Optical Fiber Sensors for Harsh Environment Fossil Energy Applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

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April 11, 2019

Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

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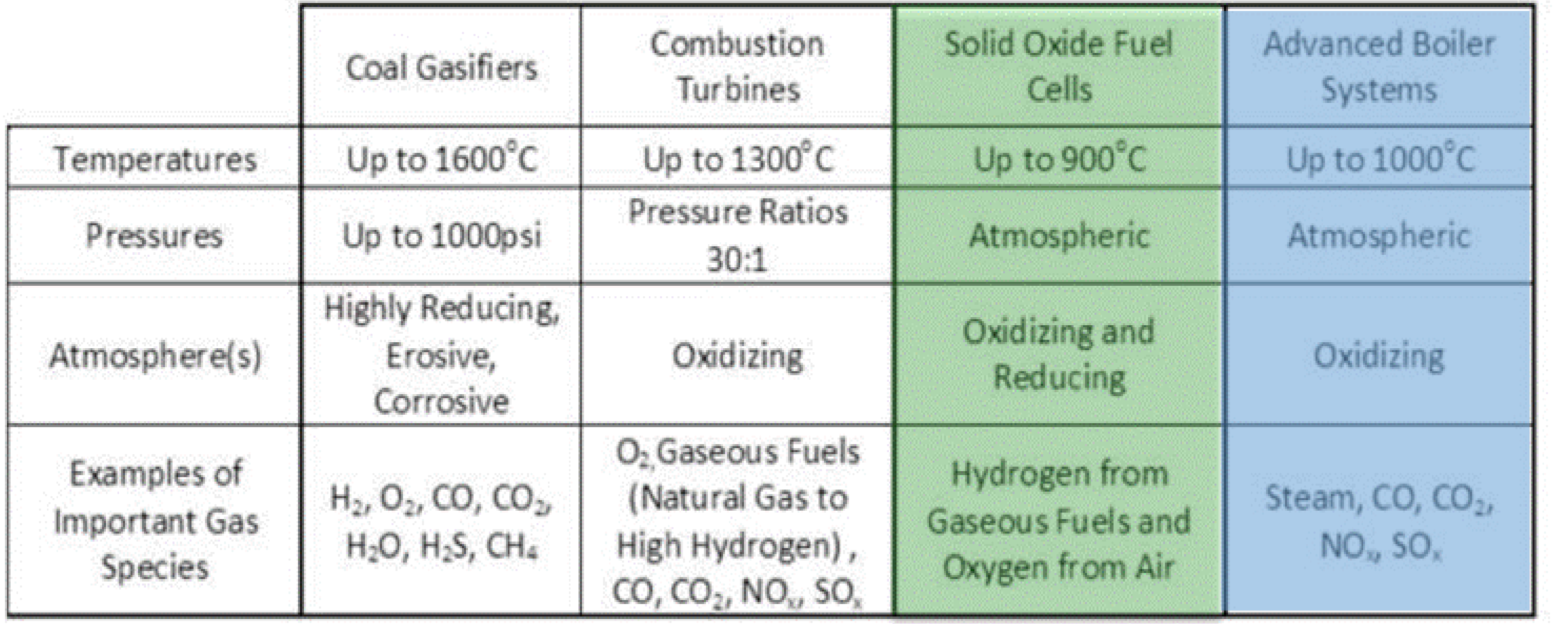
- Juddha Thapa
- Ting Jia

Presentation Overview

- NETL R&IC Sensor Material and Device Program Overview
  - Energy Infrastructure Monitoring Needs Driving Advanced Sensors
  - Enabling Materials for Harsh Environment Sensing
  - Current Capabilities and Research Thrusts
- Highlights of Recent Results and On-Going Activities
  - Summary of Past Key Results
  - Theoretical Modeling of Sensor Materials
  - Au-Nanoparticle Incorporated Conducting Oxides
  - Complex-Oxide Based O_2 Sensing Materials
  - Sapphire Fiber Cladding Research and Development Efforts
  - Custom Sapphire Fiber Distributed Interrogator Technology
  - Recent and Planned Demonstrations in SOFC and Boiler Applications
  - Aqueous Phase Compatible MOF Integrated Sensors for Carbon Storage
  - Distributed Corrosion Sensing for Natural Gas Infrastructure
- Summary and Conclusions

Harsh Environment Sensing for Power Generation

Power Generation
(Combustion, Fuel Cells, Turbines, etc.)

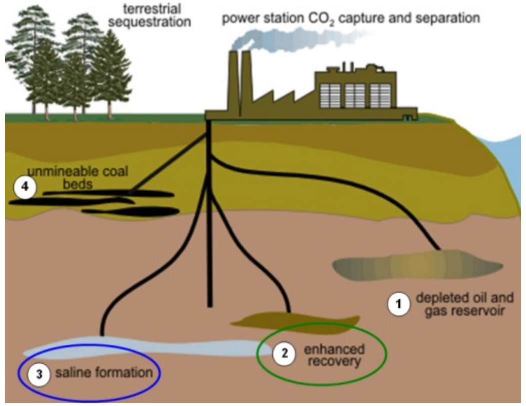


	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
Examples of Important Gas Species	H_2, O_2, CO, CO_2, H_2O, H_2S, CH_4	O_2, Gaseous Fuels (Natural Gas to High Hydrogen) , CO, CO_2, NO_x, SO_x	Hydrogen from Gaseous Fuels and Oxygen from Air	Steam, CO, CO_2, NO_x, SO_x

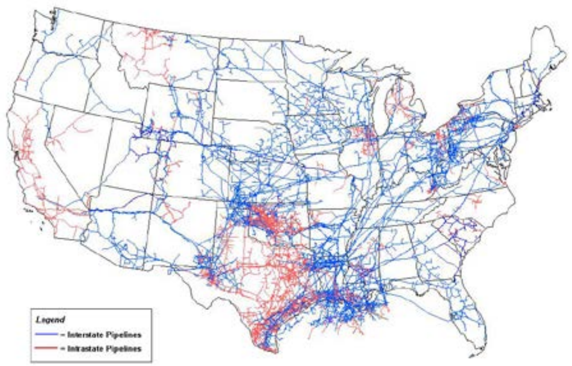
Harsh Environment Sensors are Becoming Increasingly Important for Higher Efficiency, More Flexible, and More Resilient Conventional Power Generation.

Harsh Environment Sensing: Energy Infrastructure Monitoring

CO_2 Sequestration

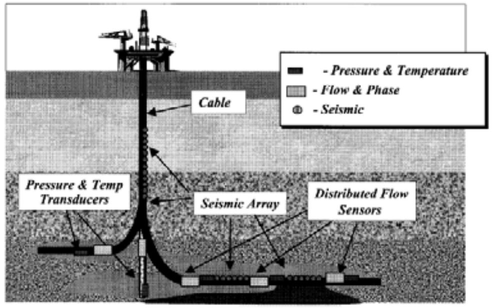


Natural Gas Infrastructure

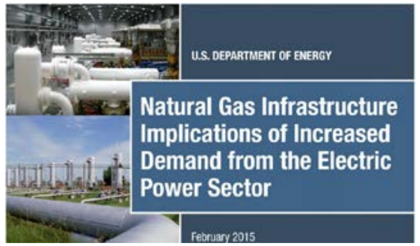


Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

Unconventional Oil & Gas



Properties of Methane	
Chemical Formula	CH4
Lifetime in Atmosphere	12 years
Global Warming Potential (100-year)	28–36



U.S. DEPARTMENT OF ENERGY

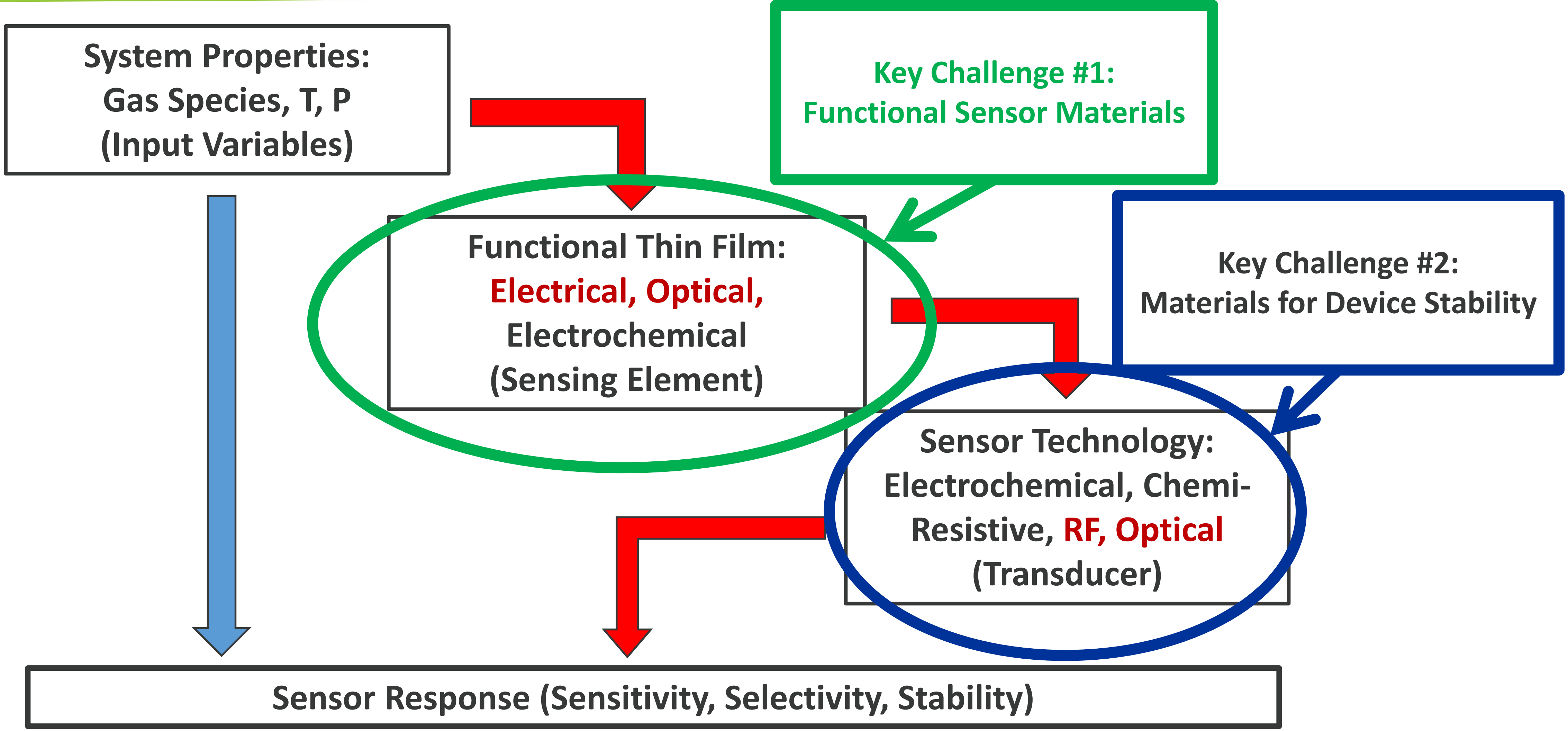
Natural Gas Infrastructure Implications of Increased Demand from the Electric Power Sector

February 2015

Electricity Infrastructure

A More Robust, Safe, and Resilient Energy Infrastructure Requires Greater Visibility Which Can Be Enabled Through Enhanced Sensing and Measurement.

Enabling Harsh Environment Sensor Materials



System Properties:
Gas Species, T, P
(Input Variables)

Key Challenge #1:
Functional Sensor Materials

Functional Thin Film:
Electrical, Optical,
Electrochemical
(Sensing Element)

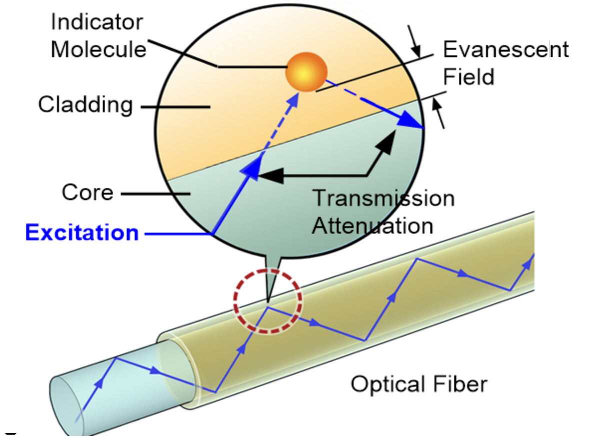
Key Challenge #2:
Materials for Device Stability

Sensor Technology:
Electrochemical, Chemi-Resistive, RF, Optical
(Transducer)

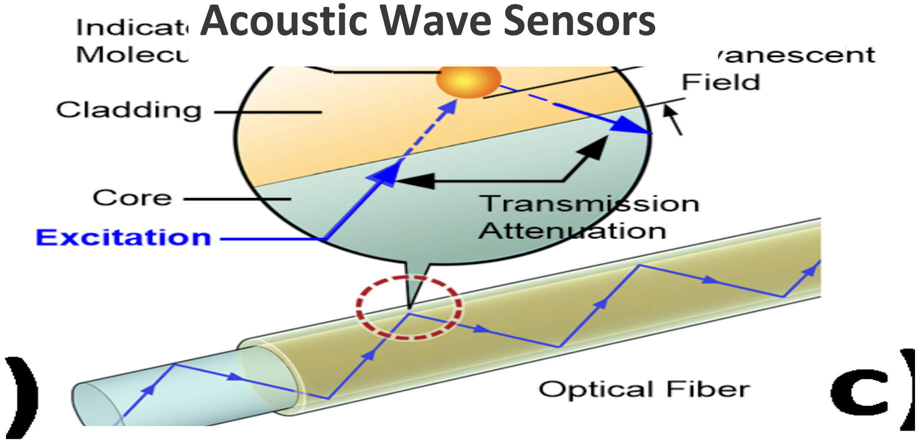
Sensor Response (Sensitivity, Selectivity, Stability)

Selected Embedded Sensor Technology Platforms

Functionalized Optical Fiber Sensors



Functionalized Surface Acoustic Wave Sensors



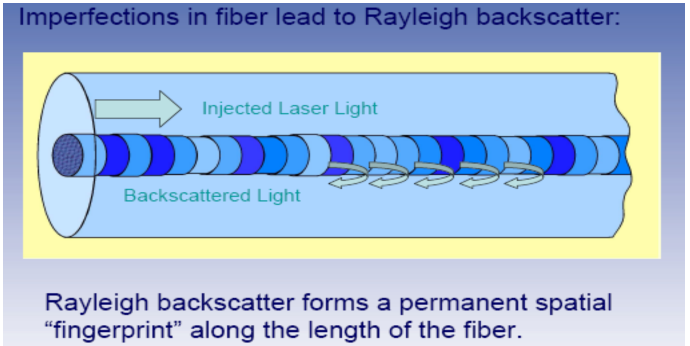
- Elimination of Electrical Wires, Contacts, and Power at Sensor
- Multifunction Capability to Maximize Value Per Sensor Node
- Potential for Low Cost and Harsh Environment Compatibility

	Geospatial Attributes	Cost	Cybersecurity
Distributed Optical Fiber Sensors	Linear Sensor Adjustable Distance and Resolution	Cost Per Sensor "Node" Low	Inherently Secure
Passive Wireless Sensors	Point Sensor	Low	Requires Precautionary Measures

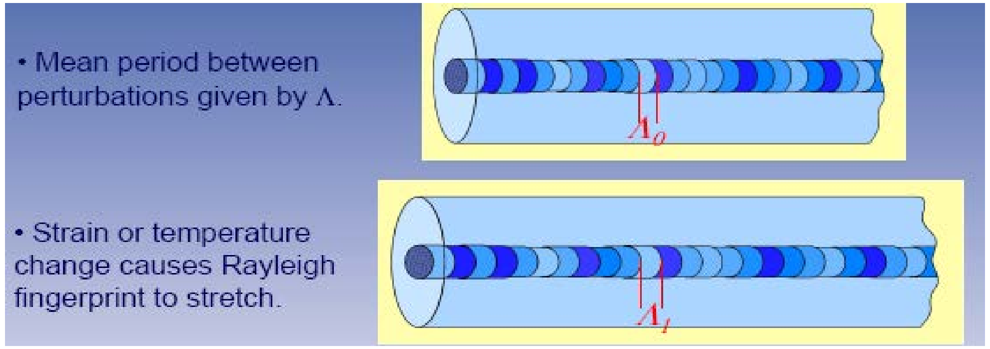
Two Technology Platforms Have Shown Unique Promise for Harsh Environment, Embedded Sensing Applications with Potential for Functionalization to Key Parameters of Interest

Focus #1 : Optical Fiber Based Sensors

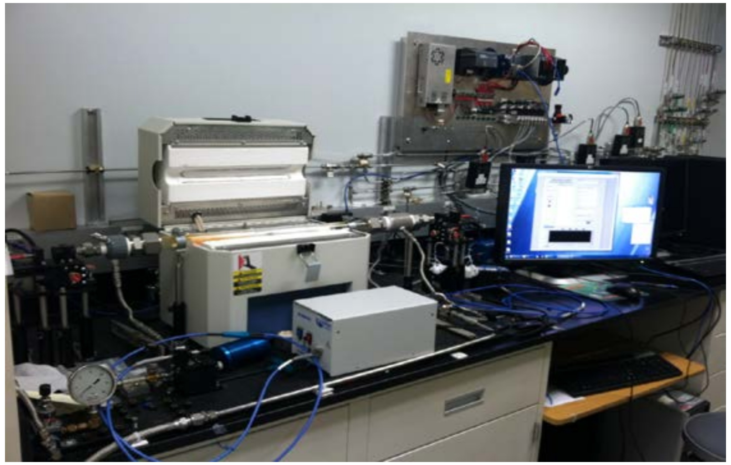
Optical Backscattering Reflectometry, Distributed Sensing in Extreme Environments

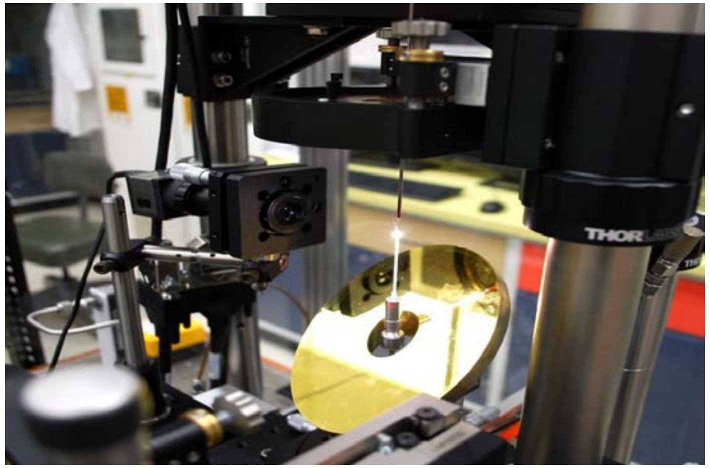

Imperfections in fiber lead to Rayleigh backscatter:

Rayleigh backscatter forms a permanent spatial "fingerprint" along the length of the fiber.


- Mean period between perturbations given by Λ.
- Strain or temperature change causes Rayleigh fingerprint to stretch.

Automated Sensor Development Testing Reactors



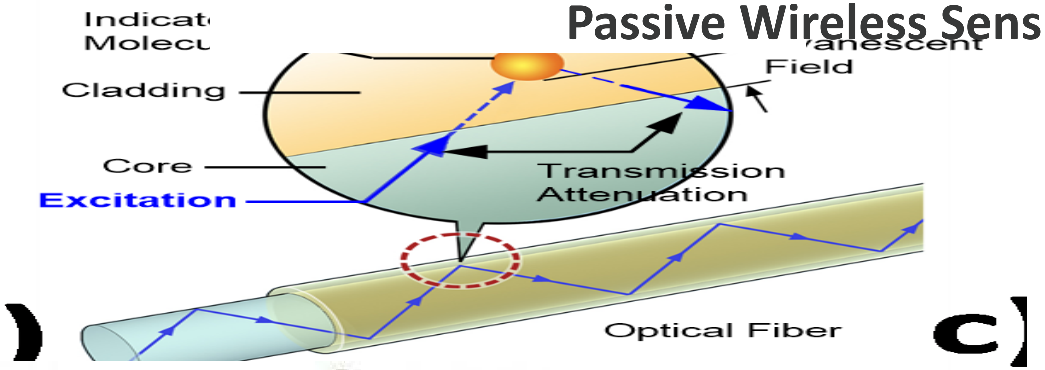


Single Crystal Fiber Growth Facilities

Research Emphasis Includes (1) Functional Sensing Materials and (2) Advanced Optical Fiber Materials for Increased Device Stability and Chemical Sensing in Extreme Environments.

