University of Pittsburgh

Kick-off Meeting

UCR-AOI2: Engineering Metal Oxide Nano-materialsfor Fiber Optical Sensor Platforms

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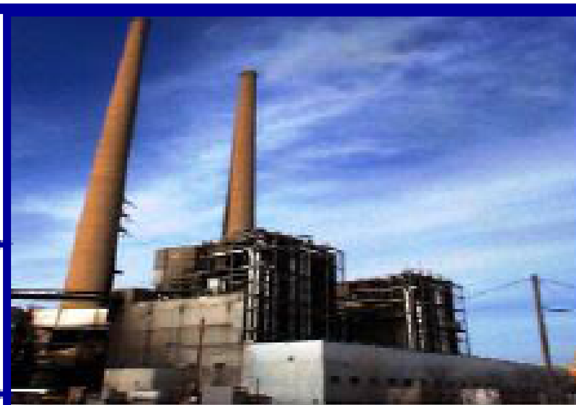
Outlines

- **Background**
- **Objective/Vision**
  - Sensing materials
  - Fiber platforms
- **Team Description and Assignments**
- **Task Descriptions**
  - Objective
  - Previous Works
  - Current Status
- **Gantt Chart**
- **Milestones**

Background: Role of Sensor for Fossil Energy Generation

FUEL COSTS
$39 Million/Year @
9,500 BTU/kw-hr,
$1.25/million BTU's

Non Fuel O&M COSTS
$6 Million/Year
(10 - 20% of total costs)



Total Fuel + O&M Budget
$45 Million - Avg. 500 MW Unit

Gaseous emissions

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

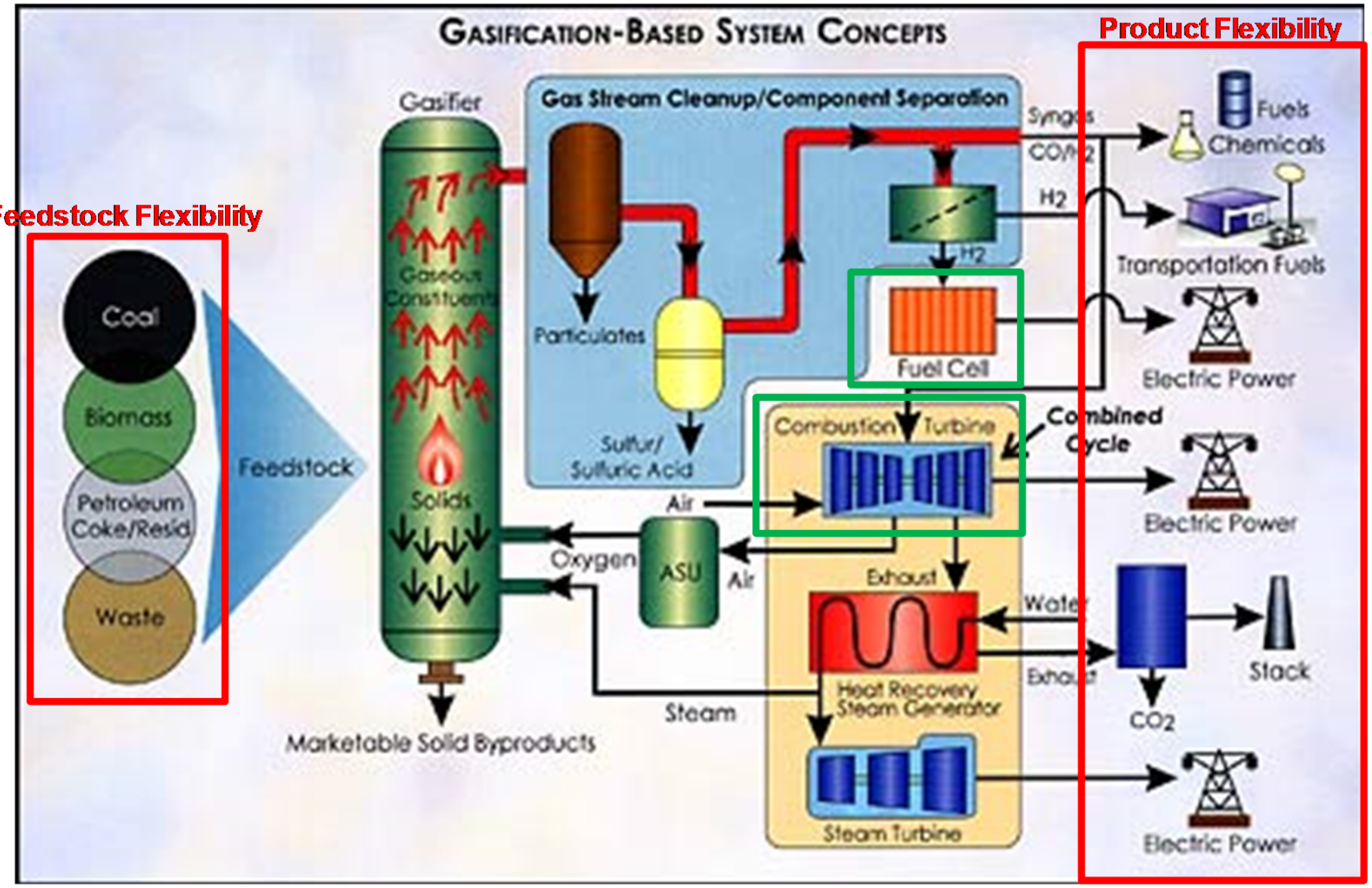
Solid wastes

Analysis for Year 2000

- **1% improvement in EFFICIENCY**
  - $390,000 savings in fuel
  - $4.1 million for entire installed fossil capacity
- **Approximately 1% REDUCTION in greenhouse gases and solid wastes**
- **1% increase in AVAILABILITY**
  - Yields 33 million kw-hr/yr added generation for a 500MW plant
  - Approximately $2 million in sales (at $60/1000kw-hr)
  - An additional 5,000 MW of power for entire installed fossil capacity

Gasification for Combined Power and Heat

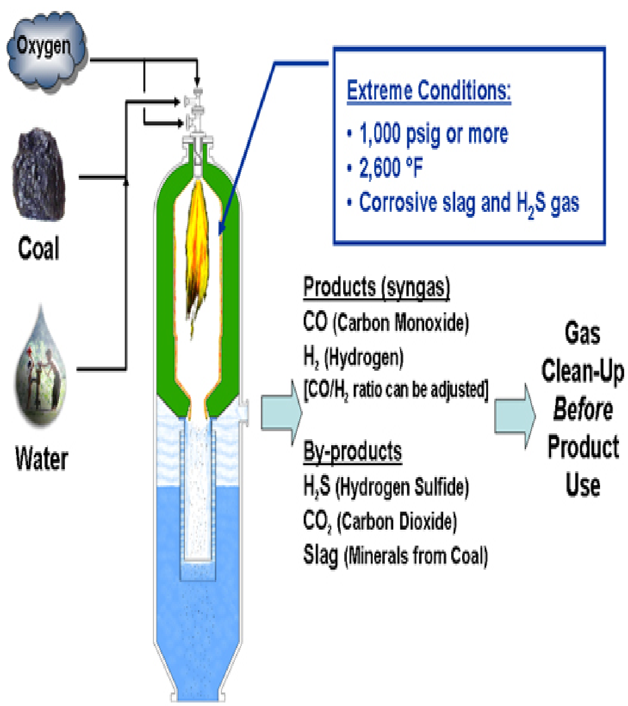
Advanced
Fossil-Based
Power Generation
Involves High
Temperature
<u>Gas Streams</u>
(Coal or Natural Gas)



http://www.fossil.energy.gov/programs/powersystems/gasification/howgasificationworks.html

Envisioned Fossil-Based Power Plants of the Future are Highly Complex Making Sensors and Controls of Crucial Importance.

