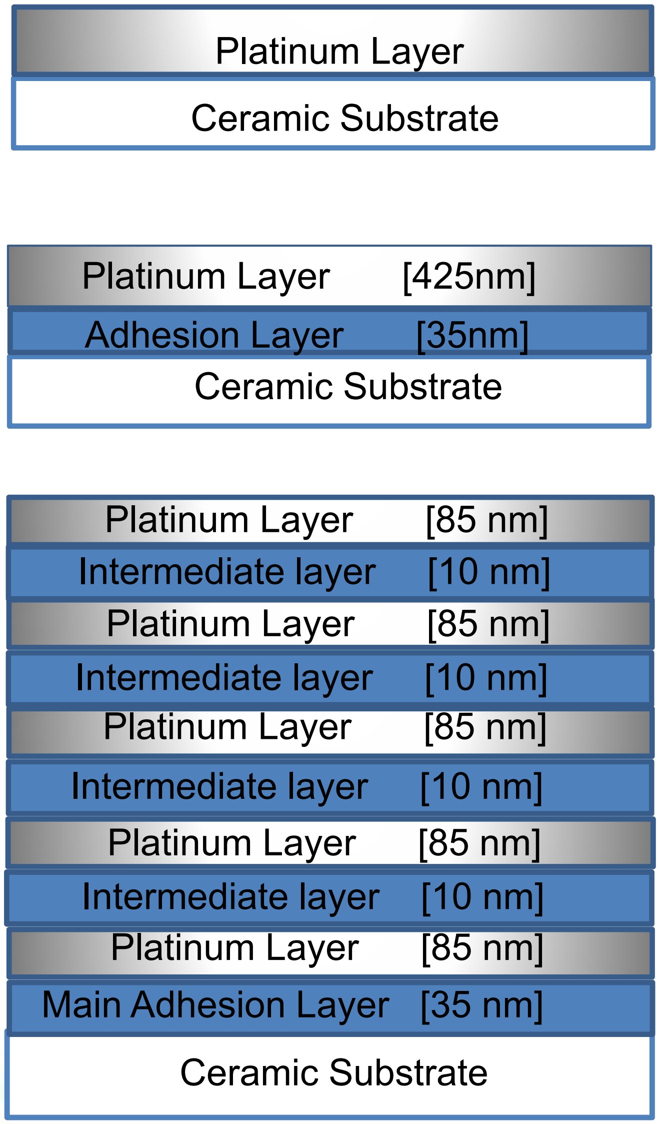
Grain Boundary Pinning Hinders Coarsening.

: Pt grain

: Second phase grain

Strategy to Stabilize IDEs

Schematic Representations

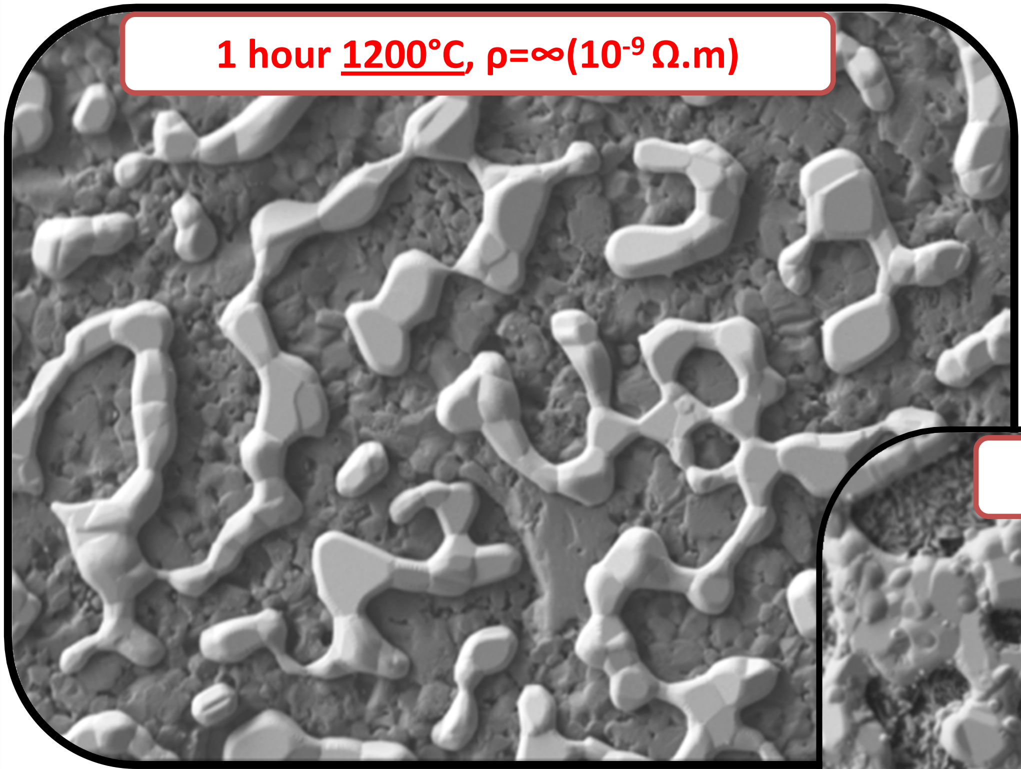


Pure Pt

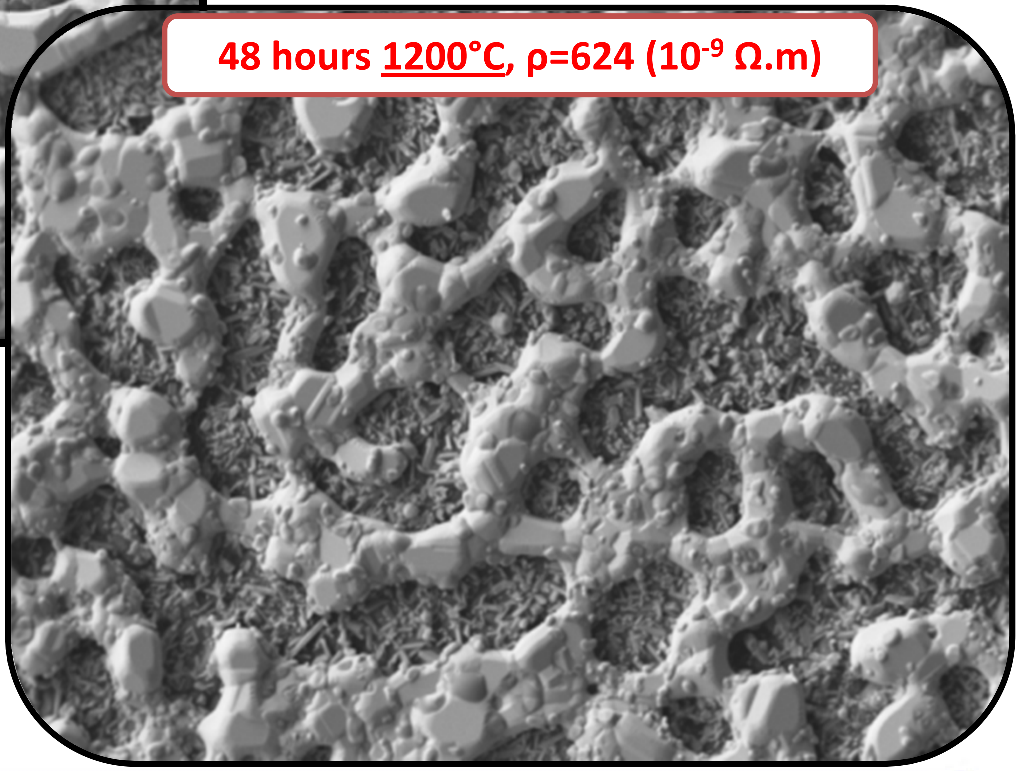
BILAYER COATING ARCHITECTURES	
Titanium	Ti+Pt
Tantalum	Ta+Pt
Zirconium	Zr+Pt
Hafnium	Hf+Pt

MULTILAYER COATING ARCHITECTURES	
Zirconium	L-Zr+Pt
Hafnium	Hf+L-Zr+Pt

Summary: IDE Stabilization



Ti or Ta adhesion layer + Pt layer



Hf adhesion layer + Zr+Pt composite

Summary: High-Temp IDE Patterning

•Simple Lift-off process for electrode manufacturing.

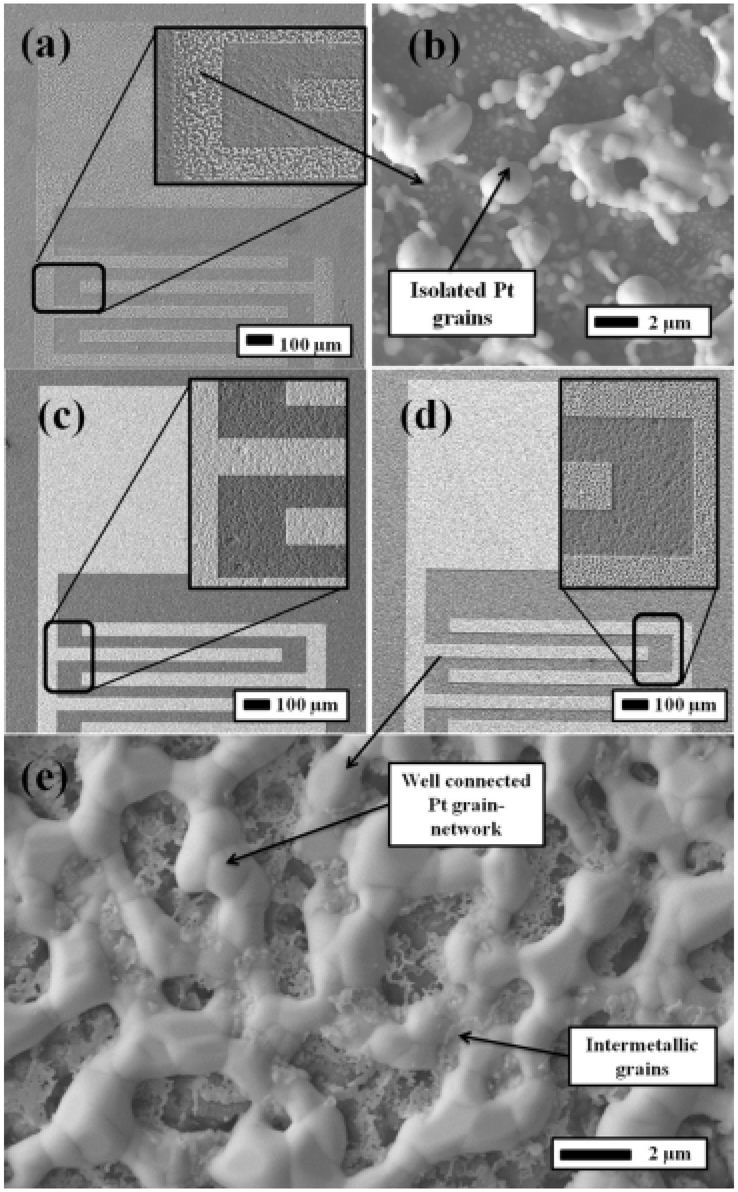
(a) Zr + Pt bilayer electrode after annealing at 1200C 15 h

(b) Close look After annealing at 1200°C for 15 h.

(c) As-deposited Hf/L-Zr + Pt multilayer electrode, inset shows the edges closely.

(d) High magnification SEM image shows the edge of 15 h 1200°C annealed electrode.

(e) High magnification SEM image shows the edge of Hf/L-Zr + Pt electrode after annealing at 1200°C for 15 h.



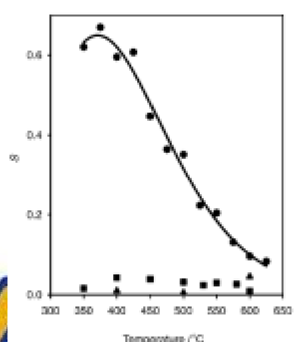
Nano-Derived Sensing Materials And Testing

Background-Sensing Materials for Sulfur Compounds

Chemiresistive and Potentiometric, and very limited number SAW devices.

Chemiresistive Type
WO_3 thick/thin film with different deposition methods
WO_3 with different noble metal loadings (Pt, Pd, Au, Ag)
TiO_2, V_2O_5 modified **WO_3** and loaded with Au
NASICON-V_2O_5/WO_3/TiO_2 and/or decorated with noble metals
$Cr_{2-x}Ti_xO_3$ (insufficient sensing at temperature range 100-350°C).
Ferrites, 0-10% even at temperatures between 100-400°C

Potentiometric Type
Na_2SO_4–$BaSO_4$–Ag_2SO_4
YSZ-LiSO-MgO
Li_2SO_4–$BaSO_4$
$(Al_{0.2}Zr_{0.8})_{10/19}Nb(PO_4)_3$
Li_2SO_4–doped $La_2O_2SO_4$
NASICON, ß-alumina and YSZ
K_2SO_4 Li_2SO_4–Ag_2SO_4



V-doped TiO_2, 1000 ppm SO_2

Morris *et al.*, J.Mat. Che, 2001

- Commercial product able to work up to 50°C.
- Not able to work at temperatures higher than 500°C
- Simple structure, design and packaging, cheap.

Background-Sensing Materials for Sulfur Compounds

General proposed reactions that occur during sensor operation.

