Strategies to enhance the selectivity in high temperature gas sensing

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Outline

Background

Research Objective

Strategies to Improve the High Temperature Gas Sensing Selectivity

Conclusions and Outlook

Backgound

Importance of Harsh Environment Gas Sensors

Environment & Energy Concerns

- Better control of **combustion**
- Reduction of **emissions** (CO, NO_x, SO_x, HCs) ➡ less environmental problems
- Improvement of **energy efficiency** ➡ more energy savings

❖ **Contribution from HTGS and Controls**

Value Derived for an Existing Coal Fired Power Plant

FUEL COSTS
$39 Million/Year ➡

➡ **Gaseous Emissions**

➡ **POWER**
3,285,000,000 kw-hr/yr
@75% Capacity Factor

➡ **Solid Wastes**

Total Fuel + O&M Budget $45 Million - Avg. 500 MW Unit (Analysis for 2000)

➢ **1% improvement in EFFICIENCY**

- $390,000 savings in fuel per year
- $4.1 million for entire installed fossil capacity

600

➢ **1% REDUCTION in greenhouse gases and solid wastes**

DOE prediction:

Energy savings per year

0.25 quadrillion BTU

- 11 million tons of coal
- 250 billion cubic feet of natural gas
- 43 million barrels of crude oil

* NETL Sensors and Controls Program Overview, 2012.

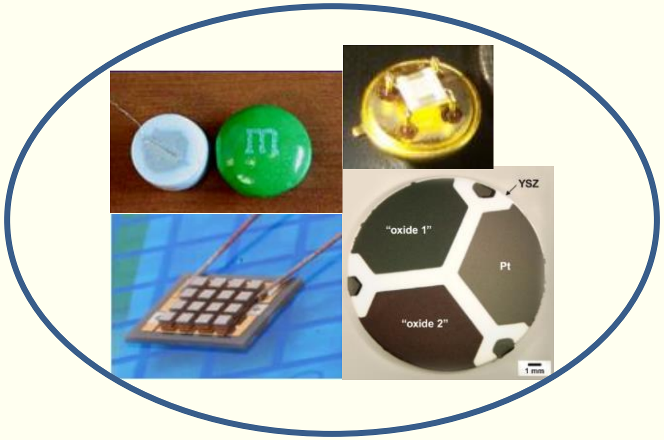
Backgound

Sensors for Harsh Environments

Solid Oxide Fuel Cells
- 650 – 1000 ^{o}C
- Atmospheric pressure

Advanced Combustion Turbines
- Up to 1300 ^{o}C combustion temperatures
- Pressure ratios of 30:1

Automotive Engine
- up to 1000 ^{o}C
- Compression ratio ~10:1



Ultra Supercritical Boilers
- Up to 760 ^{o}C temperature
- Up to 5000 PSI pressure

Gasifiers
- Up to 1600 ^{o}C, and 1000 PSI (slagging gasifiers)
- Erosive, corrosive, highly reducing environment

[1] PPT-National energy technology laboratory-Development of harsh environment sensor platform for fossil energy applications, 2008

Backgound

Sensors for Harsh Environments

❖ **Applications** — **Harsh Industrial Environment**

- Heat treating
- Glass & Ceramic
- Automotive
- Aerospace
- Pulp and paper
- Utility and power
- Metal processing and casting
- Chemical and petrochemical
- Food processing

Table 1. Example of exhaust conditions for two- and four-stroke, diesel and lean-four-stroke engines

Exhaust components and conditions [a]	Diesel engine	Four-stroke spark ignited-engine	Four-stroke lean-burn spark ignited-engine	Two-stroke spark ignited-engine
NO_x / ppm	350–1000	100–4000	≈ 1200	100–200
HC / ppm C	50–330	500–5000	≈ 1300	20,000–30,000
CO	300–1200 ppm	0.1–6%	≈ 1300 ppm	1–3%
O_2	10–15%	0.2–2%	4–12%	0.2–2%
H_2O	1.4–7%	10–12%	12%	10–12%
CO_2	7%	10–13.5%	11%	10–13%
SO_x / ppm	10–100	15–60	20	≈ 20
Temperatures / ^{o}C	r.t.–650 (r.t.–420)	r.t.–1100 [b]	r.t.–850	r.t.–1000
λ (A/F) [c]	≈ 1.8 (26)	≈ 1 (14.7)	≈ 1.16 (17)	≈ 1 (14.7)

~1000 °C
Automobile Engine

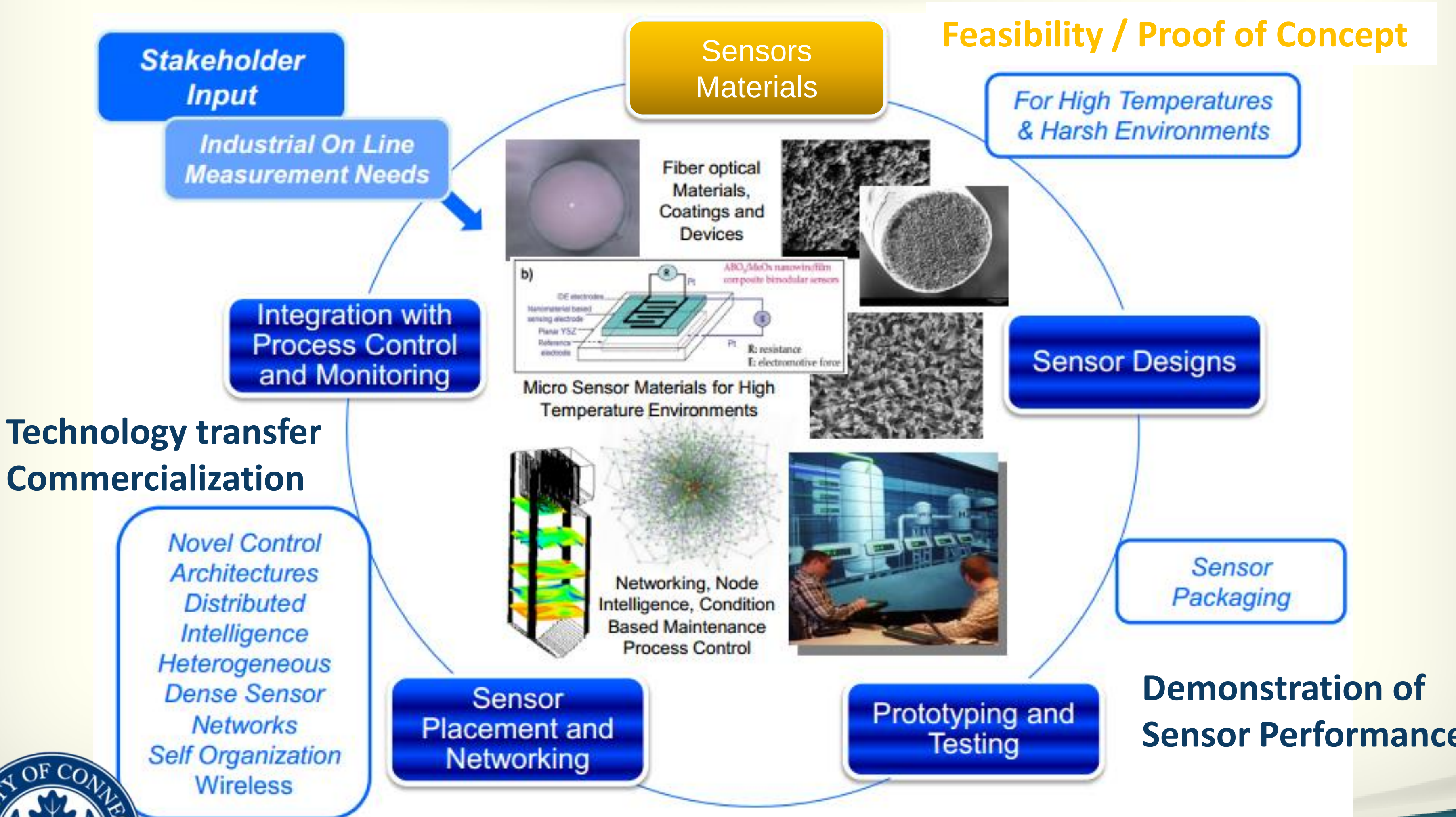
Up to 1300 °C
Advanced Combustion Turbines

650 - 1000 °C
Solid Oxide Fuel Cell

[1] J. Kaspar, P. Fornasiero, and N. Hickey, *Automotive catalytic converters: current status and some perspectives*. Catalysis Today, 2003, **77**, 419.

