Metal Oxide based Heterostructured Nanowire Arrays for Ultra-Sensitive and Selective Multi-Mode High Temperature Gas Detection

Pu-Xian Gao

Department of Materials Science and Engineering & Institute of Materials Science
University of Connecticut, Storrs, USA

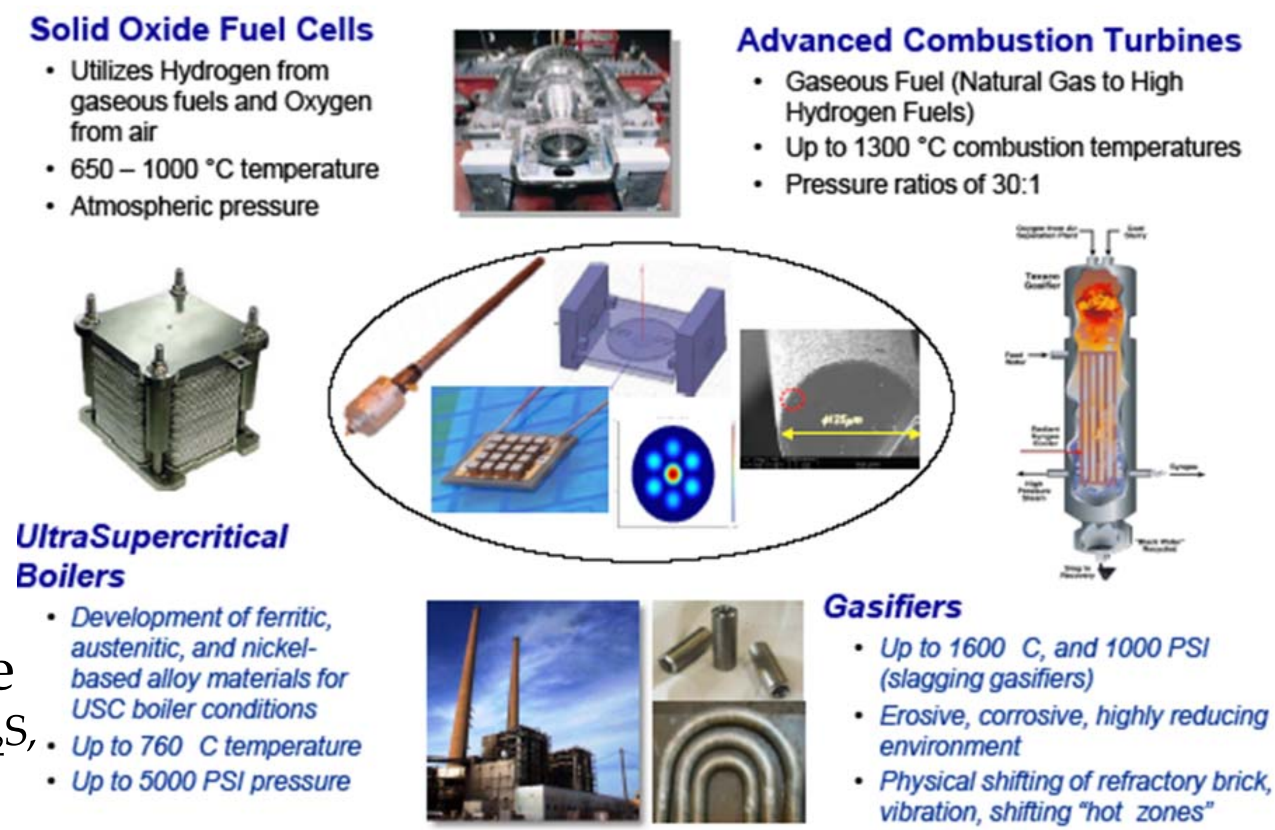
April 29, 2015
@ DOE CCR Meeting
Pittsburgh, PA

Project Overview

- Funding:
  - –DOE: $300,000
- Date: 7/17/2013 –6/30/2016
- Project Objective:
  - – To develop a new class of nanosensors using metal oxide based heterostructured nanowire arrays for gas detection at temperatures up to 1000 ^{o}C.

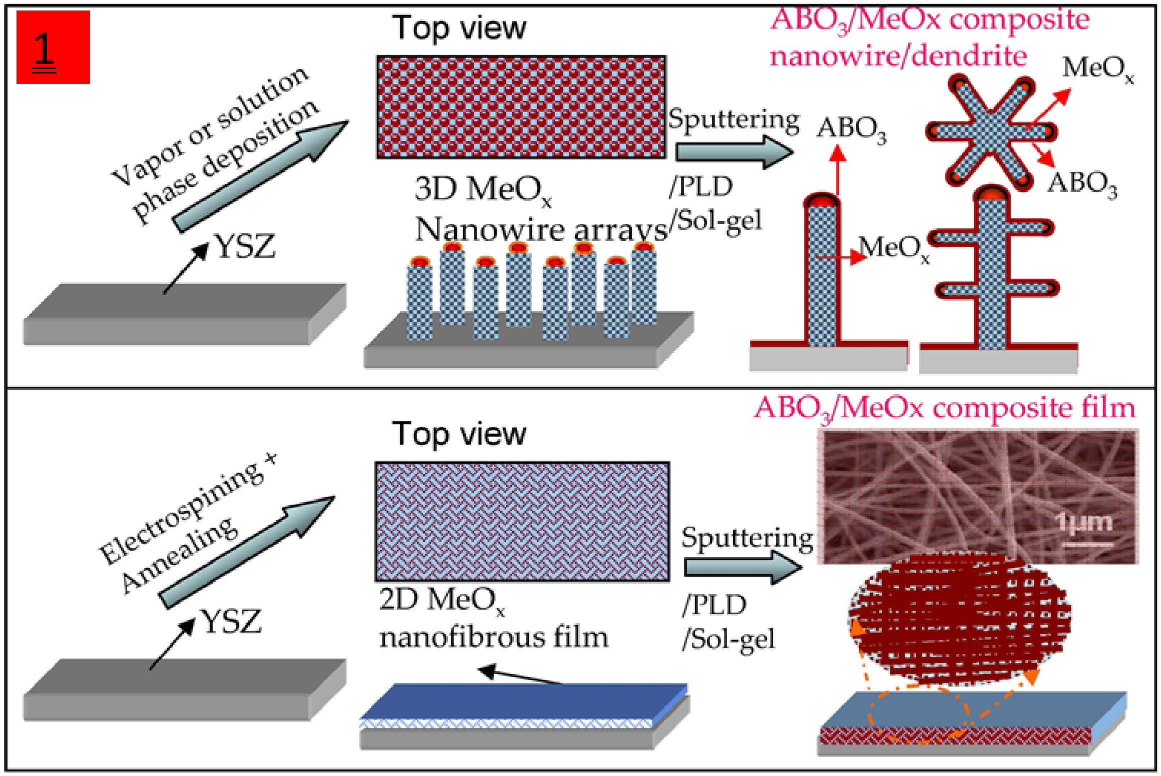
Harsh Environment in Power Systems: Sensing/monitoring Challenges

- Harsh environment
  - Pressure (-1000psi)
  - Temperature (-1600°C)
  - Atmosphere (erosive, corrosive, highly reducing)
- Materials challenge
  - Physical stability
  - Chemical stability
  - Functional stability
- Sensitivity and selectivity challenge
  - Multiple species (H_2, H_2S, CO, CO_2, CH_4, O_2, SO_x, NO_x, NH_3, etc.)
  - Cross-talk



R. Romansky, US DoE/National Energy Technology Lab, 2012

Heterostructured Nanowire Integration



MeO$_x$: metal oxide semiconductor, demonstrated in industry sensing up to 700^{o}C. → can we improve the temperature range and functionality?