Range of "Harsh-Opportunities' in Fossil Energy

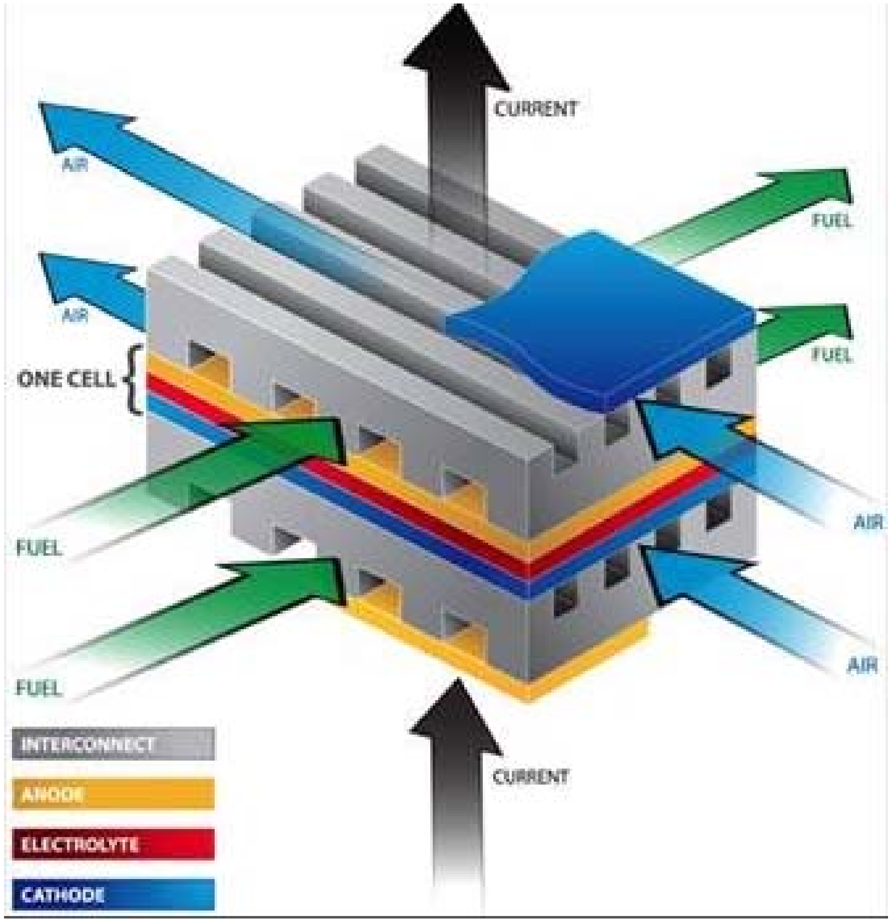


	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
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

- **Highly stable physical sensors are needed in highly reactive gas streams**
- **Probing fossil fuel chemistry at extremely high temperatures**
- **High spatial resolution measurements**

Solid Oxide Fuel Cell Basics: Fuel-in Electricity Out

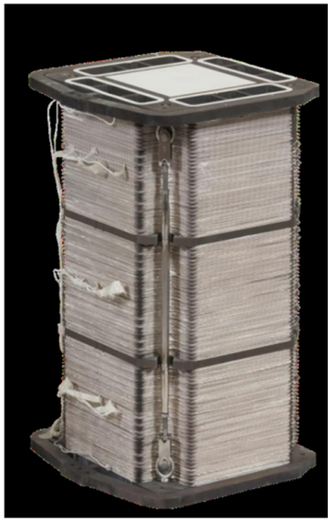
- **High-temperature (600-850C) operation**
- **Varying atmospheres**
- **0-100% H2 at the Anode**
- **0-20% O2 at the Cathode**
- **High current / stack voltage**
- **60% efficient (fuel to electric)**

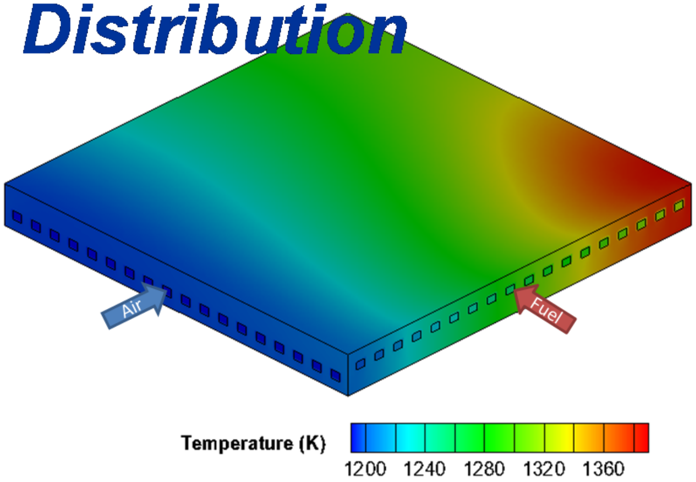


Objective/Vision: Probing High-T Chemistry in SOFC Operation

- **Develop an integrated sensor solution to perform direct and simultaneous measurements of chemical reaction and temperature in SOFC with 5-mm spatial resolution.**

Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution





Pakalapati, S. R., 'A New Reduced Order Model for Solid Oxide Fuel Cells,' Ph.D Thesis, Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV

- **Fuel consumption not uniform**
- **T profile not uniform (>150C)**

Objective- Sensing Materials: Tailoring the Refractive Indices and Chemical Responsivity

Requirement:

- 3D Geometry (Reduces unwanted anisotropy)
- $\Lambda << \lambda$ (reduce optical scattering loss)
- Processing on Arbitrary Shapes (fiber…)
- **Wide tenability of refractive indices ($\Delta n > 1.5$)**
- **Reactive to a wide array of gas species**
- **Low cost**
- **High Temperature stable**

Options

Semiconductor Processing?

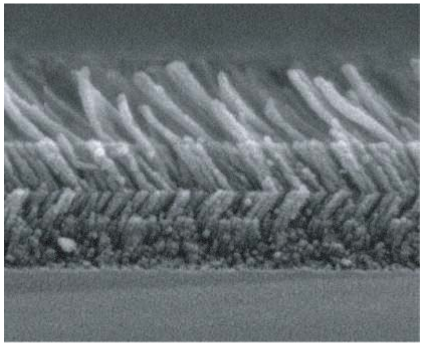
- ❖ Doping, sputtering
- ❖ Cost, not flexible

Colloidal Templating?

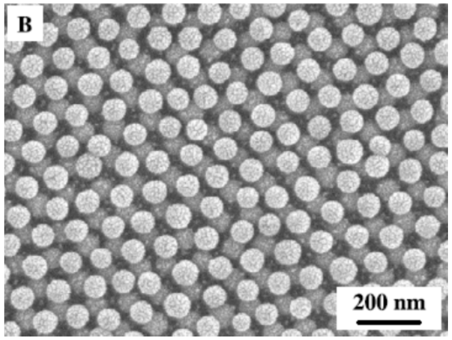
- <50-nm
- Structure limited
- Limit tuning of porosity

Block Copolymer Templating?

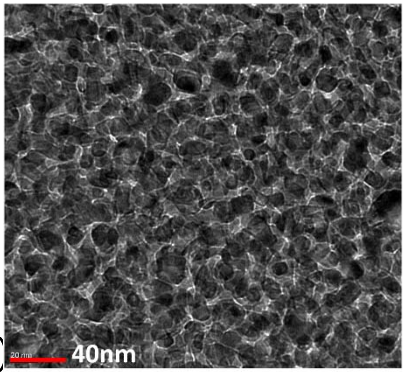
- ✓ alcohol soluble
- ✓ 5nm to 100nm
- ✓ Flexible structures
- ✓ Wide tuning of porosity



Xi (2007, Prof. Schubert's group at RPI)