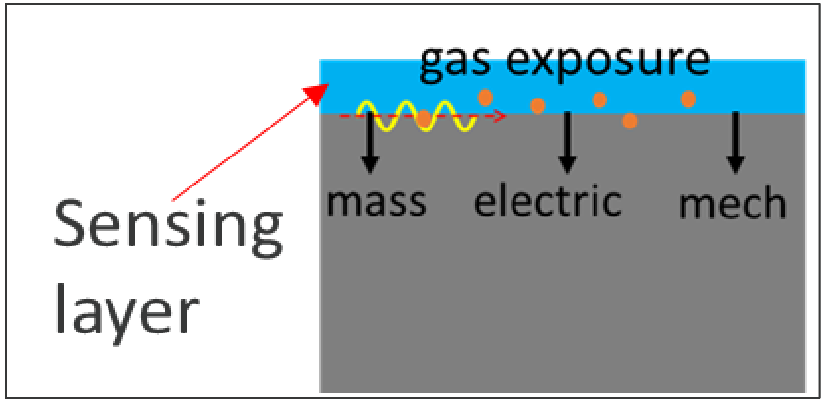
Focus #2 : Surface Acoustic Wave Sensors

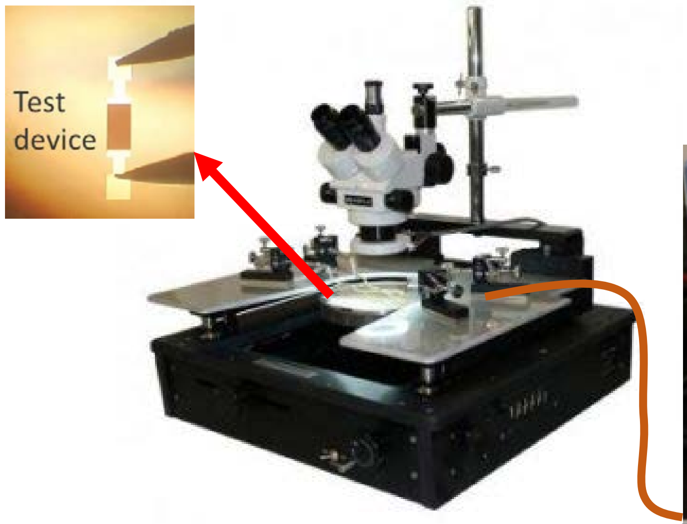
Passive Wireless Sensing in Extreme Environments

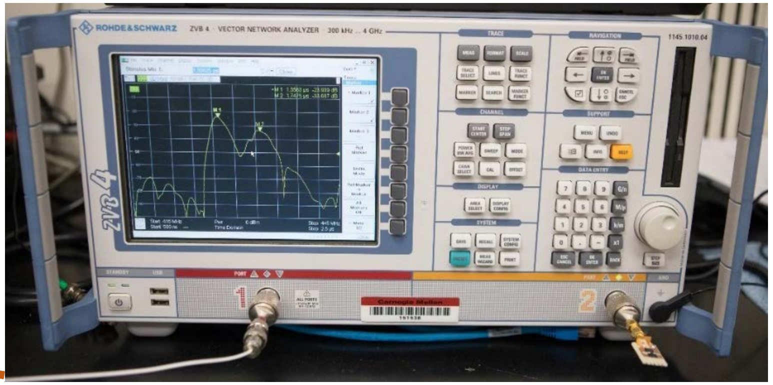


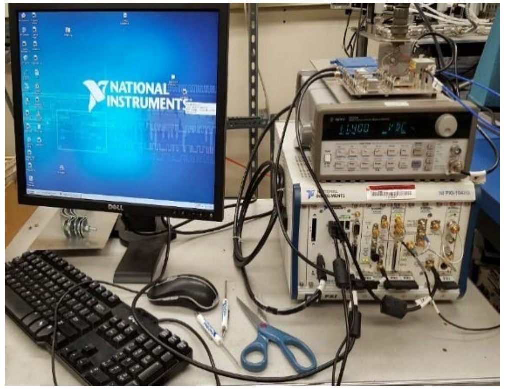
$$\frac{\Delta v}{v_0} = \frac{\Delta f}{f_0} = \frac{\Delta \phi}{\phi_0}$$

Operating frequency: ~ (100 MHz – 2 GHz)







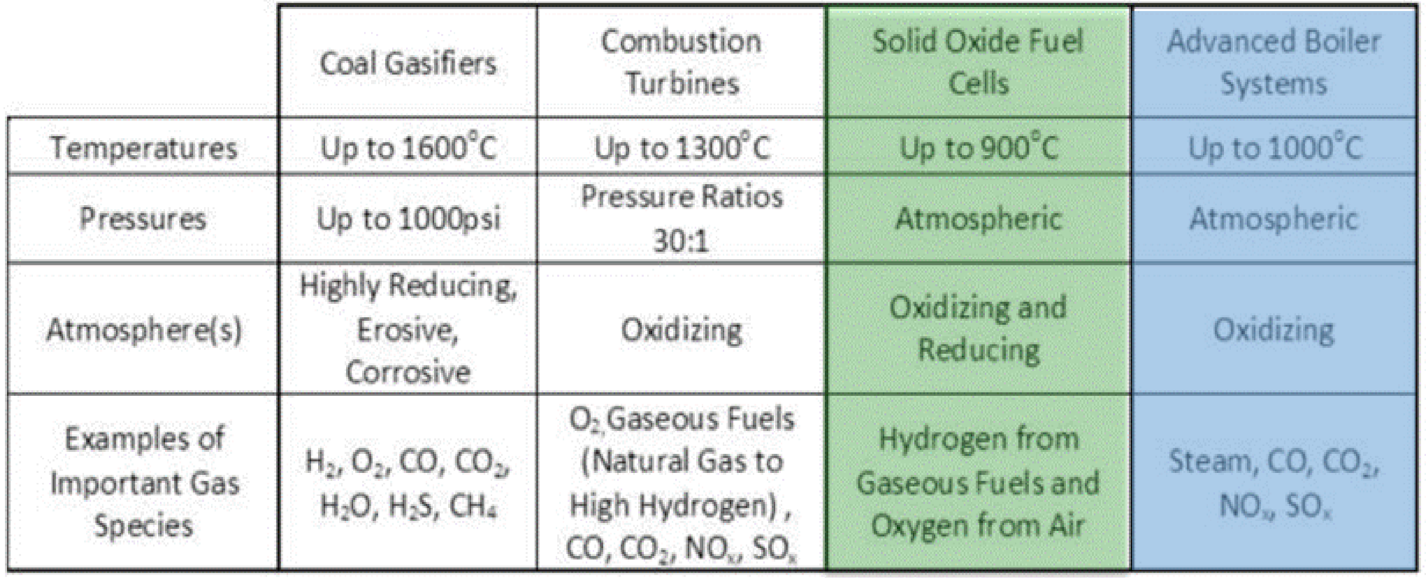


Custom
Interrogation
Instrumentation

Research Emphasis Includes (1) Functional Sensing Materials and (2) Device Stability for Chemical Sensing Capability in High Temperature and Harsh Environment Conditions.

Power Generation Sensor Technologies

Short-Term Application Focus



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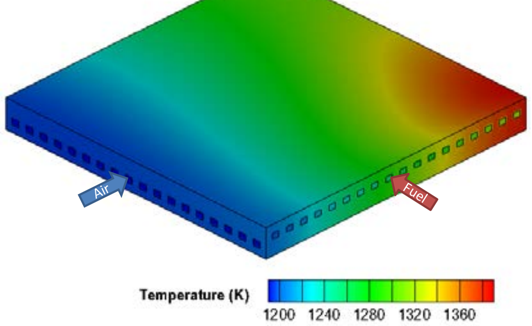
Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution



SOFC Temperature : 700-800°C
Anode Stream : Fuel Gas (e.g. H_2-Containing)
Cathode Stream : Air or O_2

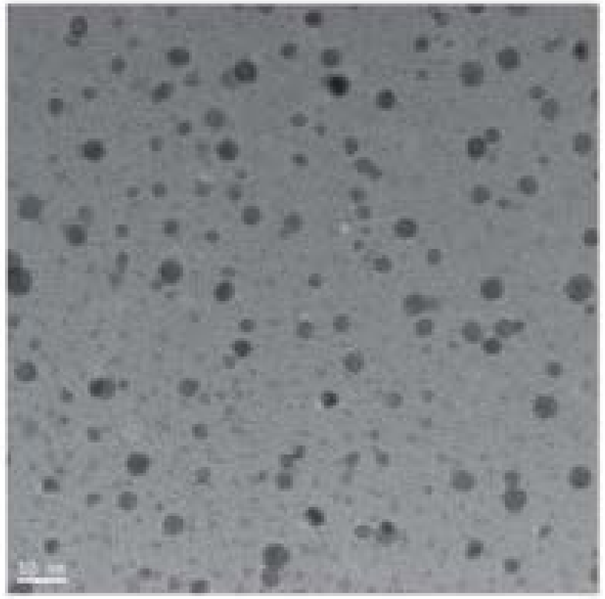
Incompatible with Traditional Sensing Technologies

1) Limits of High Temperature Electrical Insulation
2) Limited Access Space
3) Requires Multi-Point Sensing
4) Electrified Surfaces
5) Flammable Gas Atmospheres

NETL On-Site Research Has Focused on Solid Oxide Fuel Cell and Boiler Applications as Demonstration Platforms for Embedded Sensing in Advanced Power Generation Systems.

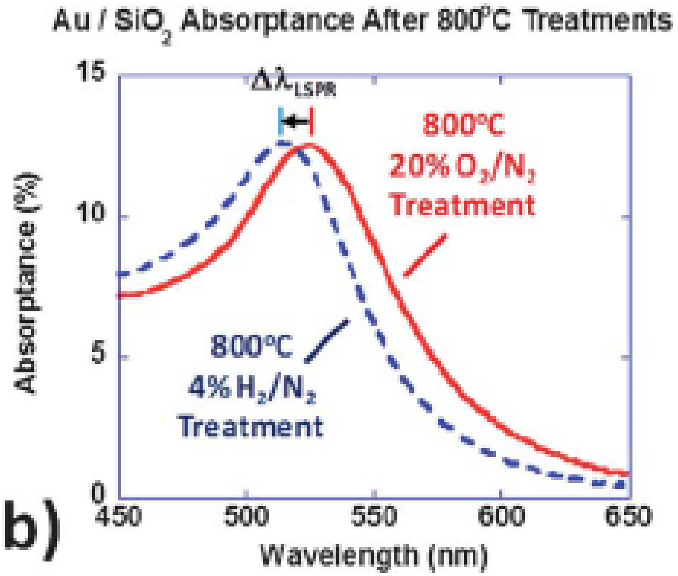
Prior Work : Au-Nanoparticle Incorporated Oxides

Au-Nanoparticle Incorporated Silica



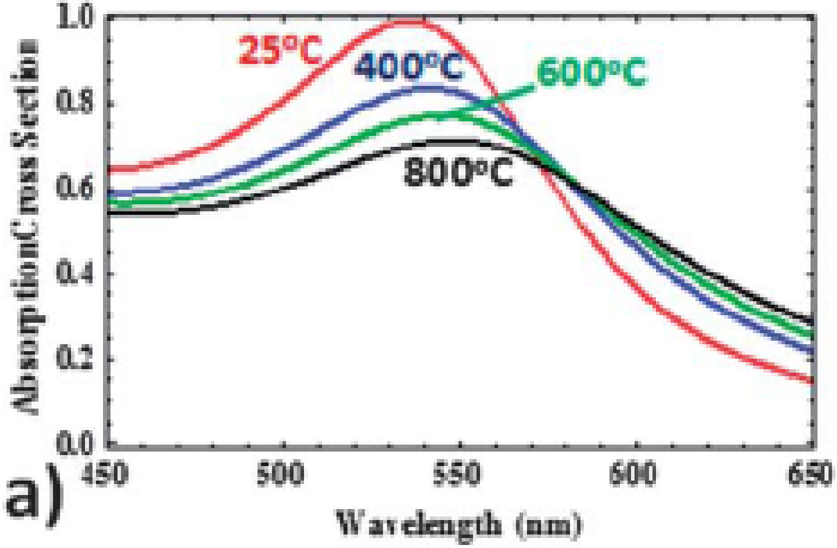
Gas Stream Response

(Free Carrier Change Dominated)



Temperature Response

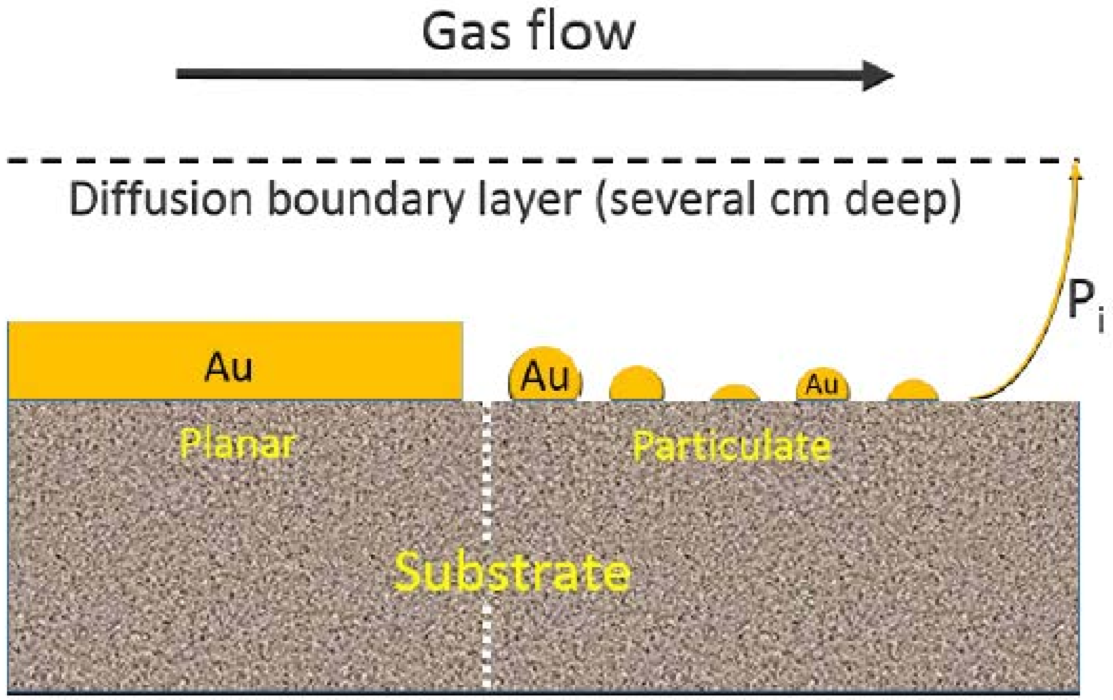
(Free Carrier Mobility Dominated)



Previous Work on Au-Nanoparticle Incorporated Refractory Metal Oxides Demonstrated Effective Gas and Temperature Sensing Responses Simultaneously.

Plasmonic nanocomposite thin film enabled fiber optic sensors for simultaneous gas and temperature sensing at extreme temperaturesPR Ohodnicki, MP Buric, TD Brown, C Matranga, C Wang, J Baltrus, ...Nanoscale 5 (19), 9030-9039 (2013).

Thermodynamic and Kinetic Modeling



H_2, H_2S, and Temperature Can All Play an Important Role in Rates of Reactive Evaporation

$$Au(s) \rightleftarrows Au(g)$$

$$Au(s) + ½\ H_2(g) \rightleftarrows \underline{AuH(g)} \leftarrow$$

$$Au(s) + H_2S(g) \rightleftarrows \underline{AuS(g)} + H_2(g) \leftarrow$$

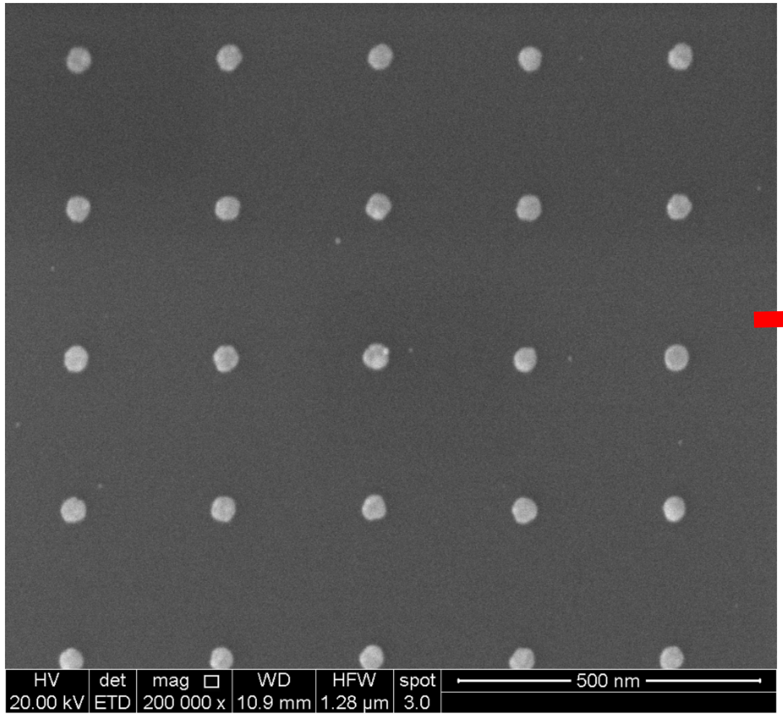
Thermodynamic and Kinetic Modeling Can Estimate the Rate of Reactive Evaporation for Various Temperature and Gas Stream Compositions.

Factors Influencing the Stability of Au-Incorporated Metal-Oxide Supported Thin Films for Optical Gas Sensing,
JP Baltrus, GR Holcomb, JH Tylczak, PR Ohodnicki, Journal of The Electrochemical Society 164 (4), B159-B167 (2017).

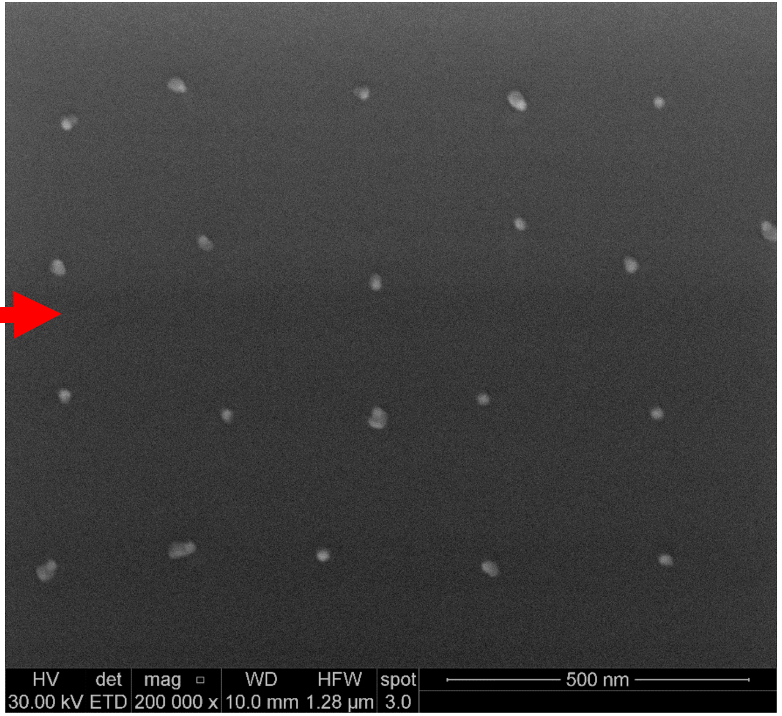
Model Experimental Systems : Quantitative Analysis