Backgound

Research in Sensors and Controls



* NETL Sensors and Controls Program Overview, 2012.

Backgound

Current Solid-State Sensing Technologies

Potentiometric
- Commercialized O_2 sensor (Zirconia)
- CO_2, SO_x (K_2CO_3, Ag_2SO_4) at mild T

Amperometric
- Diffusion limited current (linear)
- O_2, H_2, CO, NO_x, SO_2, H_2S

Mixed Potential
- Thermodynamic non-equilibrium
- More than one electrochemical reaction occurs
- The oxidation and reduction reactions are for different species
- CO, NO_x, HCs in 500 – 600 ^oC

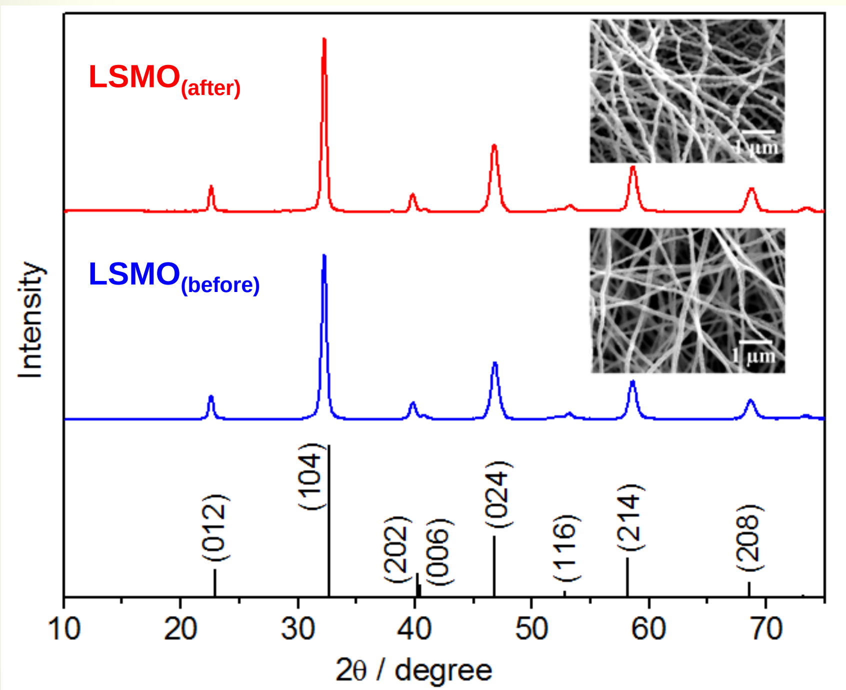
Resistive
- **Bulk conduction-based**
  O_2 at 700 – 1100 ^oC
- **Surface conduction-based**
  CO, HCs, H_2, NO_x in 200 – 500 ^oC
- **Metal/oxide junction based**
  MS/MIS, MOSFET, Schottky diodes

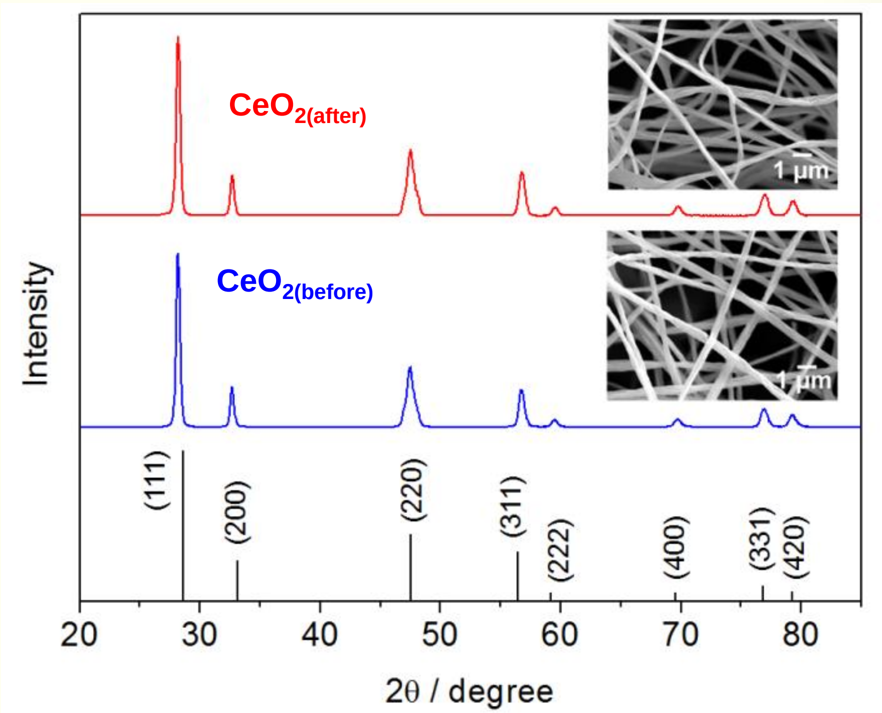
Impedancemetric
- AC measurements at a specified F
- Solid-electrolyte or resistor configured
- H_2O, CO, HCs, NO_x
- Measure total NO_x concentration
- Accurate detection on single ppm level

* **Yixin Liu**, et al., Solid-State Gas Sensors for High Temperature Application - A Review, *J Mater. Chem. A*, 2014, **DOI:** 10.1039/C3TA15008A

Easy to achieve highly stable and highly sensitive high temperature gas sensor

- Multiple cycles of heating/cooling treatment

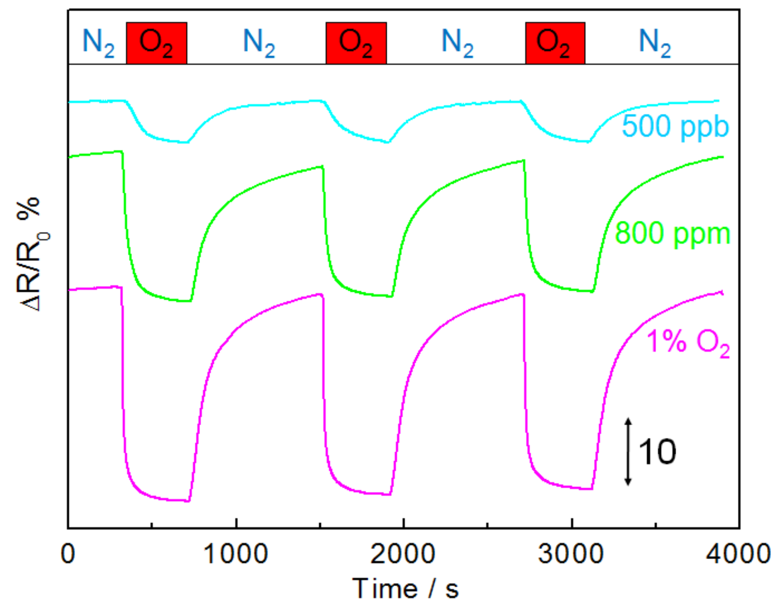


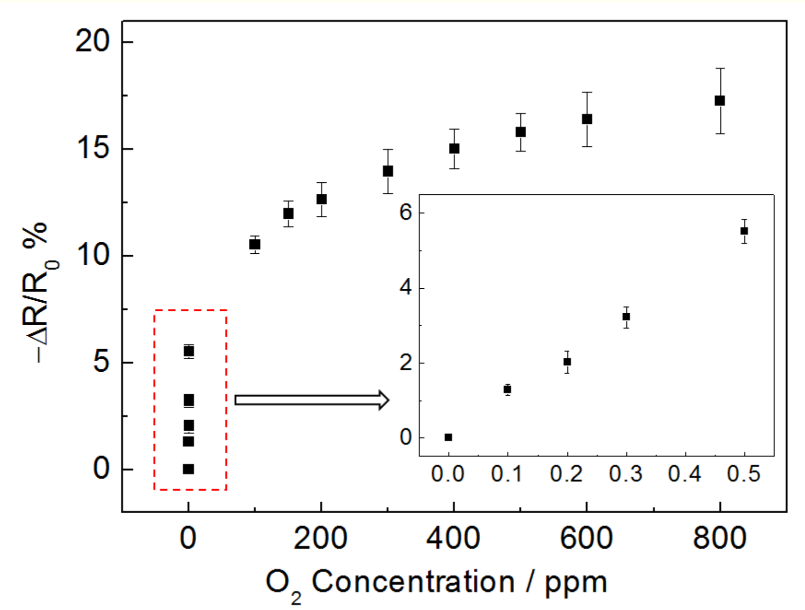


* **Yixin Liu**, et al., *RSC Advances*, 2012, 2, 3872-3877.
Yixin Liu, et al., *RSC Advances*, 2012, 2, 5193-5198.