ABO$_3$: perovskite, high stability, mixed ionic/electronic transport conductivity, catalytic filtering, A/B site doping flexibility

Metal: catalytic sensing effect, metallic conduction, optical/plasmonic effect, Shottcky junction, selectivity

Materials Advantages: 1) Ultrahigh surface area; 2) High thermal stability; 3) Strong adherence; 4) Low cost; 5) High tailoring ability

Gao et al., *DoE/NETL Sensors & Control Program Meeting*, **2009**.
Gao et al., *Proc. SPIE*, **2011**.
Gao et al., *J. Phys. D.*, **2010**.
Zhang et al., *J. Mater. Chem.*, **2012**.
Gao, et al., *Int. J. Mol. Sci.*, **2012**.
Ren, et al., *Frontier Chem*. **2014**.
Gao et al., UConn invention disclosure filed, **2012**.

Approaches:
Fabrication of Heterostructured Nanowire Arrays

I. Metal oxide nanowire growth on solid substrates

a). Hydrothermal synthesis

b). Physical and chemical vapor deposition

II. Heterostructured nanowire formation: perovskite and metal nanoparticle decoration

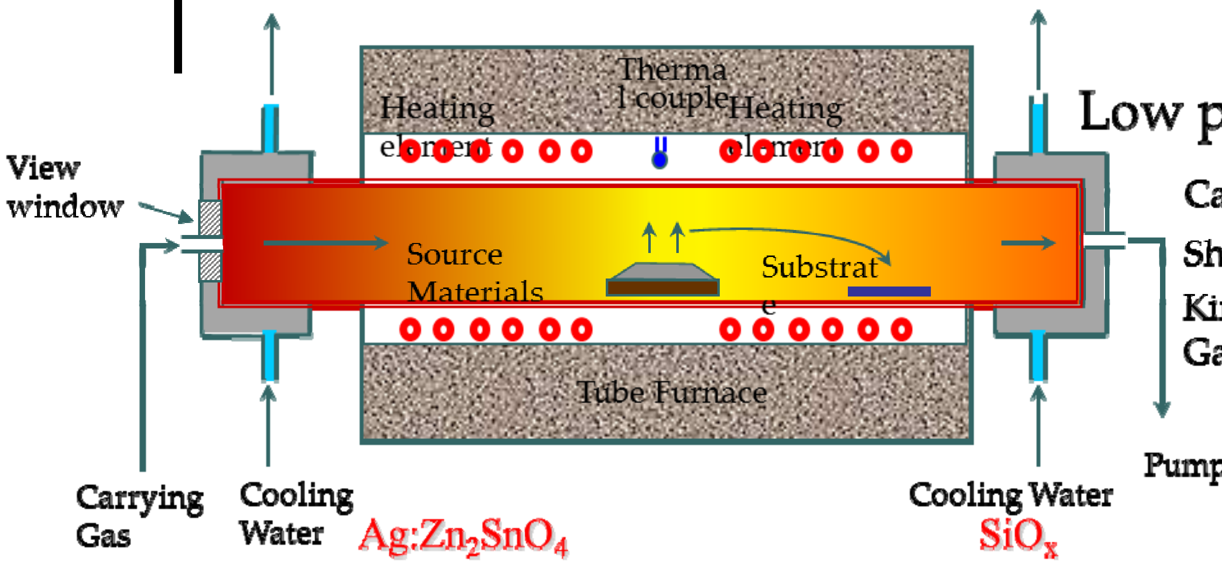
a). Sol-gel process

b). Colloidal deposition

c). Sputtering

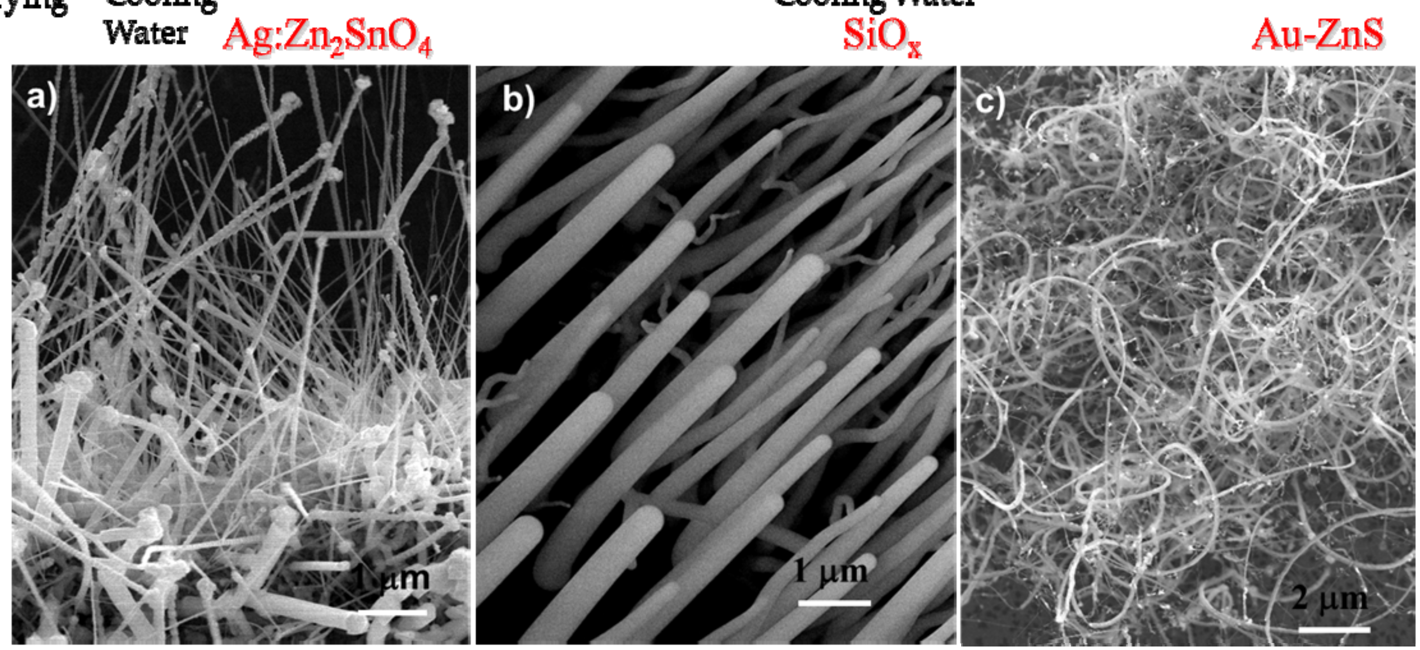
Strategy #1:

Vapor phase deposition



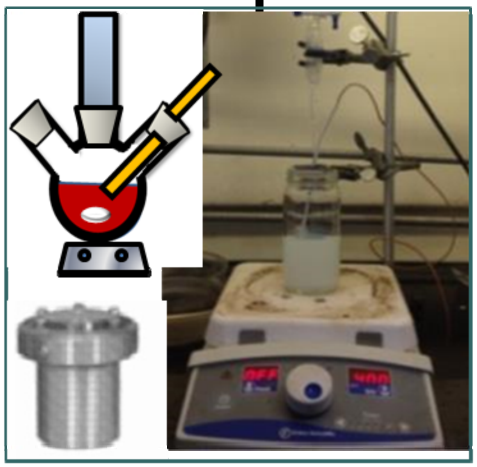
Low pressure CVD (LPCVD)