H_2S

$$H_2S_{(ads)} + 3O^{2-}_{(s)} \rightarrow SO_{2(g)} + H_2O + 6e^-$$

$$H_2S_{(ads)} + 3O^{2-}_{(s)} \rightarrow 2SO_{2(g)} + H_2O + 3e^-$$

$$H_2S_{(ads)} + 3O^{2-}_{(s)} \rightarrow SO_{2(g)} + H_2O + 6e^-$$

$$H_2 + O^-_{(ads)} \rightarrow H_2O + e^-$$

$$H_2S_{(ads)} + O^-_{(ads)} \rightarrow H_2O + SO + e^-$$

SO_2

$$SO_2 + O_{ads} \rightarrow SO_3 + V_O^X$$

$$SO_2 + O_{lattice} \rightarrow SO_3 + V_O^X$$

$$V_O^X \rightarrow V_O^{\cdot\cdot} + 2e^-$$

$$2SO_{2(gas)} + O_{2(gas)} \rightarrow 2SO_{3(gas)}$$

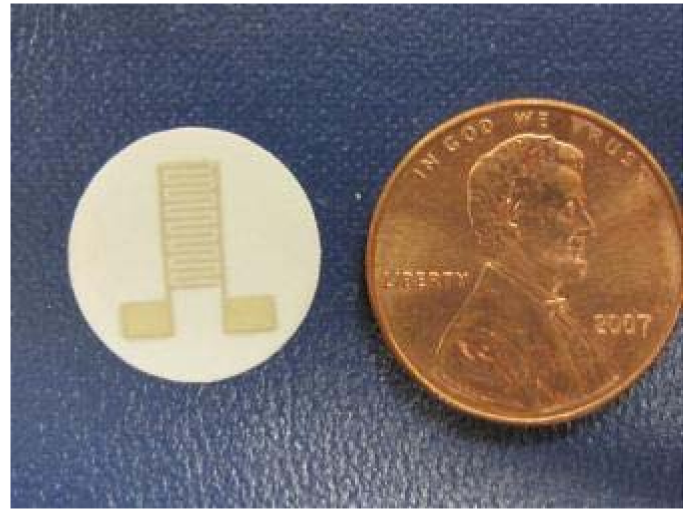
$$SO_3 + e^- \leftrightarrow SO^-_{3(ads)}$$

S. K. Pandey *et. al.*, Trends in Analytical Chemistry, Vol. 32, 2012

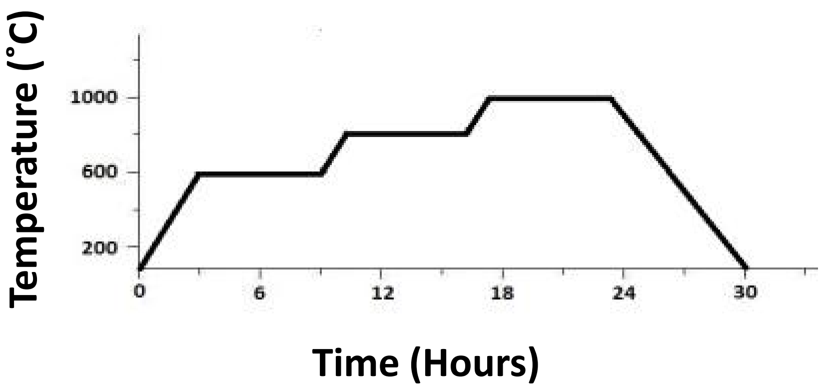
Testing Protocol

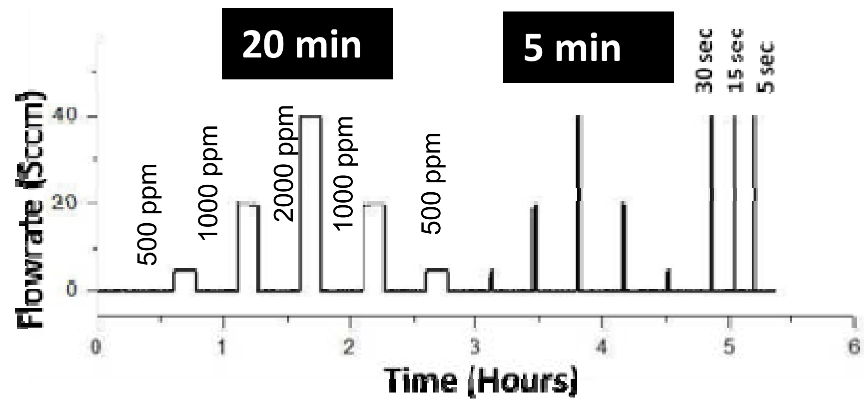
Macro Platform Properties and Testing Procedure

- Polished alumina substrates.
- Pt-IDEs screen-printed and annealed at 1200˚C.
- Sensing material printed onto electrodes and sintered at 1200˚C (~100 µm thick).
- Three different temperature regimes (600, 800, 1000°C)
- Three different O_2 partial pressures (1, 5 and 20 %)
- After each exposure to CO, H_2, SO_2 and H_2S , 30 minutes N_2 atmosphere relaxation.



Screen-printed Macro Electrode
(250 µm finger spacing)





$$Sensitivty = S = \frac{R_{gas} - R_{base}}{R_{base}}$$

Evaluation Sensing Materials for SO_2

•Tungstates and molybdates , wide band gap semiconductors (4-5 eV) and double-prevoskites

•Microstructural, chemical and morphological stability at high temperatures.

•WO_3

•WO_3 nano

•MoO_3

•MoO_3 nano

•$MgMoO_4$

•$NiMoO_4$

•$NiWO_4$

•Sr_2MgWO_6 (SMW)

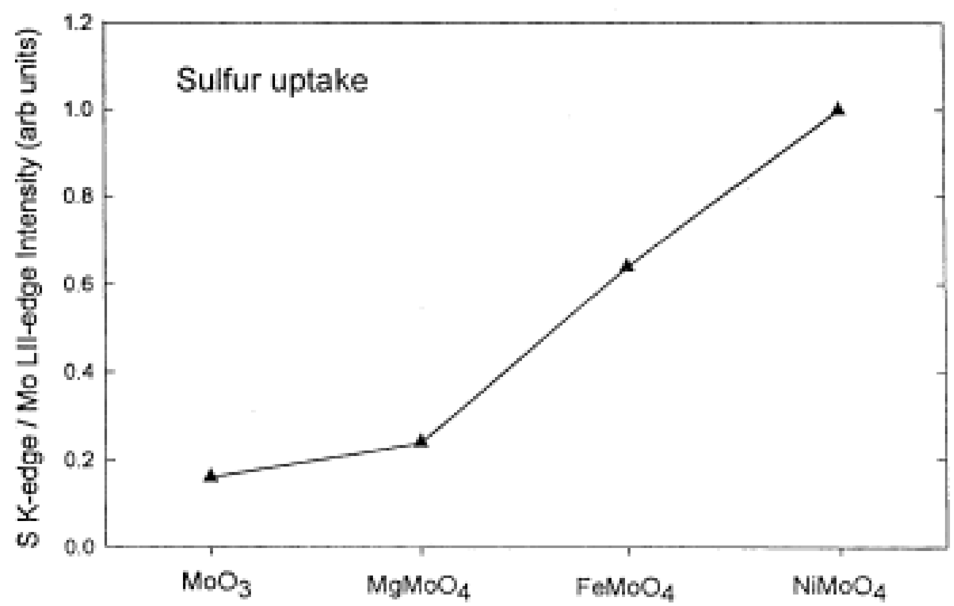
•Sr_2MgMoO_6 (SMM)

•$SrMoO_4$

•$SrMoO_4$ nano

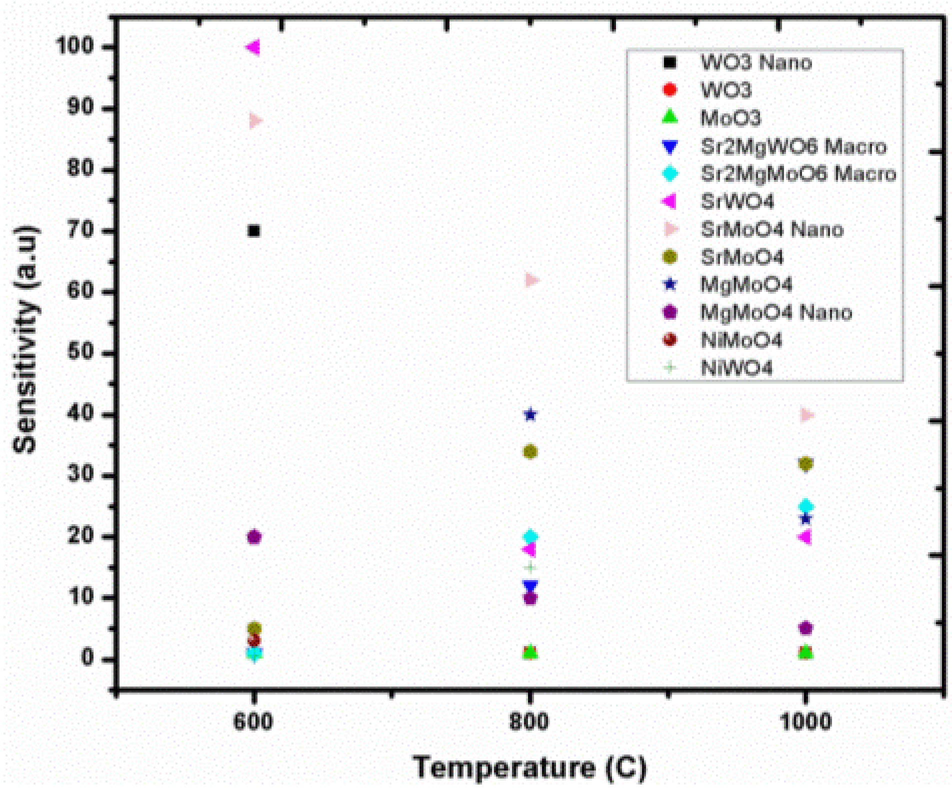
•$SrWO_4$

• Candidate compositions were tested in macro scale due to their sulfur uptake capabilities and suitable ones synthesized in nano-scale for further sensor tests.



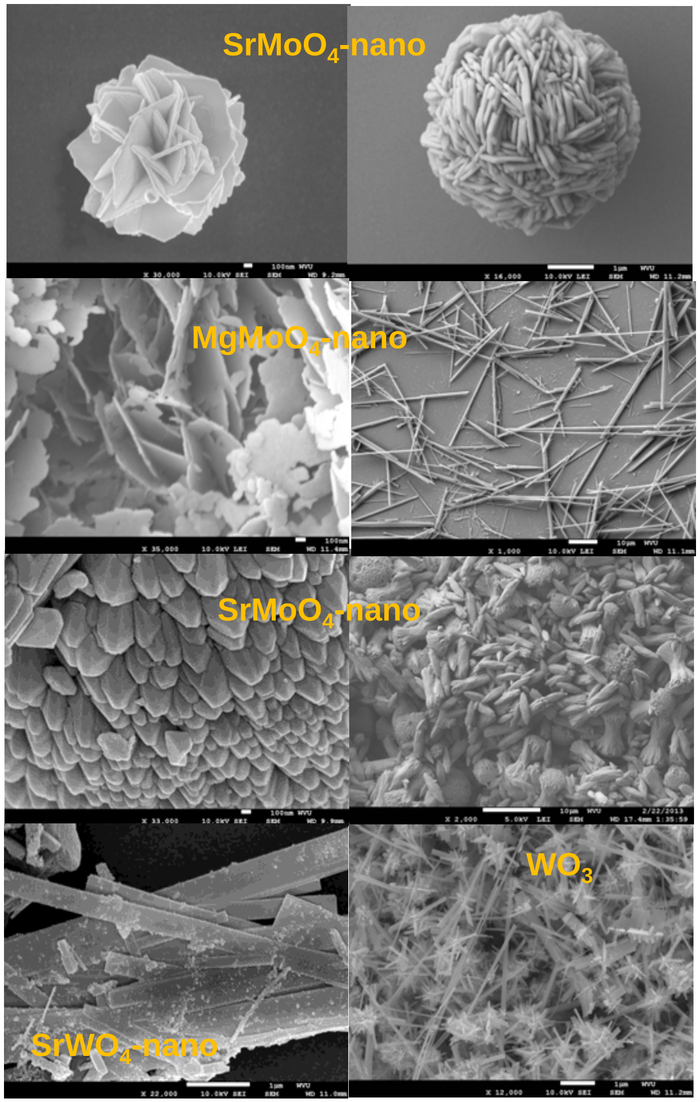
J. A. Rodriguez, Catalysis Today, 2003

Evaluation Sensing Materials for SO_2



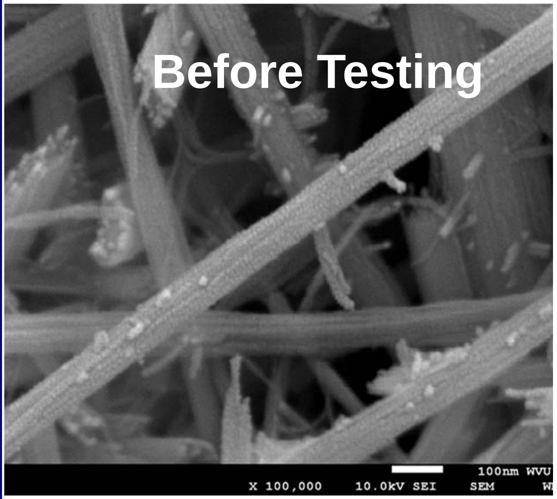
•2000 ppm SO_2 at 600, 800 and 1000 °C with 1% O_2.

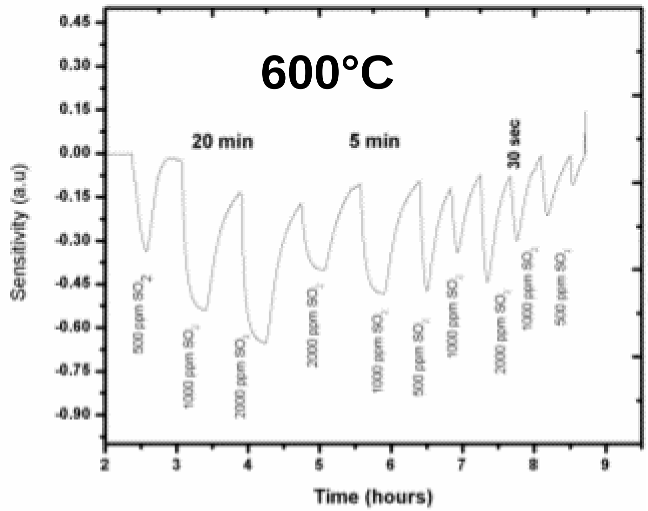
•A few of the compositions will be discussed in details

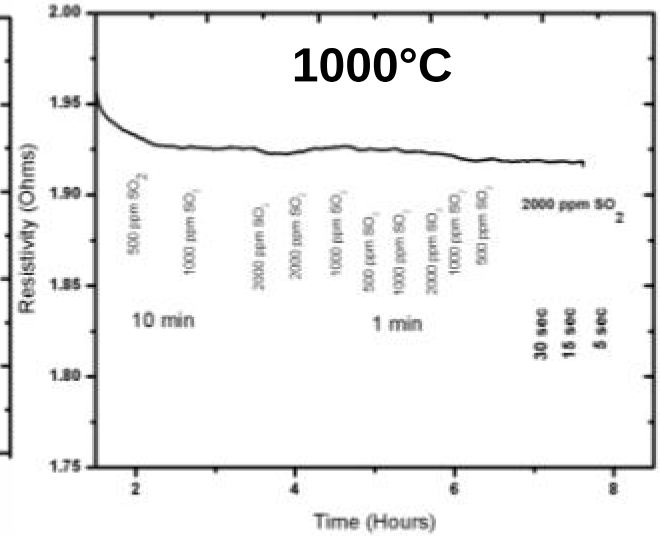


Evaluation Sensing Materials for SO_2

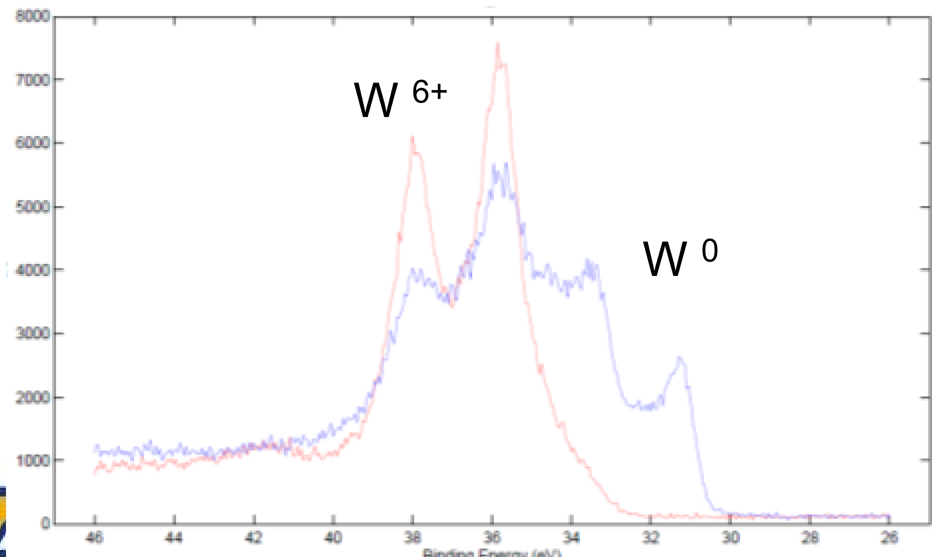
Why WO_3 is not capable of high temperature operation ?