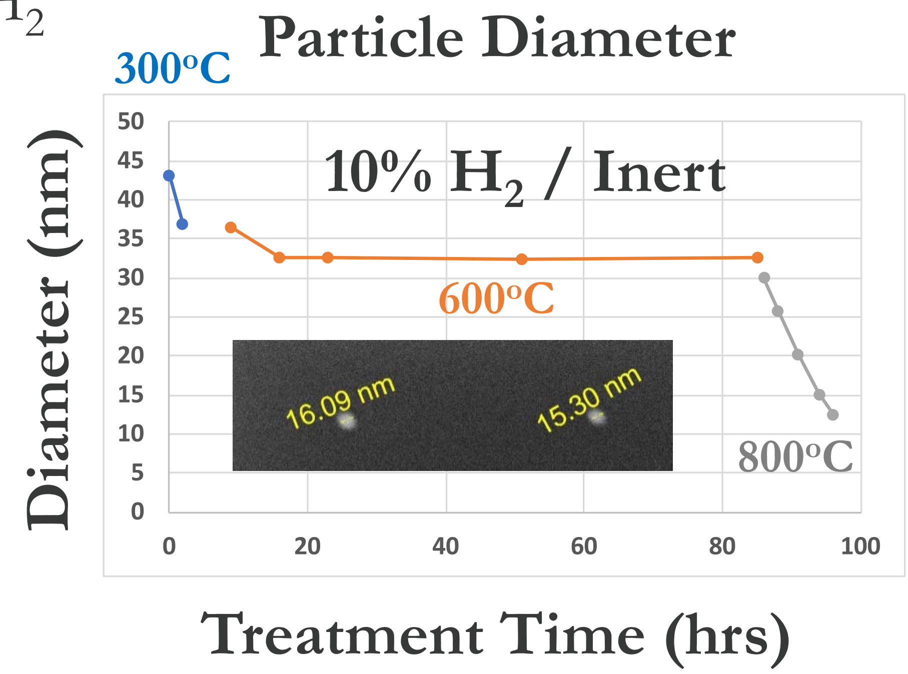
Lithographic Patterned Au-Nanodots

Pre-Treatment



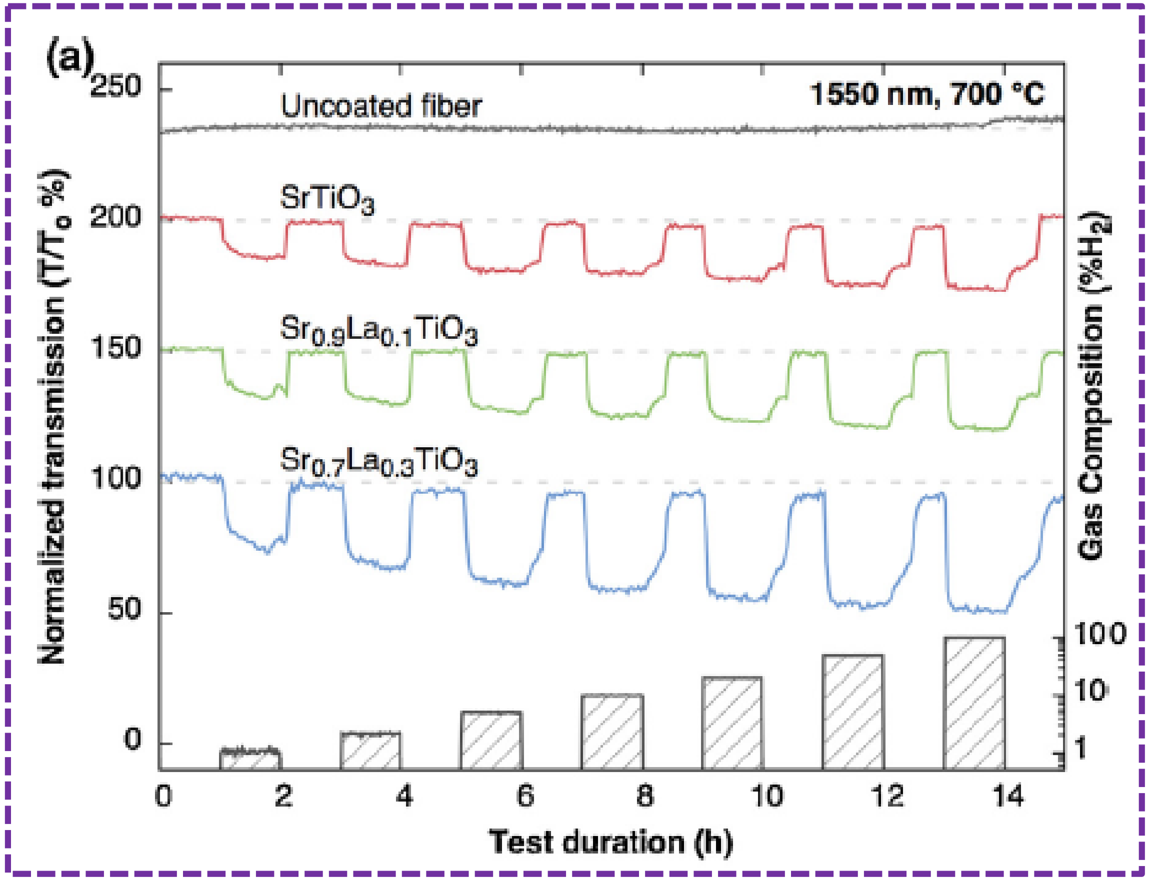
Post-Treatment @800°C, 10% H_2

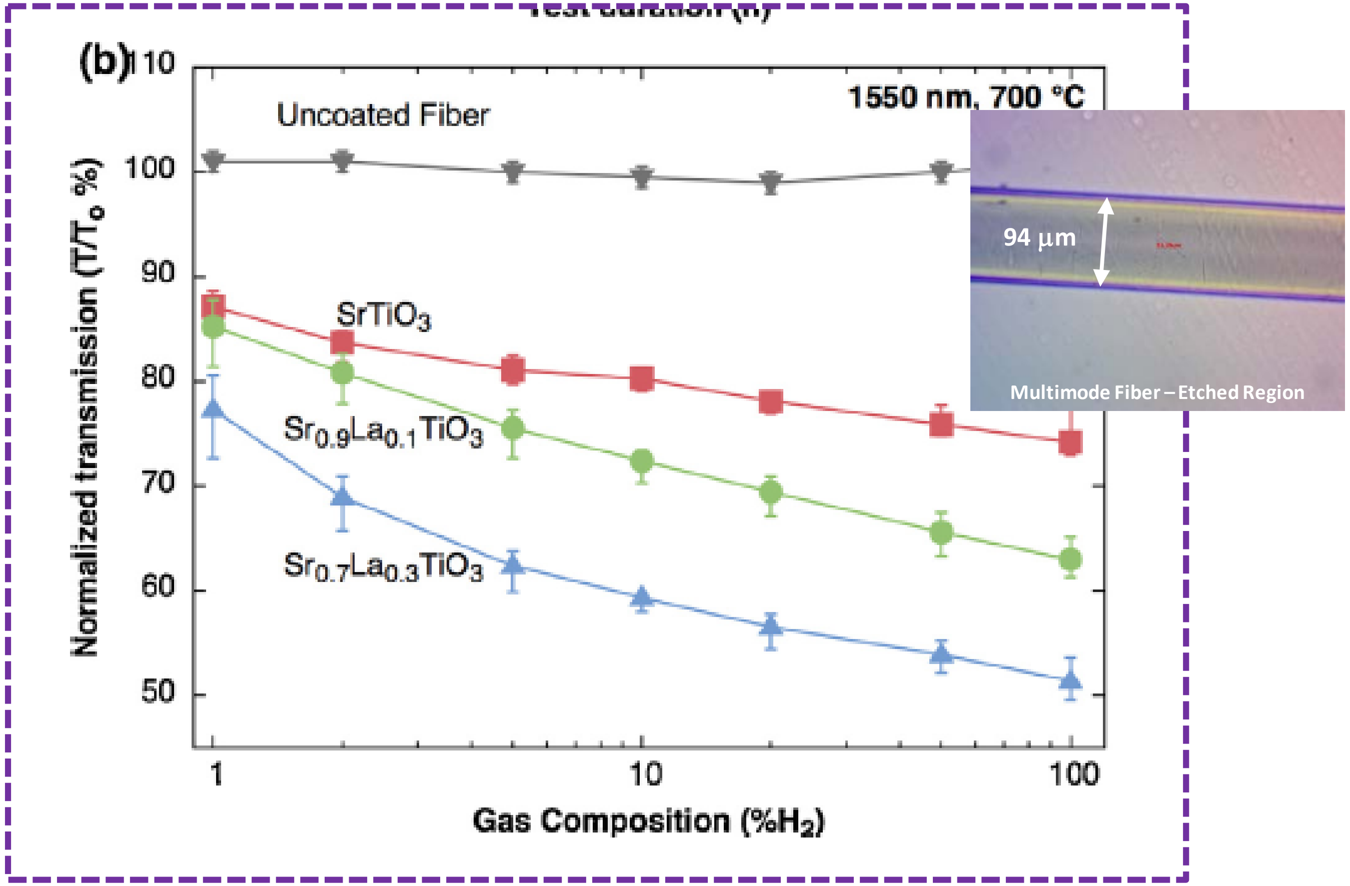




Recent Experiments are Targeting Controlled Treatments of Model Au-Nanoparticle and Other Noble Metal Systems to Explore Stability Under Various Conditions.

Previous Work : Conducting Metal Oxides

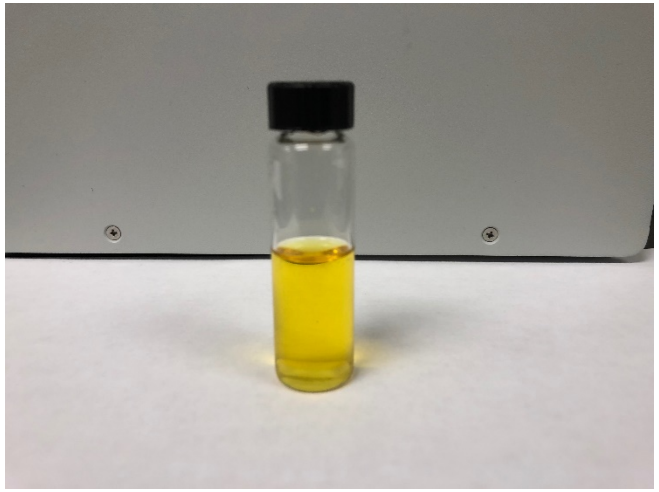


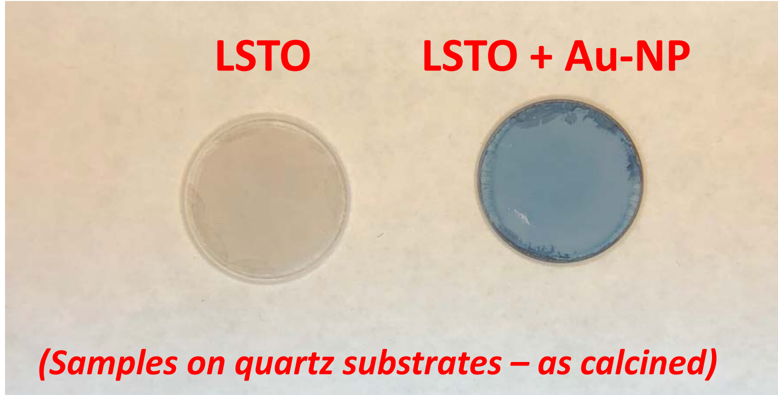


Past Work on Doped Conducting Metal Oxides Showed Enhanced Optical Response for Gas Sensing Due to Free Carrier Effects in the Near-Infrared.

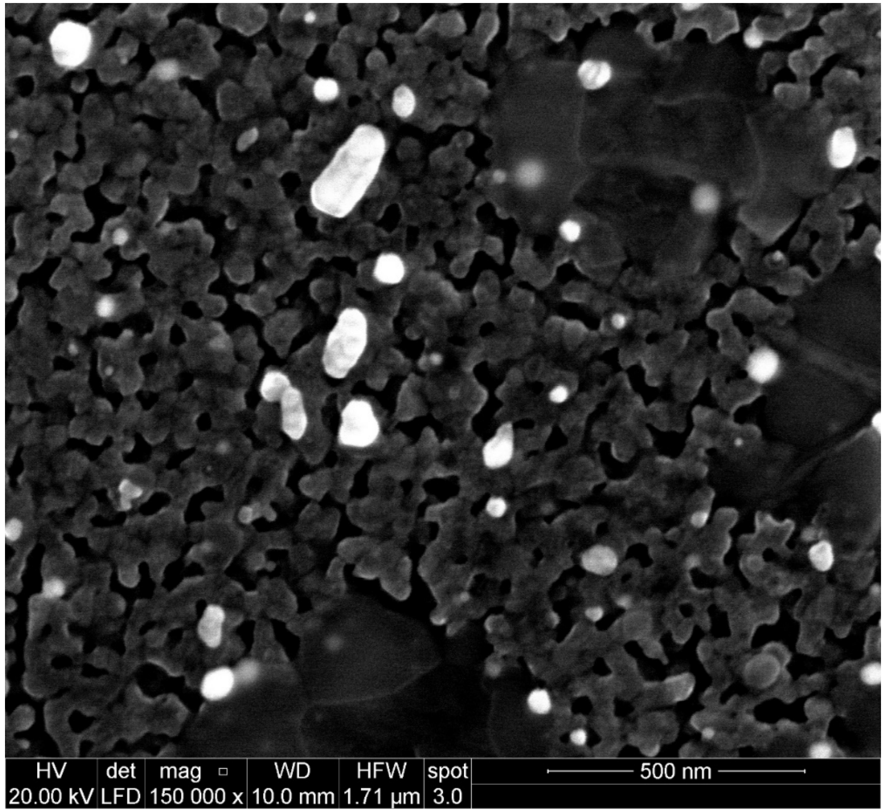
High temperature fiber-optic evanescent wave hydrogen sensors using La-doped SrTiO3 for SOFC applications,
AM Schultz, TD Brown, MP Buric, S Lee, K Gerdes, PR Ohodnicki, Sensors and Actuators B: Chemical 221, 1307-1313 (2015).

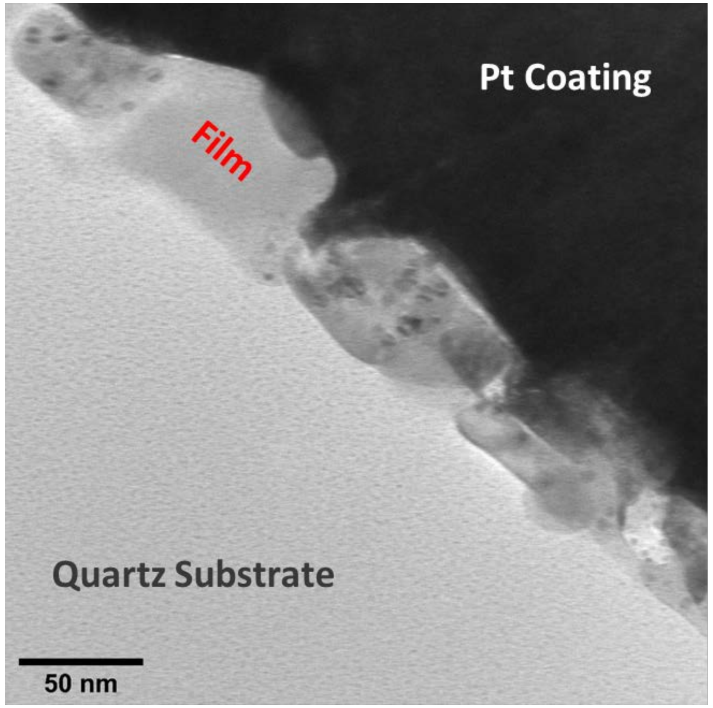
Au-Nanoparticle Integrated La-Doped STO





(Samples on quartz substrates – as calcined)

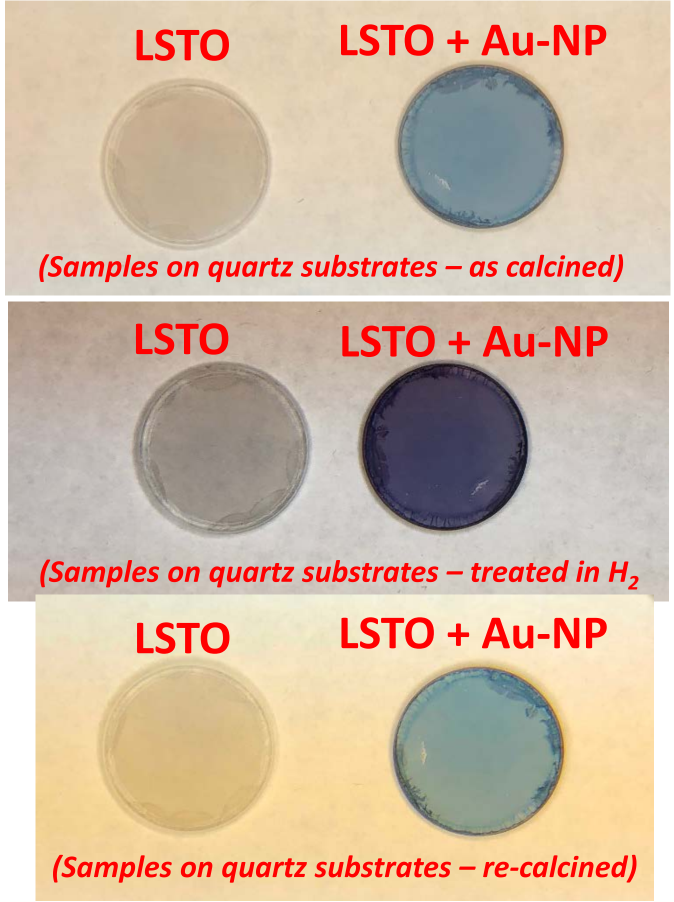




Au-Nanoparticles Are Being Incorporated Into Conducting Oxide Thin Films for Multi-Parameter Gas Sensing By Leveraging the Fiber Optic Sensing Platform.

Optical gas sensing properties of gold-nanoparticle incorporated LSTO films at high temperature,
JK Wuenschell, Y Jee, PR Ohodnicki, Oxide-based Materials and Devices X 10919, 109191X (2019).

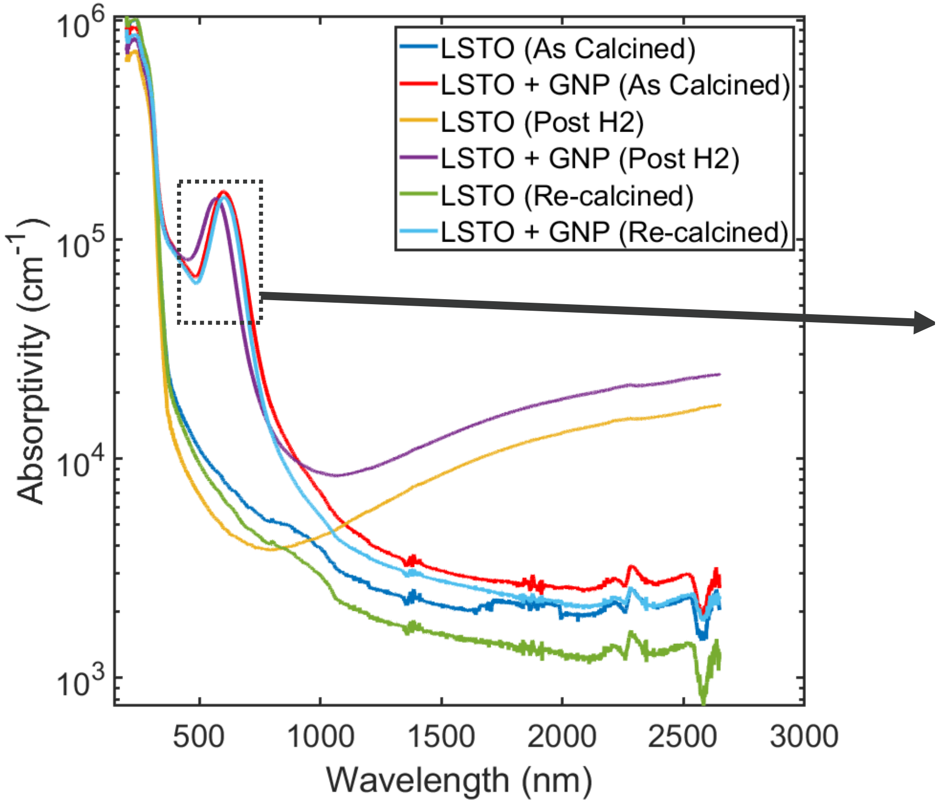
Au-Nanoparticle Integrated La-Doped STO

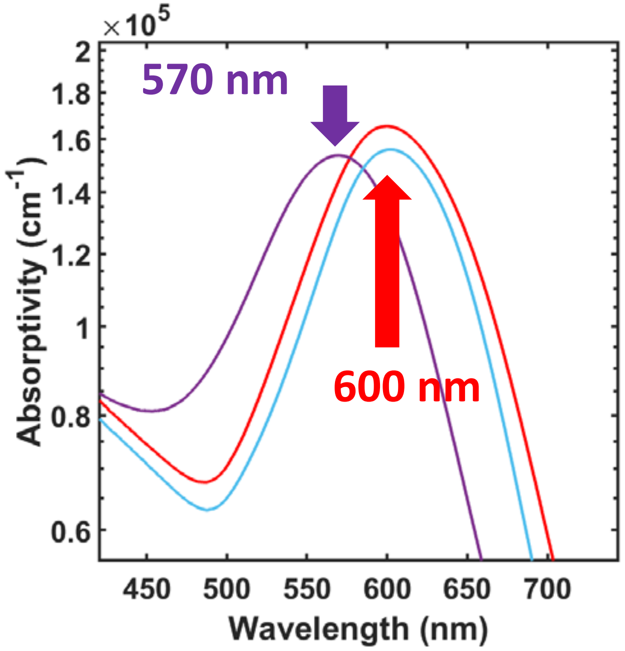


(Samples on quartz substrates – as calcined)

(Samples on quartz substrates – treated in H_2

(Samples on quartz substrates – re-calcined)





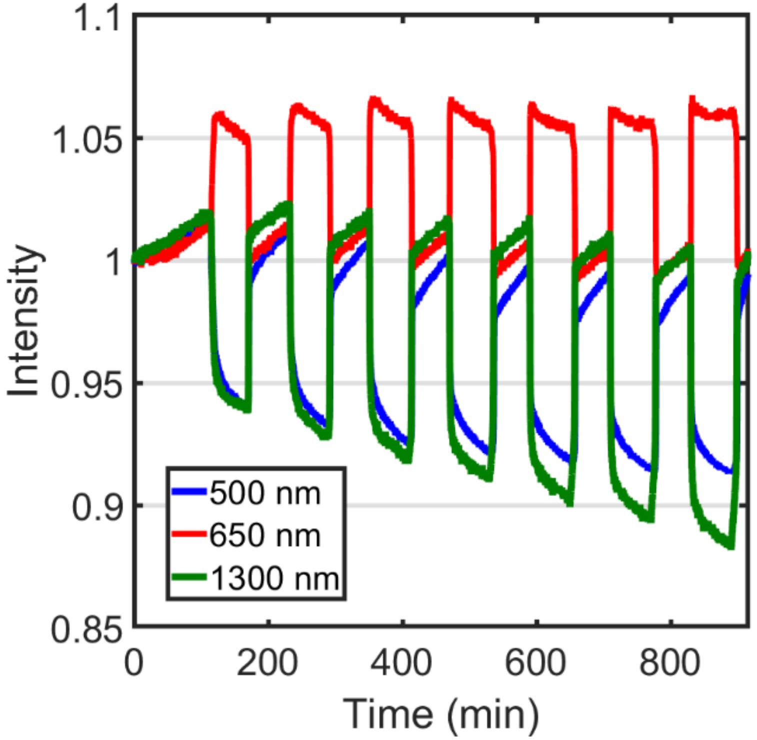
- Calcined at 950 C in air for 16 hrs.
- Treated in 10% H_2 for 16 hrs at 800 C (cool down in 10% H_2)
- Re-calcined at 950 C in air

Localized Surface Plasmon Resonances Shift Reversibly in Reducing vs. Oxidizing Gases and a Near-IR Response is Observed Due to Free Carrier Effects in the LSTO.