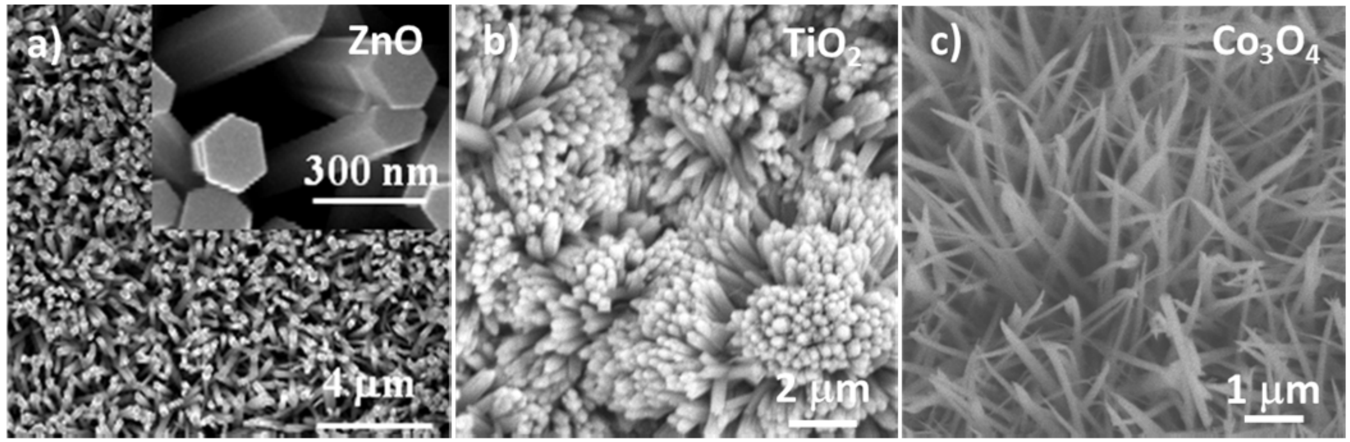
Cai, Shimpi, et al., *J. Mater. Chem.*, 201
Shimpi & Gao, *Crys. Eng. Comm.*, 2010
Kim et al., *Sci. Adv. Mater.*, 2010.
Gao et al., *Int. J. Mole. Sci.*, 2012.

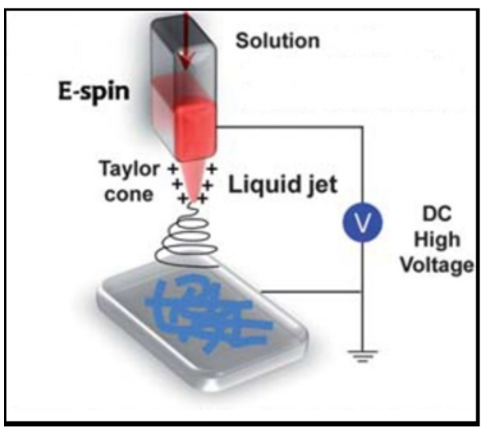


Strategy #2

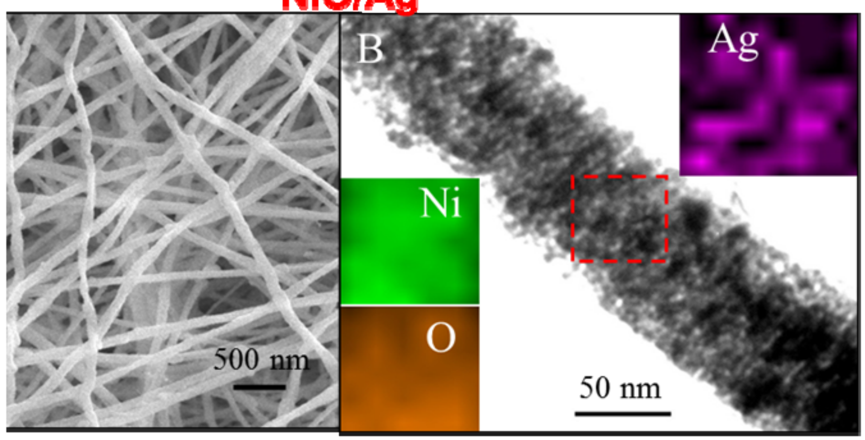
Solution phase processing and manufacturing