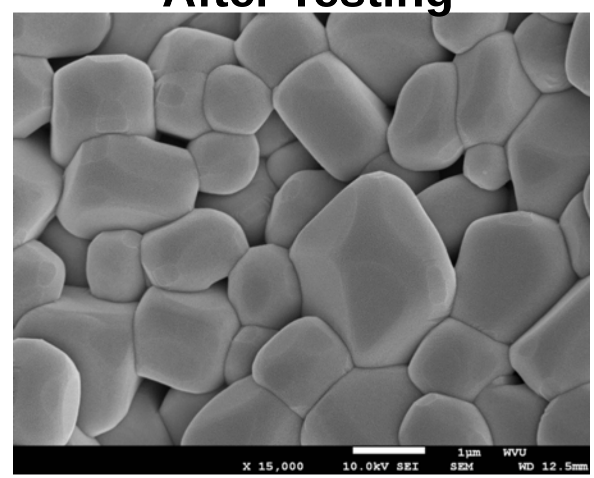




- 5-100 nm **nano-rods**
- W^{+6} are 35.67 and 37.85 and W^{+5} 34.46and 36.84 eV, color is light blue.
- 14.02% W^{+5} and 85.98% W^{+6} no other chemical state was detected.

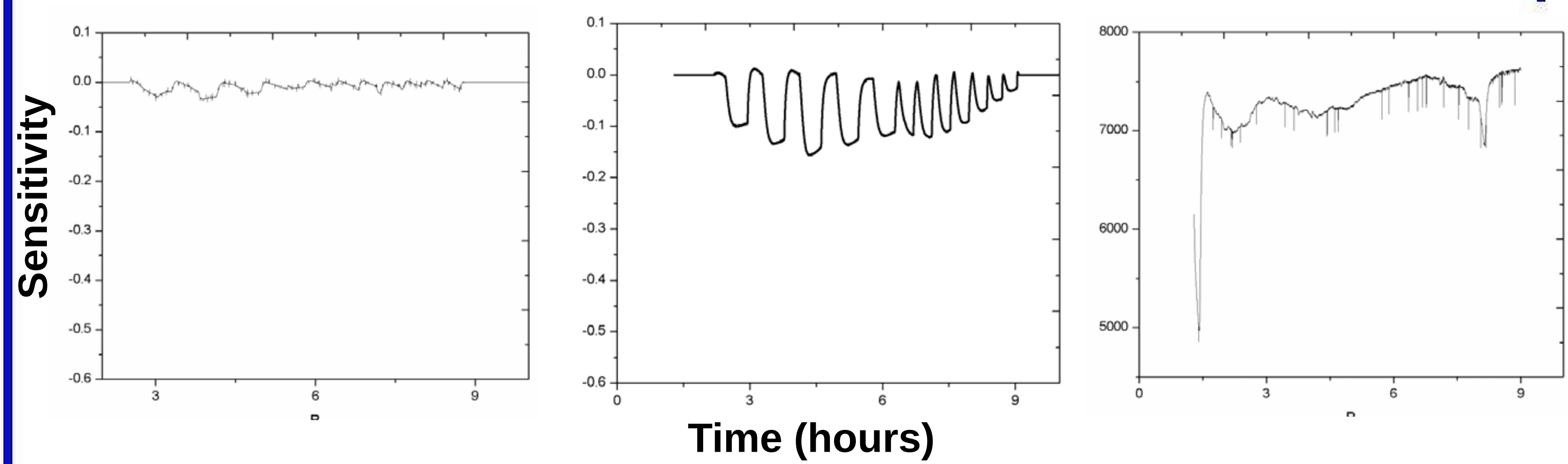


After Testing

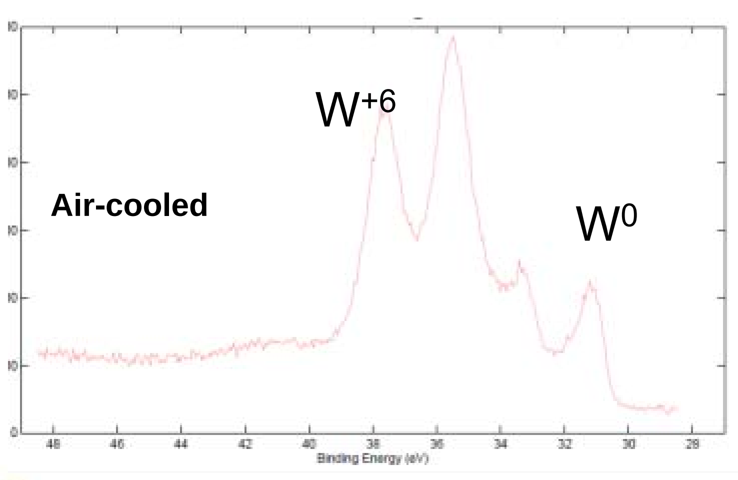


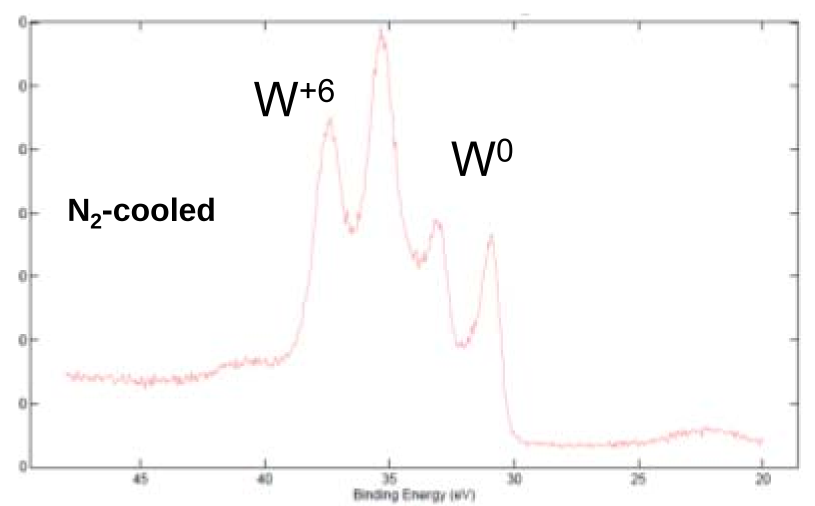
- Both macro and nano WO_3 showed similar **reduction to metallic state (W^0).**
  - Red : Air cooled
  - Blue : N_2 cooled

Evaluation Sensing Materials for SO_2



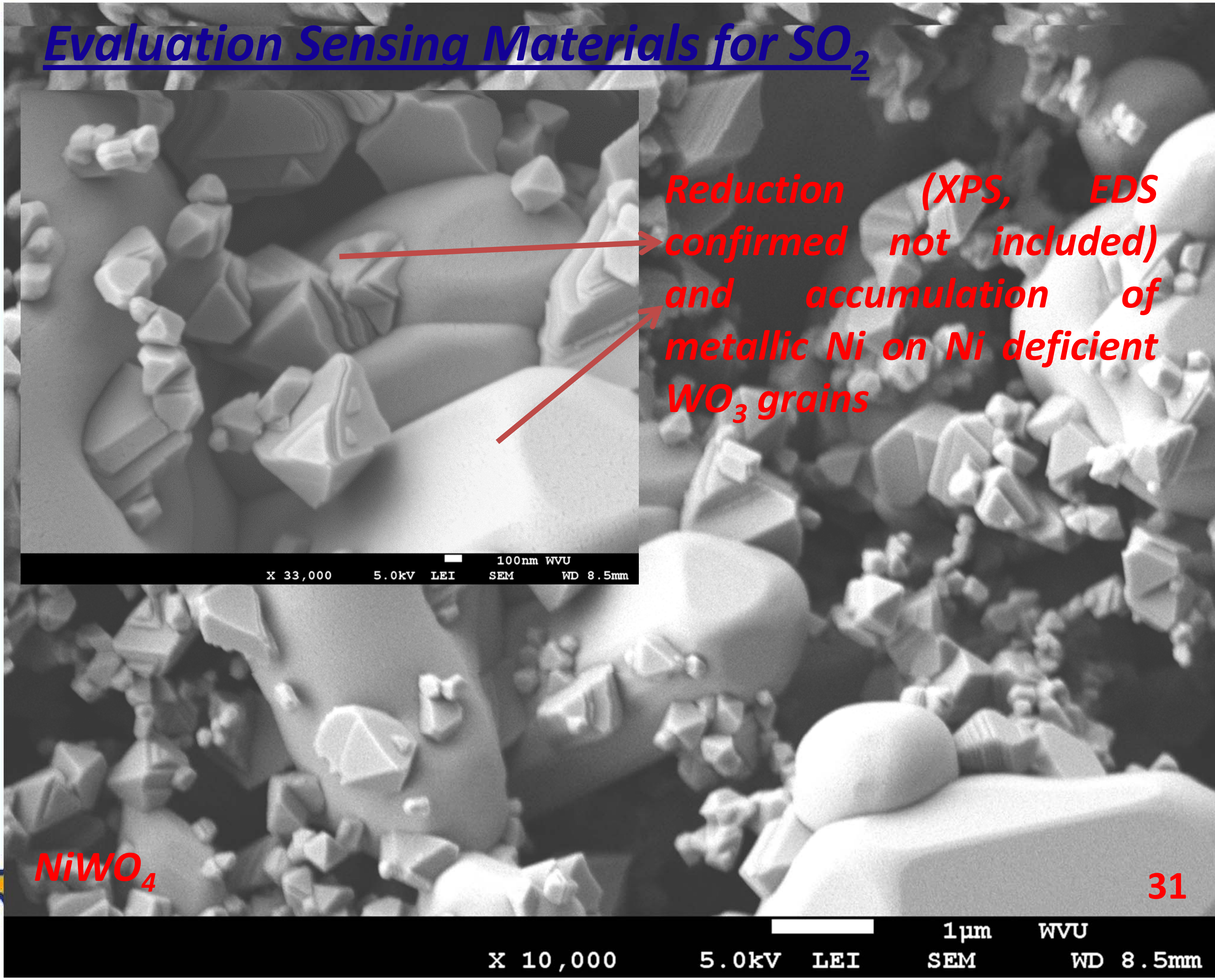
600°C 1%O_2 tested for SO_2 | 800°C 1%O_2 tested for $SO_{2,}$ | 1000°C 1%O_2 tested for SO_2





$NiWO_4$, similar reduction occurs at 1000°C

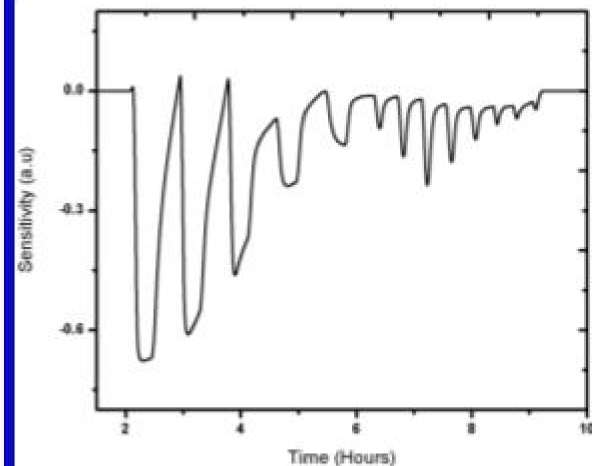
Evaluation Sensing Materials for SO_2



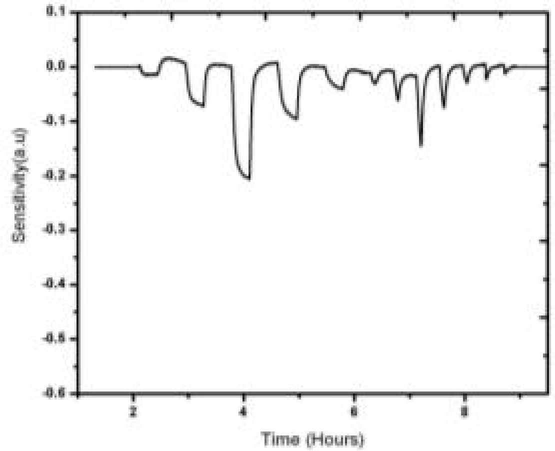
Reduction (XPS, EDS confirmed not included) and accumulation of metallic Ni on Ni deficient WO_3 grains