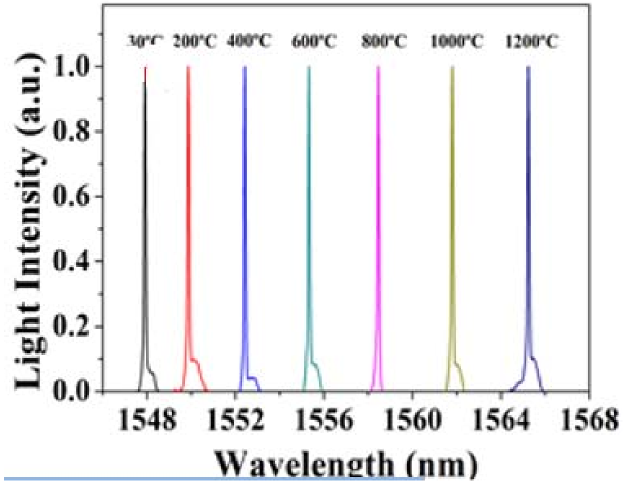


W. Min, Nanotechnol. 19, 475604 (2007)

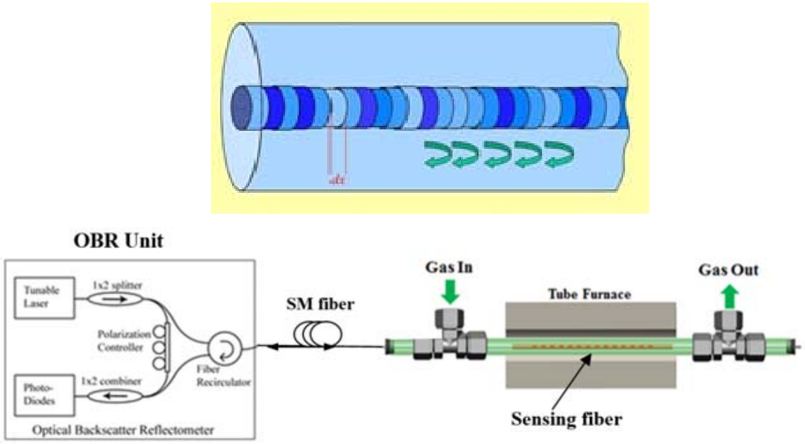


Objective/Vision – Sensing Platforms and Integration

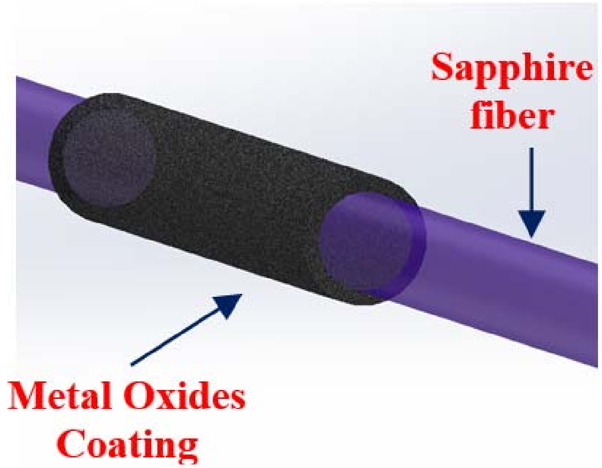
High-Temperature Stable FBG



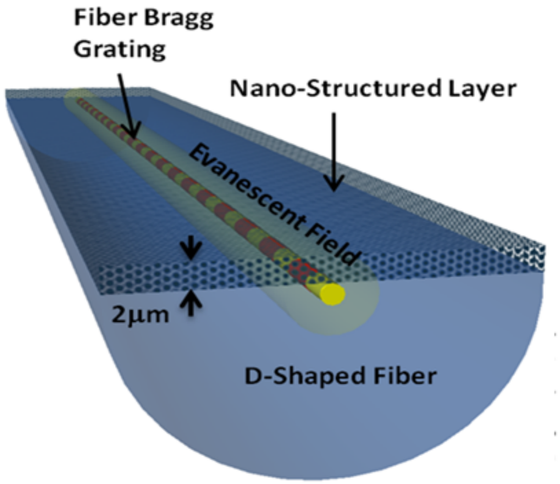
Distributed Rayleigh Scattering



Sapphire Fibers



Specialty D-shaped Fiber



Team Description and Assignments

- **University of Pittsburgh: PI: Kevin P. Chen**
  - Aidong Yan (Ph.D. student): Sensing Materials
  - Mohan Wang (Ph.D. student): Sensor Platform
  - Guangquang Liang (Research fellow): Integration
- **NETL Collaborators**
  - Dr. Paul Ohodnicki's group: Sensor Material Collaboration
  - Dr. Michael Buric's group: Sensor Platform (Silica and Sapphire) and Integration
  - NETL Fuel Cell Testing Team
- **Industry Collaborators**
  - Corning: Specialty fiber fabrication
  - University of Sydney: Specialty fiber fabrication
  - NEC America: Industry outreach

Task Descriptions

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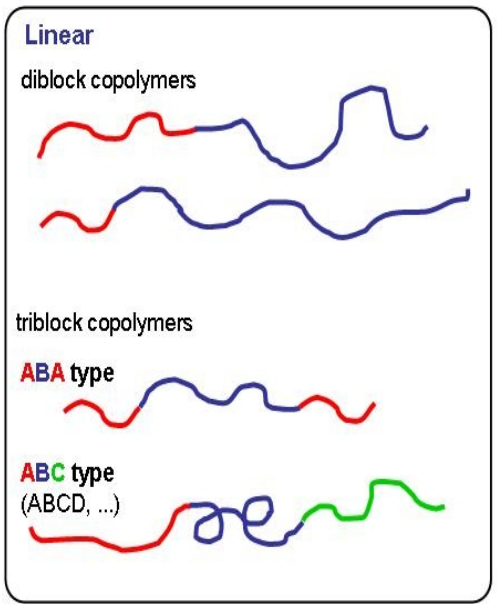
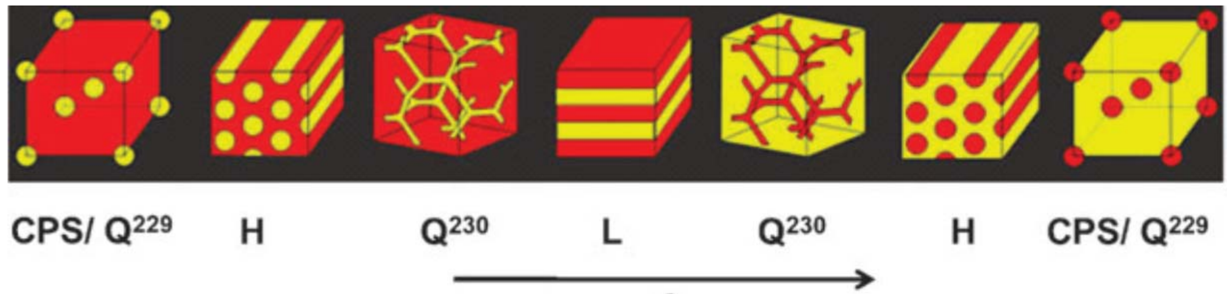
Sensing Materials: Co-Polymer Templating by F-127

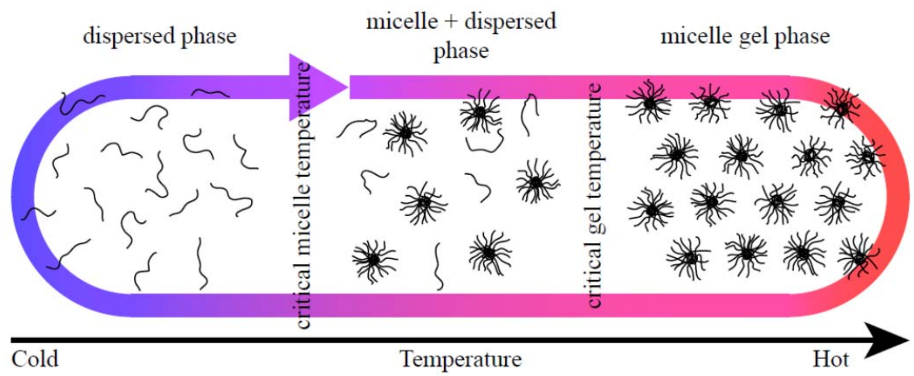
F127 Pluronic

- A triblock copolymer
- Highly Compatible with the Preferred Solvents (Alcohol)
- Has better higher temperature stability

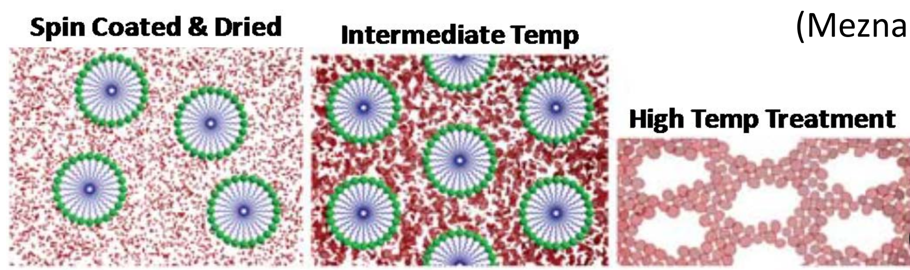


(Orilall, 2011)





(Meznarich, 2012, p. 107)