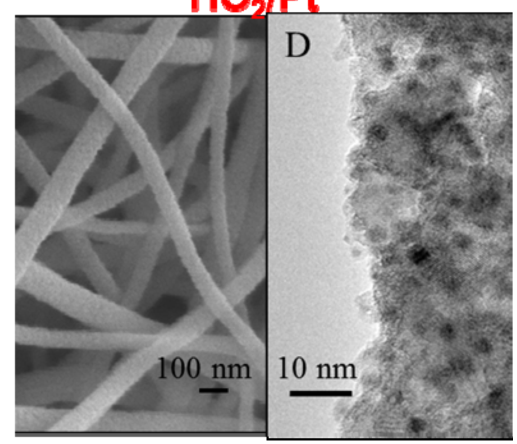




NiO/Ag



TiO_2/Pt

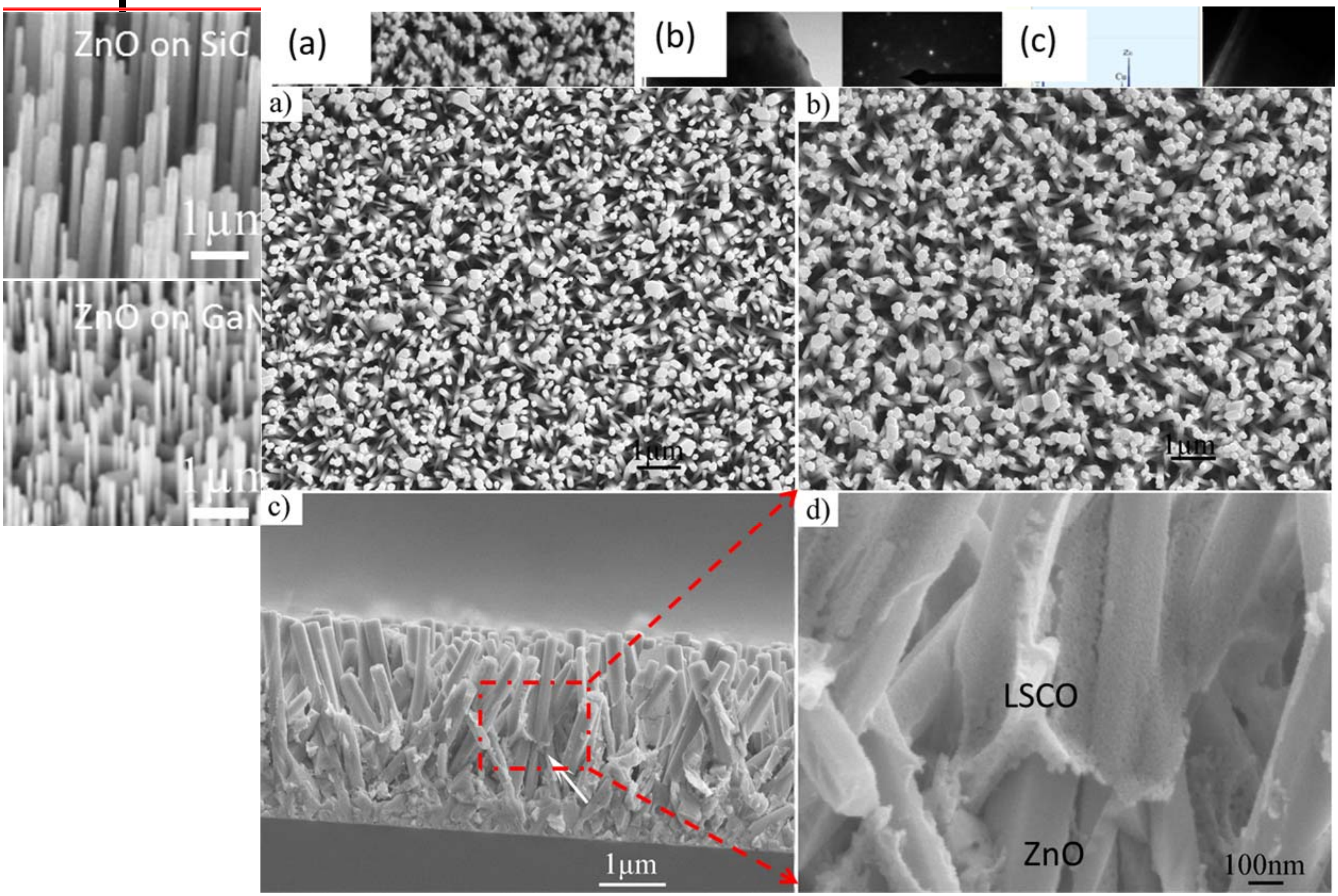


Cost-effective, large-scale, low temperature, substrate compatible.

Gao, Song, Liu & Wang, *Adv. Mater*. 2007. Wrobel, Piech, Dardona & Gao, *Crys. Growth Des.*, 2009.

Guo, Zhang, Ren & Gao, *Cat. Today*, 2012. Gao et al., *Int. J. Mole. Sci.*, 2012. Liu, Gao, et al., *RSC Adv*. 2012.

Scalable Metal oxide based Heterostructured Nanowire Integration



Mai et al., *Chem. Phys. Letts*. 2008. Gao et al., J. Phys. D., 2010.
Gao et al., *APL*, 2011 Gao et al., *Int. J. Mole. Sci.*, 2012

Project Milestones

- **FY14-15 Milestones:**
  - Q6: Growth of metal oxide nanowire arrays on various solid substrates
    - continued
  - Q6: Physico-chemical structure and morphology characterization
    - continued
  - Q8: Perovskite/metal decoration of nanowire array sensors
    - on track
  - Q8: Design and fabrication of multi-mode nanowire array sensors
    - on track

Collaborations

- National Energy Technology Laboratory: In-situ X-ray Photoelectron Spectroscopy of nanowire arrays at high temperature with Dr. Paul Ohodnicki.

- Brookhaven National Laboratory: electronic transport study of metal oxide nanowire array with Dr. Chang-Yong Nam through Center for Functional Nanomaterials (CFN).

- University of Texas at Dallas:
  metal nanoparticles as sensitizers for metal oxide nanowire sensors, with Dr. Jie Zheng at the Department of Chemistry.

Accomplishments
(Project period: 7/2013-3/2015)

1) Synthesis and characterization of ZnO and Ga_2O_3 based heterostructured nanowire array based devices.

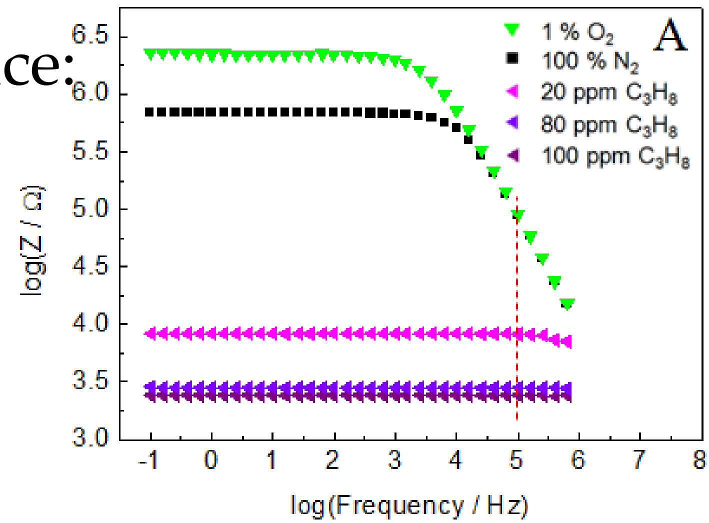
2) Demonstration of multiple sensing modes in single device.

3) Photocurrent enhancement through trace decoration of metal and perovskite.

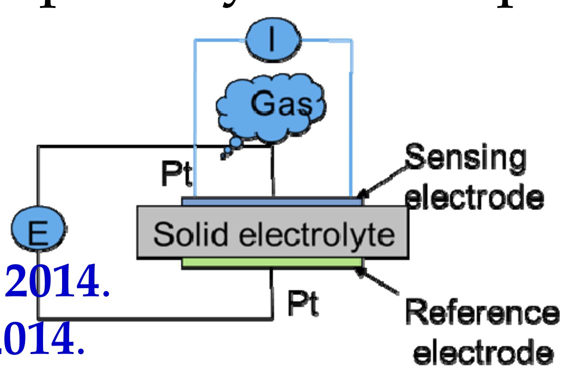
4) Sensitivity and selectivity enhancement toward CO and NO_2 detection.

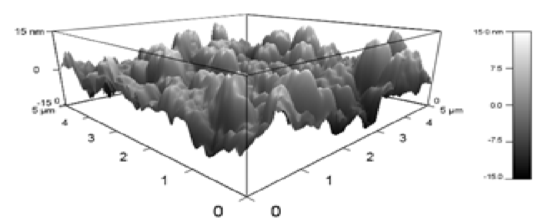
Multiple Sensing Modes in One Device

- Multiple sensing signals in one device:
  - Electrical resistance
  - Impedancemetric
  - Potentiometric
  - Photocurrent mode



- Advantages: multiple signals correlation with respect to selective species → accuracy; selectivity; sensitivity; → add new sensing capability such as physical sensing

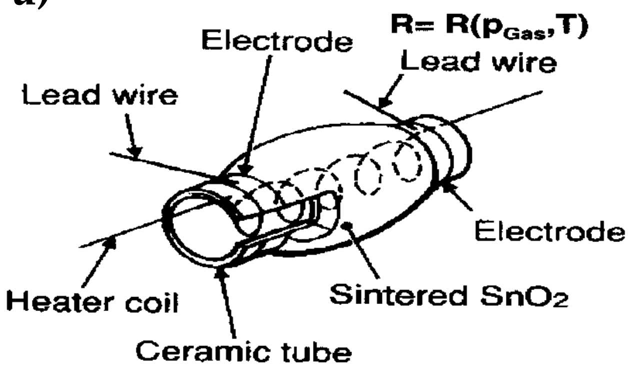




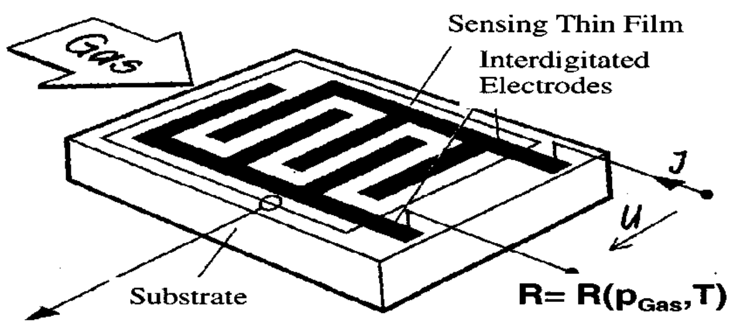
Liu, Lei, et al., *J. Mater. Chem. A*, **2014**.
Sun, Gao, et al., *Frontier Chem.*, **2014**.