Easy to achieve highly stable and highly sensitive high temperature gas sensor

LSMO NFs for O_2 Sensing at 800 °C



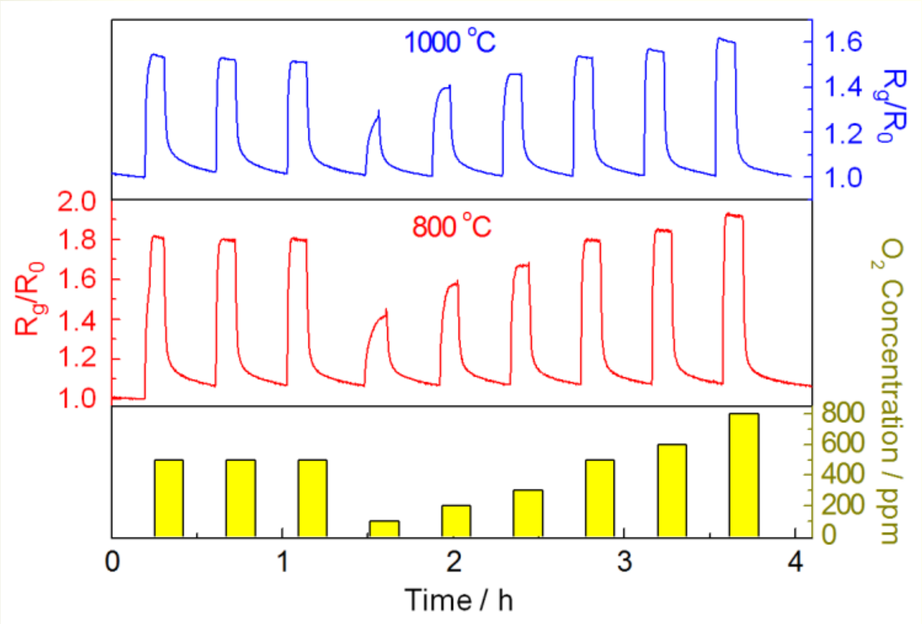


LSMO (p-type): R ↓ upon exposure to O_2

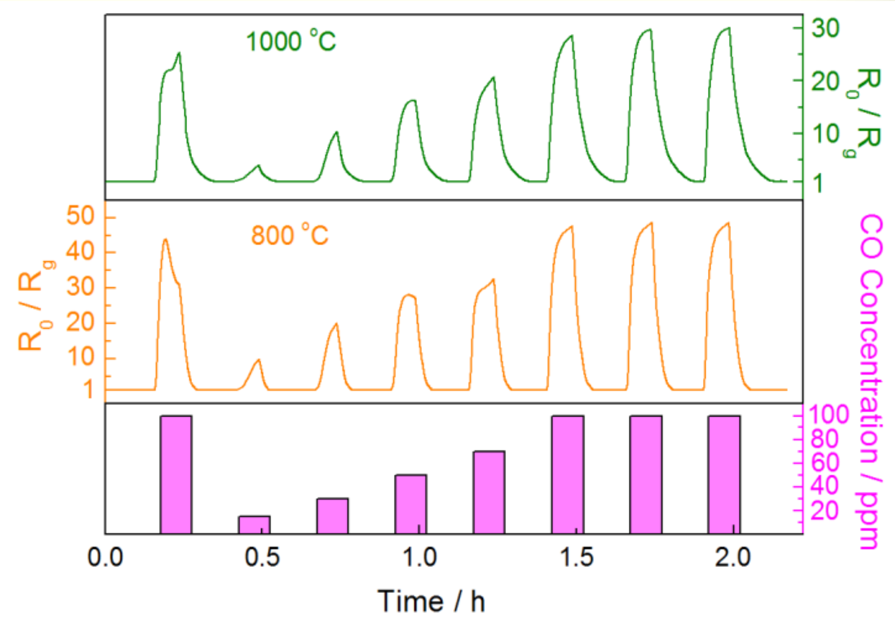
* **Yixin Liu**, et al., *RSC Advances*, 2012, 2, 3872-3877.
Yixin Liu, et al., *RSC Advances*, 2012, 2, 5193-5198.

CeO_2 NFs for O_2 and CO Sensing at 800 and 1000 °C

Oxygen sensing



CO sensing



CeO_2 (n-type):

R ↑ upon exposure to O_2

R ↓ upon exposure to CO

- **Sensitivity:**
  - In O_2 (oxidizing gas): R_g/R_0
  - In CO (reducing gas): R_0/R_g

  R_0 - initial resistance in N_2

  R_g - measured real-time resistance

✓ **Fast response**

✓ **Good recovery**

✓ **Good reproducibility**

✓ **High sensitivity**

* **Yixin Liu**, et al., CeO_2 nanofibers for in-situ O_2 and CO sensing in harsh environment, *RSC Advances*, 2012, 2, 3872-3877.

Research Objective

- <u>Selectivity</u> is the most pressing issue in high temperature gas sensing field
- Urgent need to develop gas sensors to achieve highly selective detection of gas species and concentration in high-temperature mixed gases environment

Objective

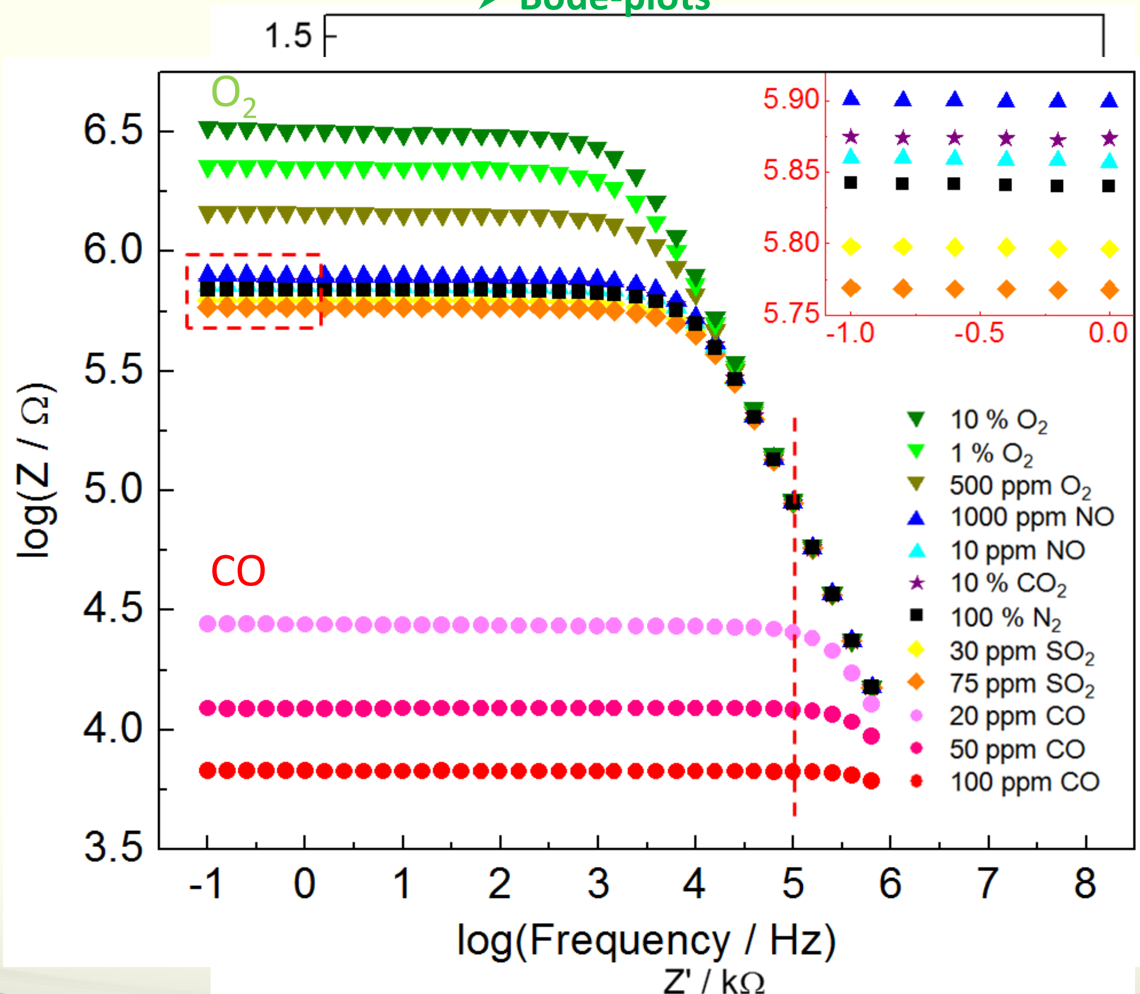
To address selectivity issue in high temperature gas sensing, following strategies are employed:

- Employing unique sensing technology for enhanced selectivity
- Engineering sensing materials for enhanced selectivity
- Developing machine learning algorithms to identify the gas concentration and species

I. Employing unique sensing technology for enhanced selectivity

Pt-CeO_2 NFs Impedancemetric Based Sensor

- ➢ Nyquist plots
- ➢ Bode-plots

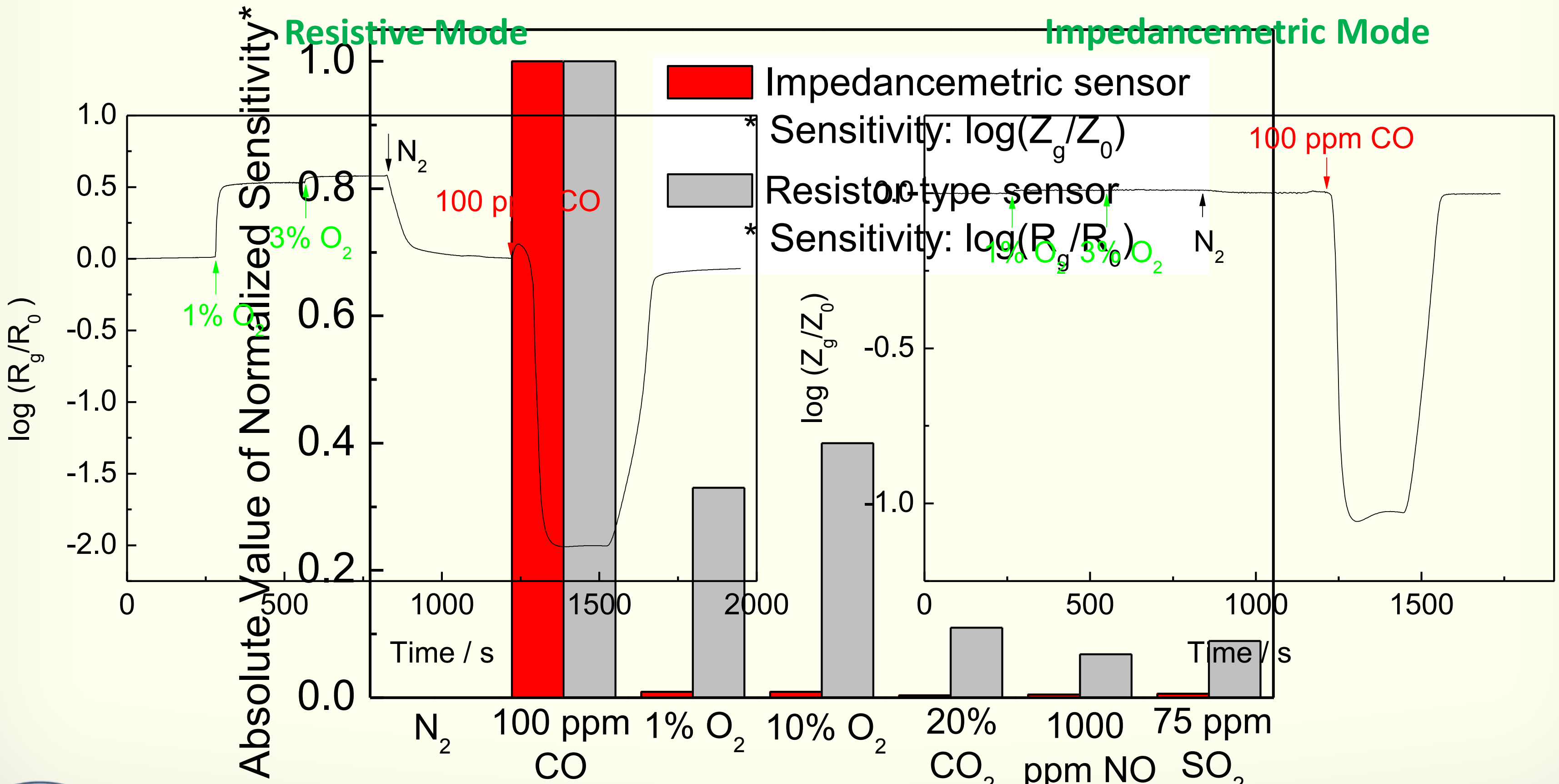


- Initial potential: 0 V
- Amplitude: 0.5 V

* **Yixin Liu** and Y. Lei, Pt-CeO_2 nanofibers based high-frequency impedancemetric gas sensor for selective CO and C_3H_8 detection in high-temperature harsh environment, *Sens. Actuators B*, 2013, 188, 1141-1147.

I. Employing unique sensing technology for enhanced selectivity

Pt-CeO_2 NFs Impedancemetric Based Sensor



* **Yixin Liu** and Y. Lei, Pt-CeO_2 nanofibers based high-frequency impedancemetric gas sensor for selective CO and C_3H_8 detection in high-temperature harsh environment, *Sens. Actuators B*, 2013, 188, 1141-1147.

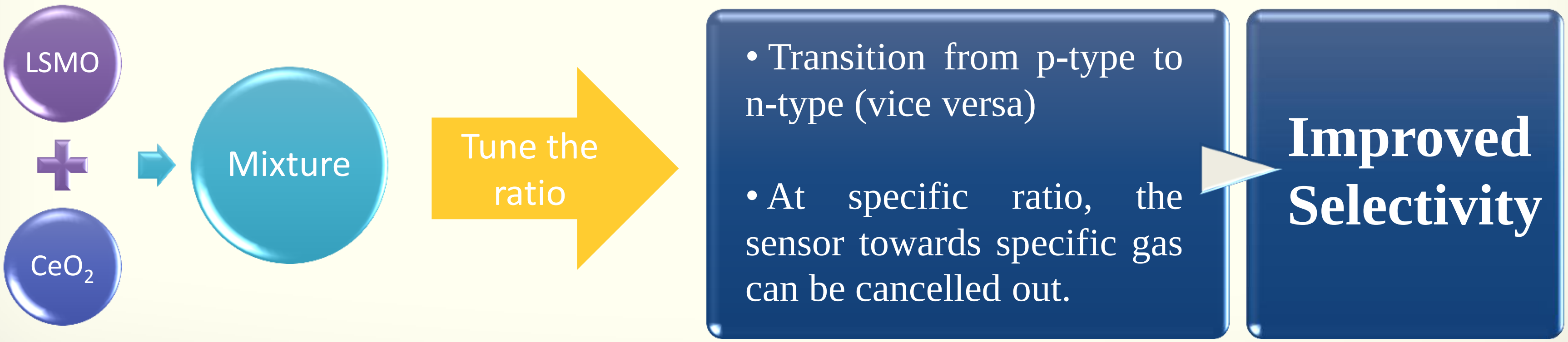
II. Engineering sensing materials for enhanced selectivity

p-LSMO/n-CeO_2 NFs heterojunction Based Sensor

❖ **Properties of LSMO (p-type) and CeO_2 (n-type)**

Material	Type	Charge carrier	Resistance	In reducing gas	In oxidizing gas
LSMO	p-type	Holes	Low	R ↑	R ↓
CeO_2	n-type	Electrons	High	R ↓	R ↑