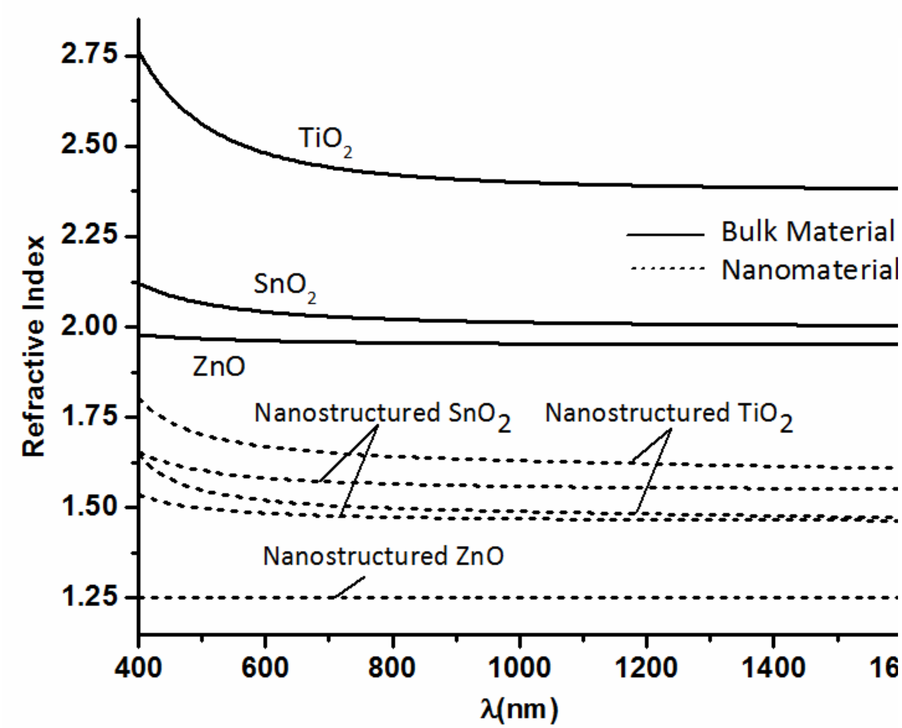
(Shao, 2010)

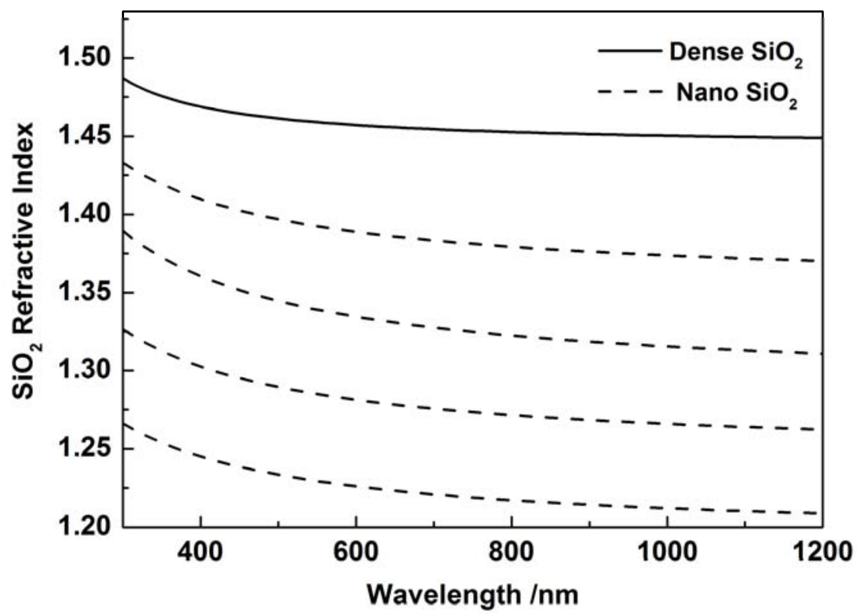
Metal Oxides and Their Dopant Variants

- Metal Source: $SnCl_4$, $TiCl_4$, and $Zn(O_2CCH_3)_2(H_2O)_2$
- Si Source: Tetraethyl Orthosilicate
- Solvent: Ethanol
- Block Copolymer: Pluronic F-127
- Stabilizer: HCl for most, NH_4OH for Zn

Controlling Refractive Indice

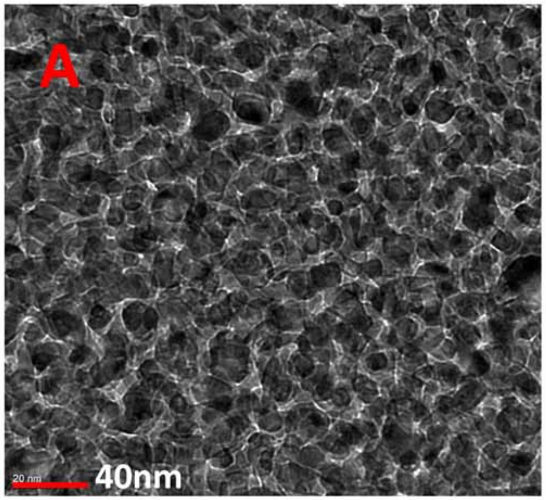
- **TiO_2: $\Delta n \sim$ 1.4 to 2.5**
- **SnO_2: $\Delta n \sim$ 1.4 to 2.1**
- **ZnO: $\Delta n \sim$ 1.25 to 2.0**
- **SiO_2: $\Delta n \sim$ 1.2 to 1.45**