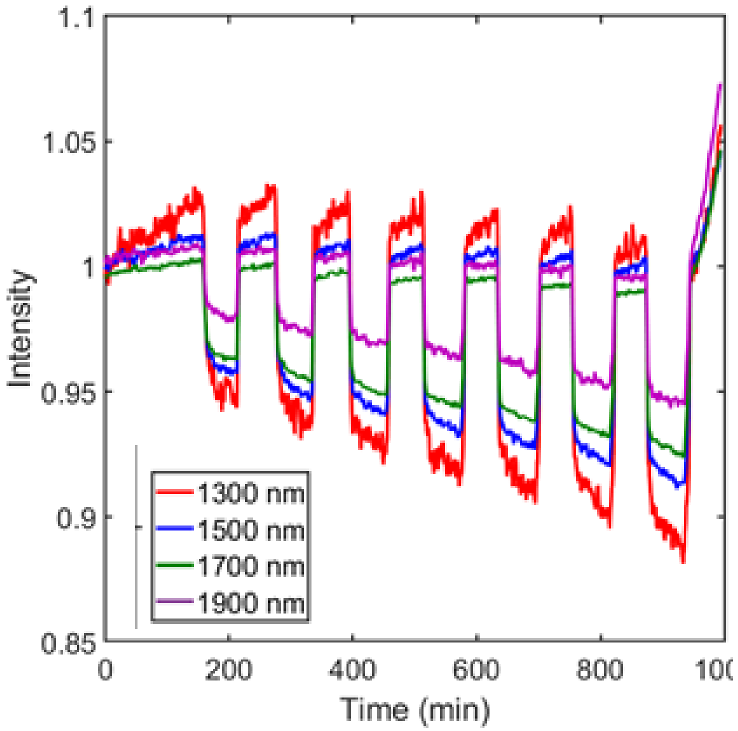
Optical gas sensing properties of gold-nanoparticle incorporated LSTO films at high temperature,
JK Wuenschell, Y Jee, PR Ohodnicki, Oxide-based Materials and Devices X 10919, 109191X (2019).

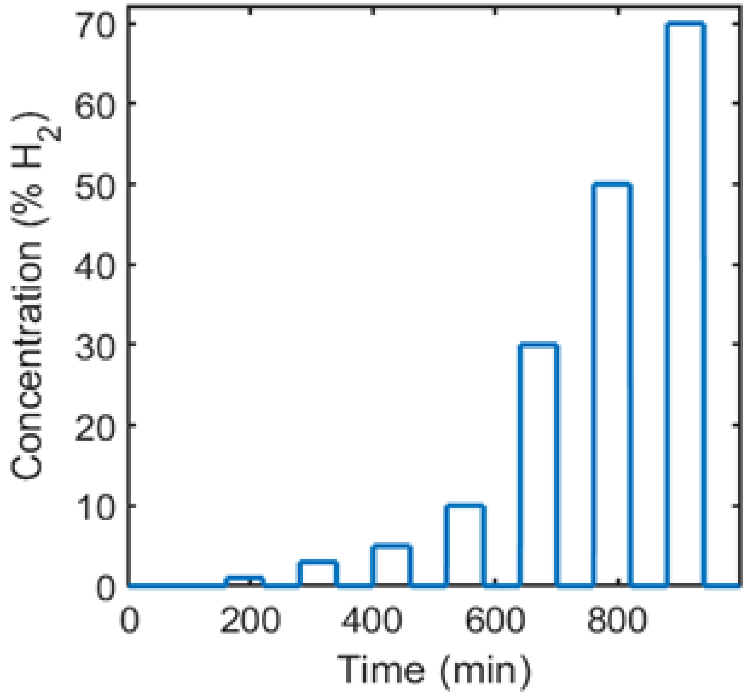
Spectrally Selective Sensing Responses

Visible Range
(Au-LSPR+Oxide Drude / Band-Edge)



Near-IR Range
(Oxide Drude)

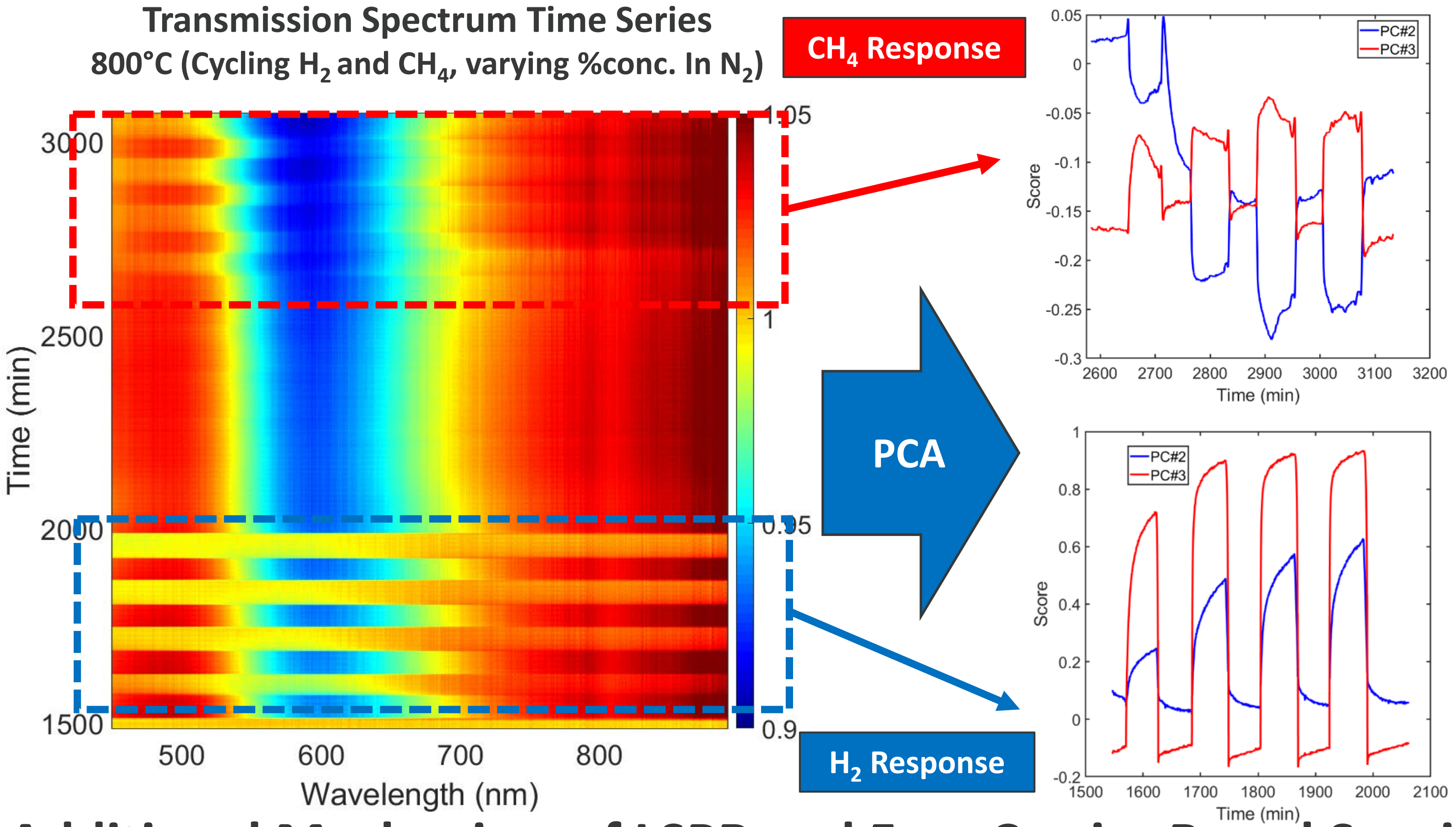




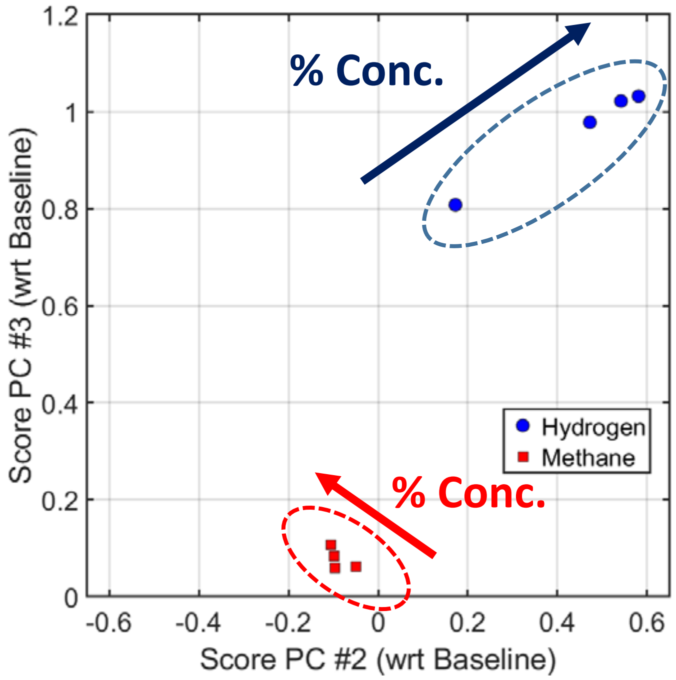
Both Visible and Near-IR Ranges Show Effective Gas Sensing Responses Due to Combined LSPR and Metal Oxide Drude Based Effects.

Optical gas sensing properties of gold-nanoparticle incorporated LSTO films at high temperature,
JK Wuenschell, Y Jee, PR Ohodnicki, Oxide-based Materials and Devices X 10919, 109191X (2019).

Multivariate Analyses : Complex Gas Streams



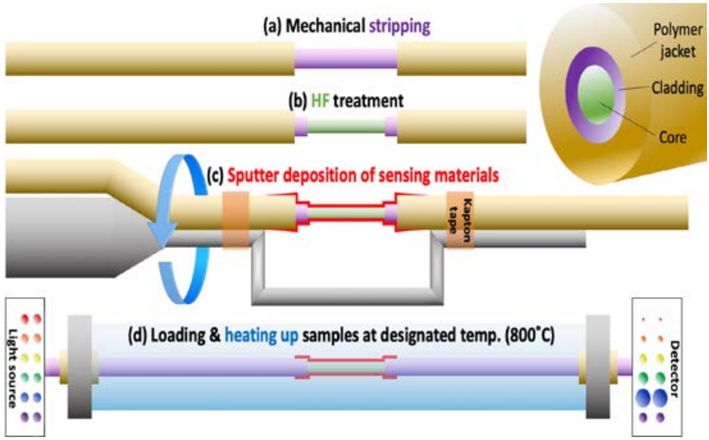
PC #2: Correlates to Oxide Film Response
PC #3: Correlates to Au NP LSPR Response

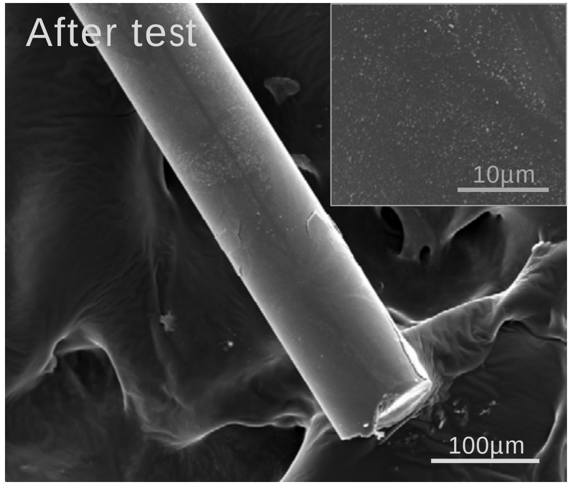


Additional Mechanism of LSPR and Free Carrier Based Sensing Response Helps to Enhance Selectivity to Various Reducing Gas Species.

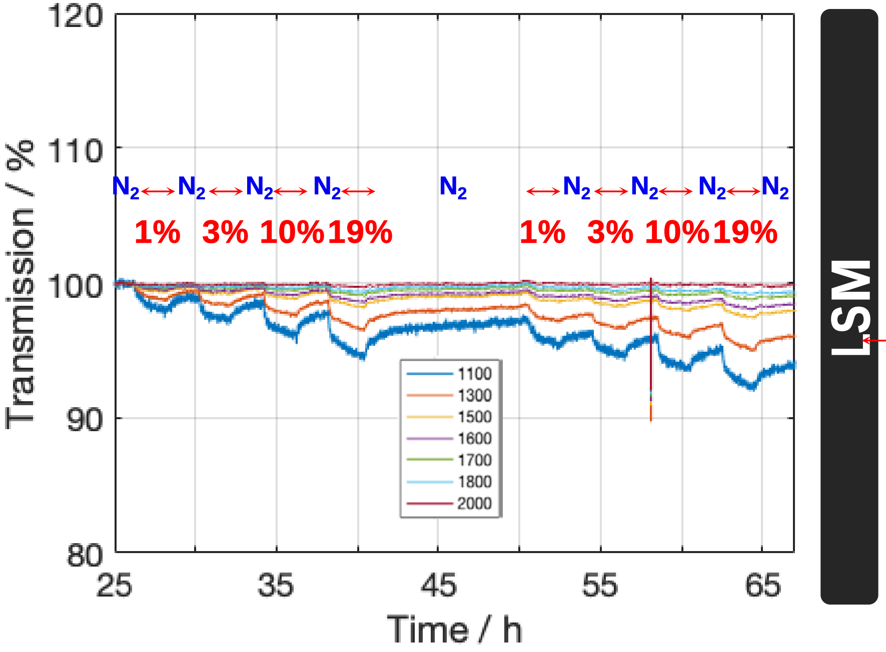
Optical gas sensing properties of gold-nanoparticle incorporated LSTO films at high temperature,
JK Wuenschell, Y Jee, PR Ohodnicki, Oxide-based Materials and Devices X 10919, 109191X (2019).

Complex Metal Oxide Functionalized Fibers

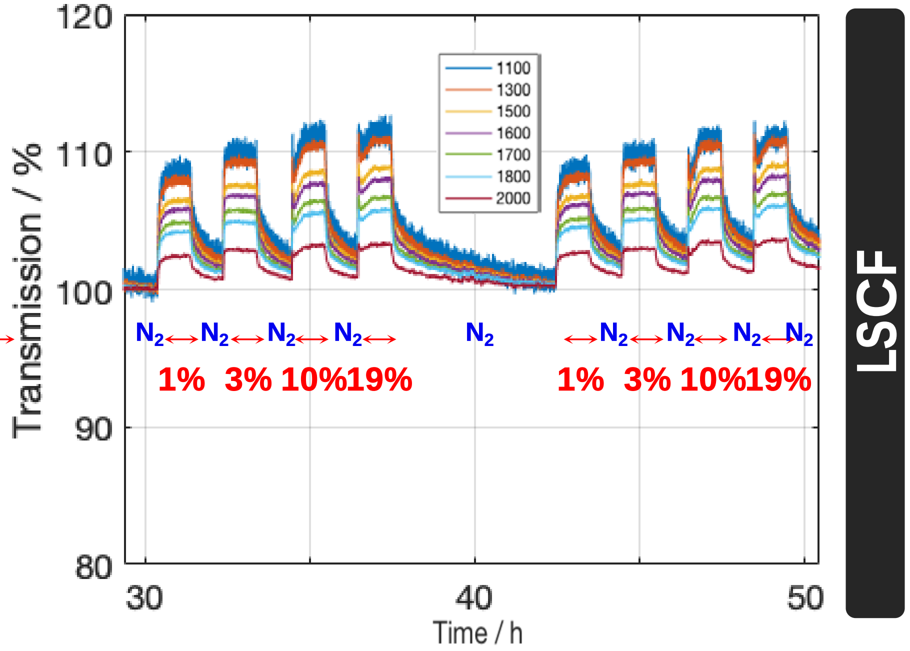




Oxygen-Defect Sensitive Optical Absorption Properties



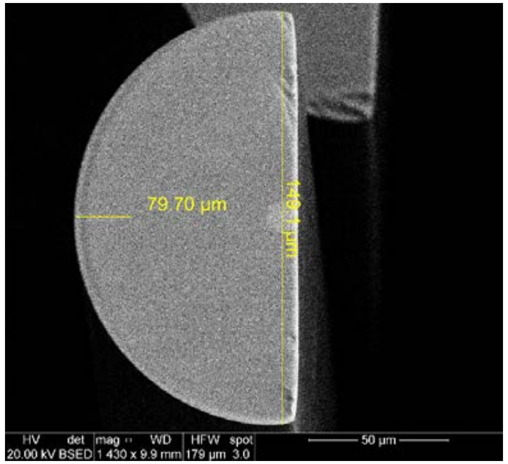
Faster Response Rate : Higher Oxygen Ion Diffusion Coefficient

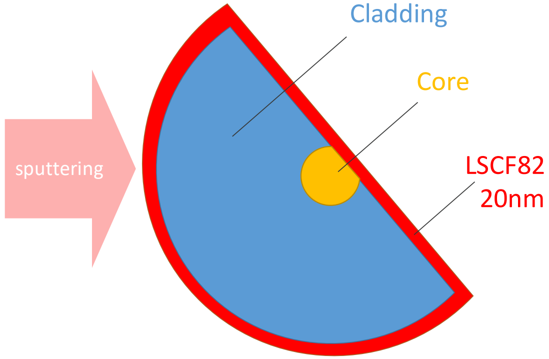


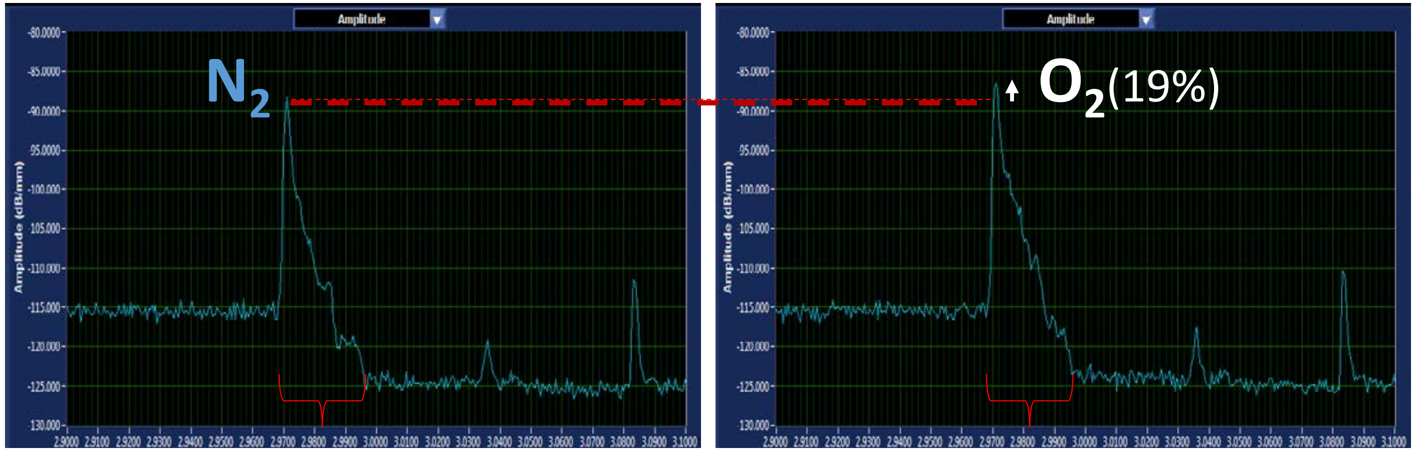
Optical O_2-Sensing Capability of Typical SOFC Cathode Materials are Being Explored.

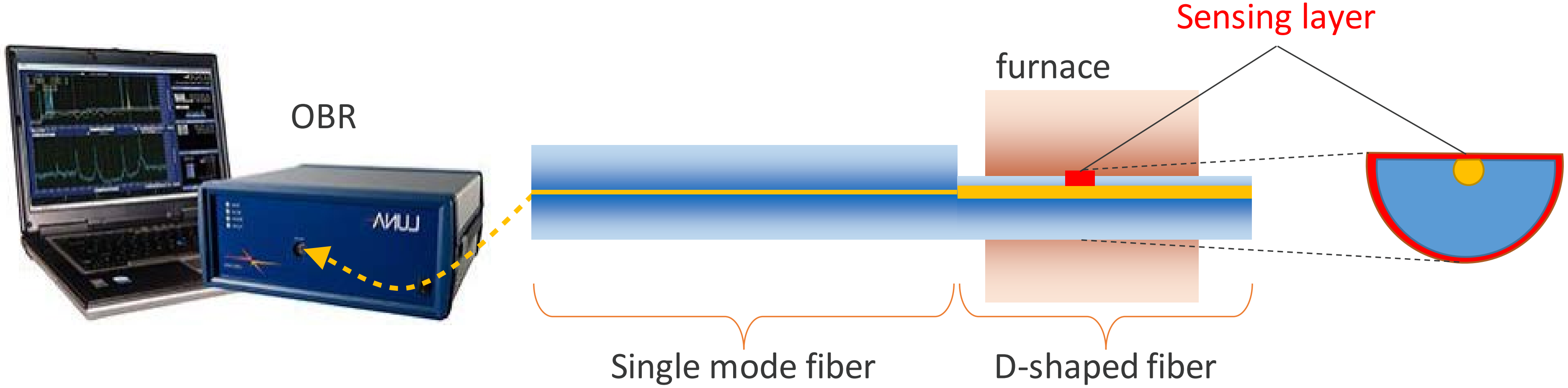
High-temperature oxygen sensing behavior of perovskite films on the optical fiber platform,
Y Jee, JK Wuenschell, HW Abernathy, S Lee, TL Kalapos, GA Hackett, Oxide-based Materials and Devices X 10919, 109192G, (2019).