Resistance and Photocurrent Sensors

a)

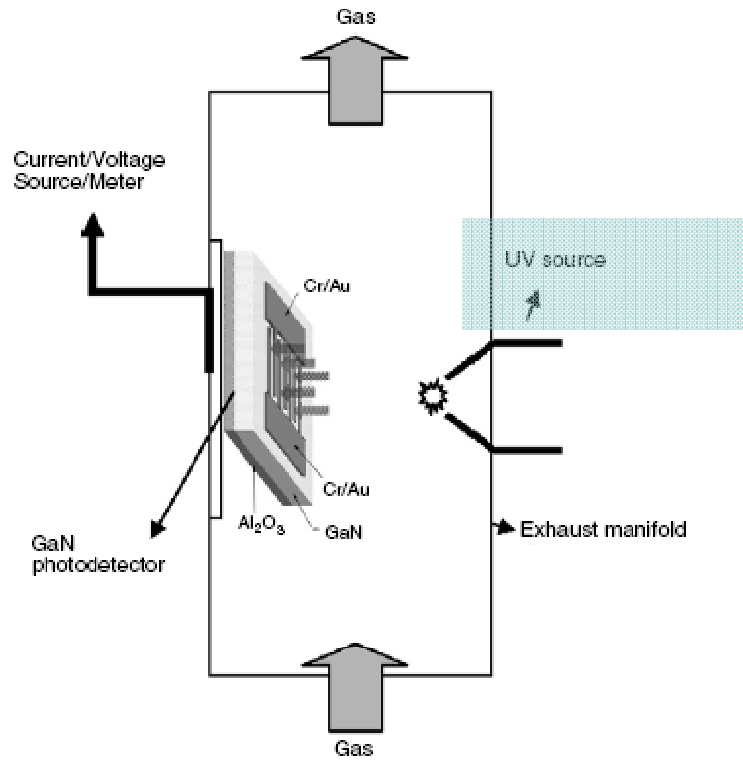


b)



Typical structures of resistor- type gas sensors: a) tubular structure; b) interdigitative electrode (IDE) chip

c)

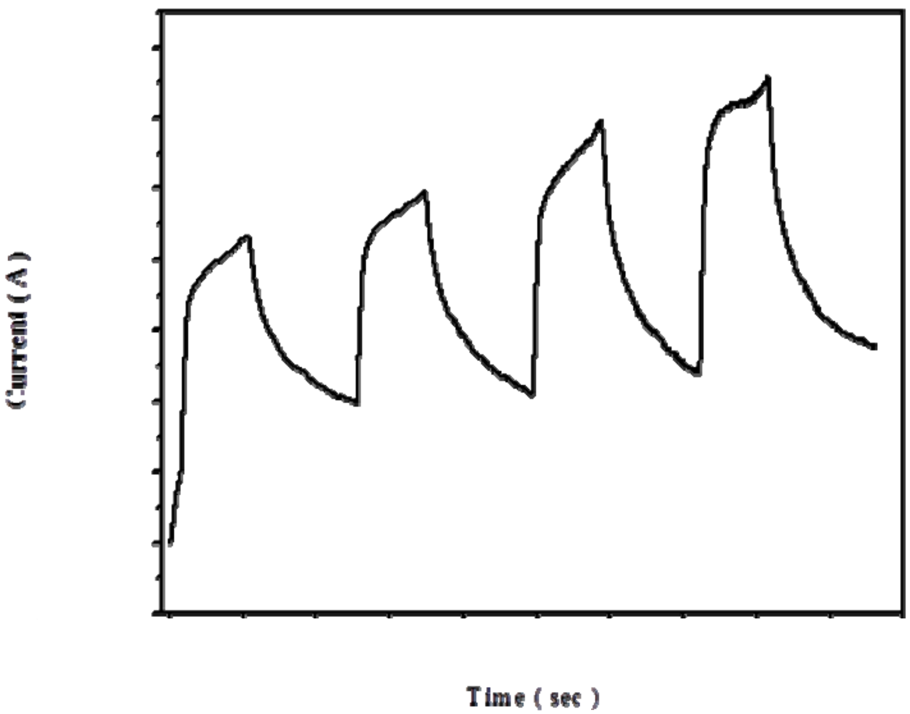


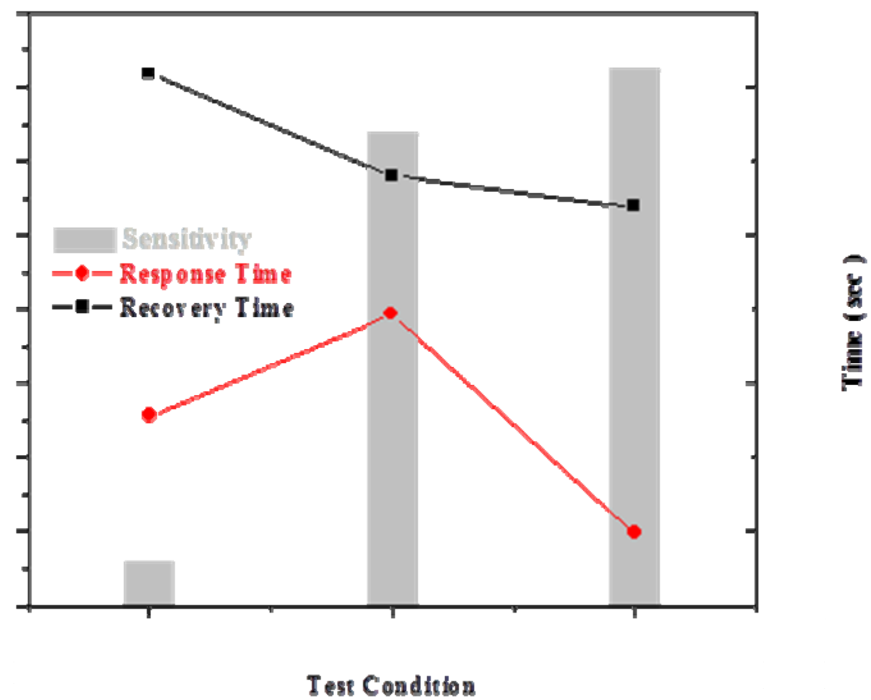
Schematic illustration of GaN based UV photodetector based gas sensor for auoto-exhaust such as NO_x and CO at temperature up to 550°C.