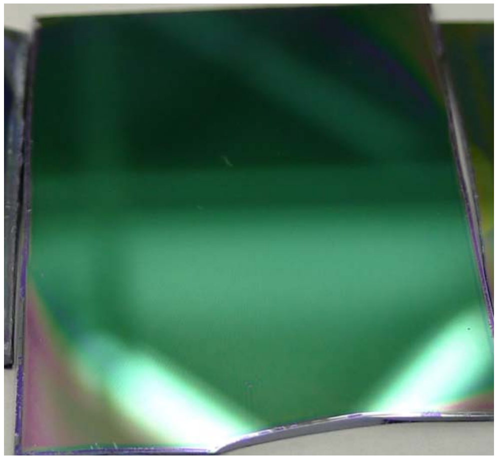




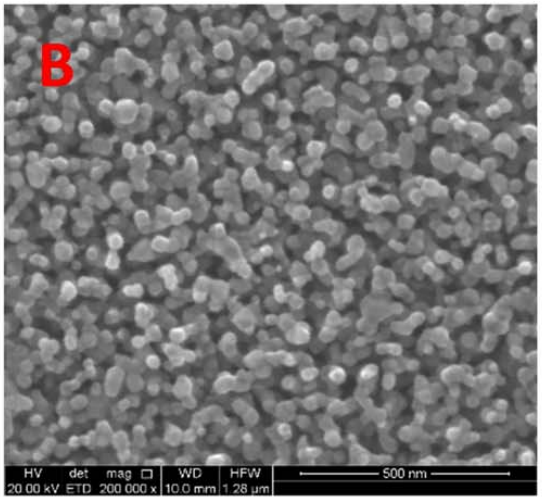
Metal Oxides and Their Dopant Variants

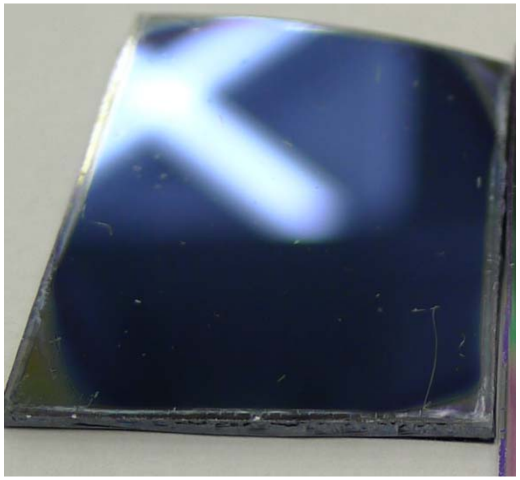
TEM of TiO_2



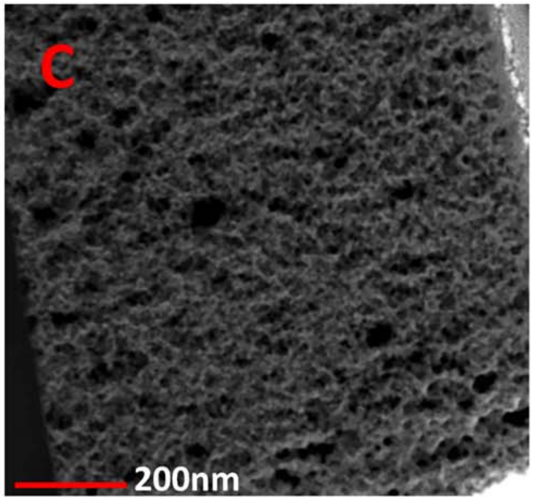


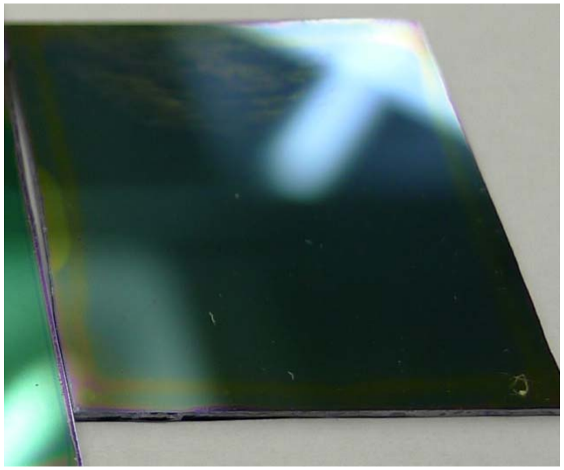
SEM of ZnO





SEM of SnO_2

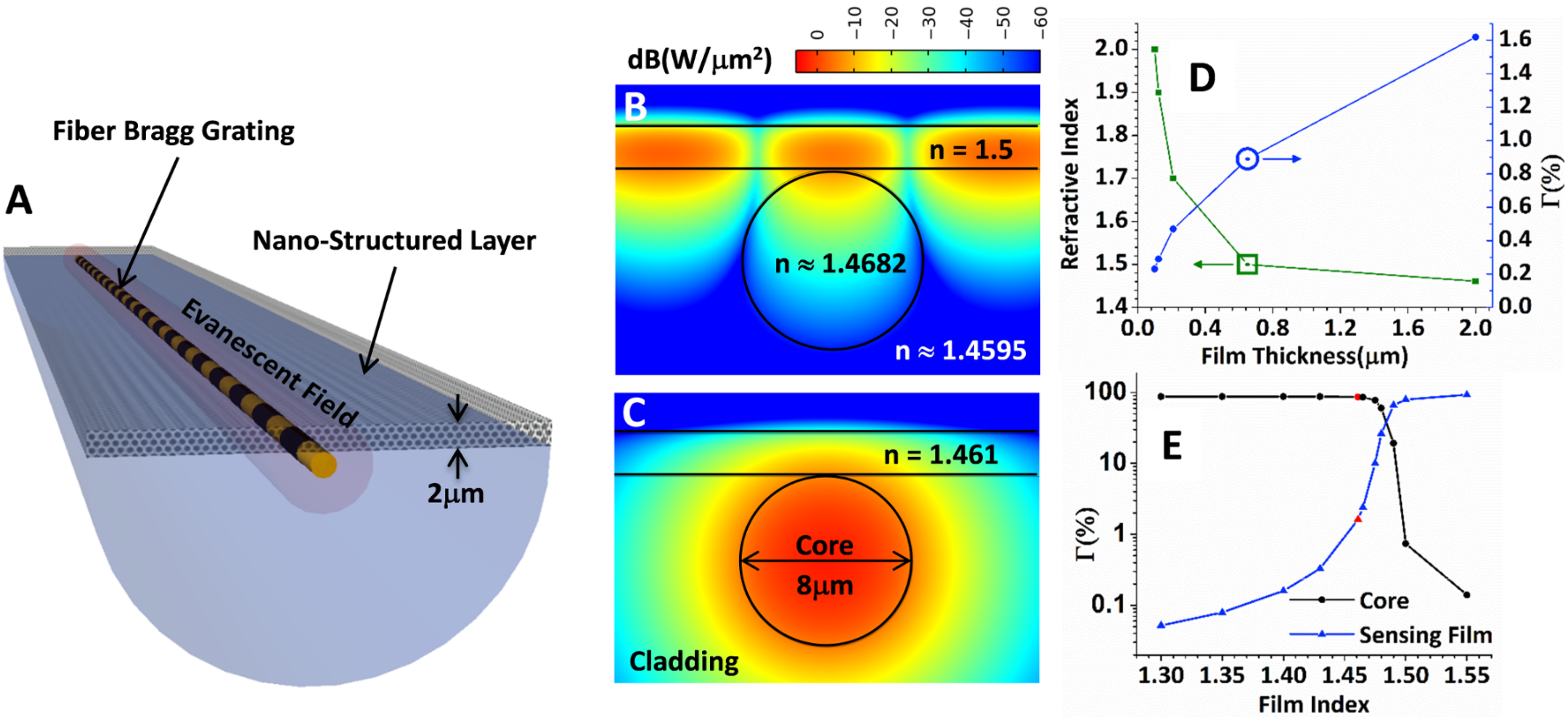




Optical Sensing: Metal Oxide on Optical Fiber Platform

In the evanescent wave configuration

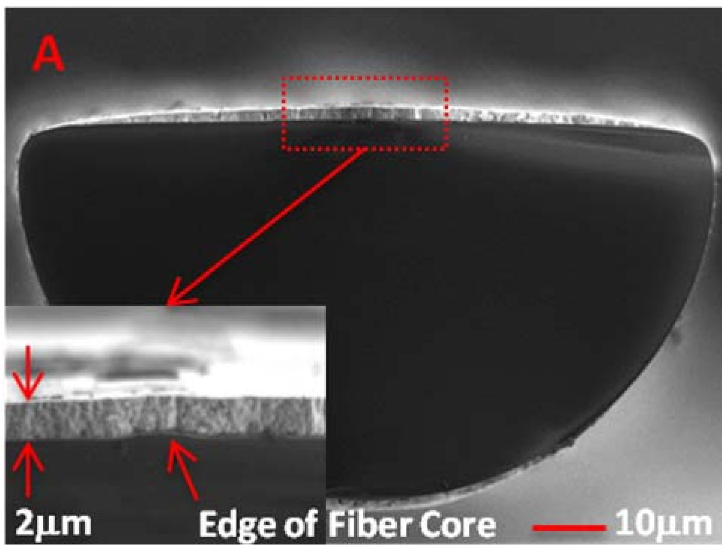
Refractive Index Matching is Critical

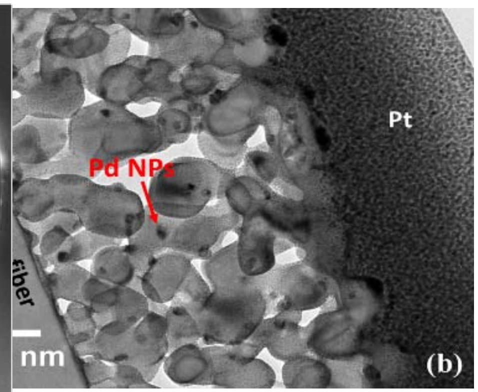


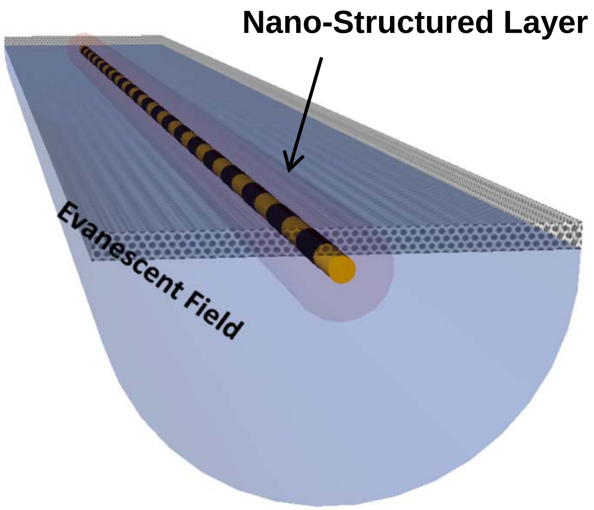
Finite Element Simulation of the Power Distribution of the Fundamental Mode

Metal Oxides Enabled Chemical Sensors

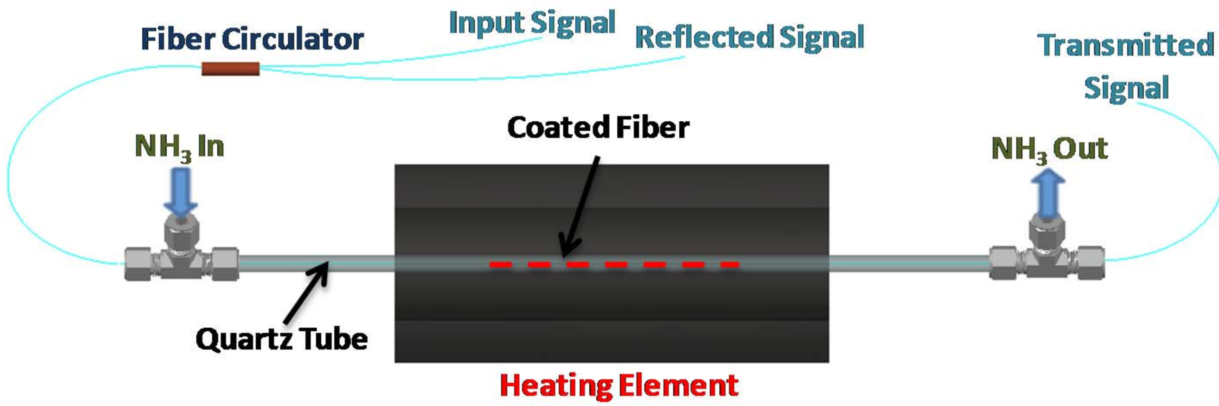
- **Nano-Engineered metal oxide sensory film**
  - **Porosity control for refractive index matching**
  - **Rare-earth or noble metal dopants for specificity**
  - **Pd-TiO2**
- **Sensor can operate >700C**
- **No electrical components in target environment**