Distributed Oxygen Sensing in Cathode Stream







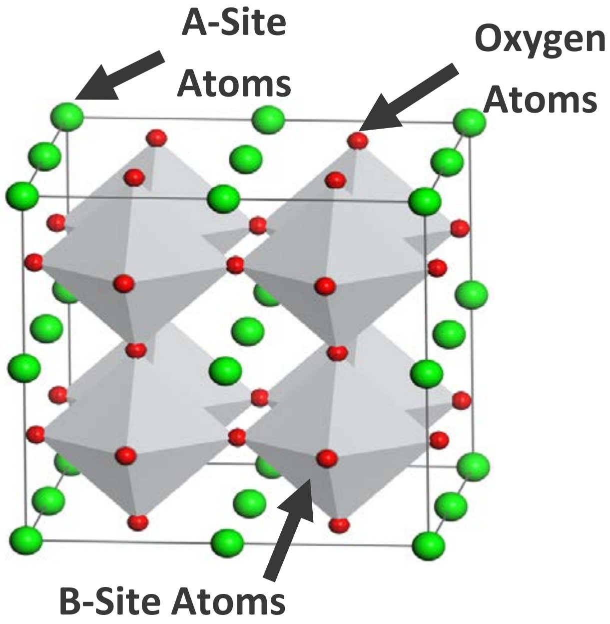


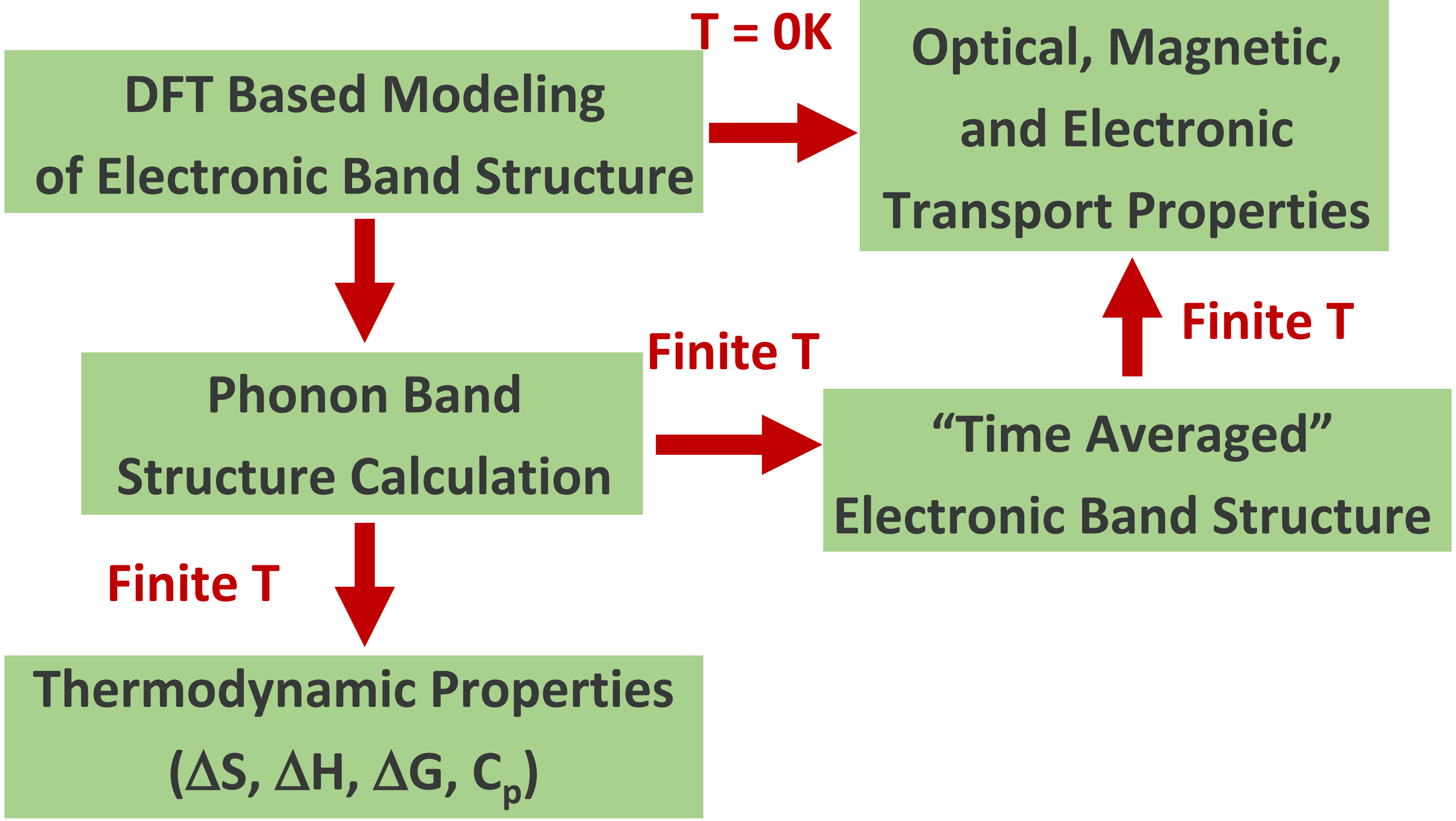
First Distributed O_2-Sensing Efforts Relevant for SOFC Cathode Monitoring are Underway.

Computational Methods Applied to Sensor Materials

Perovskite Type : ABO_3

Examples: STO, LSTO, LSM, LSC, LSCF, etc.





DFT Based Modeling of Electronic Band Structure

T = 0K

Optical, Magnetic, and Electronic Transport Properties

Phonon Band Structure Calculation

Finite T

"Time Averaged" Electronic Band Structure

Finite T

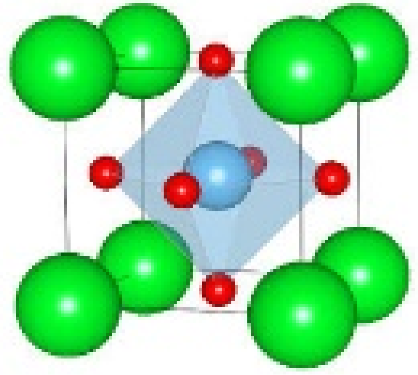
Finite T

Thermodynamic Properties (ΔS, ΔH, ΔG, C_p)

We are Developing and Applying Computational Methodologies and Techniques with a Goal of Obtaining High Temperature Functional Properties from First Principles.

First Principle Predictions : Optical Properties

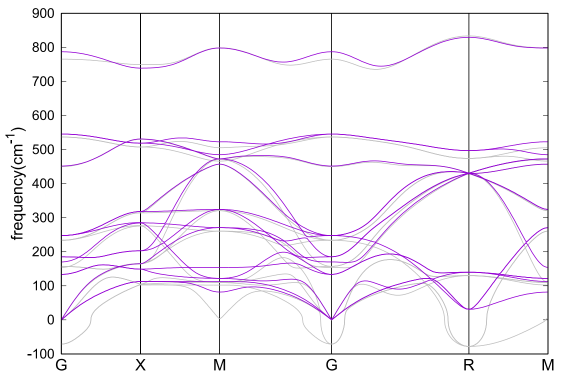
Cubic Perovskite (e.g. $SrTiO_3$)



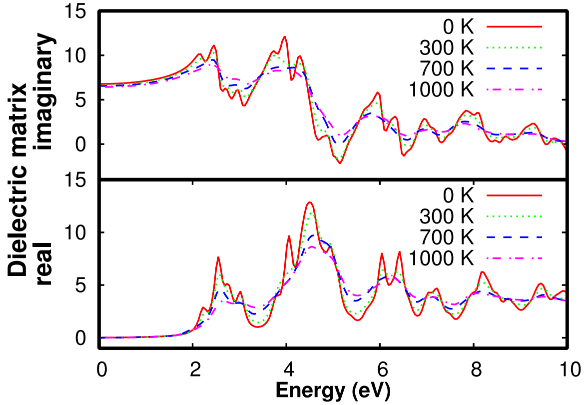
- Calculation of Phonon Spectrum
- Calculation of Band Structure at Finite Temperatures

- Estimate Bandgap, Dielectric Constants, Optical Constants, etc.

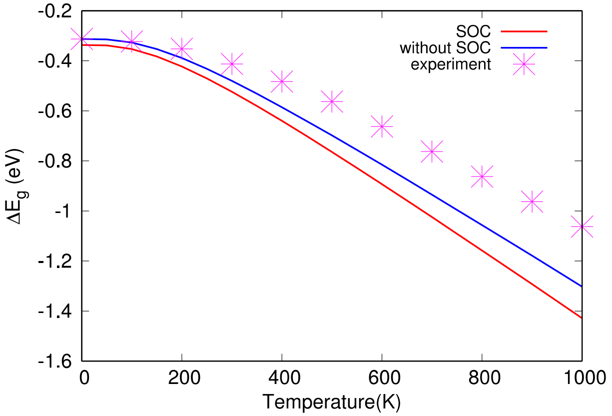
Phonon Spectrum



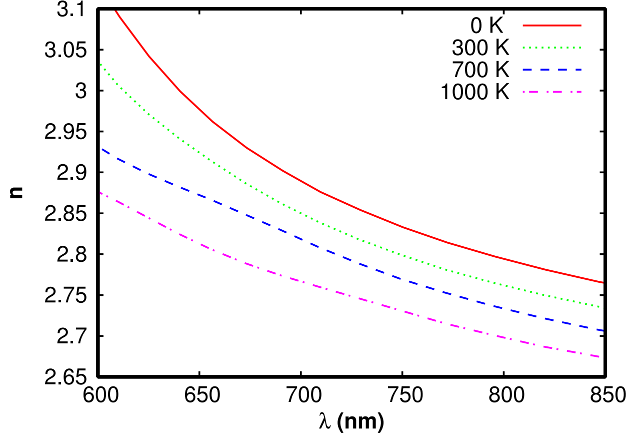
Electronic Band Structure



Band Gap vs. Temperature



Optical Constant vs. Temperature

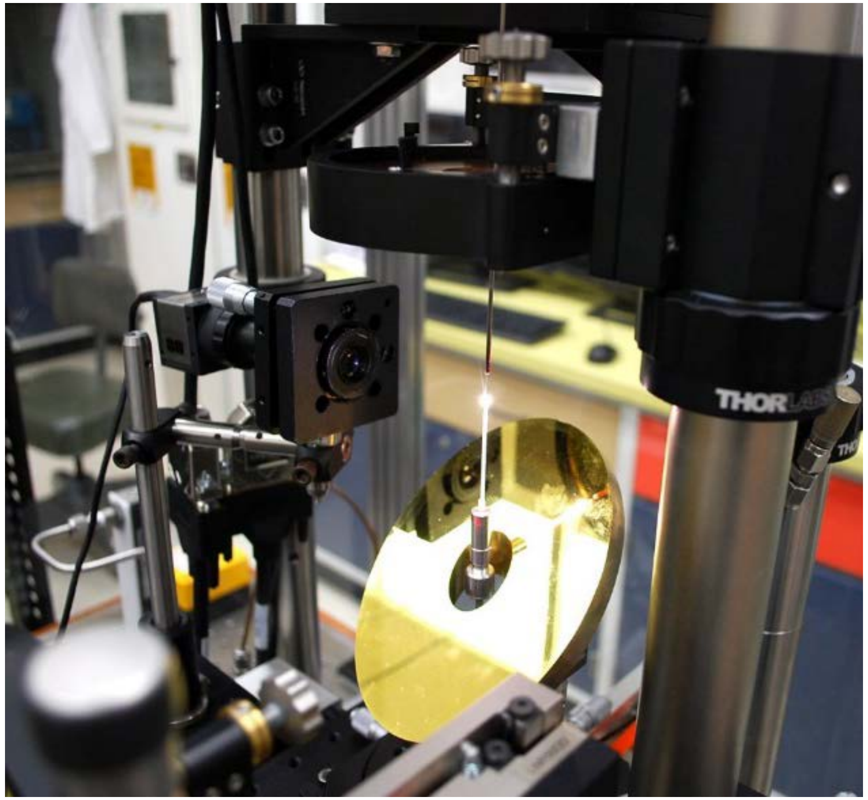


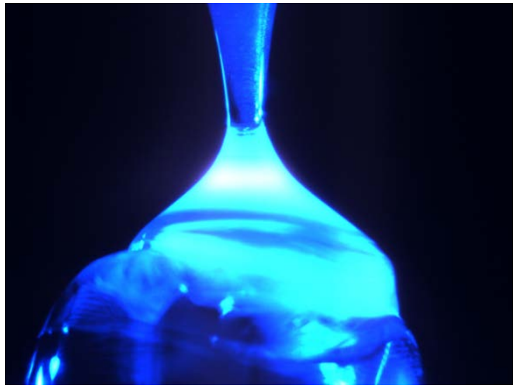
Computational Methods are Being Developed and Applied for Finite Temperature Optical and Electronic Property Predictions to Inform and Accelerate Sensor Material Research.

First-Principles Investigations of the Temperature Dependence of Electronic Structure and Optical Properties of Rutile TiO_2
YN Wu, WA Saidi, P Ohodnicki, B Chorpening, Y Duan, The Journal of Physical Chemistry C 122 (39), 22642-22649, (2018).

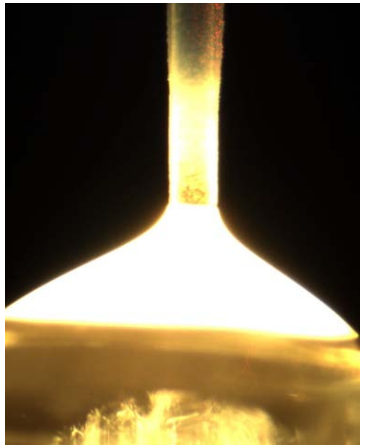
Alternative Optical Fiber Material Investigations

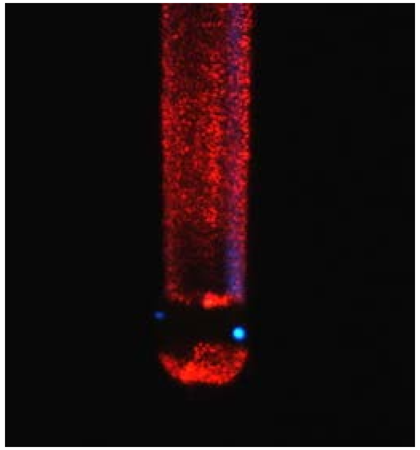
Laser Heated Pedestal Growth Processing

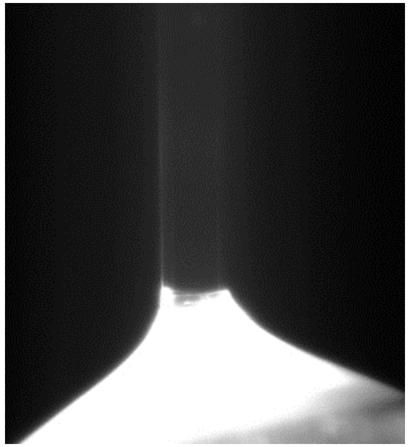




Novel Sensor Fabrication Through LHPG Process Controls



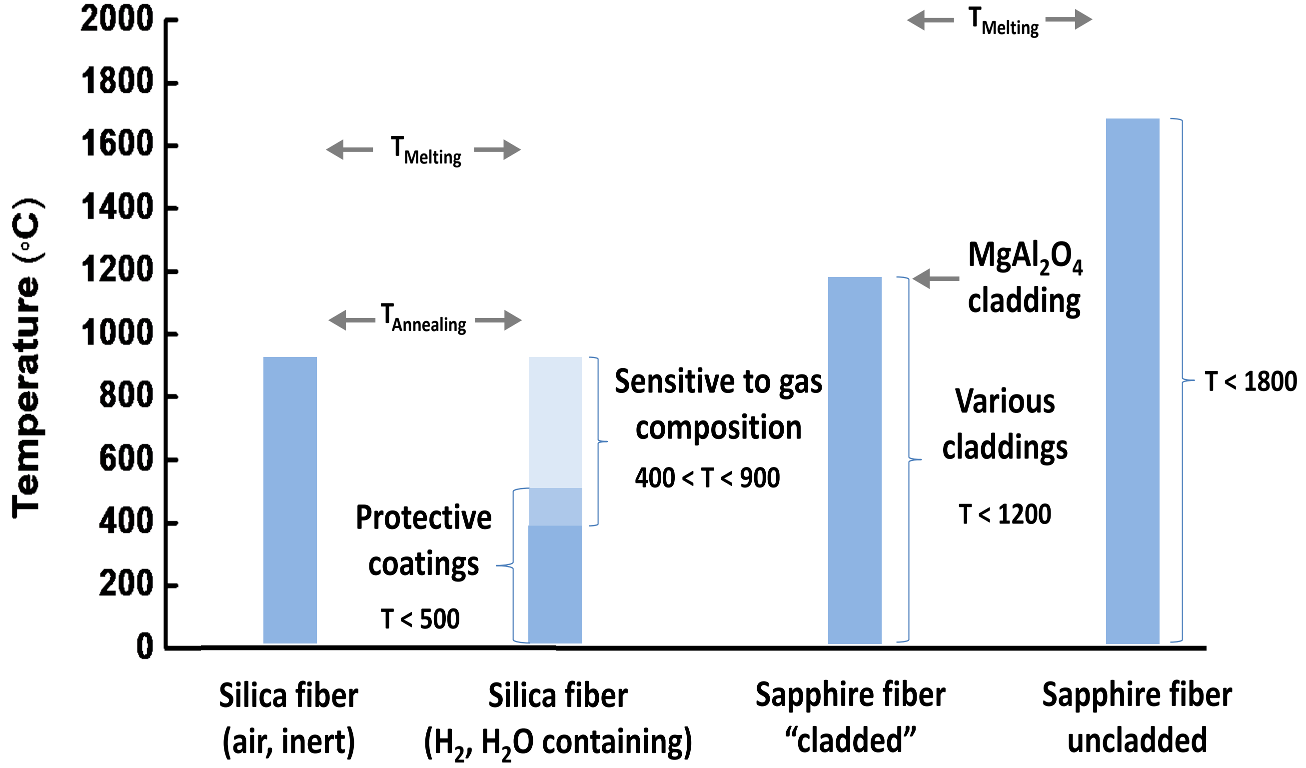




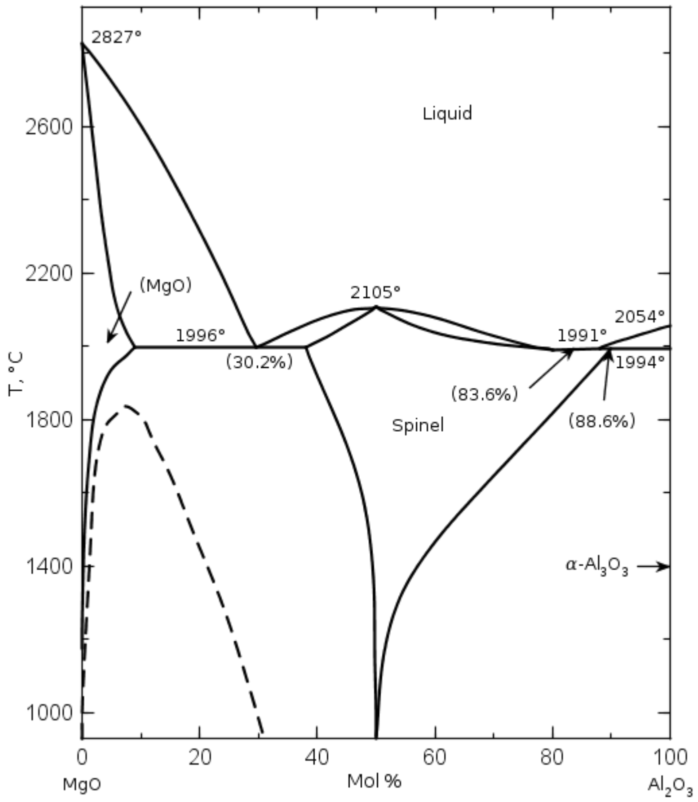
Relatively New Efforts are Focused on Fabrication of Single Crystal Sapphire Based Fiber Sensors and In-Line Processing for Sensor Functionality and Ultimately Cladding Integration.

New Sapphire Fiber Cladding Approaches

High Temperature Stable Sapphire Cladding Materials



e.g. $MgAl_2O_4$

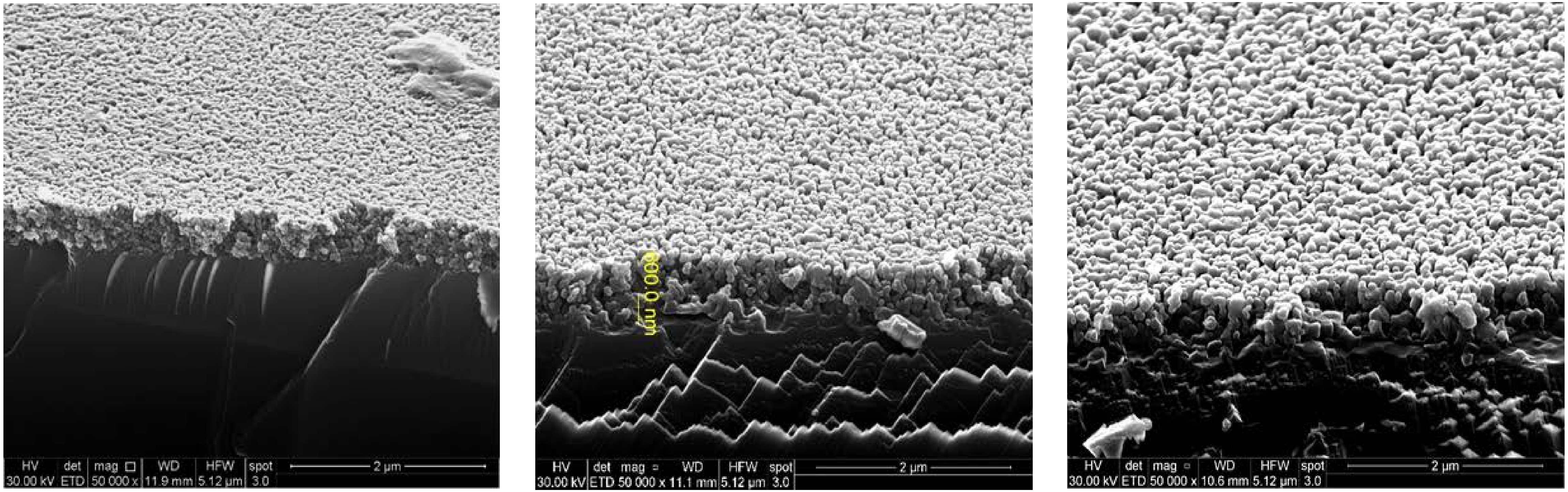


New Research Efforts Target Development of Cladding Layer Approaches for Sapphire Fibers.