$NiWO_4$

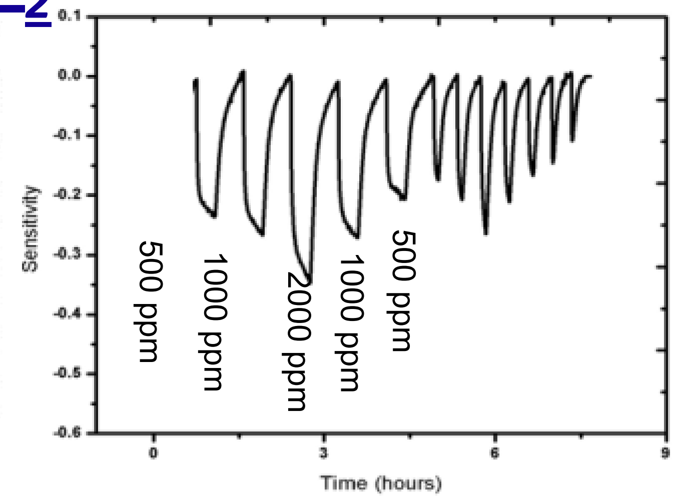
Evaluation Sensing Materials for SO_2



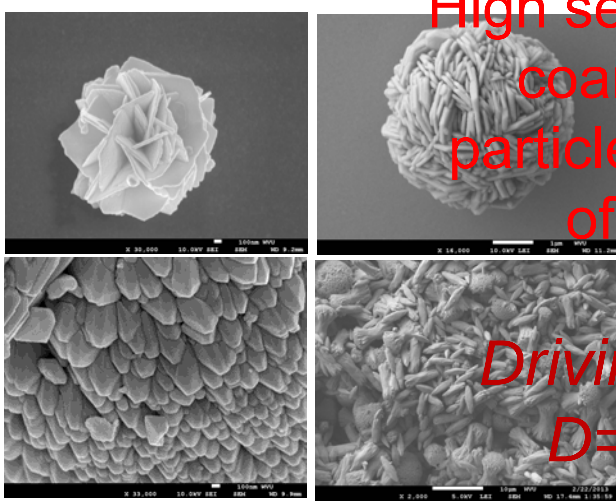
600°C 1%O_2 tested for SO_2,



800°C 1%O_2 tested for SO_2,



1000°C 1%O_2 tested for SO_2,



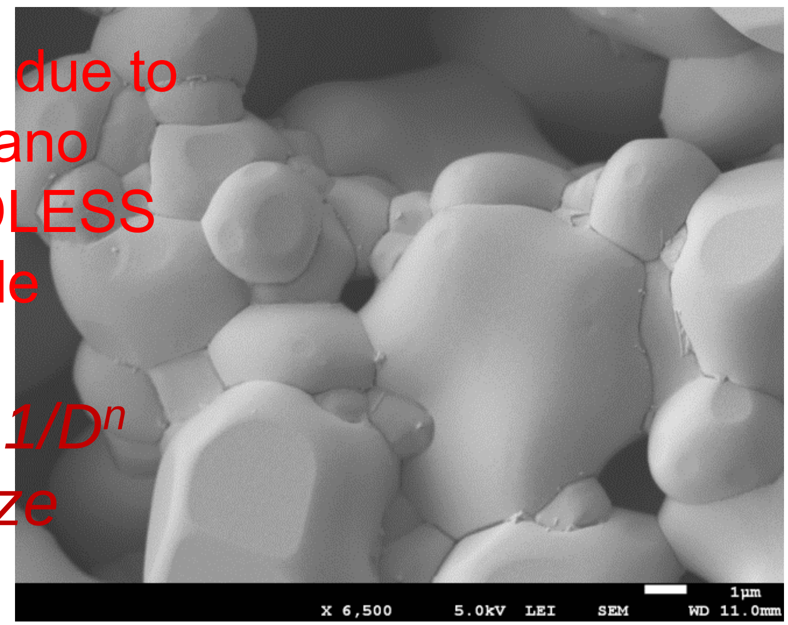
SrMoO$_4$ powders with different morphologies, confirmed by XRD not included.

High sensitivity lost due to coarsening of nano particles REGARDLESS of nano particle morphology

Driving Force ≈ $1/D^n$

D= particle size

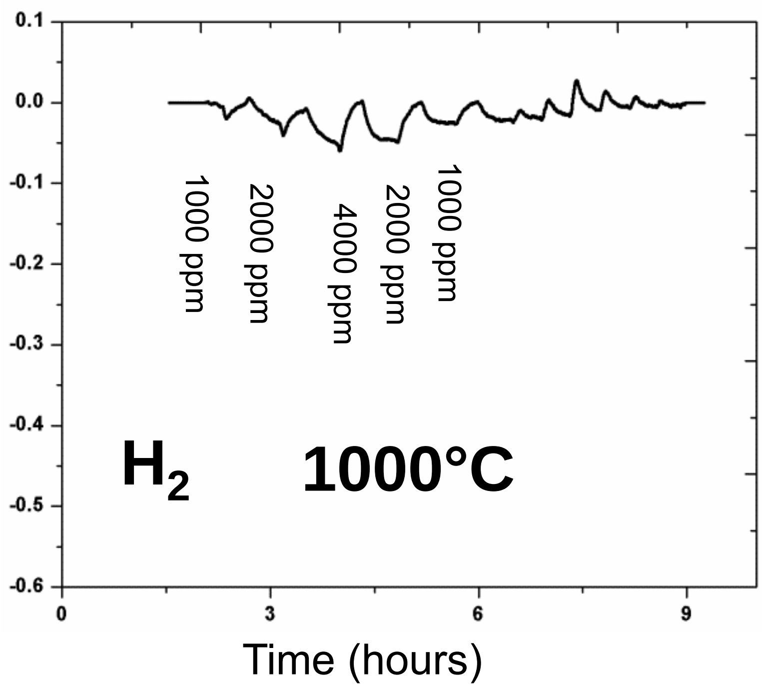
n=1,2,



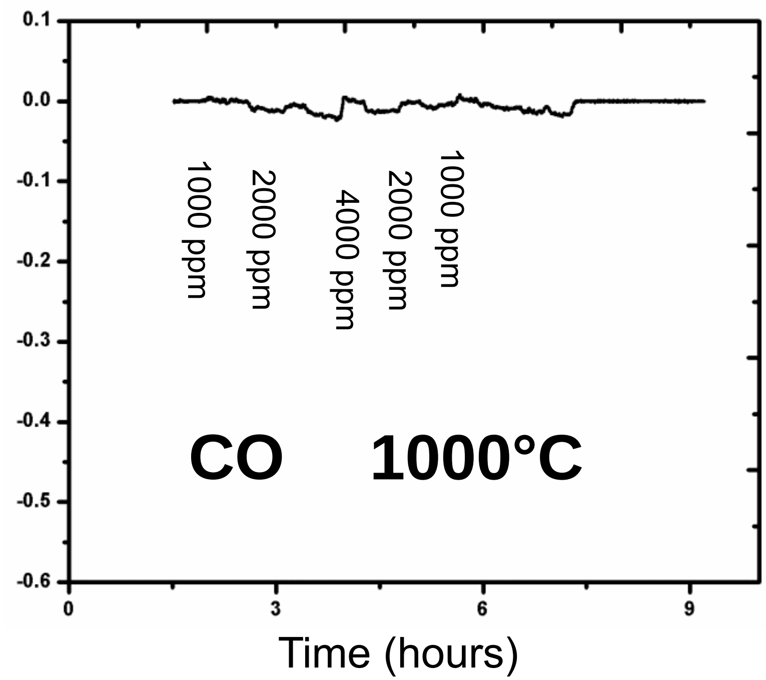
Nano-$SrMoO_4$

Evaluation Sensing Materials for SO_2-Cross-Sensitivity Tests

H_2 concentration (4000 ppm) level is always two times than that of SO_2 (2000 ppm)



CO concentration (4000 ppm) level is two times than that of SO_2 (2000 ppm)



•CROSS-SENSITIVITY ! TESTS SHOWED APPLICABILITY of nano-$SrMoO_4$ further !

Summary: Evaluation Sensing Materials for SO_2

$SrMoO_4$ and $SrWO_4$ showed

- **Highest sensitivities at high temperature**
- **Lowest cross-sensitivities against CO and H_2**
- **Long term stability (100 h)**

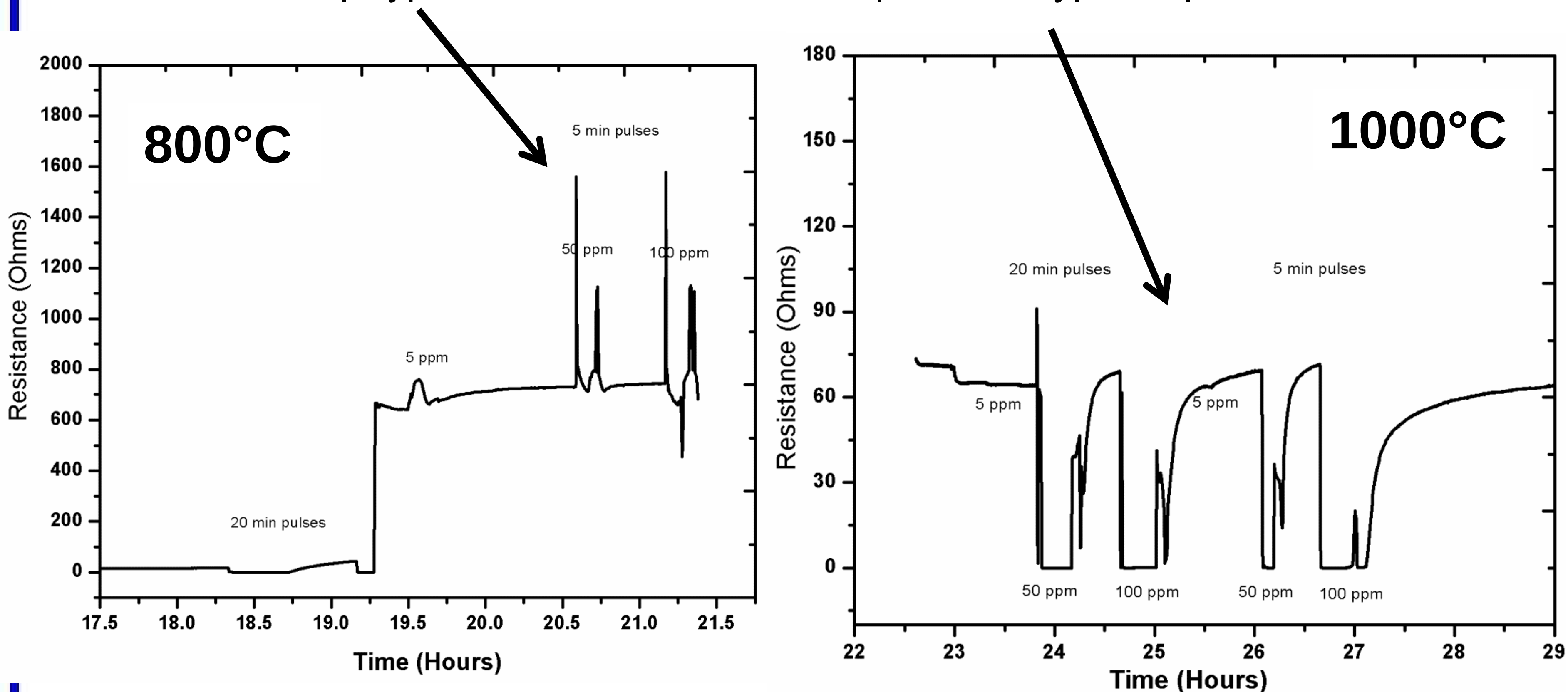
Evaluation Sensing Materials for H_2S

$SrMoO_4$, $SrWO_4$, $NiWO_4$

•The tests were conducted with 5, 50 and 100 ppm H_2S balanced with H_2 and 1% O_2 Background.

Evaluation Sensing Materials for H_2S

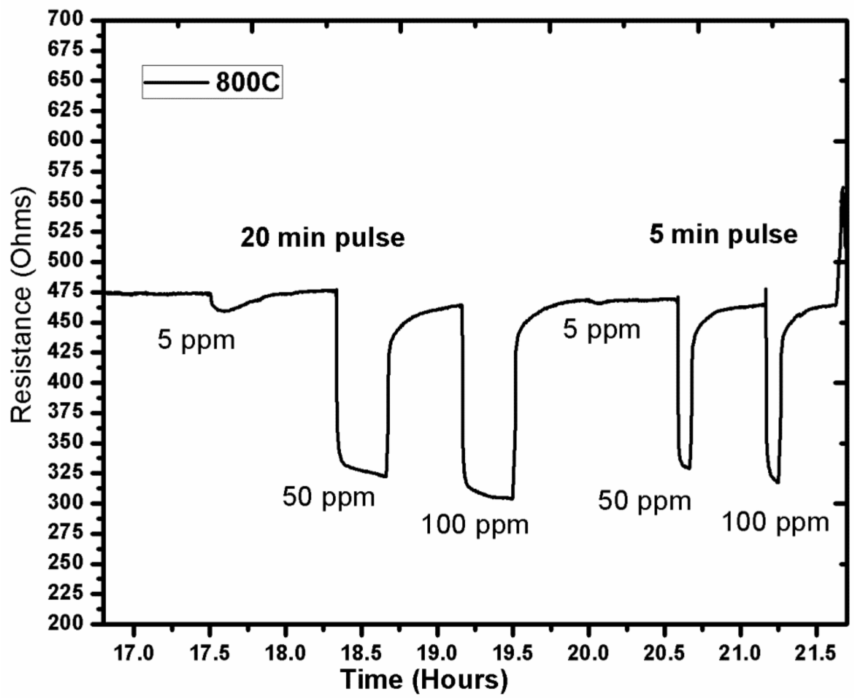
•800°C p-type, however 1000°C as expected n-type response.