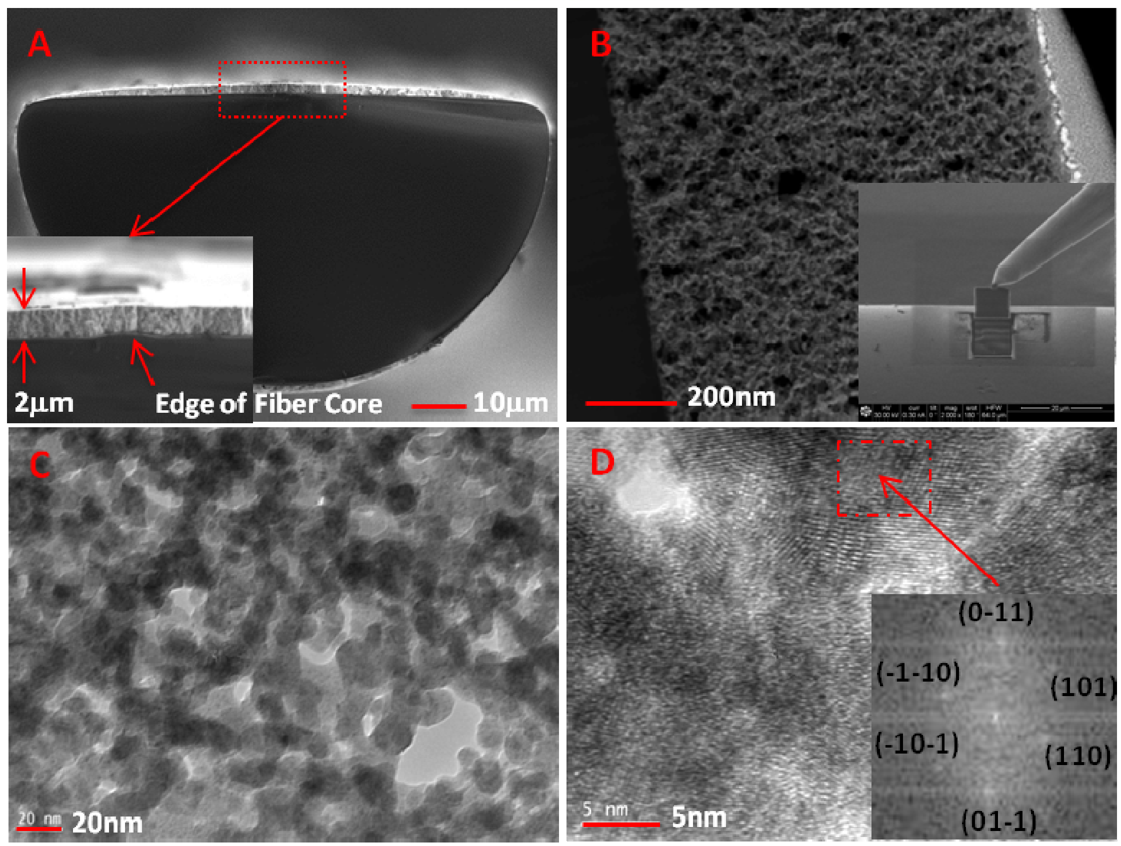






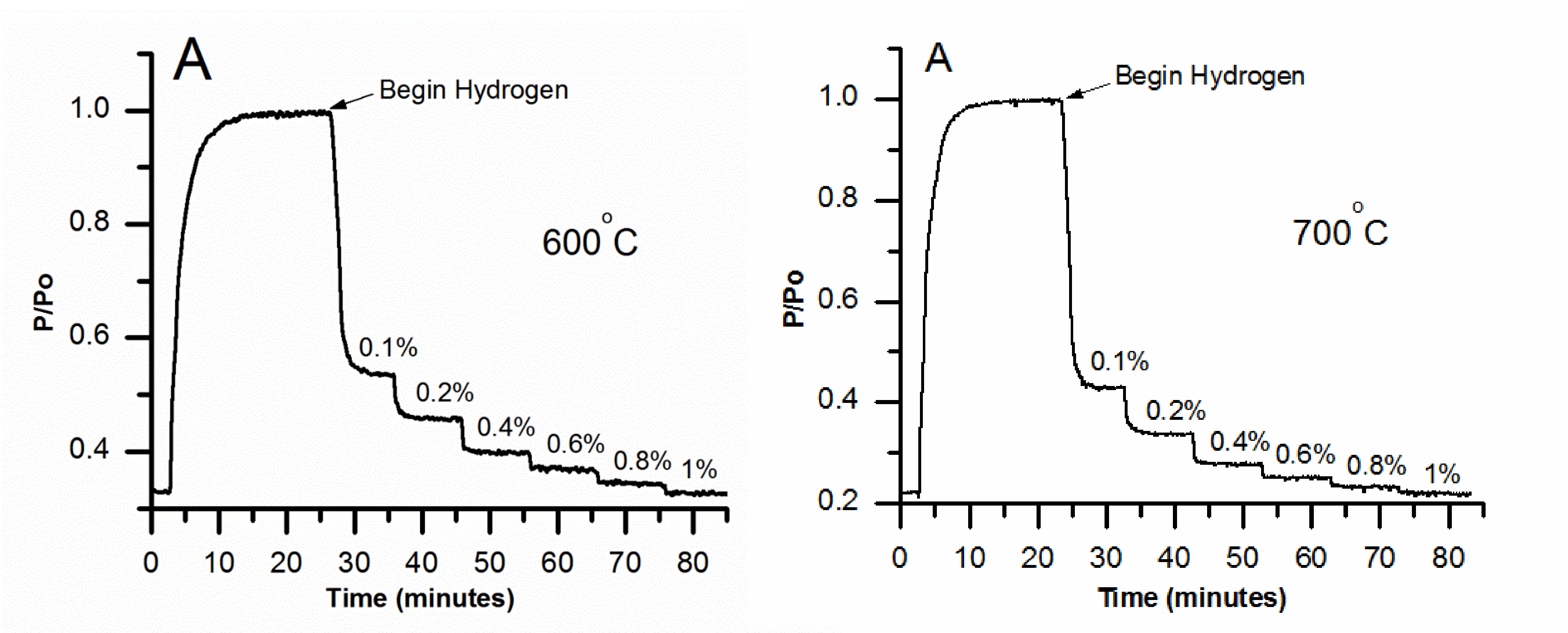
High-Temperature Chemical Sensor on D-shaped Optical Fiber