Review and perspective: Sapphire optical fiber cladding development for harsh environment sensing,
Hui Chen, Michael Buric, Paul R. Ohodnicki, Jinichiro Nakano, Bo Liu, Benjamin T. Chorpening, Applied Physics Reviews **5**, 011102 (2018).

Current State-of-the-Art : $MgAl_2O_4$ Spinel on Sapphire

Coated Sapphire Wafers



1100°C 3 hours

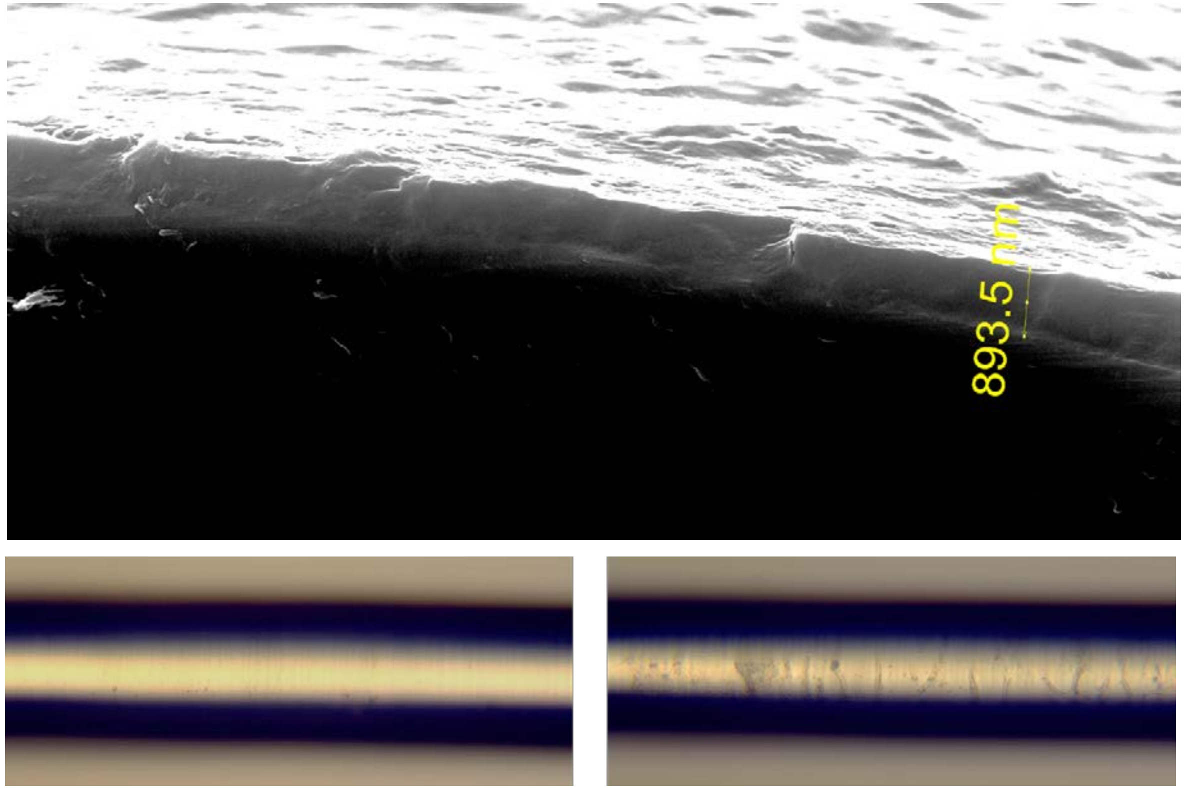
1200°C 3 hours

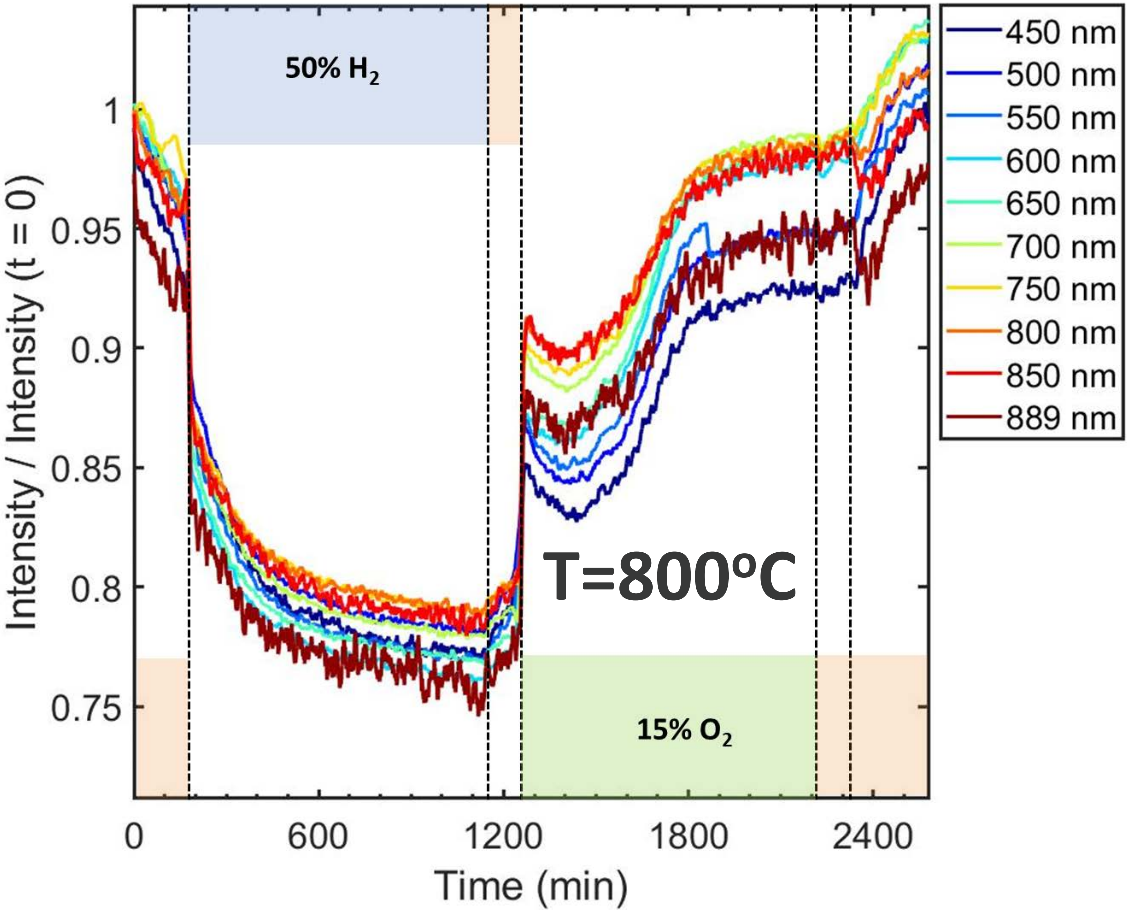
1300°C 3 hours

Recipes for Sol-Gel Coating of Thick-Film $MgAl_2O_4$ on Sapphire Has Been Demonstrated.

Spinel Coated Sapphire Fibers Fabrication

Coated Sapphire Fibers

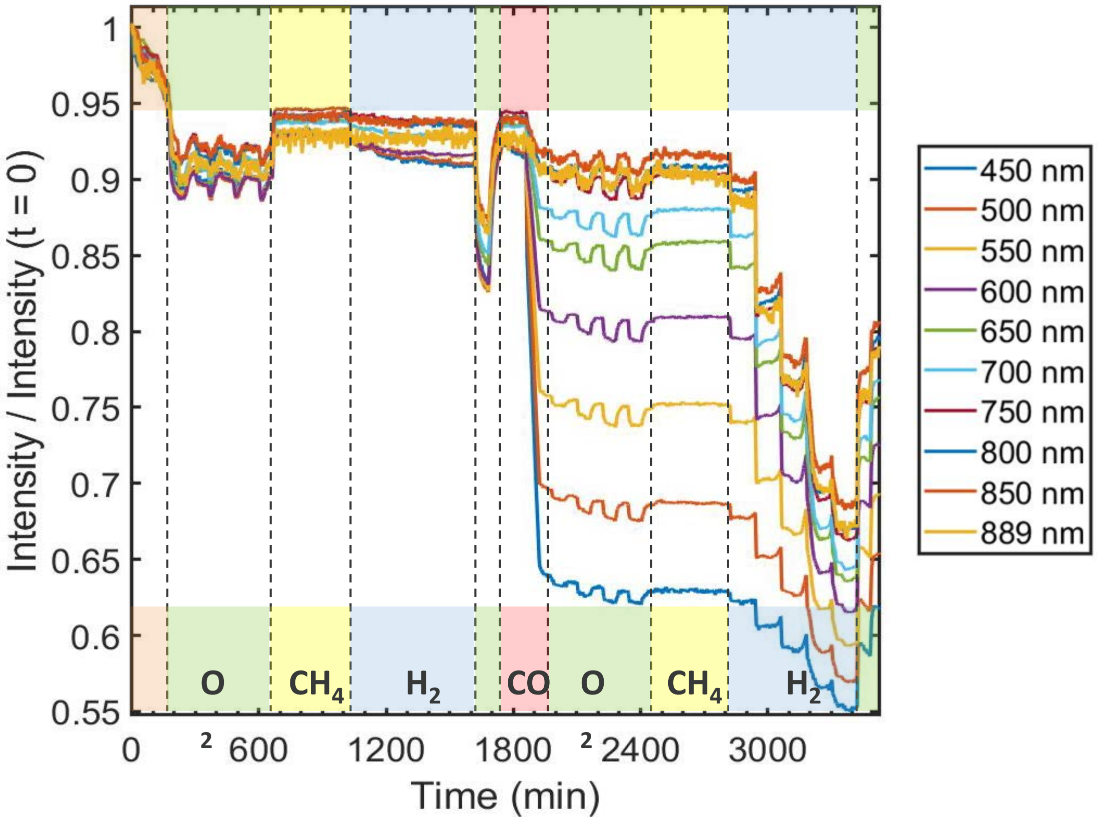




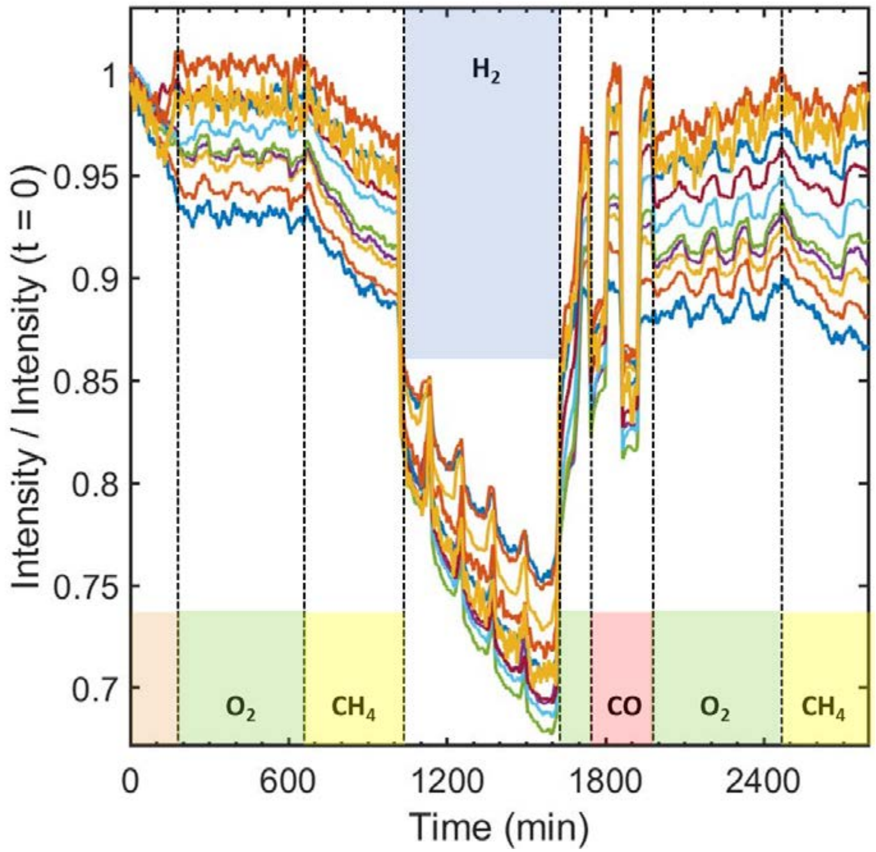
Coating of Spinel Cladding on Significant Length of Sapphire Fiber Was Fabricated and Tested.

Spinel Coated Sapphire Fibers Testing

Uncoated Fiber



Coated Fiber



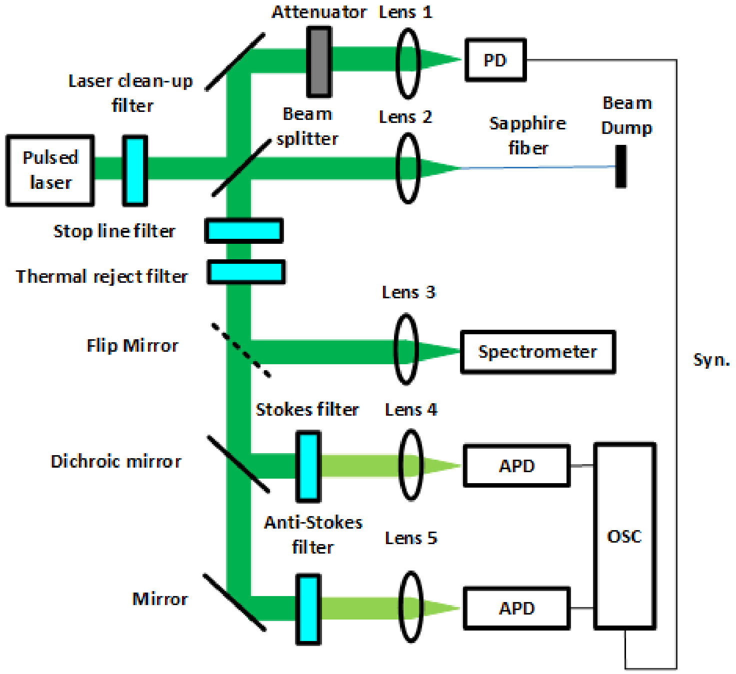
T=800°C

O_2	1, 5, 10, 15
CH_4	1, 5, 10
H_2	1, 5, 10, 25, 50
O_2	15
CO	1, 3
O_2	1, 5, 10, 15
CH_4	1, 5, 10
H_2	1, 5, 10, 25, 50
O_2	15

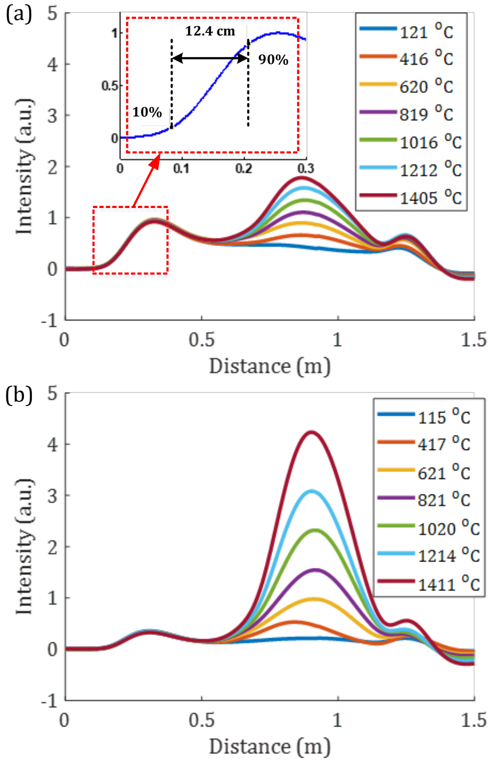
First Information About Responses / Stability for $MgAl_2O_4$ Coated Sapphire is Being Developed.

Raman Based Distributed Temperature Monitoring

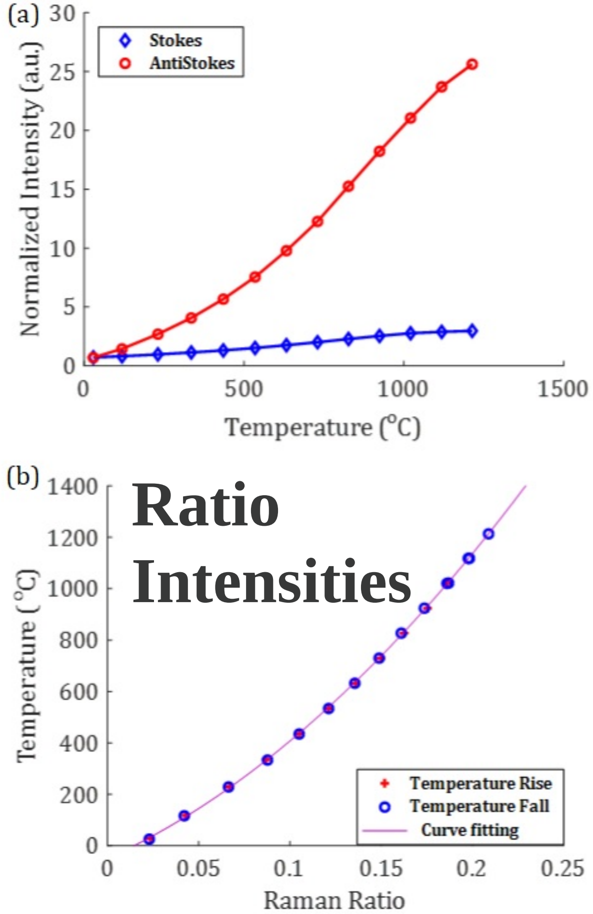
Sapphire-fiber-based Raman DTS



Time-Resolved Raman Stokes / Anti-Stokes



Ratio Intensities



Custom Interrogation Hardware Has Been Developed and Demonstrated for Sapphire Fibers.

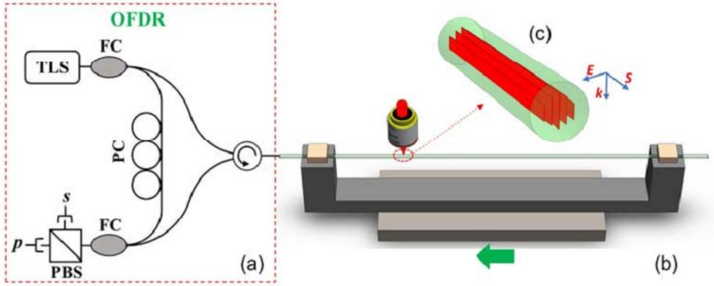
*B. Liu, at al, Journal of Lightwave Technology, 2018

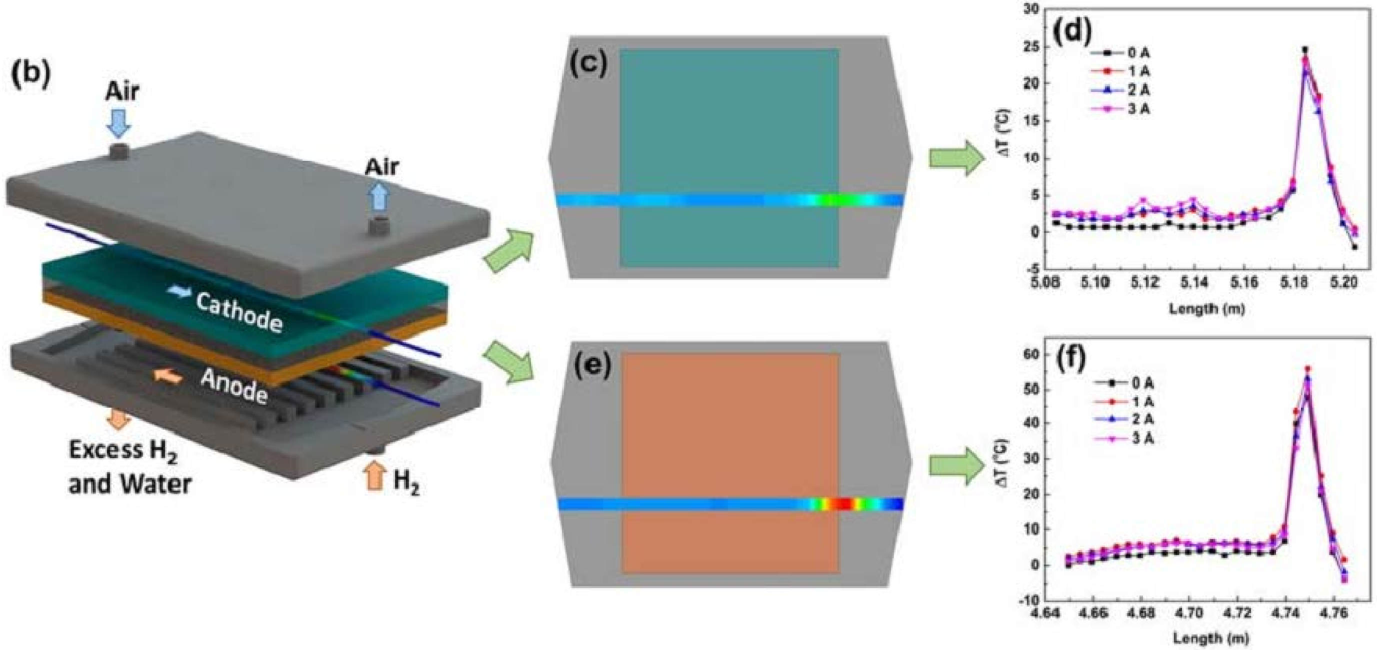
Solid Oxide Fuel Cell Integrated Optical Fiber Sensors

NATIONAL ENERGY TECHNOLOGY LABORATORY

University of Pittsburgh

Elevated Temperatures Near the Anode Stream Inlet Due to the High Thermal Conductivity of the Fuel Gas Stream and Elevated Temperatures Relative to Cell Operating Temperature.