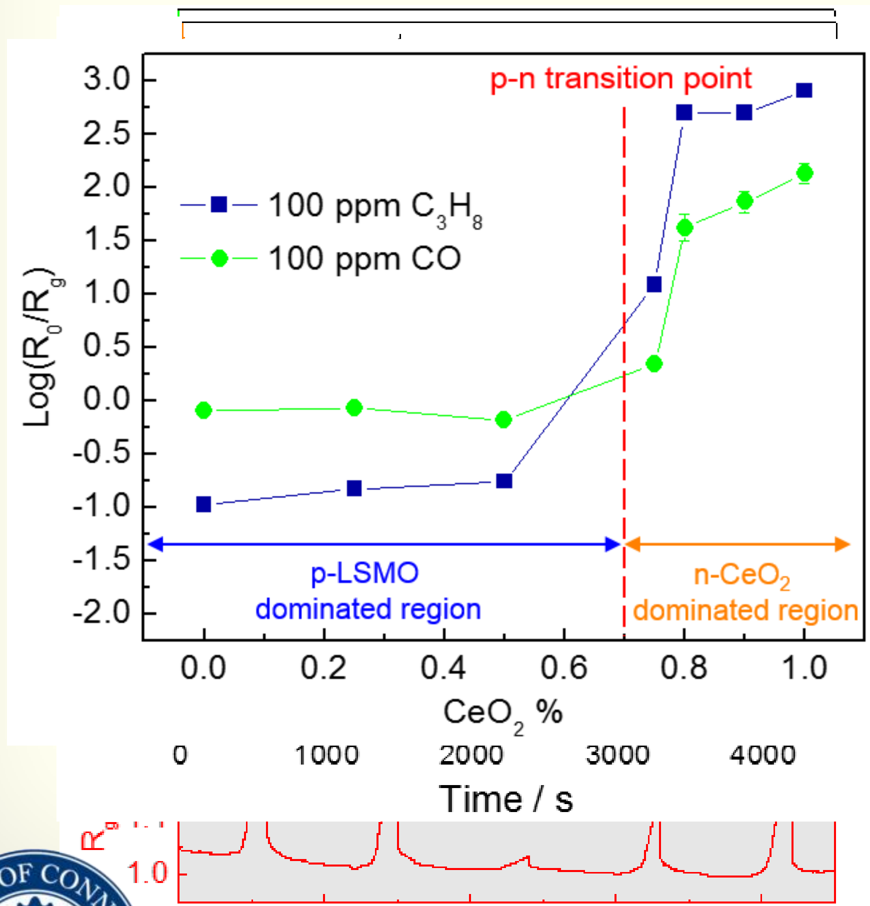
❖ **Rationale**



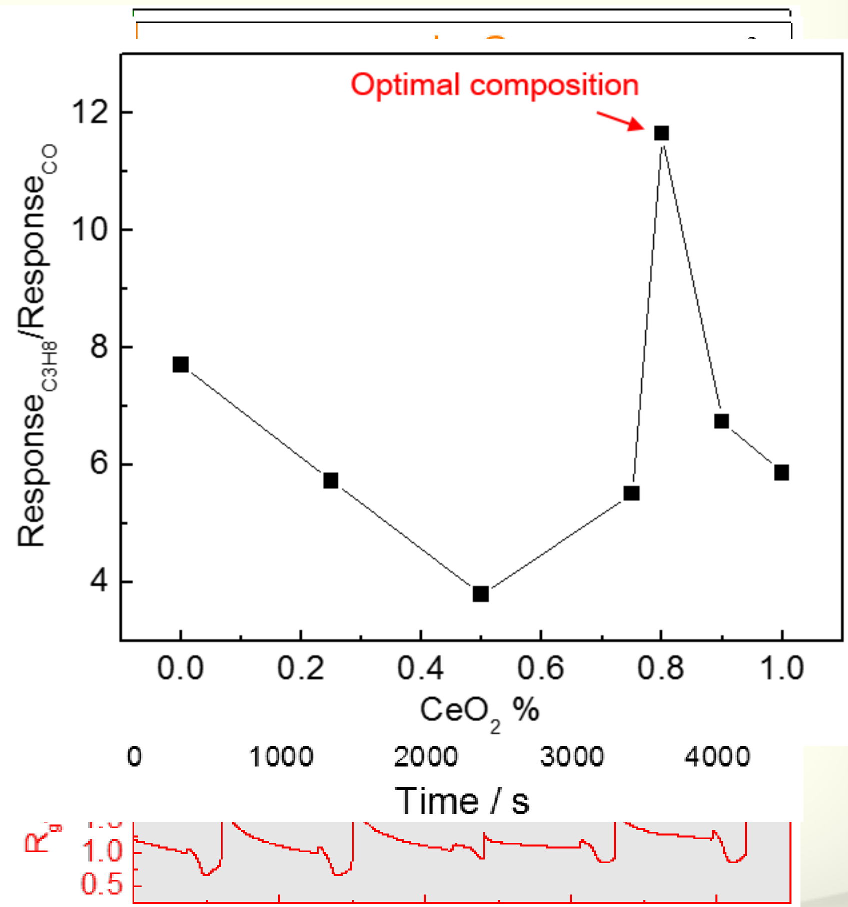
II. Engineering sensing materials for enhanced selectivity

p-LSMO/n-CeO_2 NFs heterojunction Based Sensor

CO detection



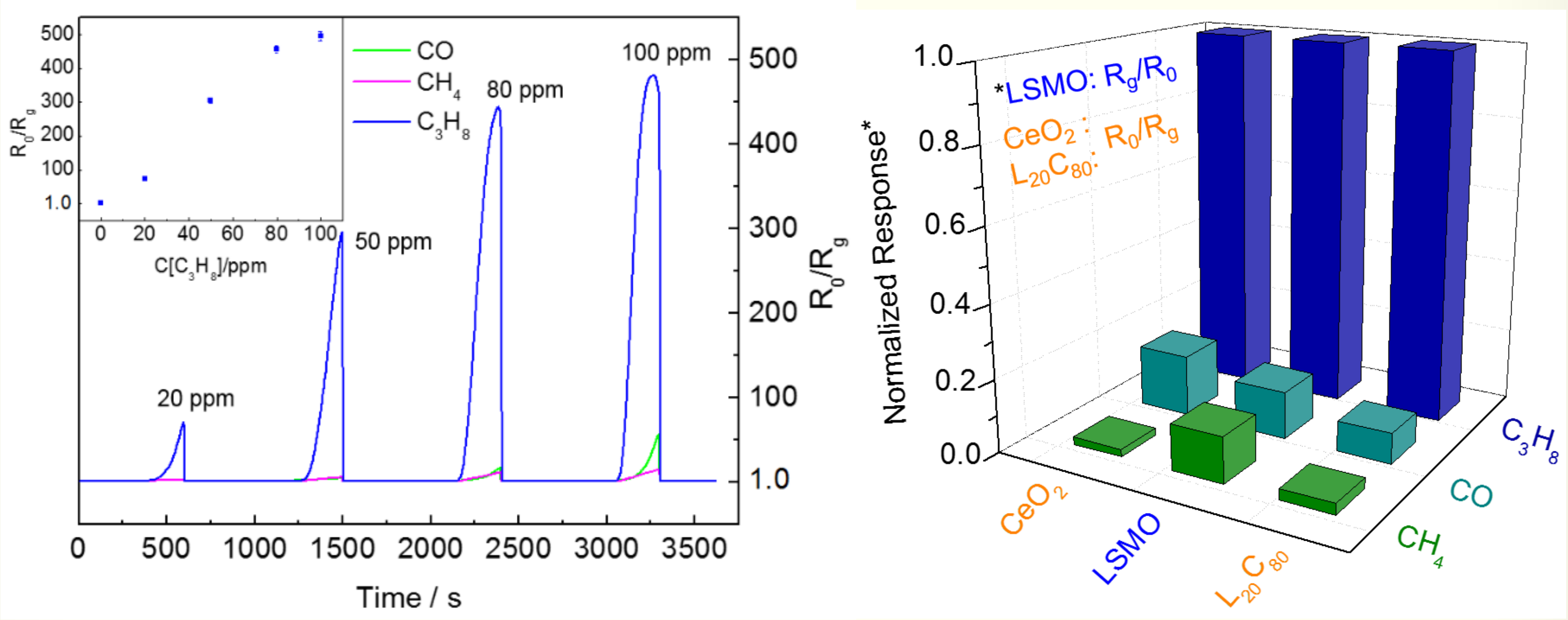
Propane detection



* **Yixin Liu**, et al., Tunable p-n transition behavior of p-$La_{0.67}Sr_{0.33}MnO_3$/n-CeO_2 nanofibers heterojunction for the development of highly selective high temperature propane sensors, *J. Mater. Chem. A*, 2014.