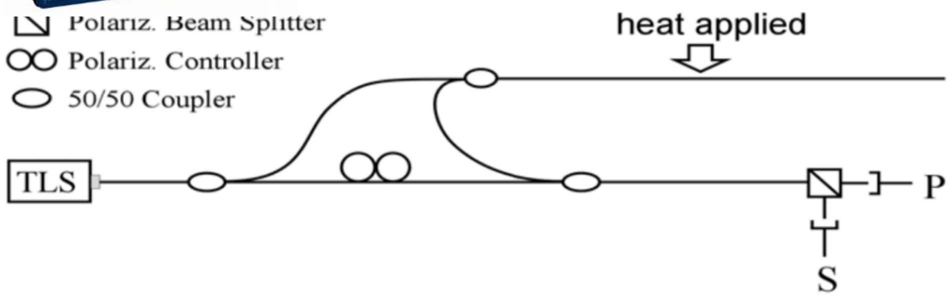
Fiber Optic Hydrogen Sensor at 700C

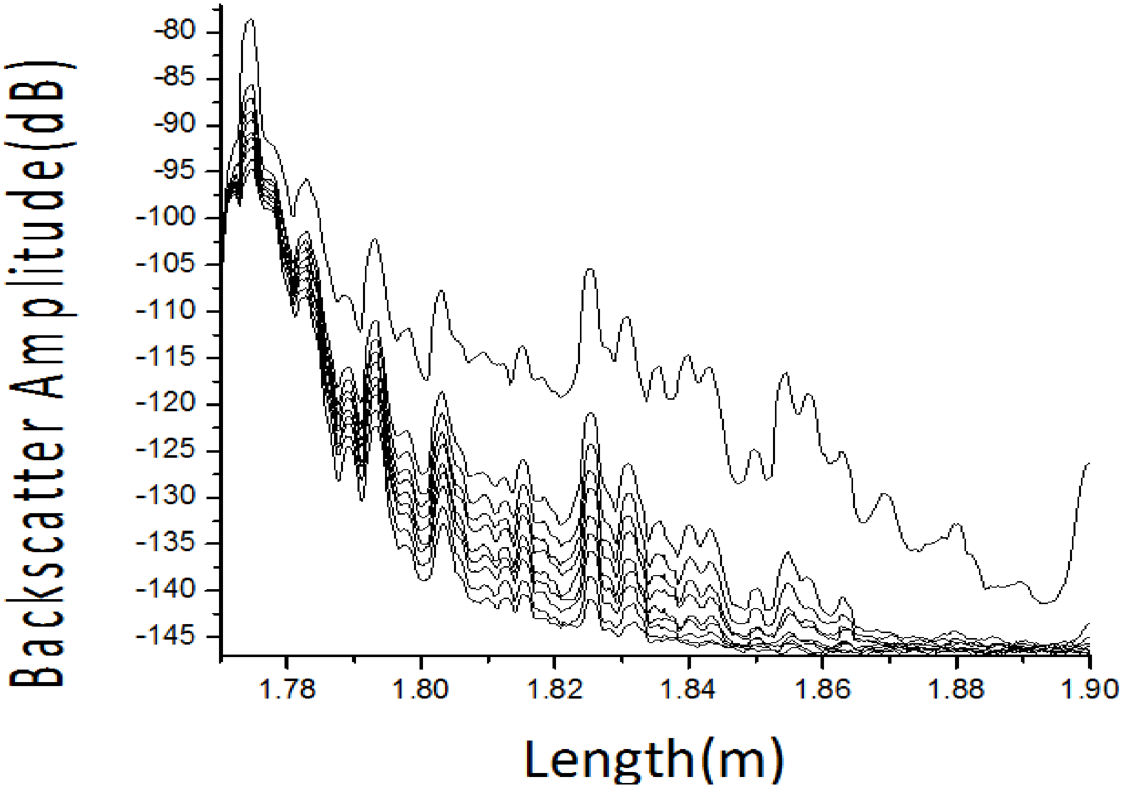
Optical Transmission vs. Hydrogen Concentrations



Exposed to various concentrations of hydrogen in nitrogen, recovered with nitrogen
Ideal for hydrogen driven energy conversion systems

Distributed H2 Measurements (Distributed Loss)



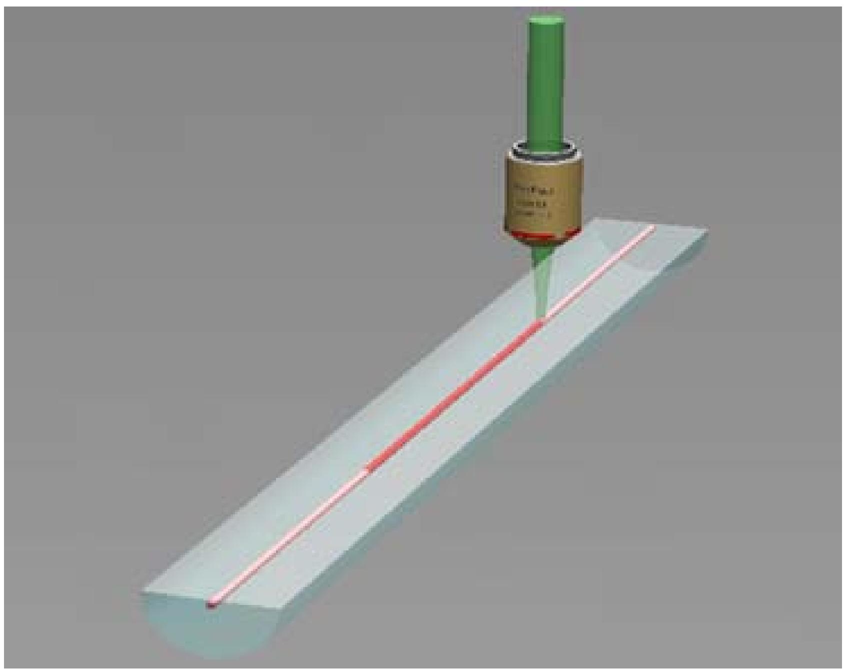


Why….?

Our fiber is too "good" for sensing applications…

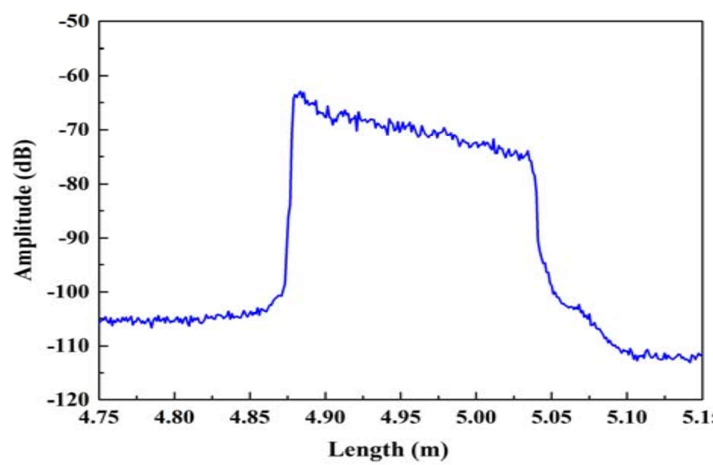
Rayleigh scattering profile is too weak (like weak type I FBG)