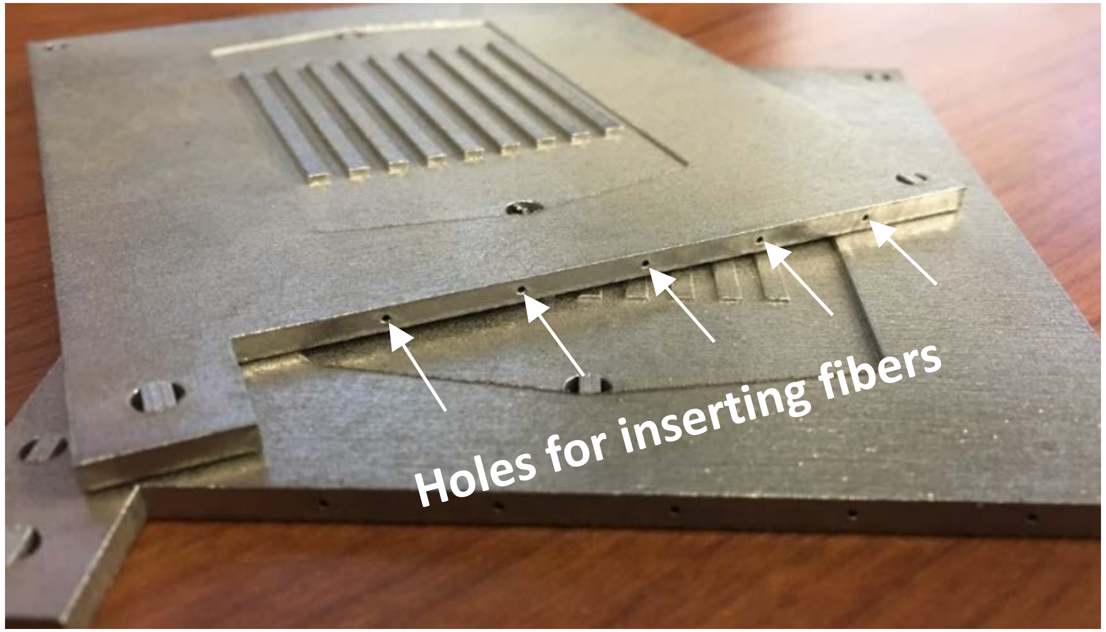
Anode and Cathode Stream Sensing Demonstrations Have Been Performed for Distributed Temperature Sensing with Initial Efforts on Distributed Gas Chemistry Monitoring.

Distributed Optical Fiber Sensors with Ultrafast Laser Enhanced Rayleigh Backscattering Profiles for Real-Time Monitoring of Solid Oxide Fuel Cell Operations, Aidong Yan et al, *Scientific Reports* **volume 7**, 9360 (2017).

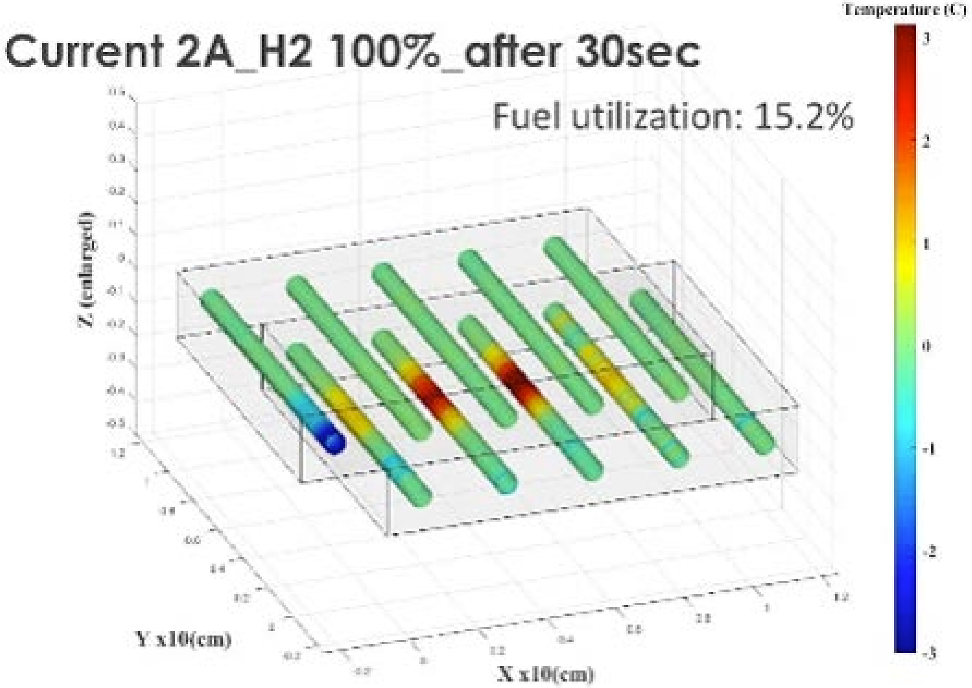
Solid Oxide Fuel Cell Integrated Optical Fiber Sensors

University of Pittsburgh

Additively Manufactured SOFC Interconnects



Furnace Temperature setting at 750°C

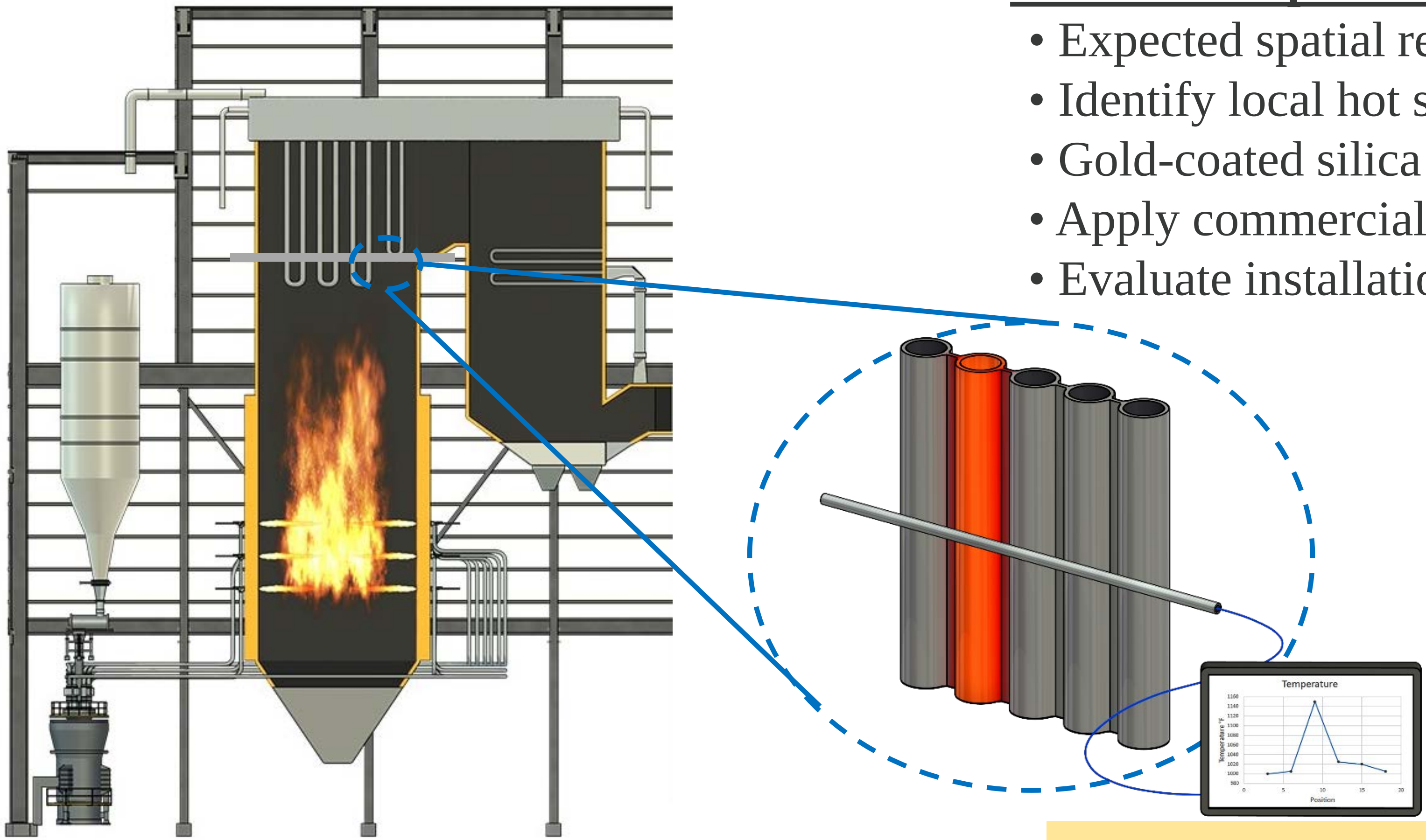


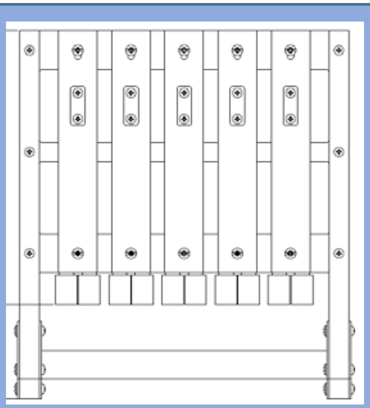
Embedding of Optical Fiber Sensors within Additively Manufactured Interconnects Has Enabled 2-D Profiles of Temperature Distribution During Cell Operation.

Multi-Point Boiler Tube Monitoring

Measure temperatures from every tube

- Expected spatial resolution 1 inch (200 ft long)
- Identify local hot spots, low-load maldistribution of steam
- Gold-coated silica fiber for <1200°F (650°C), air
- Apply commercial optical fiber instrument
- Evaluate installation, performance for application





Heated bar lab test

FY21 field testing in hotter locations with sapphire fiber

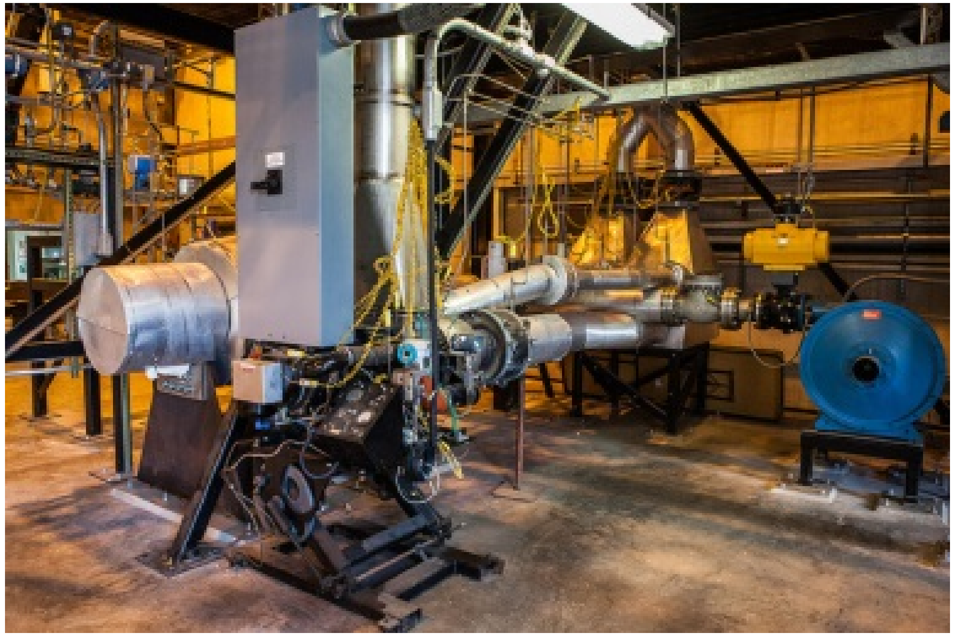
Optical Fiber Based Boiler Tube Temperature Monitoring will Be Pursued w/ Industry Partners.

Pilot-Scale Facilities Available at NETL

High-Pressure Combustion Facility (Aerothermal Rig)

- Simulates hot gas path of a turbine
- Natural gas or hydrogen fuel
- Temperature: up to 1300°C

Hybrid Performance Facility (Hyper)



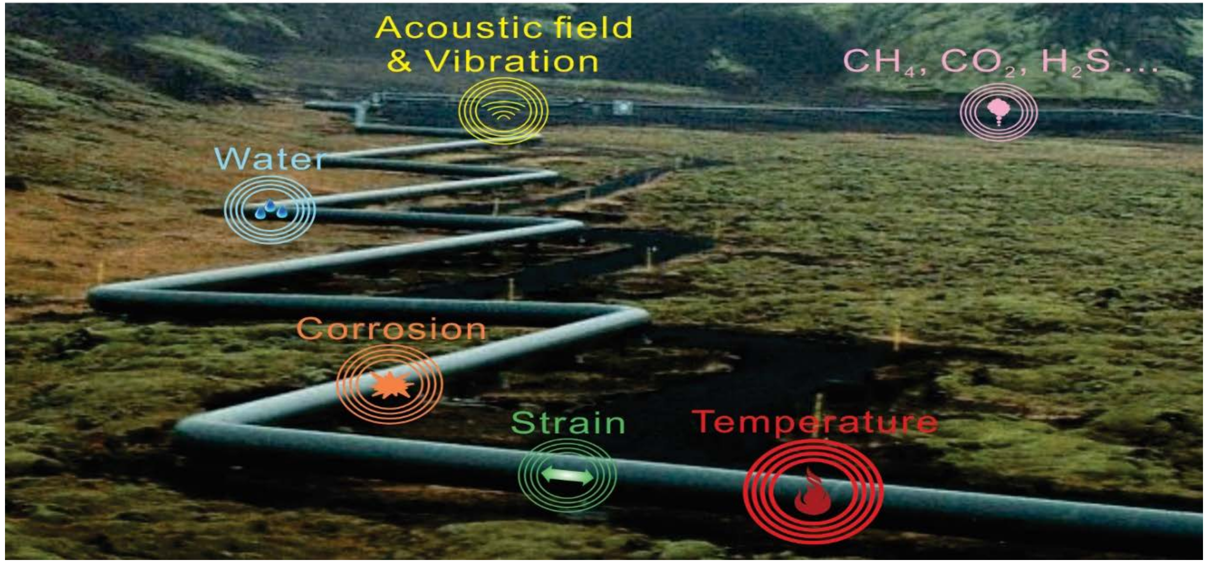
- A 300kW solid oxide fuel cell gas turbine (SOFC-GT) power plant simulator
- 120 kW Garrett Series 85 APU with single-shaft turbine, 2-stage radial compressor, and gear driven generator

Pilot Scale Facilities Exist at NETL for Demonstrations of Prototype Sensor Concepts Under Application Relevant Conditions (Turbine, Combustion, SOFC).

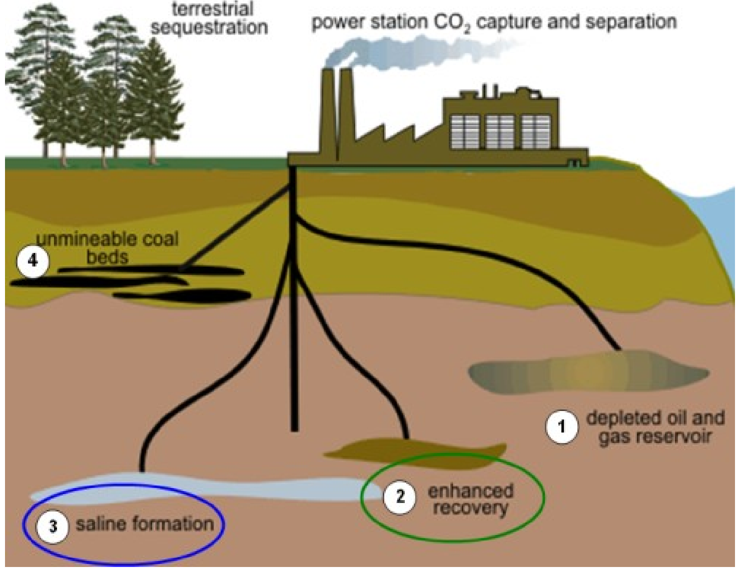
Natural Gas & Subsurface Sensor Technologies

NATIONAL ENERGY TECHNOLOGY LABORATORY

Natural Gas Infrastructure Including Pipelines



Carbon Sequestration



Emphasis Within NETL Research & Innovation Center:

- Early Corrosion On-Set Detection
- Methane Leak Detection & In-Pipe Gas Composition Monitoring

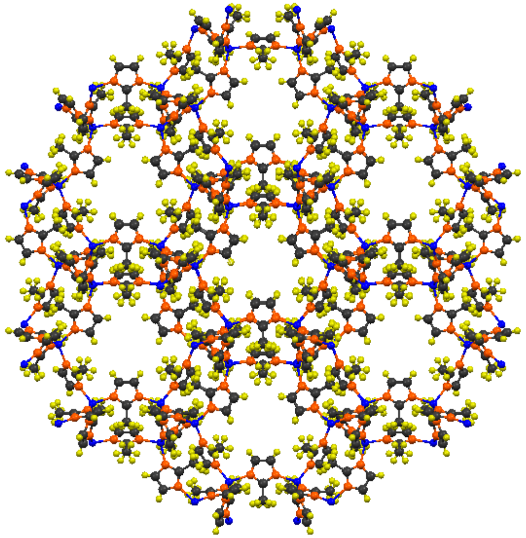
Emphasis Within NETL Research & Innovation Center:

- Distributed CO2 Sensing Throughout a Formation
- Both Direct CO2 and Proxy Parameters (e.g. pH)

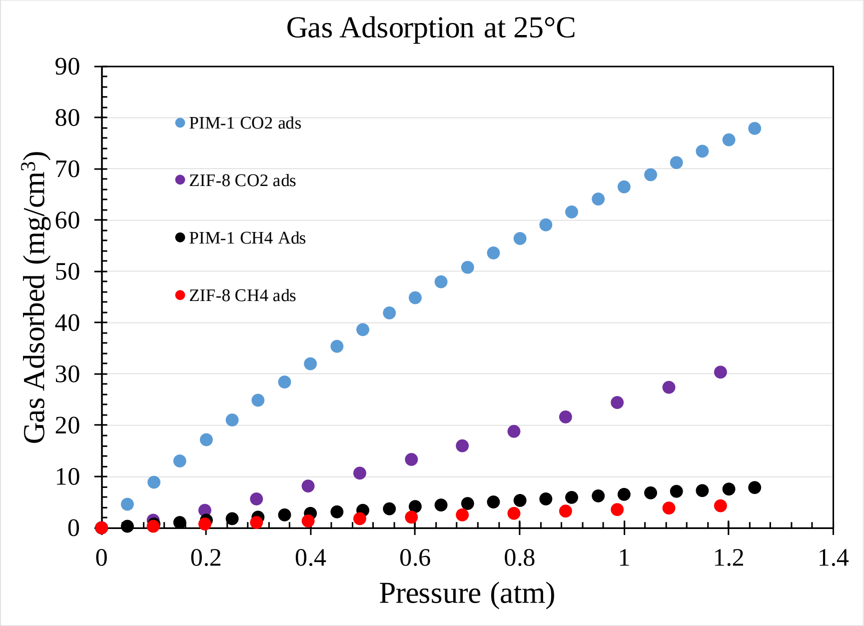
Distributed Measurements of Key Chemical Constituents Including CO_2, CH_4, Early Corrosion Onset Detection, and pH are all Relevant for These Applications.