II. Engineering sensing materials for enhanced selectivity

p-LSMO/n-CeO_2 NFs heterojunction Based Sensor



Real-Time Detection on $L_{20}C_{80}$ – Based Sensor

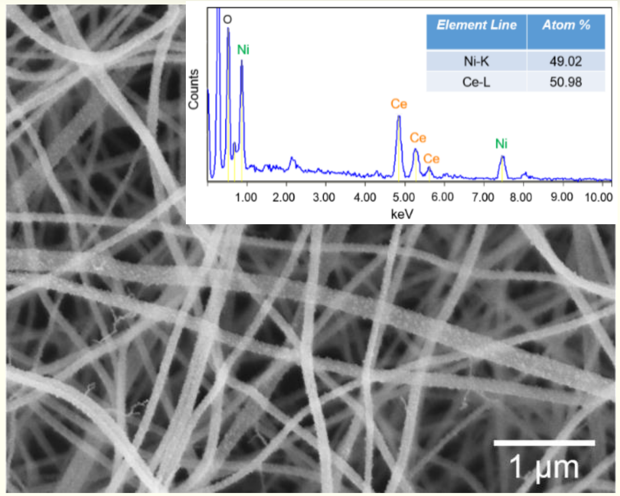
* **Yixin Liu**, et al., Tunable p-n transition behavior of p-$La_{0.67}Sr_{0.33}MnO_3$/n-CeO_2 nanofibers heterojunction for the development of highly selective high temperature propane sensors, *J. Mater. Chem. A*, 2014.

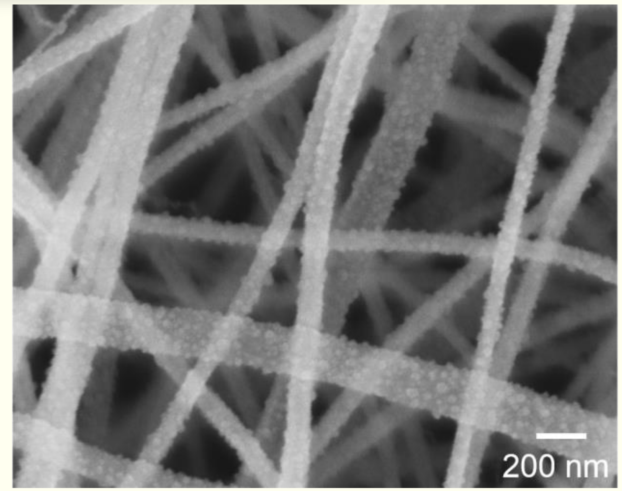
II. Engineering sensing materials for enhanced selectivity

Ce-Ni-O NFs Based Sensor

Nanofiber
d ~ 89 ± 10 nm

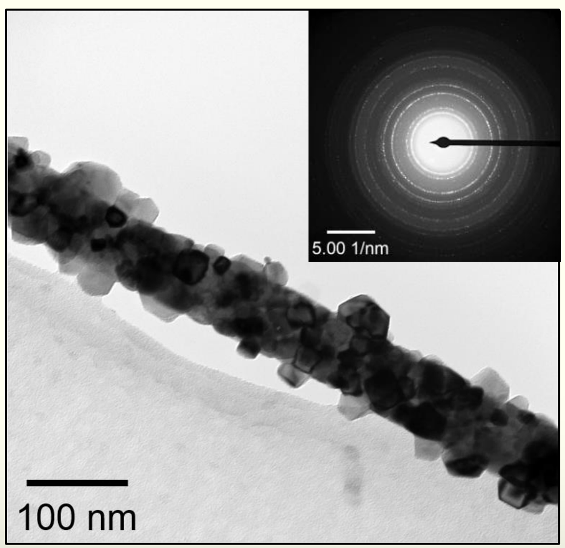
Nanobelt
d ~ 176 nm

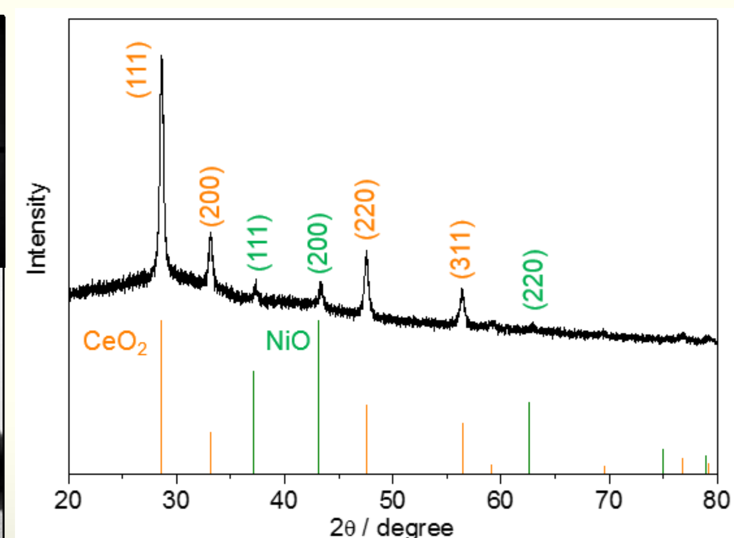




Nanofiber
d ~ 80 nm

Nanoparticles
d ~ 25 ± 7 nm

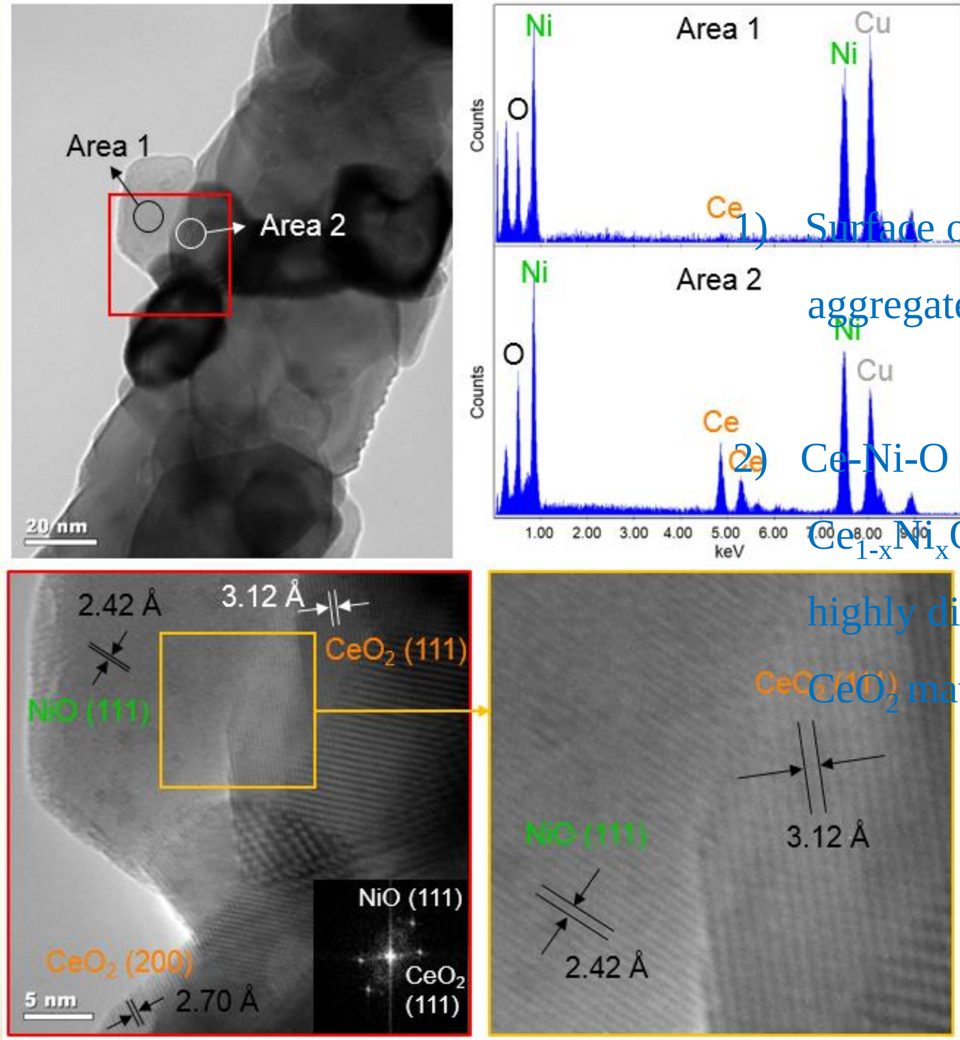




* **Yixin Liu**, et al., Electrospun Ce-Ni-O Composite Nanofibers for Highly Selective Propane Detection at High Temperature Based on Its Rapid Reaction Mechanism, *J. Mater. Chem. A*, 2014.