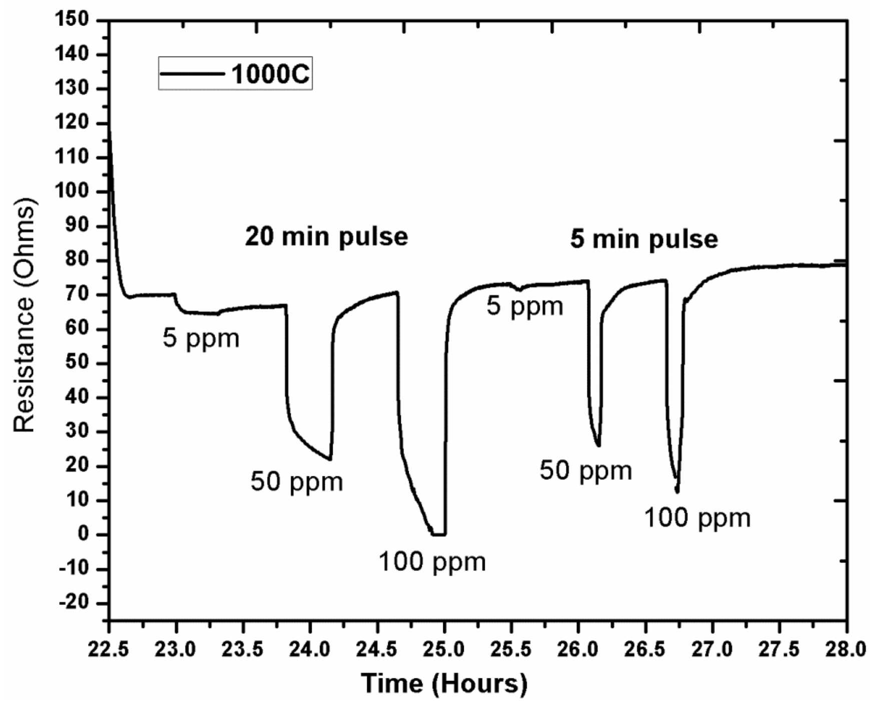


•**Not able to distinguish, 5, 50, and 100 ppm H_2S at 800 and 1000°C**
•**Long term stability (48 h testing) test showed similar reduction behavior.**

$NiWO_4$

Evaluation Sensing Materials for H_2S

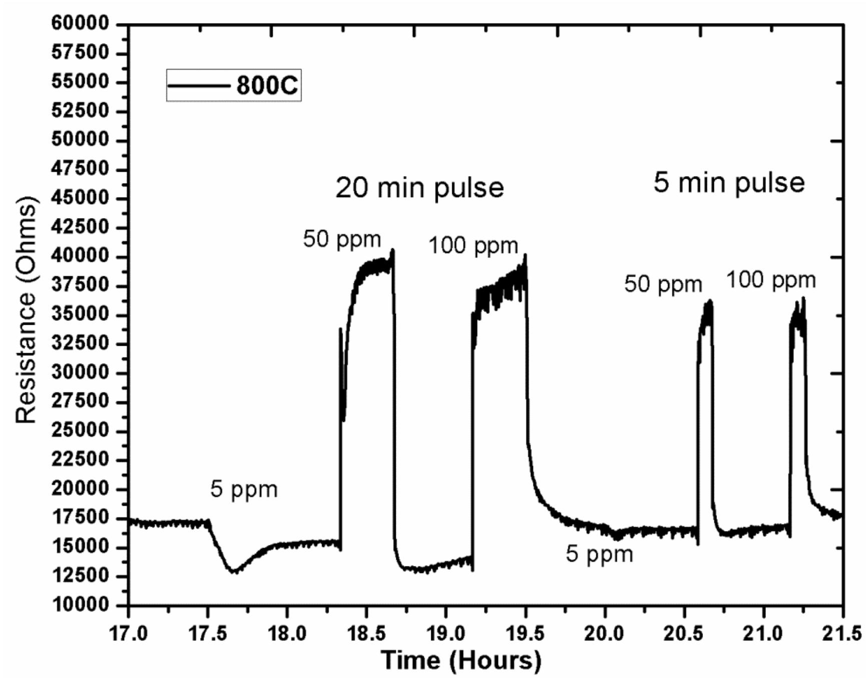


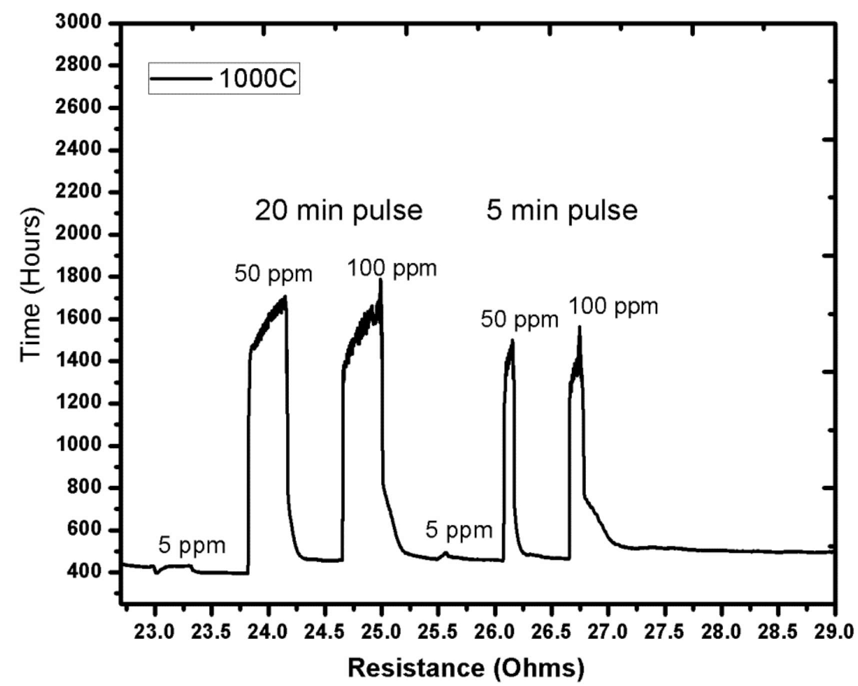


- Sensitive towards 5, 50, and 100 ppm H_2S at 800 and 1000°C
- N-type behavior
- Long term stability (48 h testing) test showed similar sensing behavior.

Nano- $SrMoO_4$

Evaluation Sensing Materials for H_2S

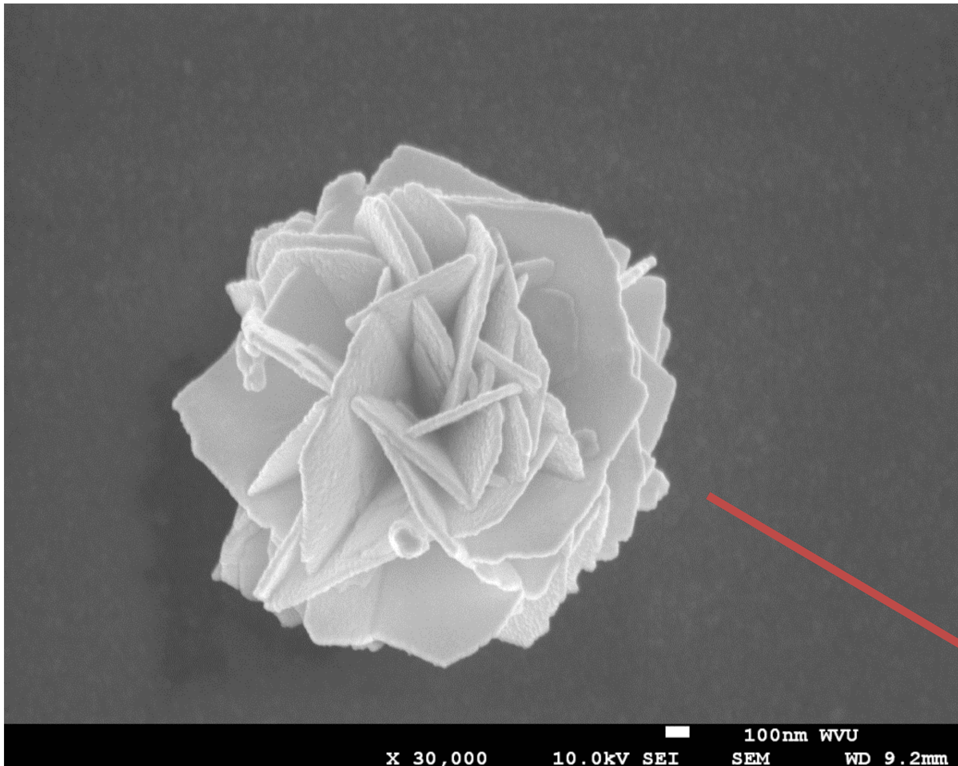




- Sensitive towards 5, 50, and 100 ppm H_2S at 800 and 1000°C
- P-type behavior
- Long term stability (48 h testing)

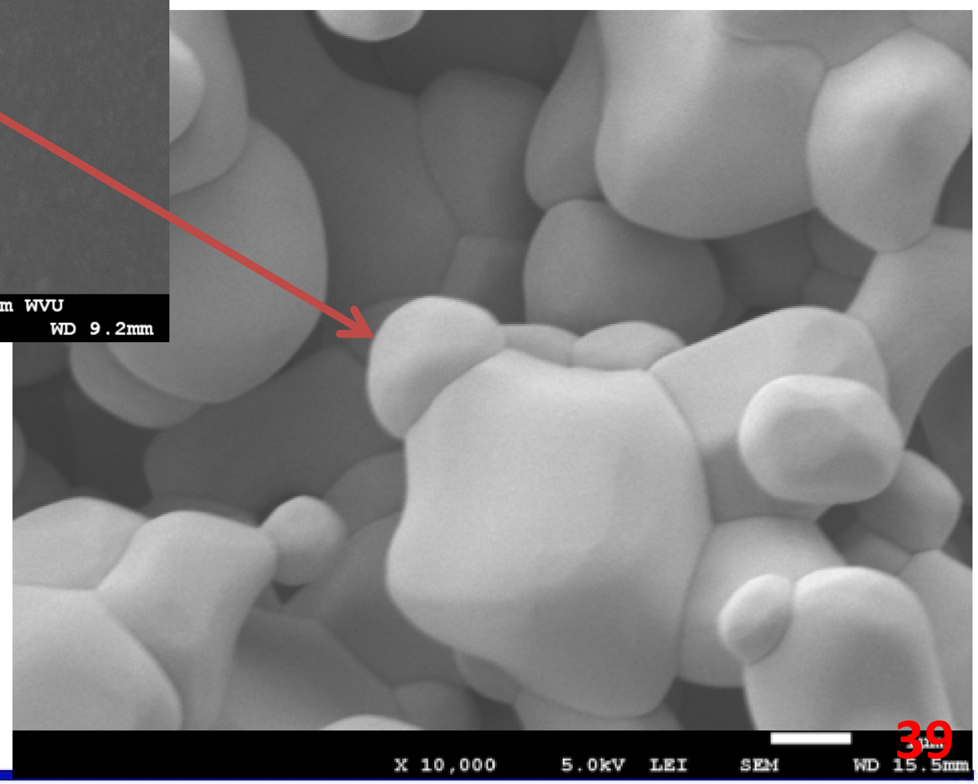
$SrWO_4$

NANOMATERIAL STABILIZATION EFFORTS



Regardless of morphology (5 different morphology were tried) this is what happens at elevated temperature !!!

Nano- $SrMoO_4$

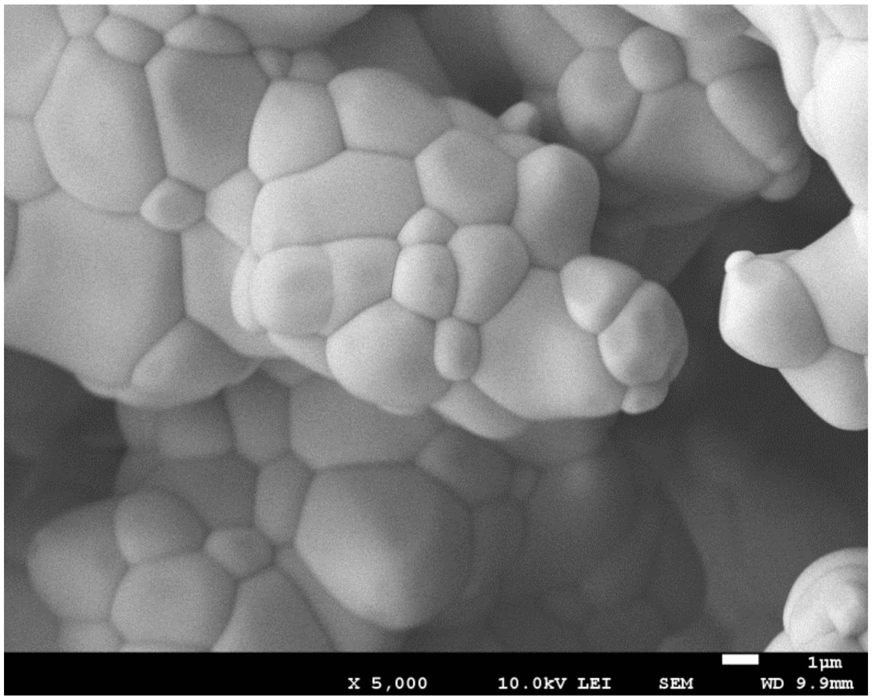


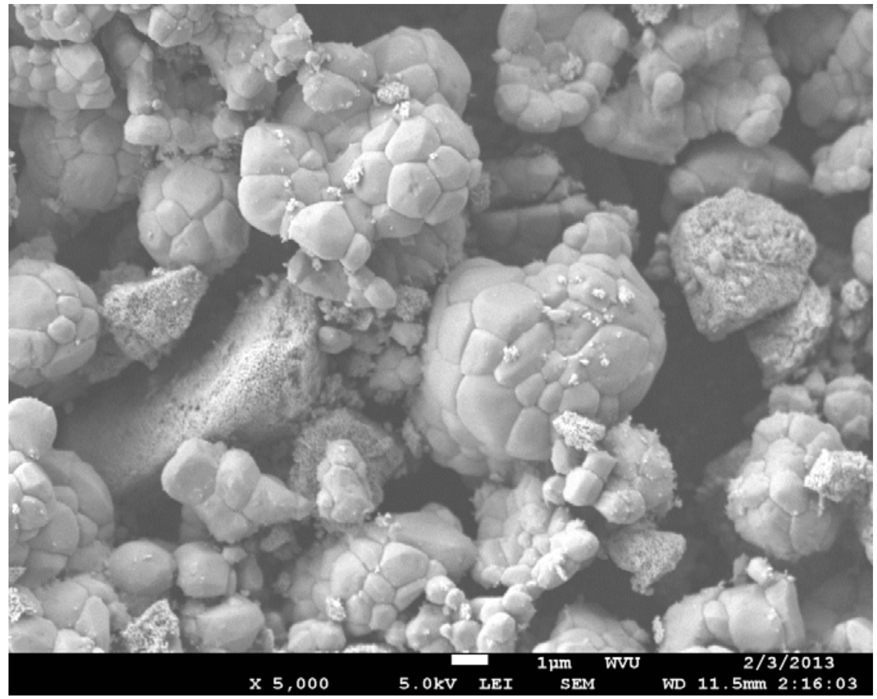
Possible Solutions to stop the coarsening of nano-$SrMoO_4$