M. Mello, et al., *J. Opt. A: Pure Appl. Opt. 8 (2006) S545–S549*.

Photocurrent Module:
ZnO Nanowire CO Sensors

- 325 nm UV excitation: photocurrent addition to the current signal
- Enhanced CO sensitivity by 30-40%, faster response and recovery upon UV excitation

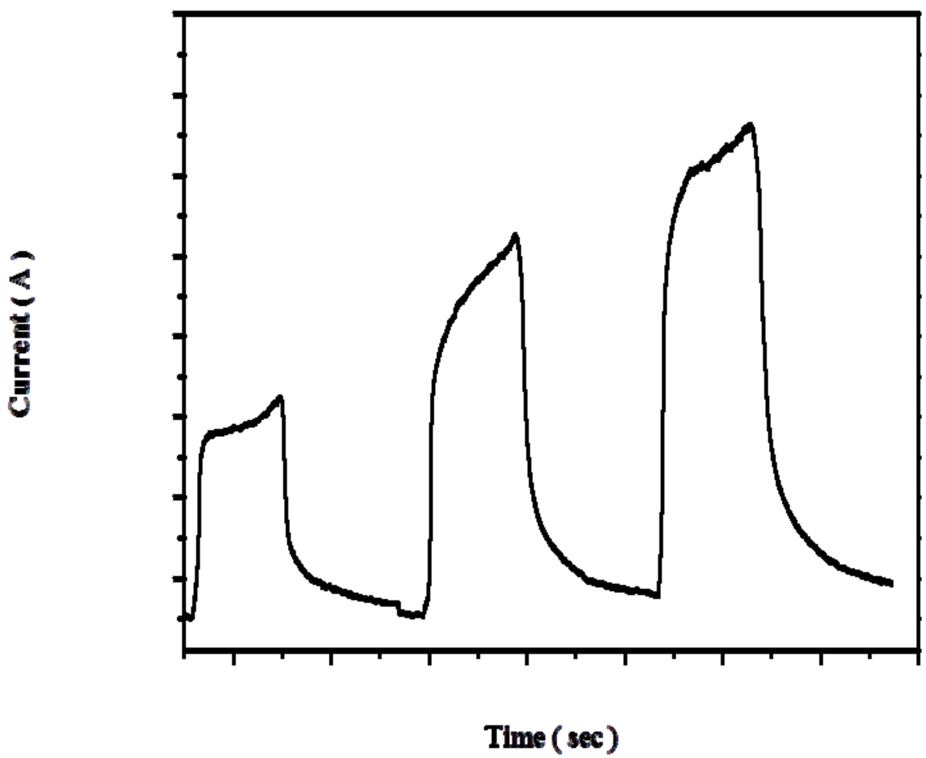


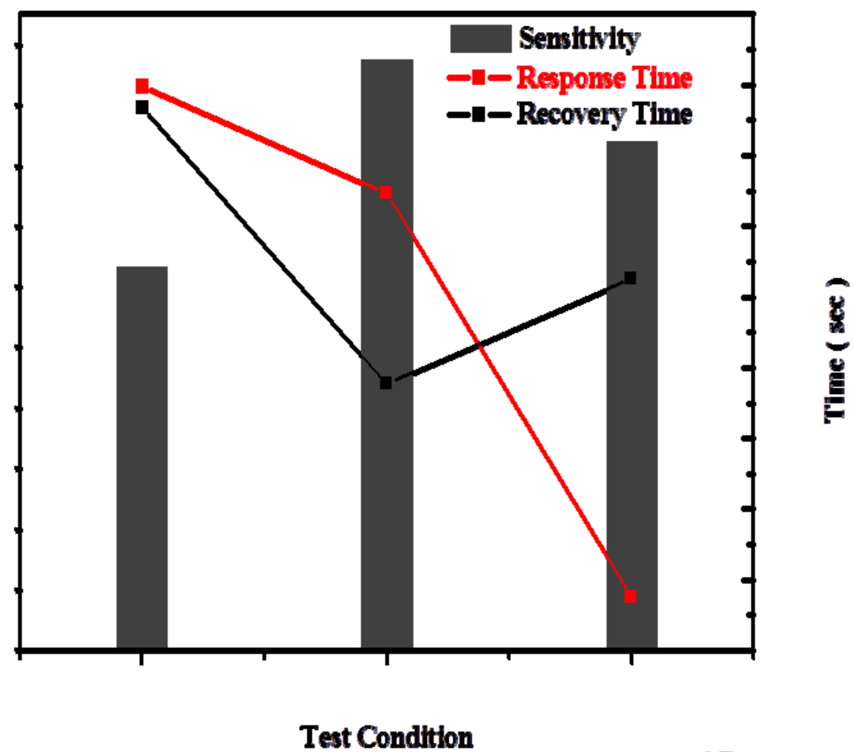


Lin, et al., **2015**, to be submitted.

Photocurrent Module:
Ga_2O_3 Nanowire CO Sensors

- 325 nm UV excitation: photocurrent addition to the current signal
- Enhanced sensitivity by 40-60%, faster response and recovery upon UV excitation
- UV excitation current sustained in the later cycles.



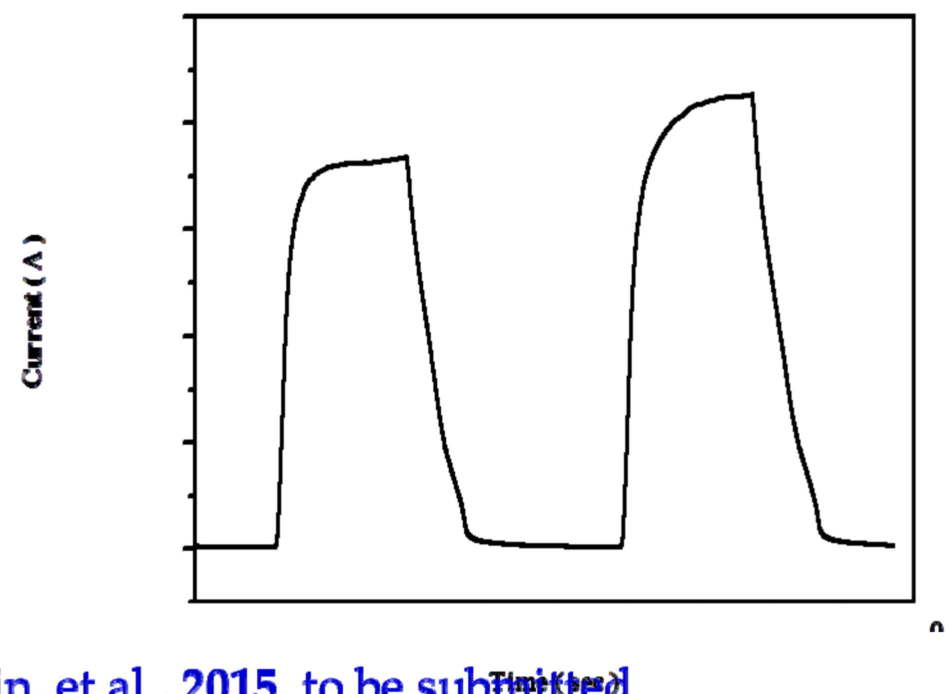


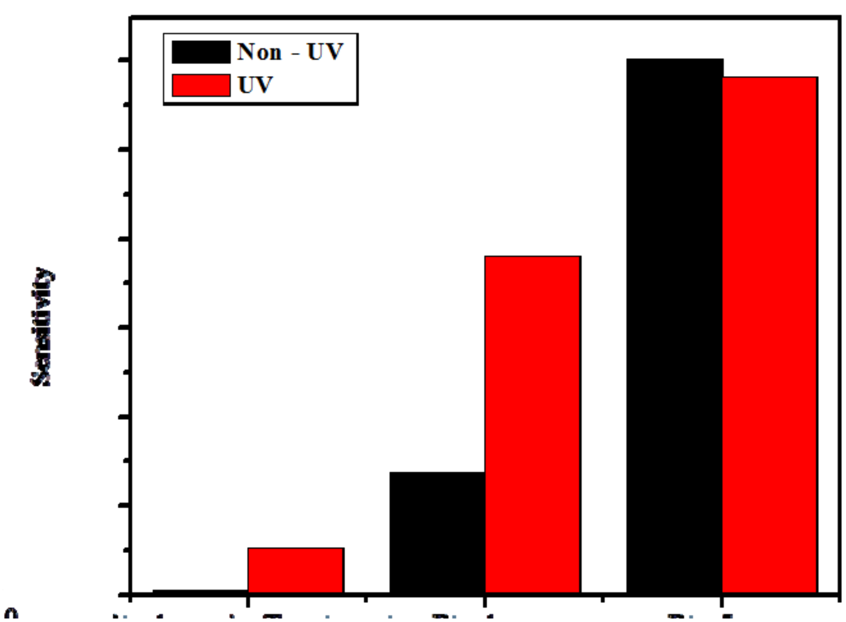
Lin, et al., 2015, to be submitted.