II. Engineering sensing materials for enhanced selectivity

Ce-Ni-O NFs Based Sensor

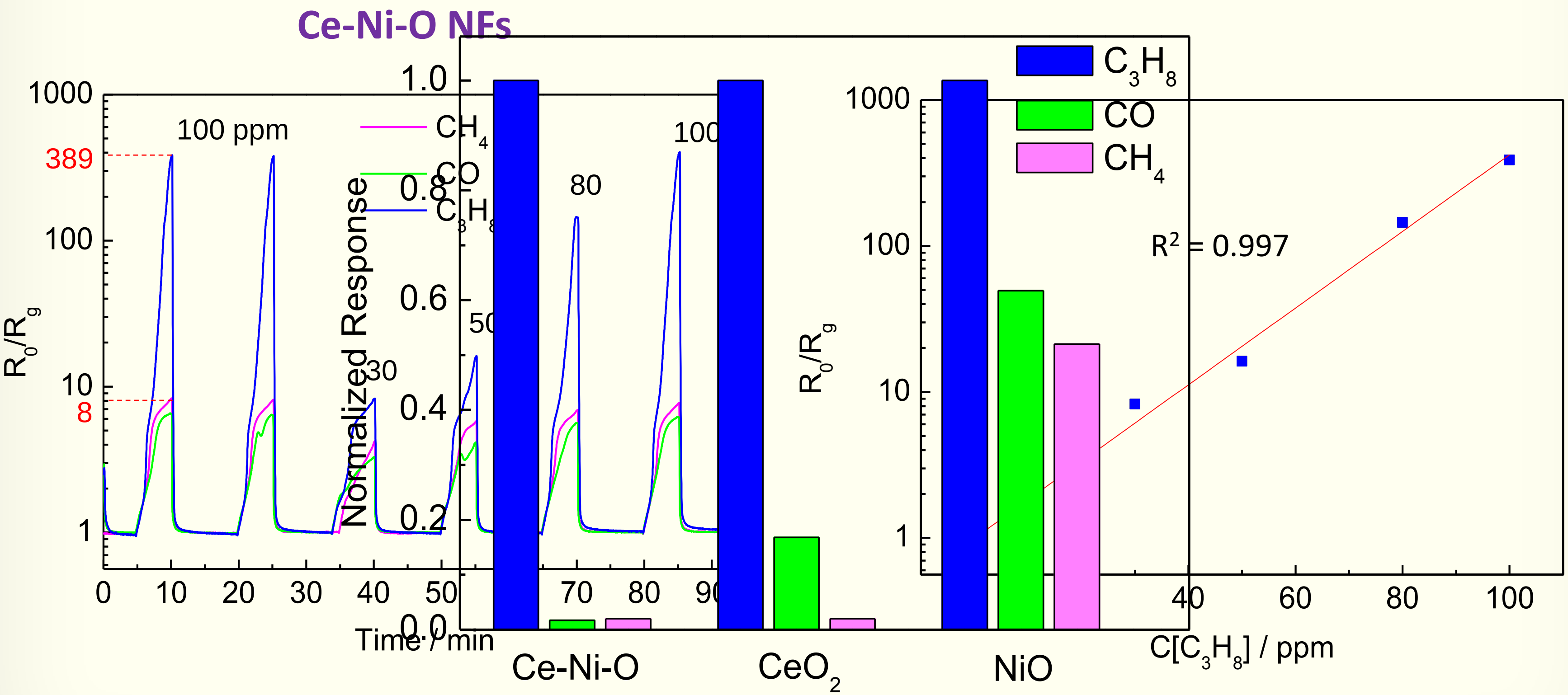


1) Surface of nanofibers:
   aggregated NiO nanoparticles

2) Ce-Ni-O backbone:
   $Ce_{1-x}Ni_xO_2$ solid solution
   highly dispersed NiO
   CeO_2 matrix

II. Engineering sensing materials for enhanced selectivity

Ce-Ni-O NFs Based Sensor



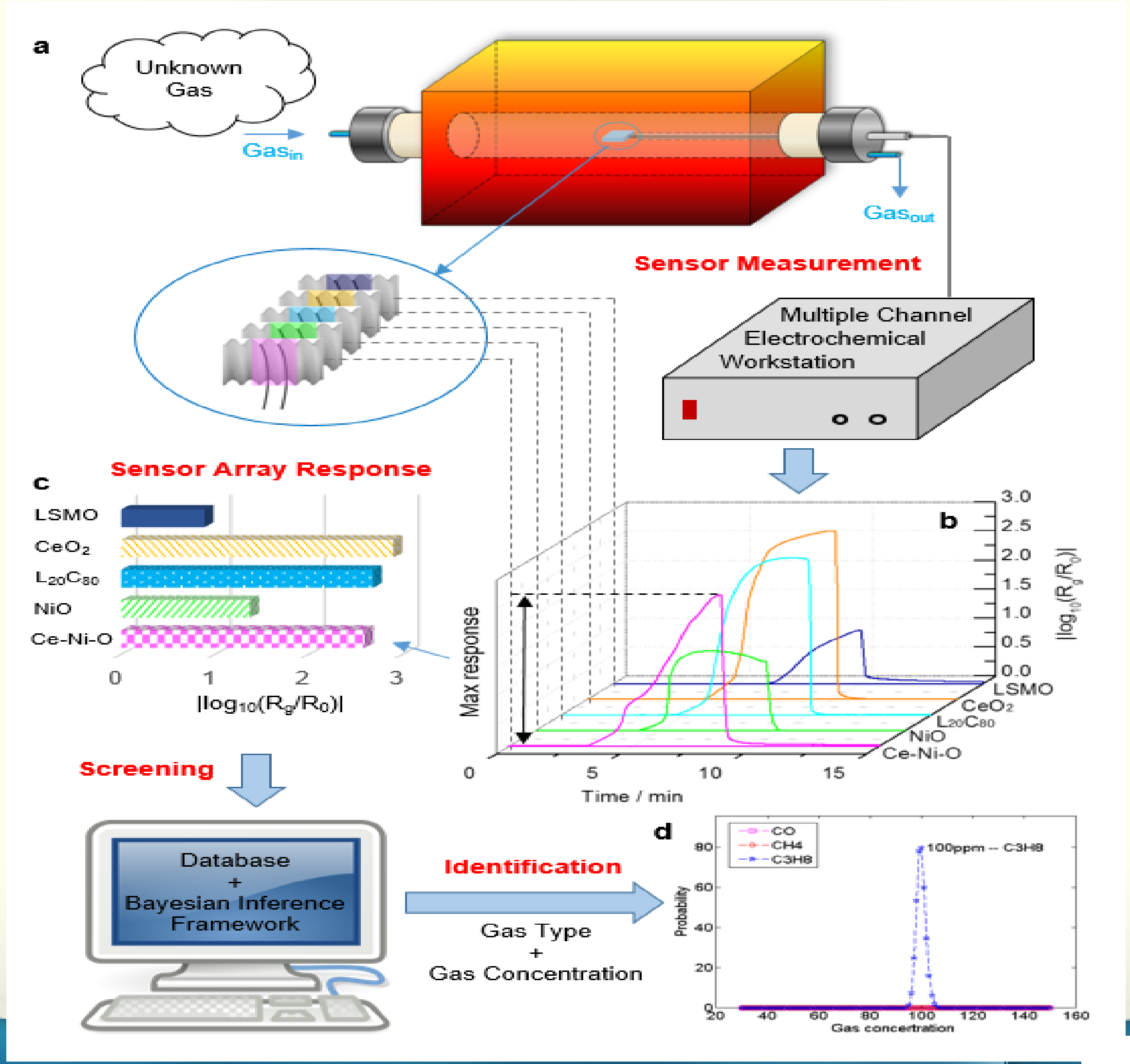
* **Yixin Liu**, et al., Electrospun Ce-Ni-O Composite Nanofibers for Highly Selective Propane Detection at High Temperature Based on Its Rapid Reaction Mechanism, *J. Mater. Chem. A*, 2014.

III. Developing machine learning algorithms to identify the gas concentration and species

Why to develop advanced machine learning algorithms for improved identification of target species and concentration?