1. Grain pining
2. Templated growth of $SrMoO_4$, over a core refractory-oxide structure

NANOMATERIAL STABILIZATION EFFORTS

1. Grain pining

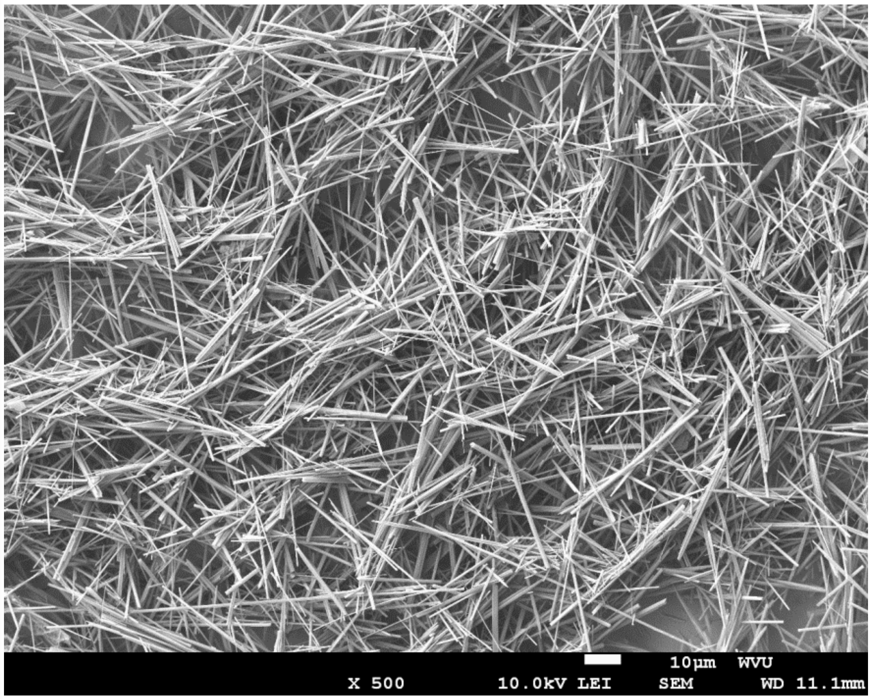


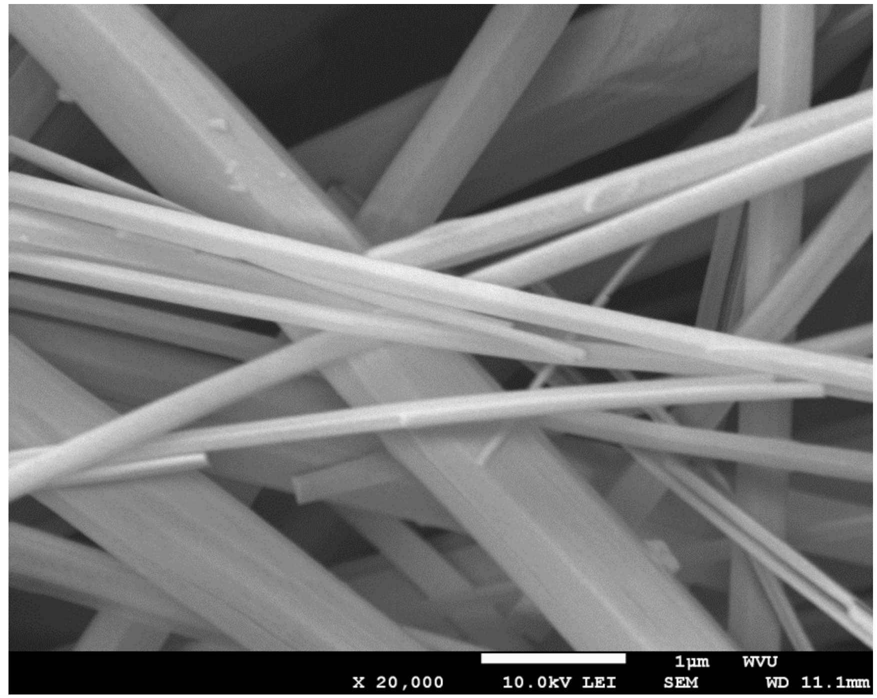


•Limited success !!!

NANOMATERIAL STABILIZATION EFFORTS

2. Templated growth of $SrMoO_4$, over a core refractory-oxide structure.

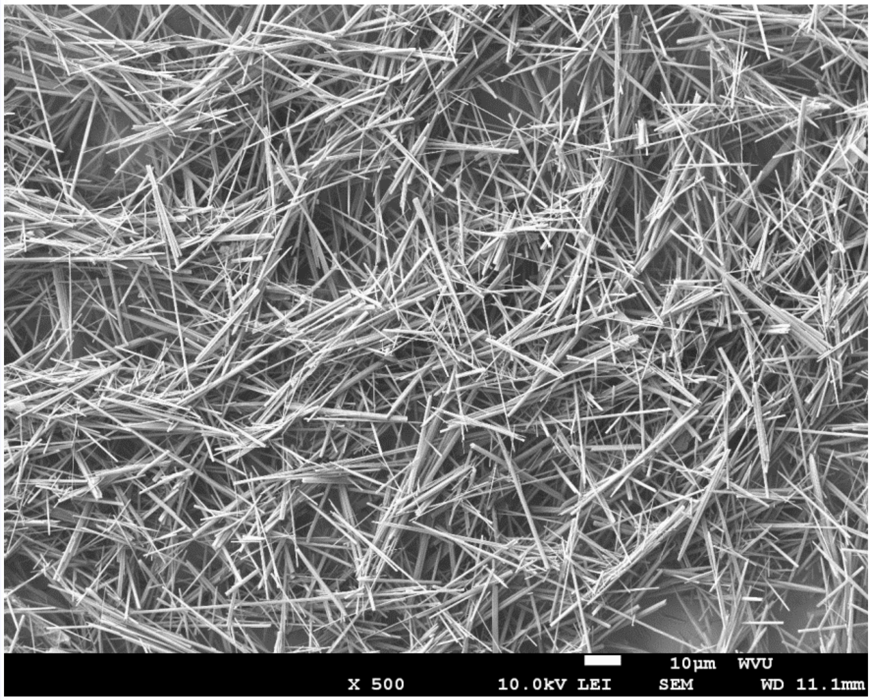


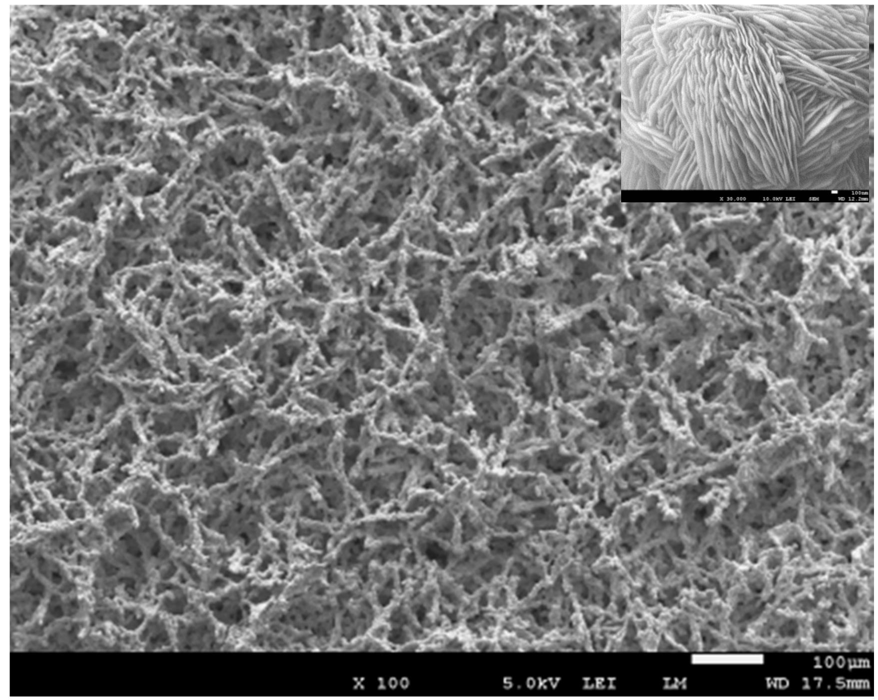


•For this purpose, MgO nanorods were synthesized.

NANOMATERIAL STABILIZATION EFFORTS

2. Lost-Template Growth , over a core refractory structure with nano-features. Core structure totally lost, confirmed by XPS, EDS and XRD not included.



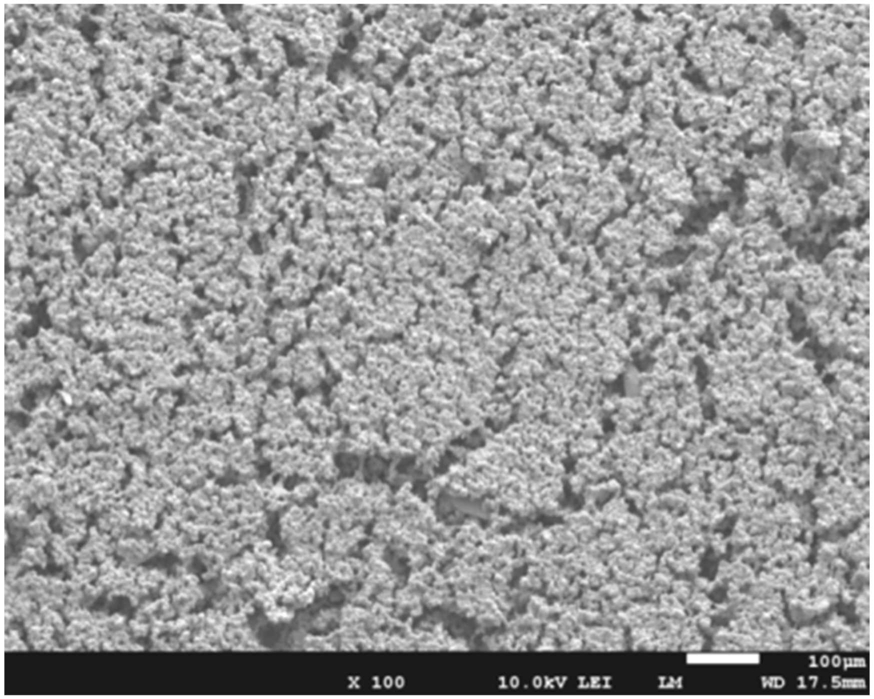


And tried grow ***$SrMoO_4$ over MgO, worked…***

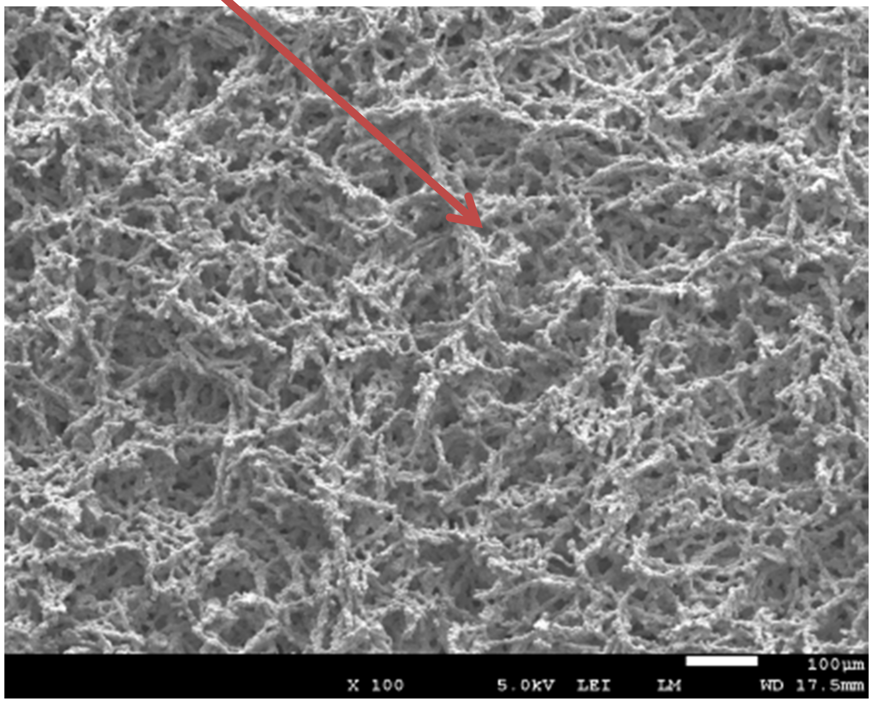
NANOMATERIAL STABILIZATION EFFORTS

COMPARISON

•Higher surface area and very porous network for efficient gas penetration survived…Temporary testing facility established and this material about to be tested.



•$SrMoO_4$ nano-flowers after 5 h 1000°C in air.



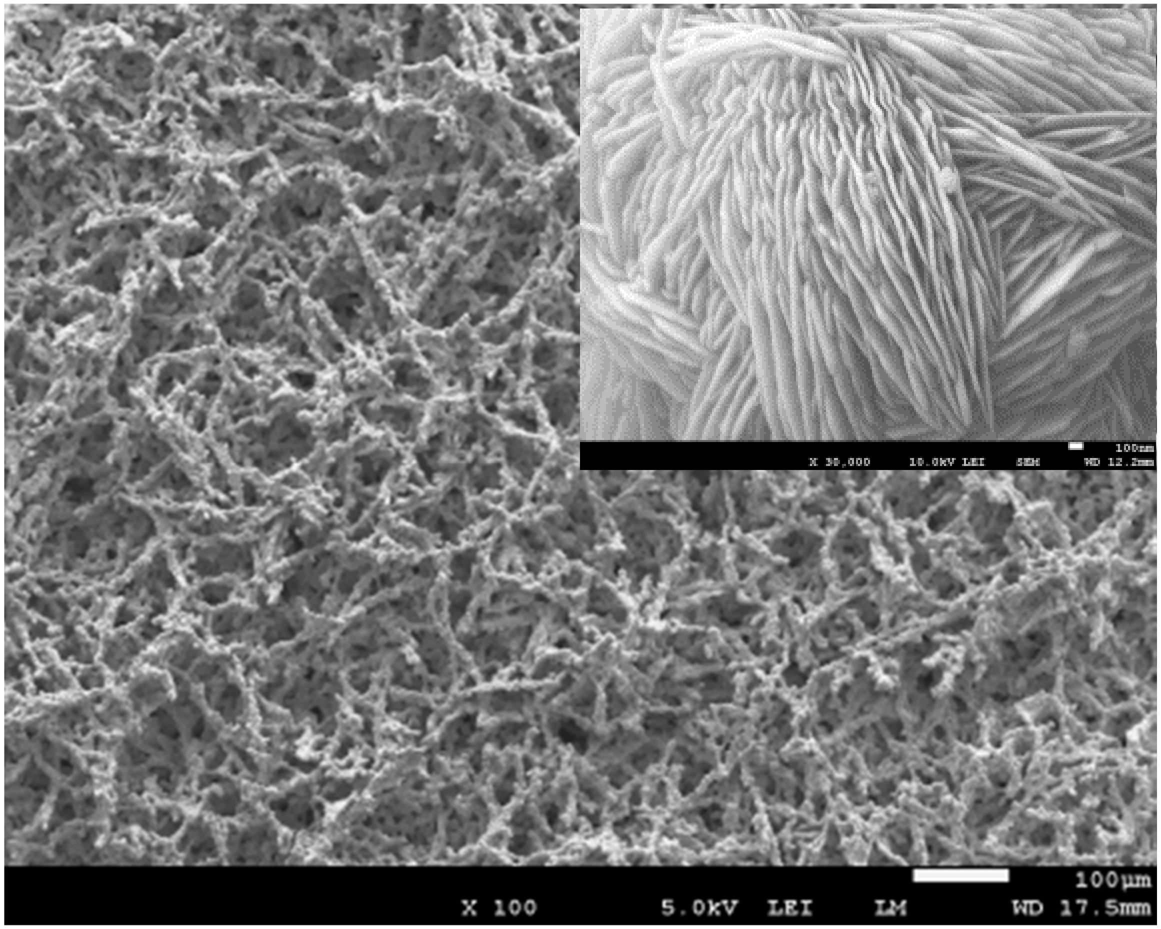
•$SrMoO_4$ nano-flowers over MgO after 5 h 1000°C in air.