Photocurrent Module:

Metal decorated Ga_2O_3 nanowire CO sensors (I)

- UV excited photocurrent → addition to the sensing signal
- UV excitation and metal decoration enhanced the sensitivity by 10-60 times



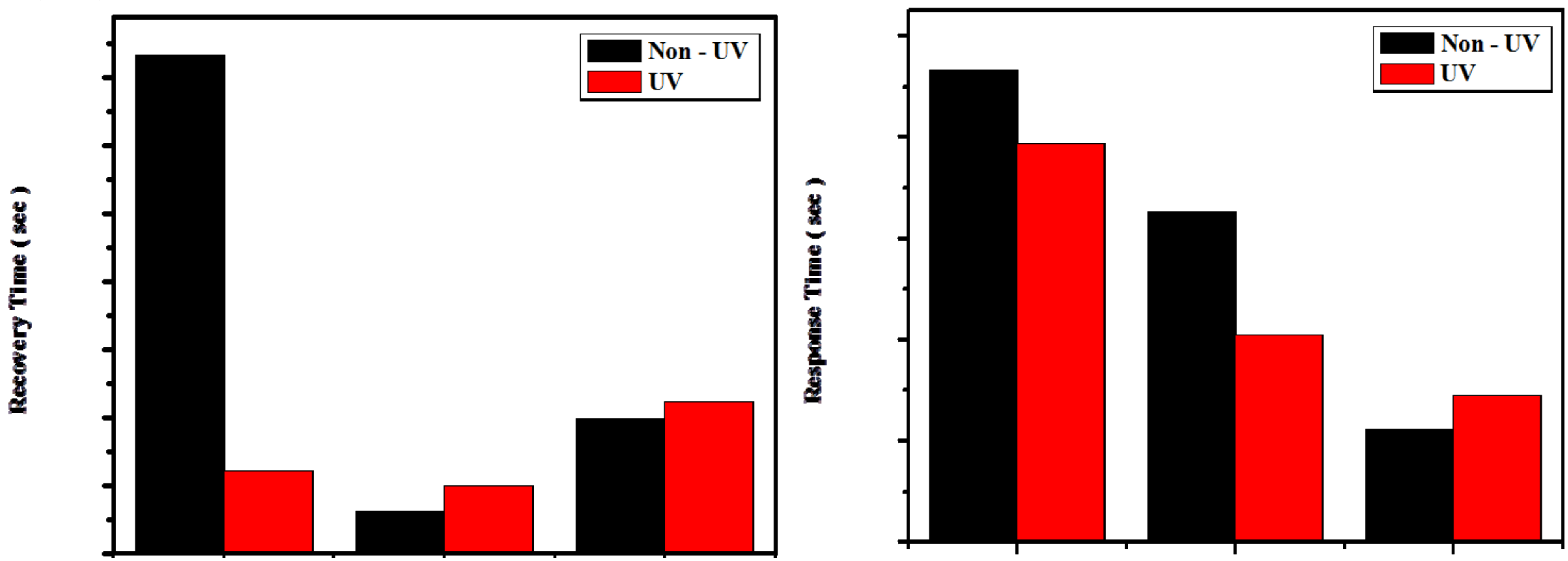


Lin, et al., 2015, to be submitted.

Photocurrent Module:

Metal decorated Ga_2O_3 nanowire CO sensors (II)

- UV excitation induced current enhancement
- UV excitation and metal nanoparticle enhanced response and recovery in CO detection at high temperature