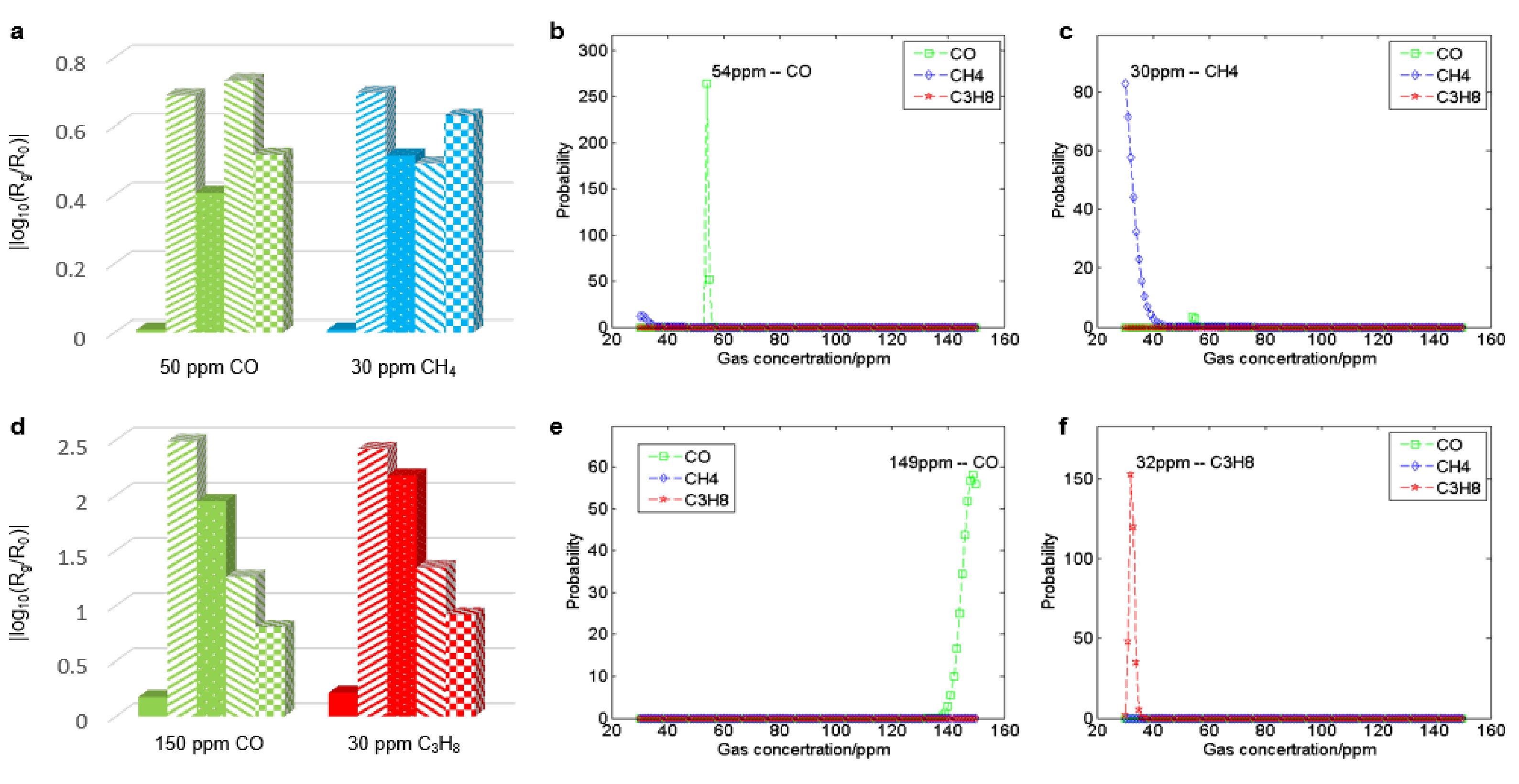
- A sensor array could provide a specific and unique response patterns (fingerprints) for different individual chemical species or mixtures of species.
- With subsequent data analysis, the gas sensor array could be used to qualitatively identify gas species using pattern recognition approaches and quantitatively determine gas composition based on learning and regression methods.
- We can think of a learner as an entity that tries to guess a concept or function. Let this function be $f(x_1, x_2, \ldots, x_n)$ where $x_1, x_2, \ldots, x_n$ are the underlying variables. A learner is supplied with examples. An example is nothing but a specific assignment of values to the variables and the corresponding value of the function.
- After having seen a sufficient number of examples, the learner comes up with an estimate of the function. In general the estimate may not be the same as f but possibly a close approximation to f.

III. Developing machine learning algorithms to identify the gas concentration and species



* **Yixin Liu**, et al., *J. Sensors*, 2015.

III. Developing machine learning algorithms to identify the gas concentration and species



The comparison of sensor array response input of a) 50 ppm CO and 30 ppm CH_4, d) 150 ppm CO and 30 ppm C_3H_8. The output of gas identification program for b) 50 ppm CO, c) 30 ppm CH_4, e) 150 ppm CO and f) 30 ppm C_3H_8, respectively.

* **Yixin Liu**, et al., *J. Sensors*, 2015.

III. Developing machine learning algorithms to identify the gas concentration and species

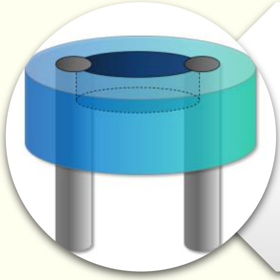
Gas concentration predicted by gas identification program

Gas Type	CO				CH_4				C_3H_8			
Real Conc./ppm	50	80	100	150	30	50	80	100	30	50	80	100
Predicted Conc./ppm	54	72	104	149	30	51	77	101	32	45	81	100

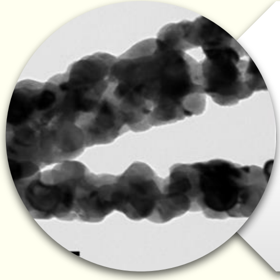
*Conc.: gas concentration.

Conclusions and Outlook

Conclusions



High temperature gas sensors working in harsh exhaust environment are of paramount importance to improve combustion efficiency and control emissions.

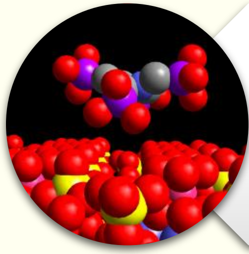


Compared to **stability** and **sensitivity**, **selectivity** is a major issue for high temperature gas sensing.

Three strategies (sensing technology, sensing materials and machine learning algorithm) have been employed to improve the high temperature gas sensing selectivity.

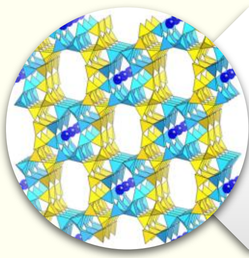
Conclusions and Outlook

Outlook



Fundamental studies for better understanding of sensing mechanisms and the relation between sensing element and sensing properties.

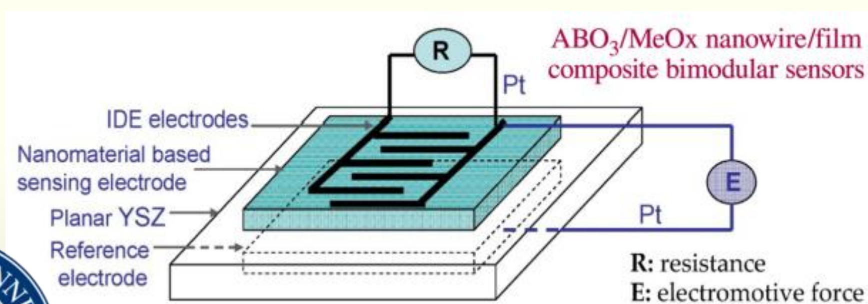
- Modeling and Simulation



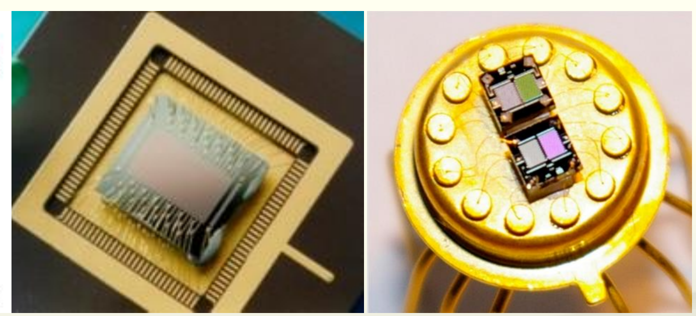
New or improved materials synthesis, novel sensor designs, combination of sensing technologies and advanced device fabrication techniques.

- Sensor array, bi-modular sensor, catalytic/physical filter

Bi-modular Sensor



Sensor Arrays



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- Students: Dr. Yu Ding, Dr. Ying Wang, Dr. Yixin Liu, Dr. Liang Su, Dr. Joseph Parisi, Dr. Xiangcheng Sun, Xiaoyu Ma, Jun Chen, Qiuchen Dong, Sichen Zhang, Sana Alshahrani
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U.S. DEPARTMENT OF ENERGY

Thank You !

Questions ?