SUMMARY: Nano-Derived Sensing Materials And Testing

•$SrMoO_4$ and $SrWO_4$ showed superior sensing capabilities at high temperature.

•High-temperature coarsening resistant $SrMoO_4$ was synthesized by lost-template method showed increased sensitivity.

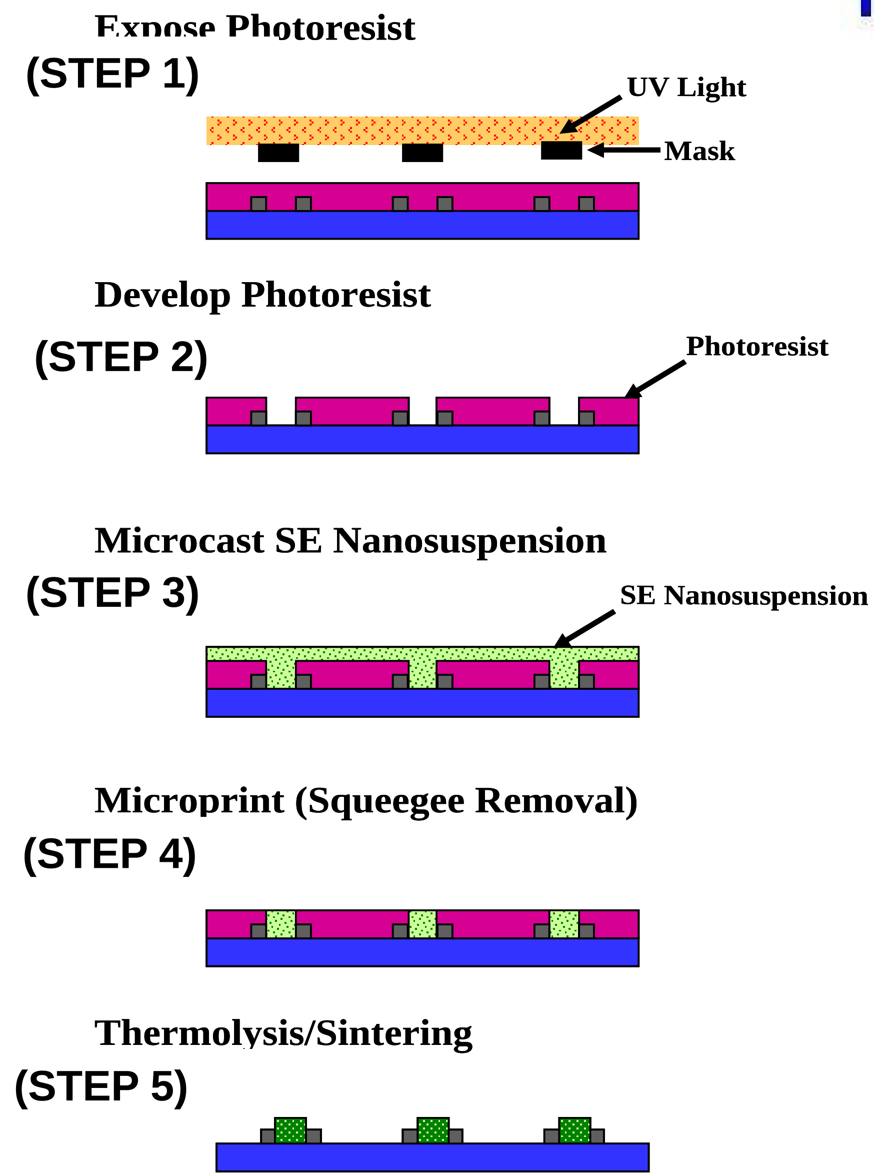
•Long term stability tests showed reliability of the $SrMoO_4$ and $SrWO_4$



Micro-Sensor and -Array Fabrication and Testing

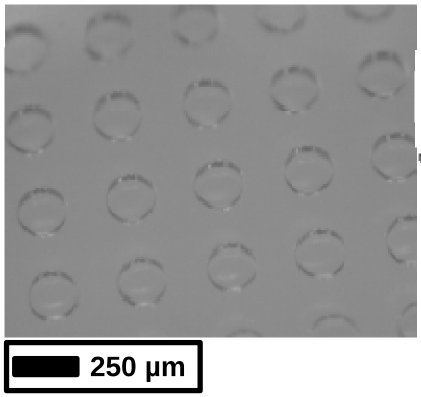
Micro-sensor Array Fabrication

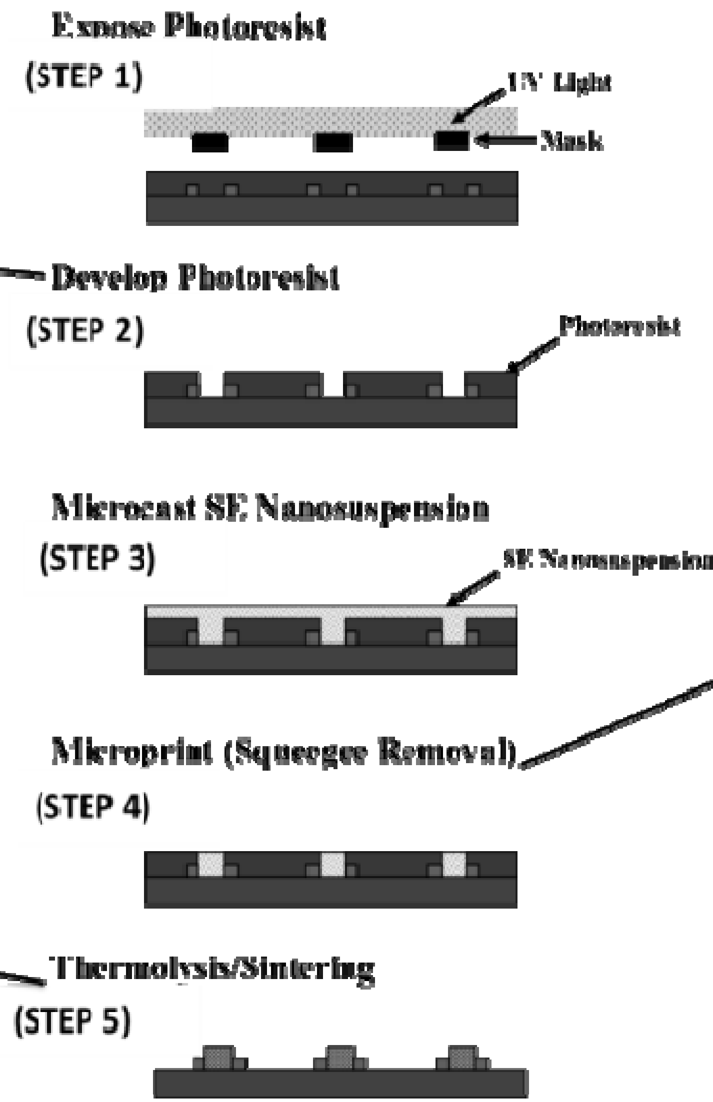
1) Negative lithography used for micro-molds
   - SU8-25 (Microchem)
     - From 20-90 µm depth depending on spin rate
   - OAI UV Flood Exposure System
   - SU8 developer
2) Sensing material is casted into mold.
3) Mold is burned off and material is sintered or bonded to substrate.



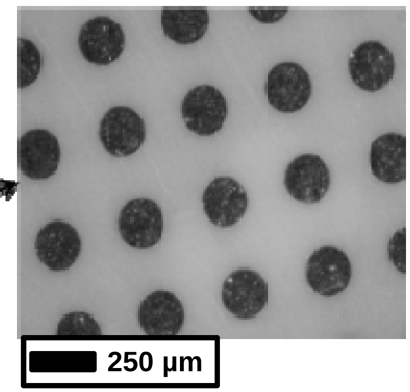
Micro-sensor Array Fabrication

SU8 Micro-mold

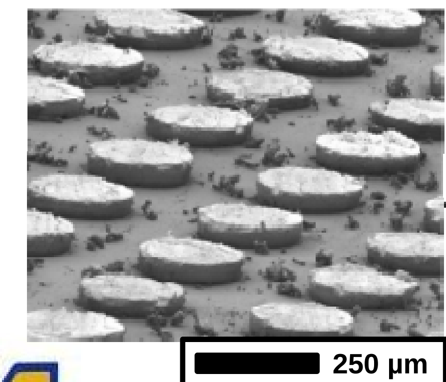




Micro-casted into Micro-molds

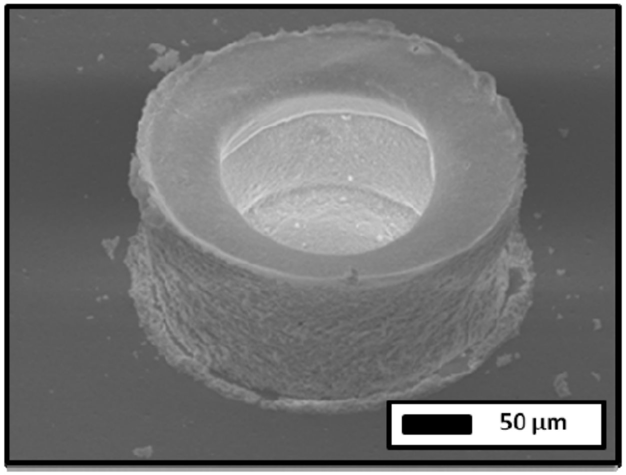


Thermally Processed Features

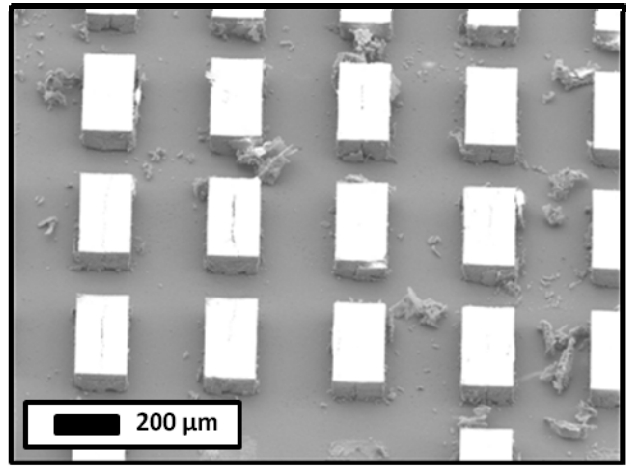


Micro-Casting - SEM

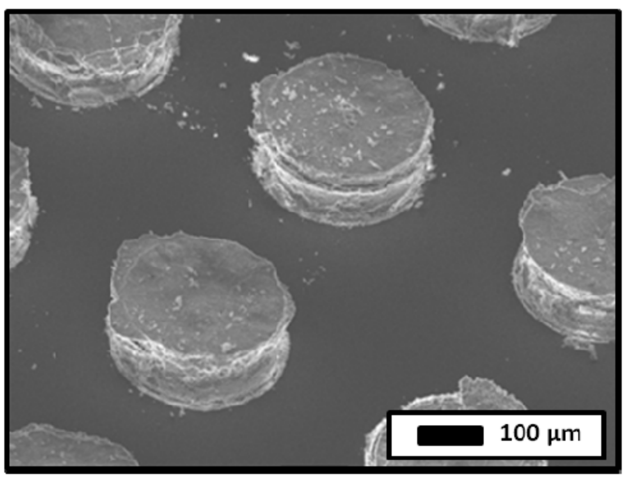
- Casted single layer on YSZ substrate
- Casted double layer on YSZ substrate



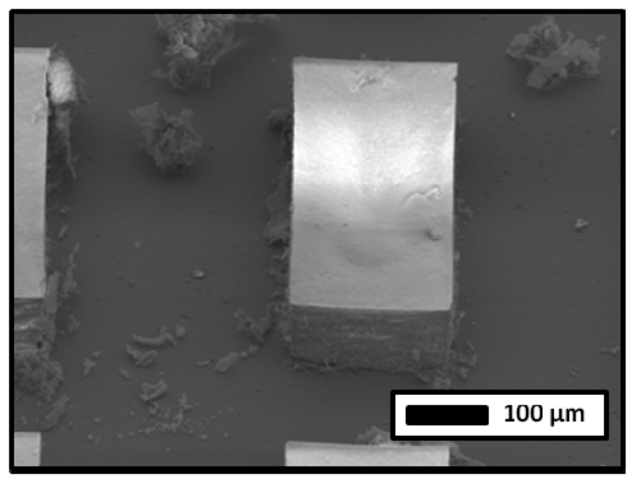
(a)



(b)



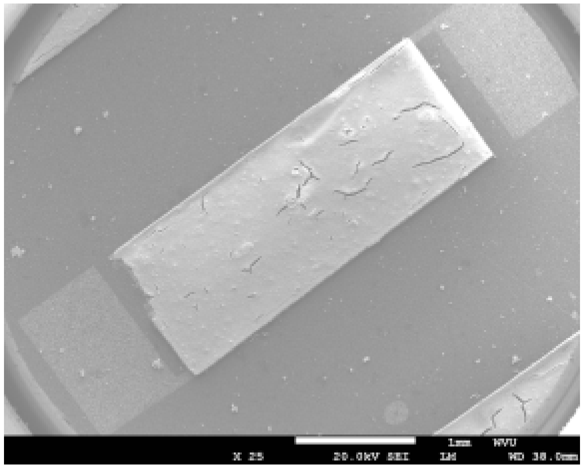
(c)



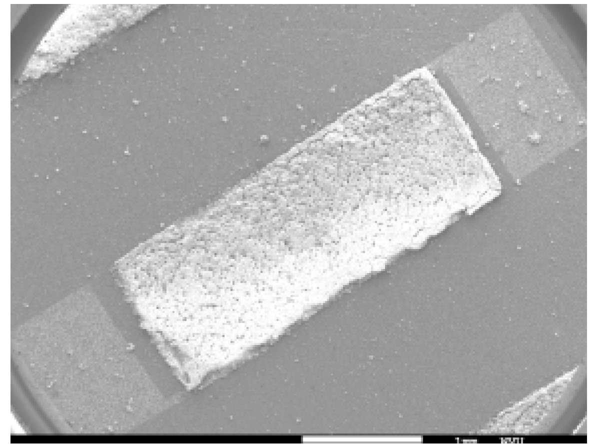
(d)