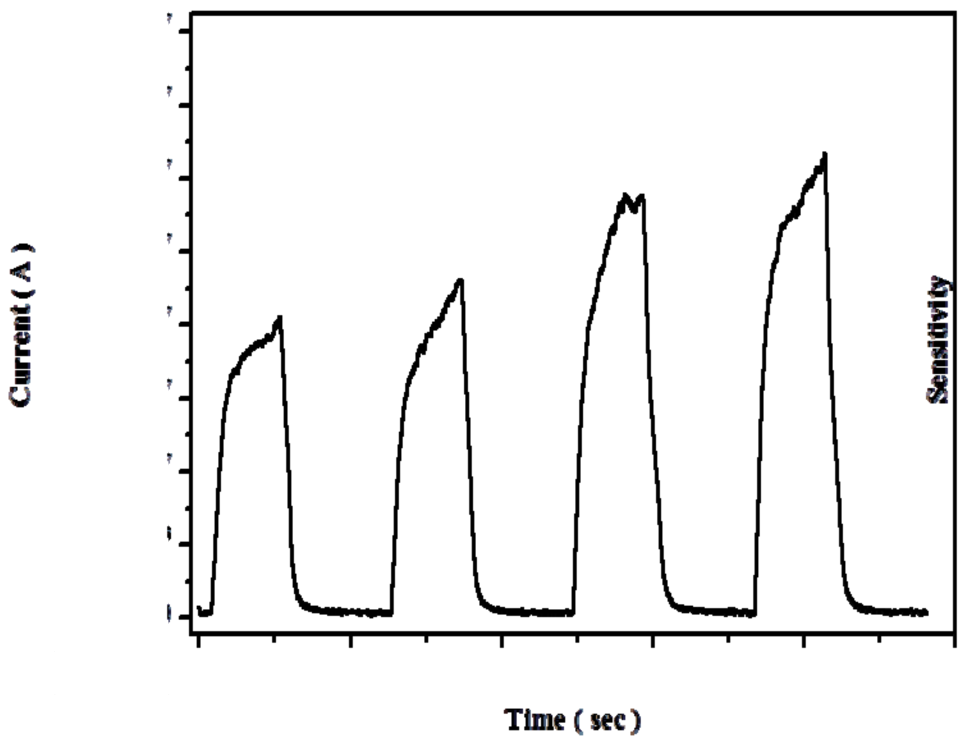


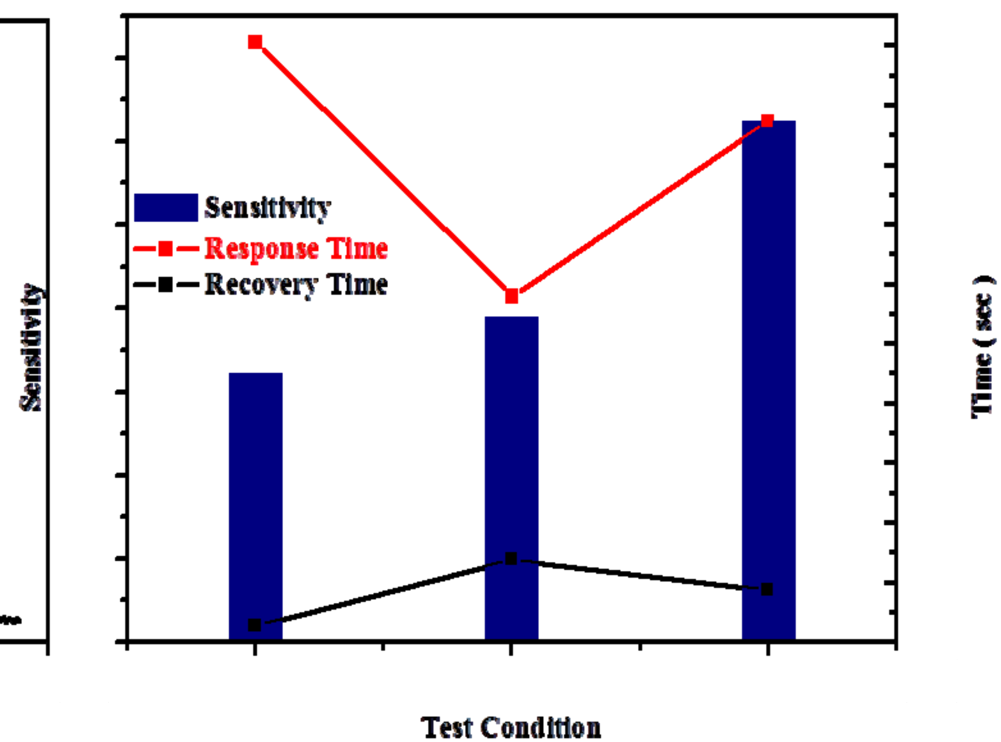
Lin, et al., 2015, to be submitted.

Photocurrent Module:

Perovskite decorated Ga_2O_3 nanowire CO sensors

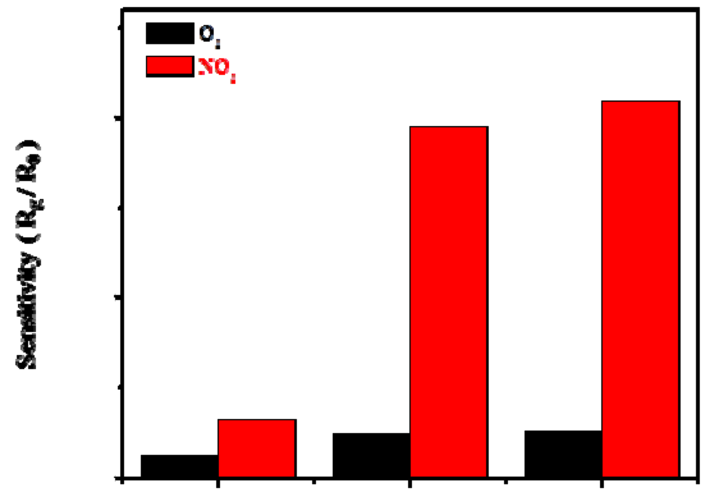
- UV excitation induced current enhancement
- UV excitation and perovskite nanoparticle enhanced response and recovery in CO detection at high temperature





Lin, et al., 2015, to be submitted.

Selective Resistance Module:
Perovskite decorated Ga_2O_3 nanowire sensors (I)

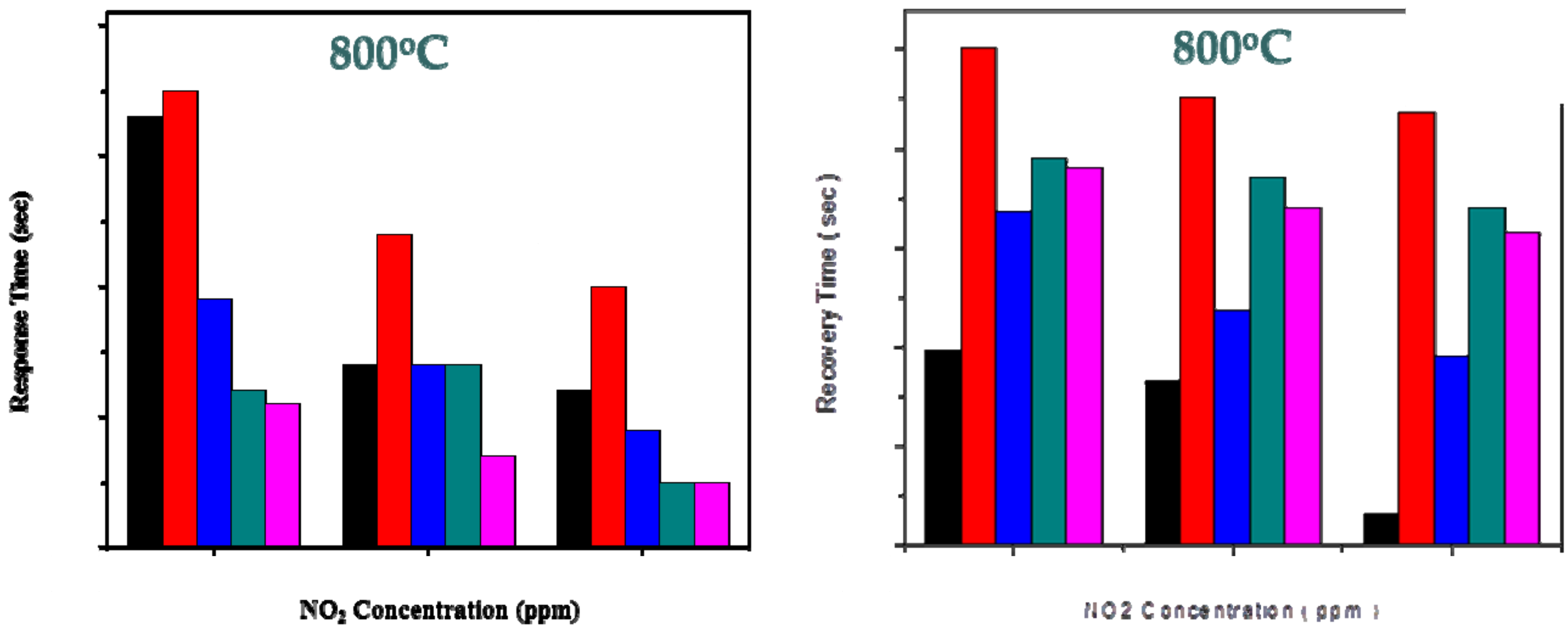


- Trace decoration of perovskite nanoparticles on Ga_2O_3 nanorod arrays.
- Enhanced NO_2 differentiation from O_2 using perovskite nanoparticles at high temperature.

Lin, et al., **2015**, to be submitted.

Selective Resistance Module:

Perovskite decorated Ga_2O_3 nanowire NO_2 sensors (II)



- Trace decoration of perovskite nanoparticles on Ga_2O_3 nanowire arrays.
- Enhanced NO_2 differentiation from O_2 using perovskite nanoparticles.

Lin, et al., **2015**, to be submitted.

Future work

1) Growth of selective metal oxide and nitride based heterostructured nanowire arrays.

2) Decoration of metal and perovskite nanoparticles on selective nanowire array sensors.

3) Continuing of the structure, morphology and stability characterization of nanowire array sensors

4) Design and validation of nanowire array sensors with multiple sensing modes.

Acknowledgement

- Postdocs: Drs. Yanbing Guo, Haiyong Gao

  Graduate students: Hui-Jan Lin, Bo Zhang, Xiangchen Sun, Yixin Liu
- Co-PI: Prof. Yu Lei (UConn)
- Collaborators: Drs. Paul Ohodnicki, John Baltrus (NETL); Dr. Chang-Yong Nam (BNL), Dr. Jie Zheng (UT Dallas)
- DoE/NETL project manager: Rick Dunst
- Funding: DoE/NETL; NSF, and UConn Research Foundation