Key Sensing Materials Under Investigation

Metalorganic frameworks (MOF)

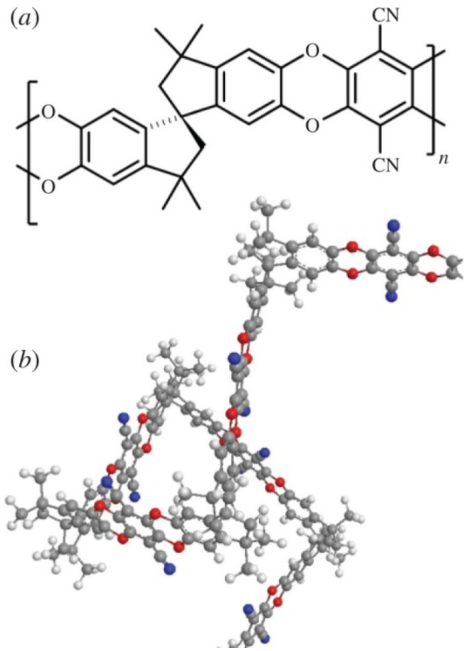


ZIF-8



Leveraging engineered sorbent materials and modifying them for sensing applications

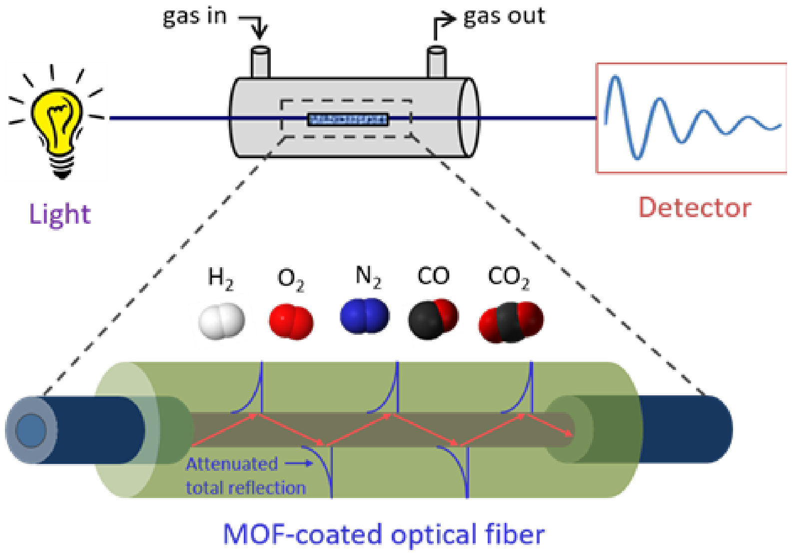
Polymers with engineered porosity

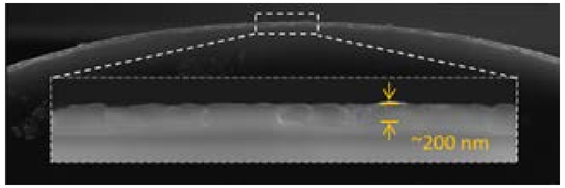


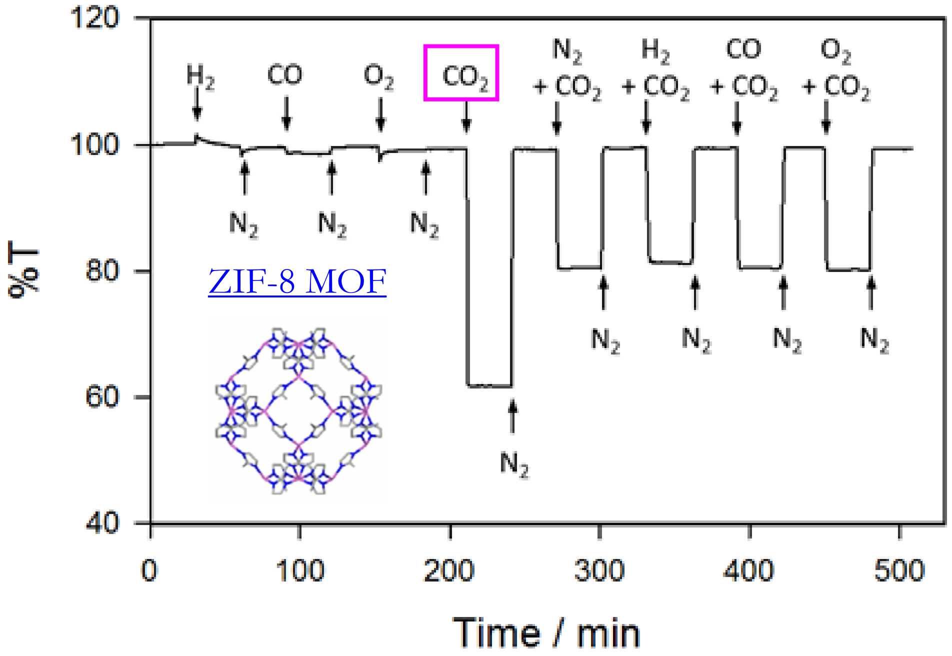
Carbon Capture Materials Development Efforts are Being Leveraged Including Metalorganic Framework Materials and Polymers of Engineered Porosity with Emphasis on CH_4 and CO_2.

Metalorganic Framework(MOF) Integrated Sensors

Optical Fiber Sensor Integrated with MOF Thin Film for Gas Sensor





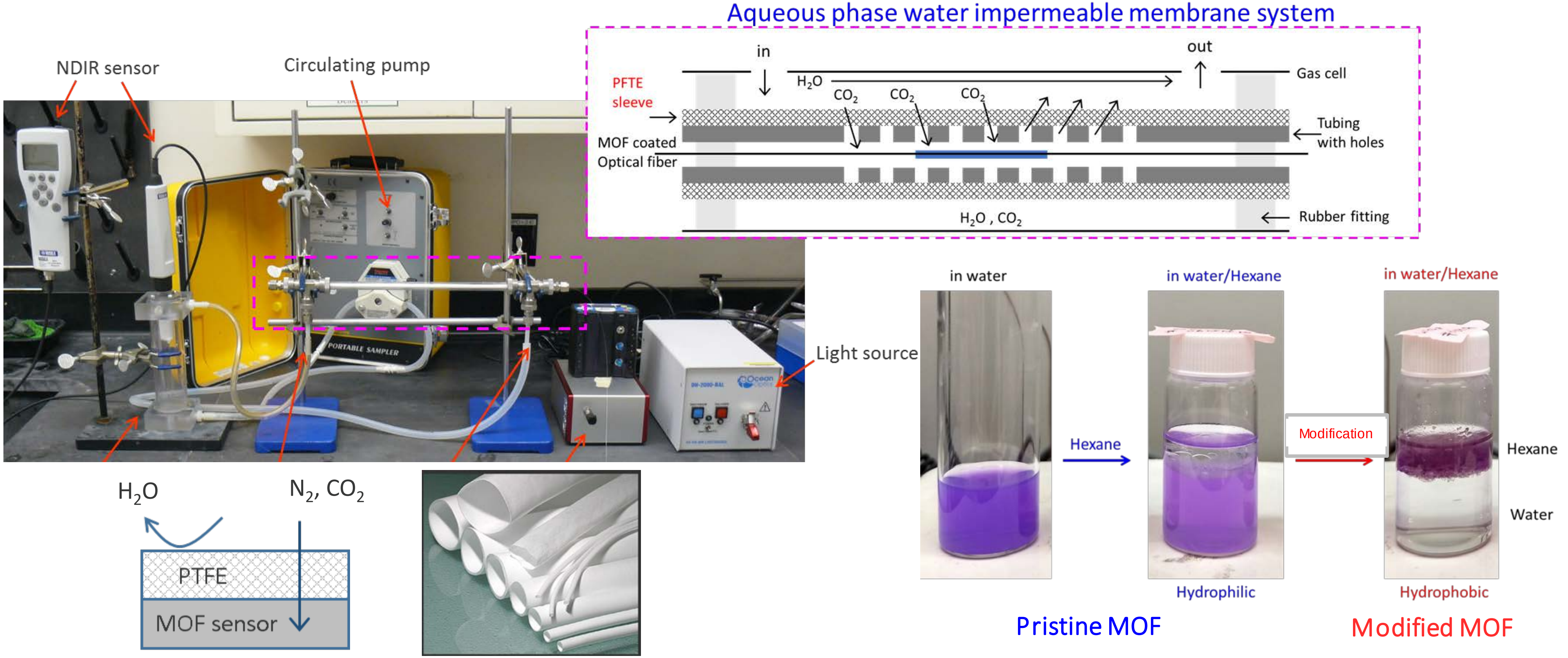


- Clear selectivity to CO_2 relative to other gases.
- Very fast (< 1 minute) response times and excellent reversibility

As One Example, Metalorganic Frameworks Have Been Applied to Thin Film Fiber Optic Based Sensors Showing Rapid and Selective Responses to CO_2 Which are Fully Reversible.

Metal–Organic Framework Thin Film Coated Optical Fiber Sensors: A Novel Waveguide-Based Chemical Sensing Platform,
KJ Kim, P Lu, JT Culp, PR Ohodnicki, ACS sensors 3 (2), 386-394, (2018).

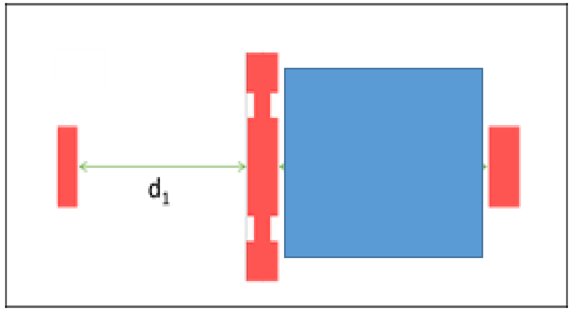
Functionalized MOFs for Improved Water Stability

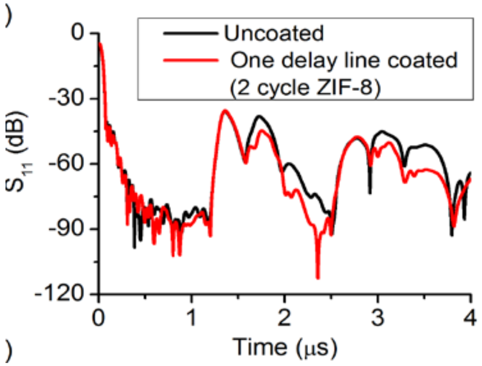


Packaging and Surface Modifications to Existing Metalorganic Frameworks to Improve Stability.

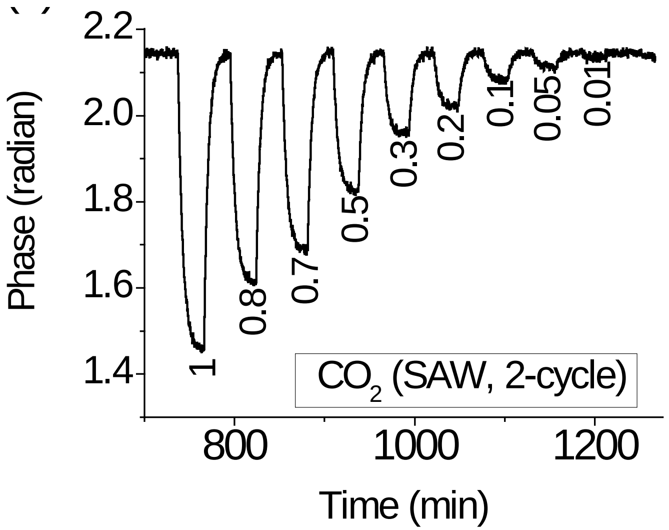
Metalorganic Functionalized SAW Sensors

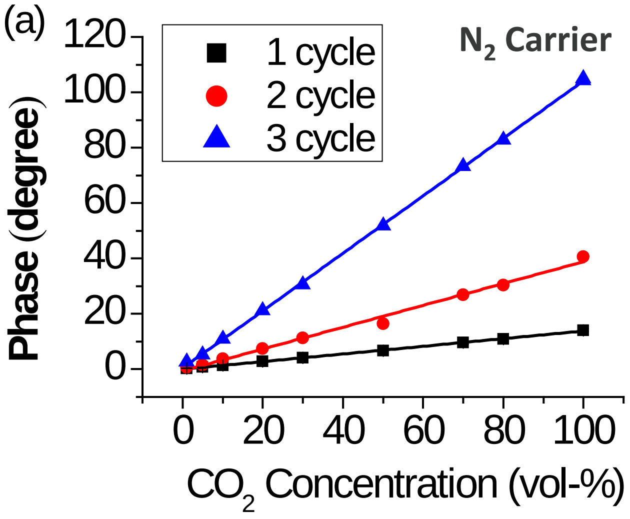
Schematic of Device Operation

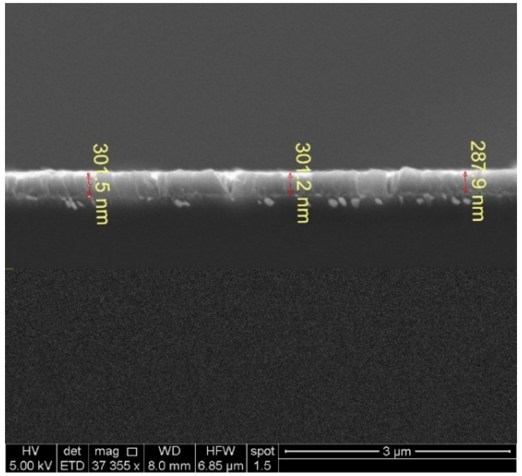




Wired Device Operation With and Without ZIF-8





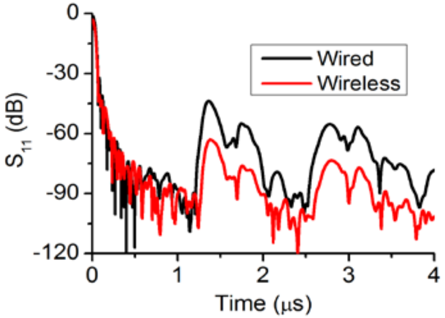


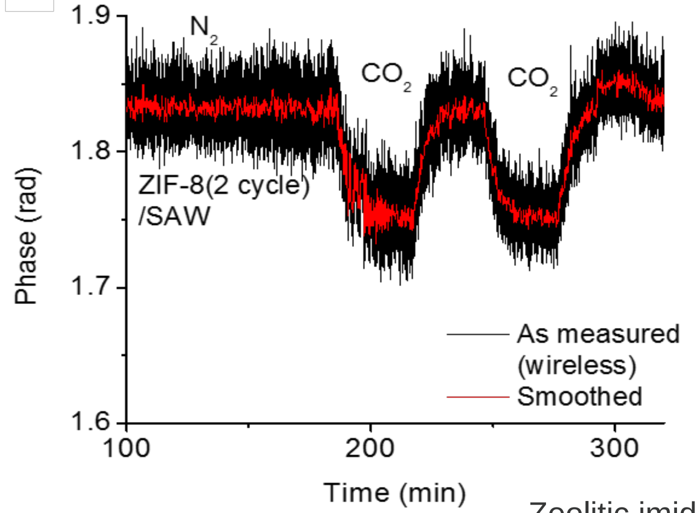
Metalorganic Framework Materials Integrated with Surface Acoustic Wave Based Devices are Also Being Explored Through a Mass Uptake Based Mechanism.

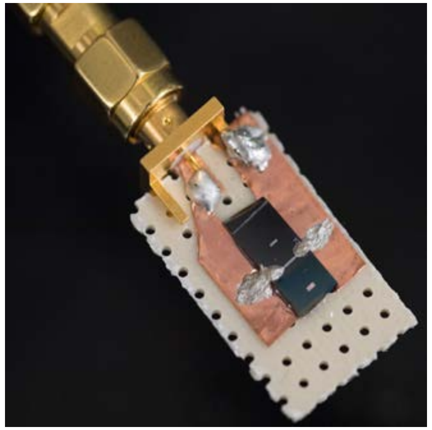
Zeolitic imidazolate framework-coated acoustic sensors for room temperature detection of carbon dioxide and methane,
J Devkota, KJ Kim, P Ohodnicki, JT Culp, D Greve, JW Lekse, Nanoscale, (2018).

Demonstrated Wireless Gas Sensing

Interrogation Distance > 45 cm With a Commercial Antenna







Demonstration of Wireless and Real Time Sensing Capability of the SAW sensors to Monitor Gases

Zeolitic imidazole framework-coated acoustic sensors for room temperature detection of carbon dioxide and methaneJ Devkota, KJ Kim, PR Ohodnicki, JT Culp, DW Greve, JW Lekse, arXiv preprint arXiv:1712.08468

Real-Time, Wireless Gas Sensing with MOF Based Sensors Have Been Demonstrated.

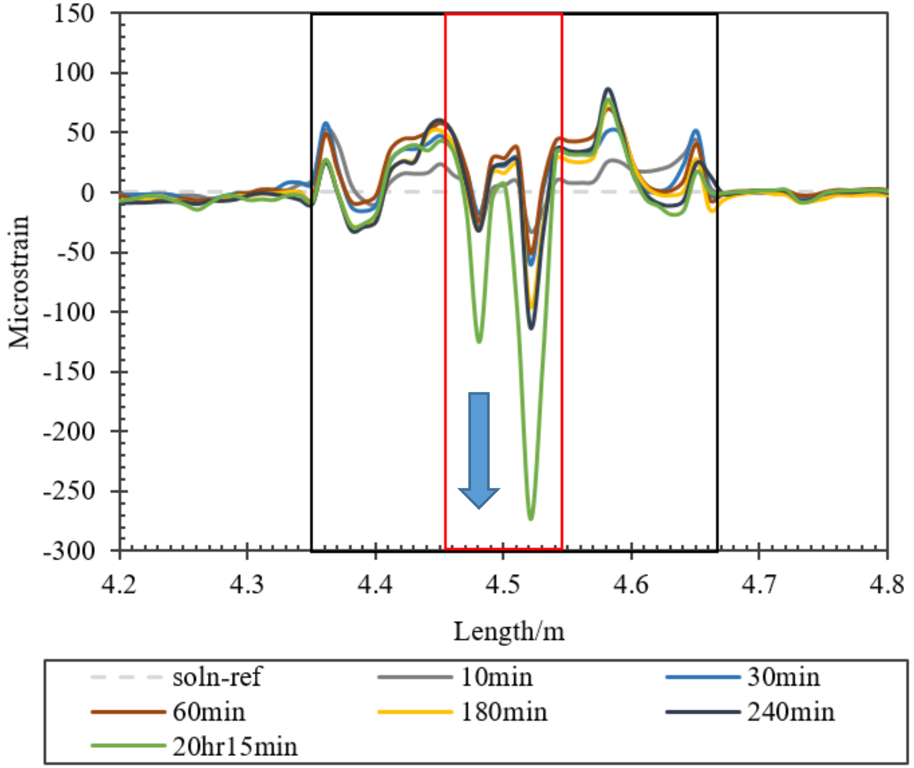
Zeolitic imidazolate framework-coated acoustic sensors for room temperature detection of carbon dioxide and methane,
J Devkota, KJ Kim, P Ohodnicki, JT Culp, D Greve, JW Lekse, Nanoscale, (2018).

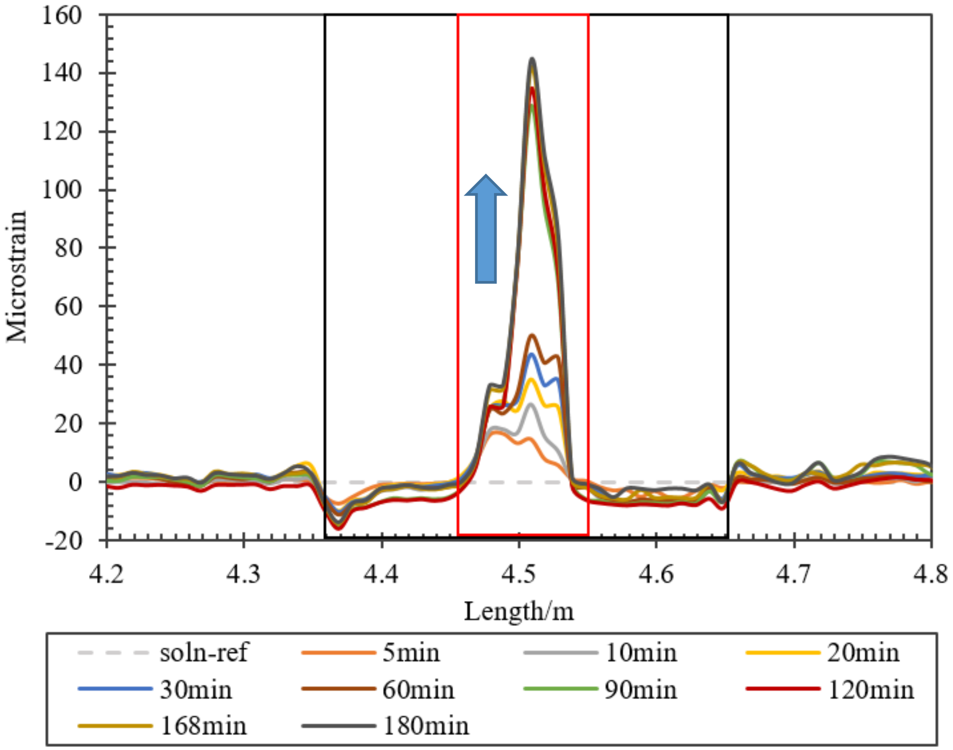
Distributed Corrosion On-set : Thick Film Proxies

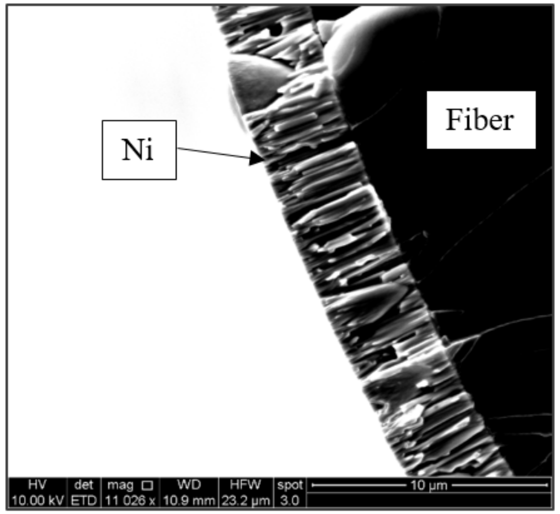
Single-mode jacketed fiber

Strain-based, fully distributed signal

- Ni Electroless Deposition
- Ni film Dissolution (HCl solution, pH 0)







Integration of Thick Film Corrosion Proxies into Distributed Sensing Schemes is Being Pursued.

Review on corrosion sensors for structural health monitoring of oil and natural gas infrastructure, RF Wright, P Lu, J Devkota, F Lu, M Ziomek-Moroz, PR Ohodnicki, Smart Structures and NDE for Energy Systems and Industry 4.0 10973, 109730N, (2019).

Summary and Conclusions

- **NETL Has a Well Established Focus Area in Enabling Materials for Harsh Environment Sensing Applications**
- **NETL Has Excellent Capabilities for High Temperature and Harsh Environment Sensor Development**
- **Functionalized Optical Fiber and SAW Sensors Show Promise for a Range of Energy Related Applications**
- **NETL R&IC Has Active In-House Research In a Broad Range of Areas with an Emphasis on Sensing Materials**
  - **Power Generation**
  - **Subsurface CO_2 Storage / Oil & Gas**
  - **Natural Gas Infrastructure**
  - **Electricity Infrastructure**
- **We are Always Interested in Collaboration Opportunities as Well as Joint Technology Development and/or Licensing of Patented Concepts**