Micro-casting of Sensor Arrays

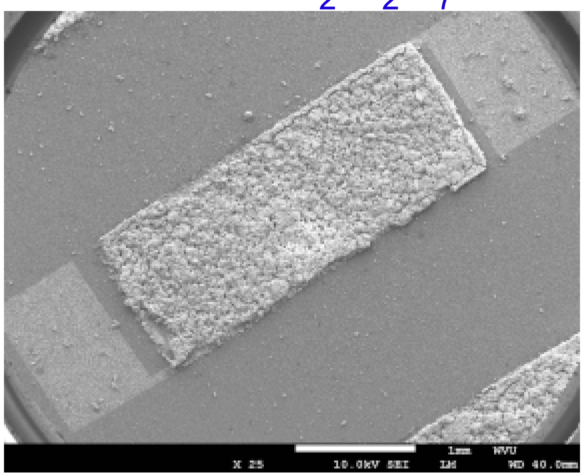
Nano-SnO_2



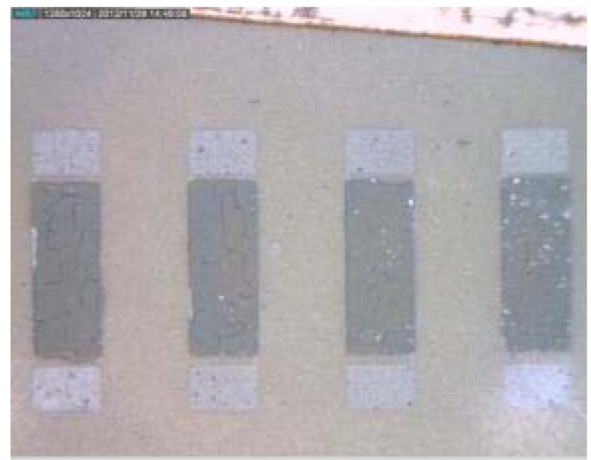
Nano-10% SnO_2/90% $Gd_{1.8}Y_{0.2}Zr_2O_7$



Nano-$Gd_2Zr_2O_7$



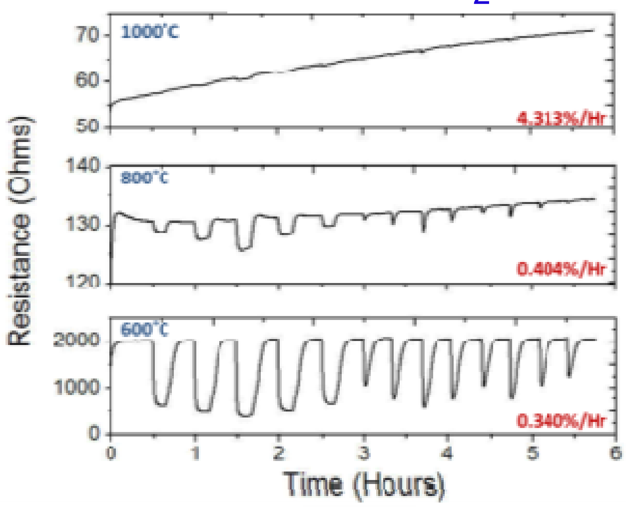
Nano-SnO_2 and $Gd_{1.8}Y_{0.2}Zr_2O_7$ Arrays



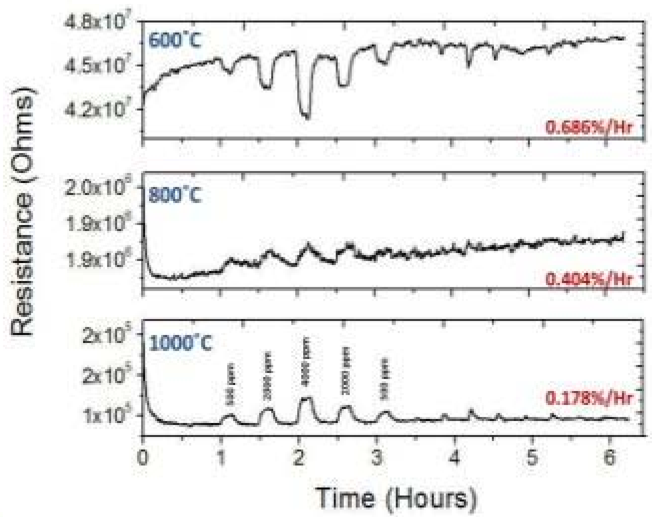
Micro-sensor and arrays fabricated with nano-SnO_2 and nano-SnO_2/zirconate materials.

Initial Micro-sensor Testing (with Nanomaterials)

Nano-SnO_2



Nano-10% SnO_2/90% GZO



(b)

- Micro-IDEs were fabricated by sputtering process.
- 29 fingers were spaced 50 µm apart with a sensing area of 1.2 mm x 3 mm.

SnO_2 sensor

- Sensitivity of 0.812 and 0.010 at 600 and 800°C to 4000 ppm of H_2

10% SnO_2/90% GZO sensor

- Sensitivity of 0.097 and 0.047 sensitivity at 600 and 1000°C, respectively, to 4000 ppm of H_2

Compared to Macro-Sensors

~63% increase in response rate

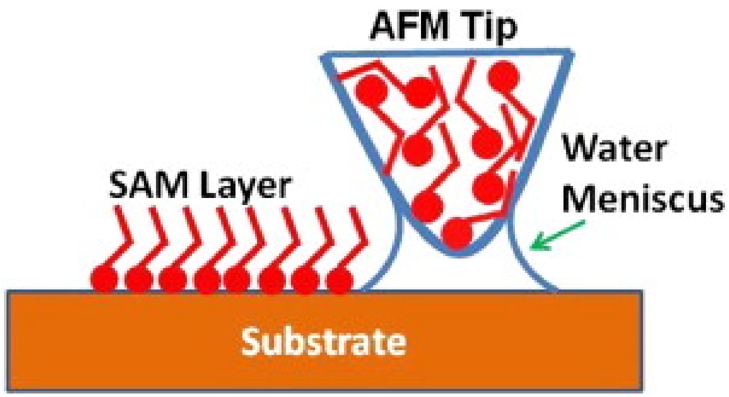
~200% increase in sensitivity

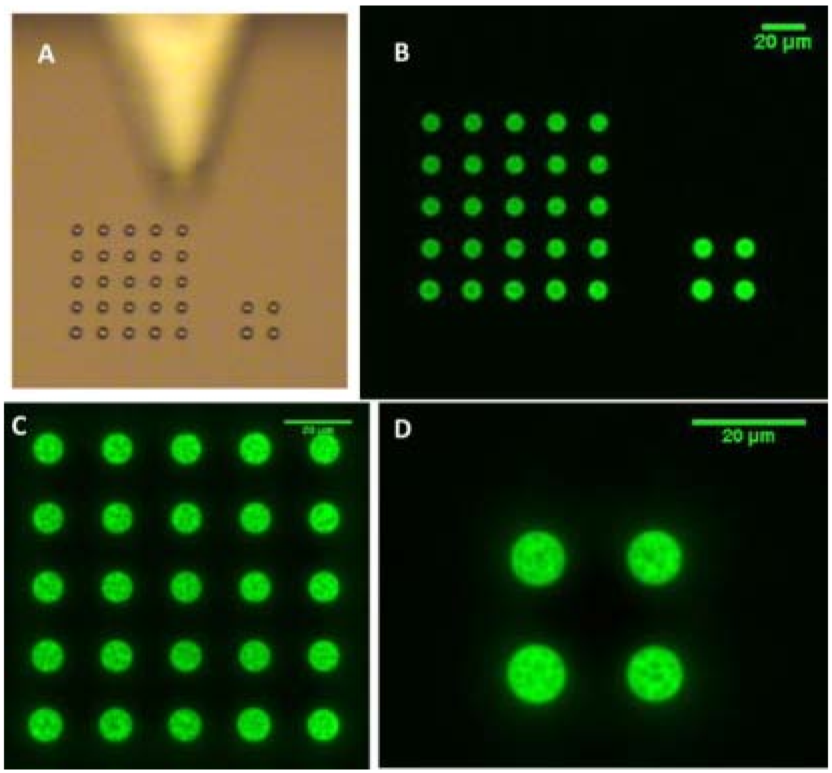
N_2 with ppm H_2 (10% oxygen atmosphere)

Micro-Patterning Techniques

Dip Pen Nanolithography (DPN)

•Direct drawing delivers multiple materials onto a single substrate.
•Typically used to deposit organic material (DNA, cells, peptides, polymers).

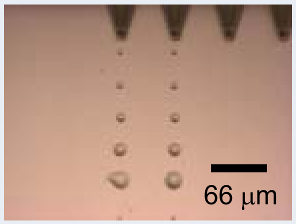
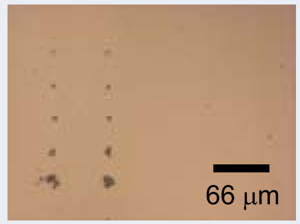
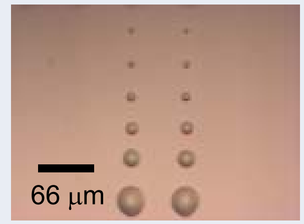
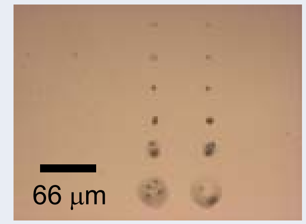
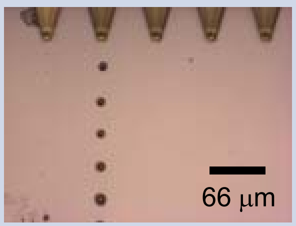
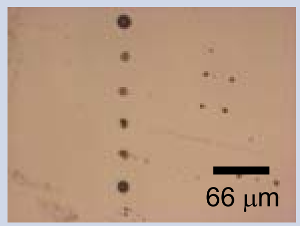
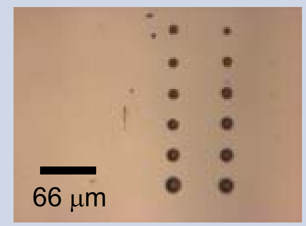




Thompson et al., Biosensors and Bioelectronics, 26 (2011).

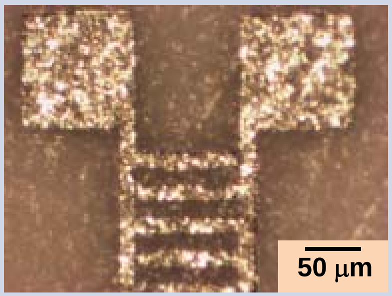
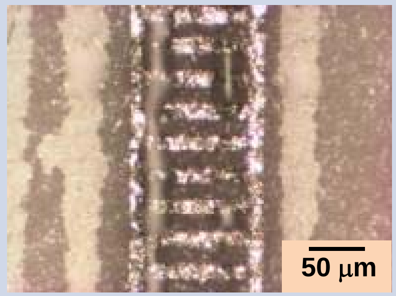
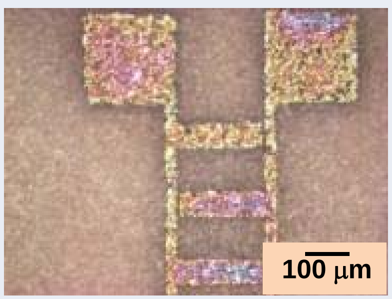
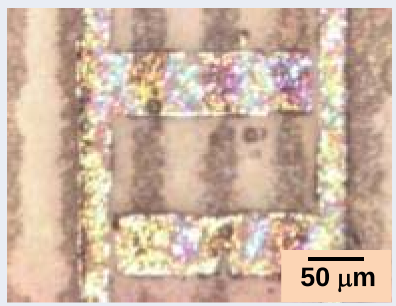
Agarwal et al., Thin Solid Films, 519(2010).

DPN of Nano-Inks on Untreated Substrate

	Ink #1		Ink #2	
	Wet	Dry	Wet	Dry
Glass				
Alumina				

- Ink shows $\theta \approx$**35°** on both substrates.
- Uniform size and shape dots (5-10 μm) possible on alumina substrate.
- Ink #2 dots on alumina substrate retain shape through drying.
- Direct-writing of continuous line not possible on neither substrates **(contact angle too high, >25° for line drawing).**

<u>DPN of Nano-Inks on Electroded Ceramic Substrates</u>

	Substrate	Pattern with Ink #2
No coating		
CTAB coating		

- Patterning on ceramic (polycrystalline) substrate with metallic electrodes.
- Difficult due to difference in wetting characteristics of each grain and metal vs. ceramic.
- Ink pattern on a substrate ***without a coating*** shows the ink **stumbling over the metallic/ceramic interchanges.**
- CTAB coating provides a single chemistry surface over the IDEs on multigrain ceramic substrate.
- CTAB coating enables patterning of inks.

Work Summary

1. High-temperature interdigitzed electrodes (IDEs).

- ***High temperature IDEs (stable to 1000℃) were developed and method for micro-patterning.***

2. Sensing Materials for Sulphur Compounds.

- **Ternary tungstates and molybdates were synthesized at the micron- and nano-scale, and tested for H_2, SO_2 and H_2S.**
- **High sensitivities were measured >800°C, but the as-synthesized nanomaterial morphologies was not stable.**

3. High-temperature Stablization of Ternary Mo/W Nanomaterials

- **Nano-$SrMoO_3$ (which showed high sensitivity to SO_2) was grown over nano-fiber MgO to form a high-temperature stable nano-morphology.**

4. Micro-sensors and Array Fabrication

- **Micro-molding process was developed to deposit forms down to ~10μm.**
- **Micro-sensors and basic arrays (with synthesized nanomaterials) were fabricated on stable IDEs.**

Future Work

- Alternative core structures for templated growth of nanomaterials.
- Fabrication and testing of the micro-sensor platform for SO_2, H_2 and H_2S.
- Longer term testing of the micro-sensors for >100 h.
- Further investigation of sensing mechanism by ECR (electrochemical relaxation) supported by XPS and FT-IR.

Acknowledgments

- This research was funded by US Department of Energy University Coal Research (UCR) program under contract DE-FE0003872. We want to thank DOE for their support.

- WVU Shared Research Facilities.

- We also would like the acknowledge Dr. Kolin Brown, Dr. Wei Ding. Mr. Harley Hart for their assistance.