Technical Solutions… Enhanced Backgroundd Rayleigh Scattering …



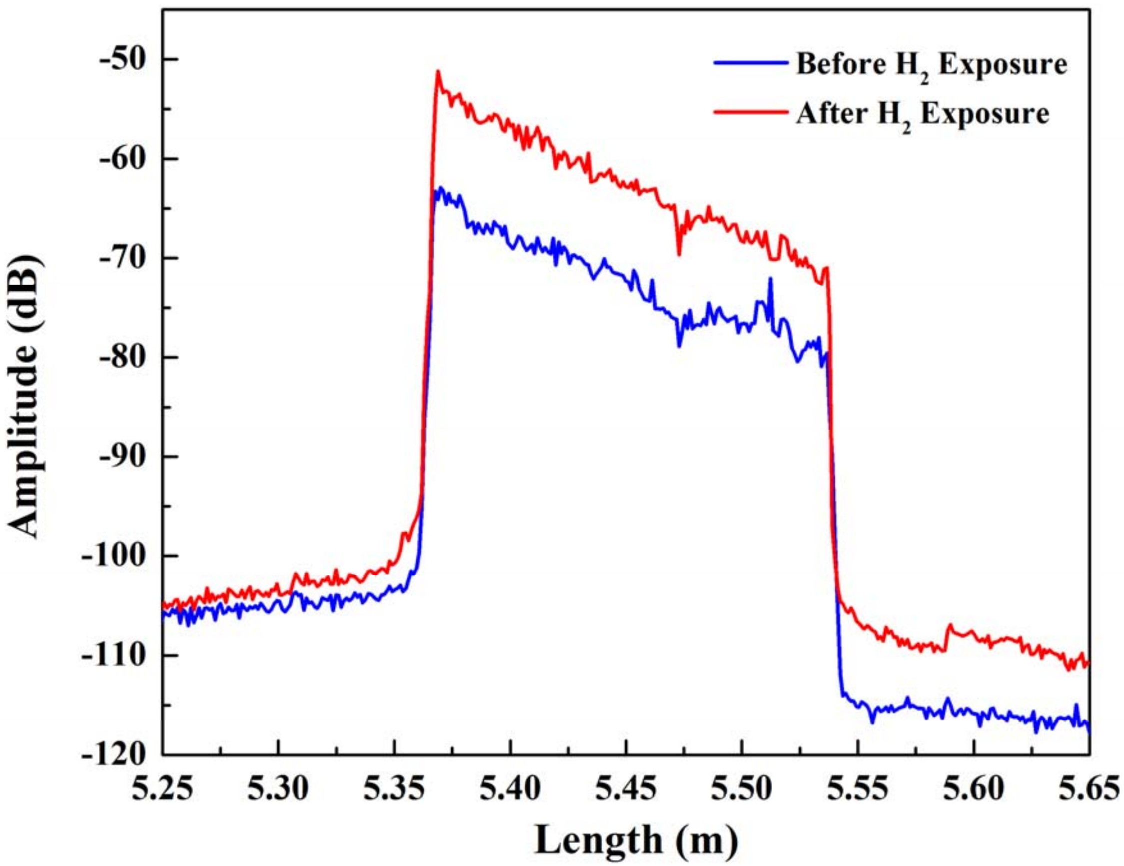
Ultrafast laser irradiation

- **Ti:Sapphire 250-kHz, 180-fs, 780-nm**
- **0.2-0.5 μJ**
- **0.5-10 mm/s**



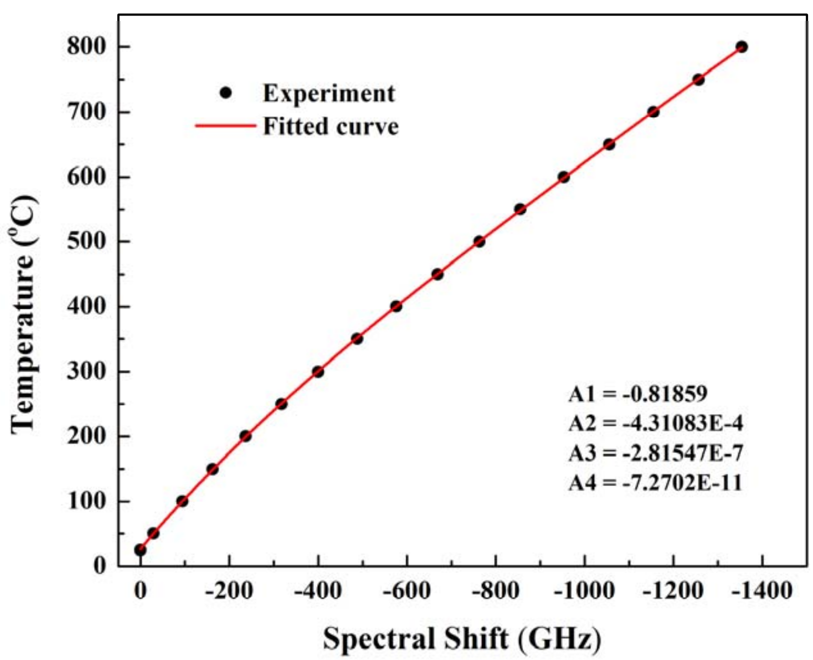
Increasing Rayleigh scattering stability

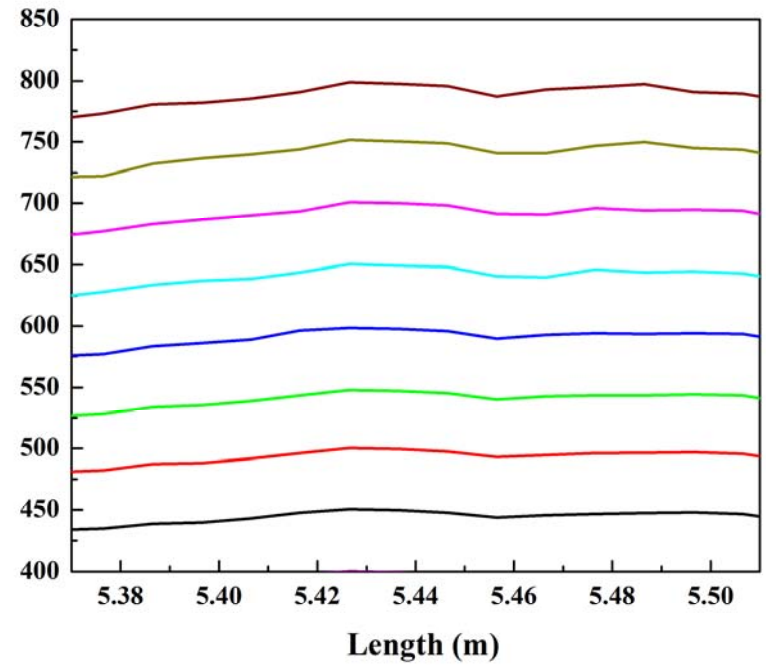
- **Hydrogen exposure still increases loss and scattering**
- **However, this change is permanent .**
  - **Based on 72-hr heating in 7% hydrogen at 800C**
- **Cross-correlation is more effective with increased scattering features that do not change with temperature**



Temperature coefficients determined to 800C

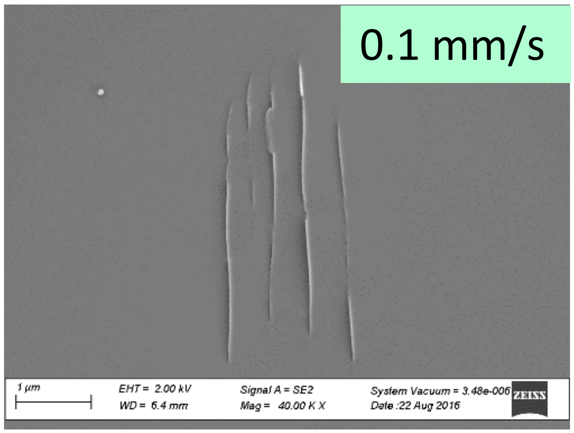
- Temperature can now be measured at 800C with H_2 atmosphere
- Stability verified for ~72 hours at 800C
- 4C accuracy with heat/reheat cycles (10 cycles tested).

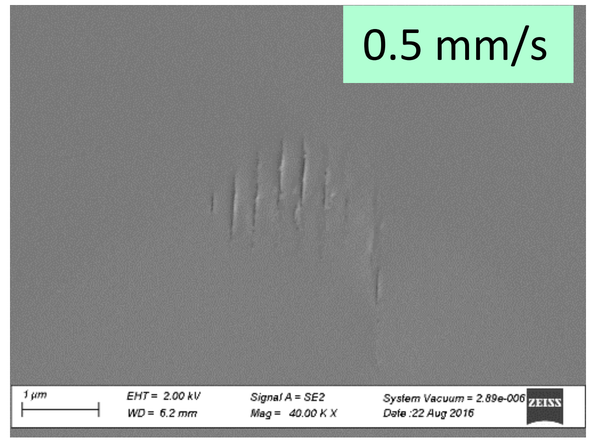


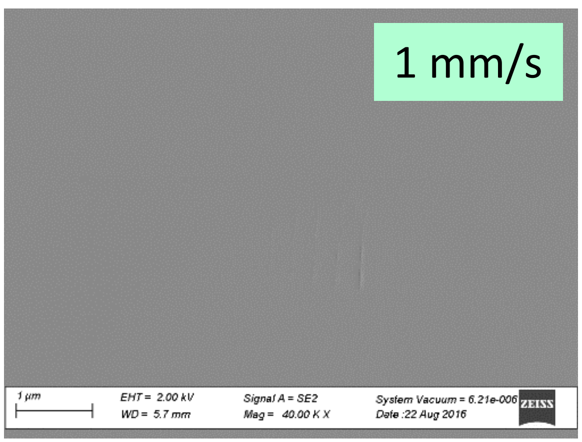


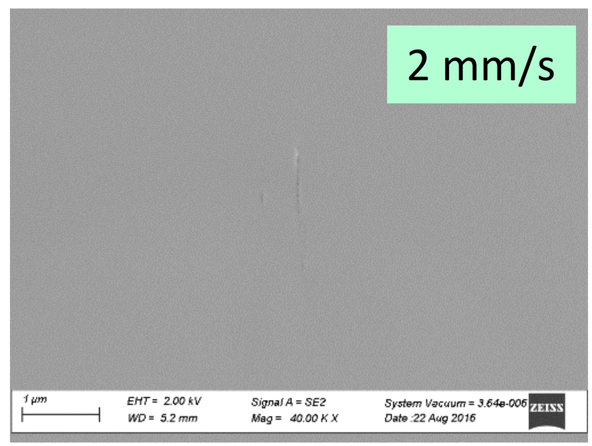
Increasing Rayleigh scattering stability

- **SEM image of the fiber cross section at different scanning speed**
- **Minimize the transmission loss and smooth the profile**

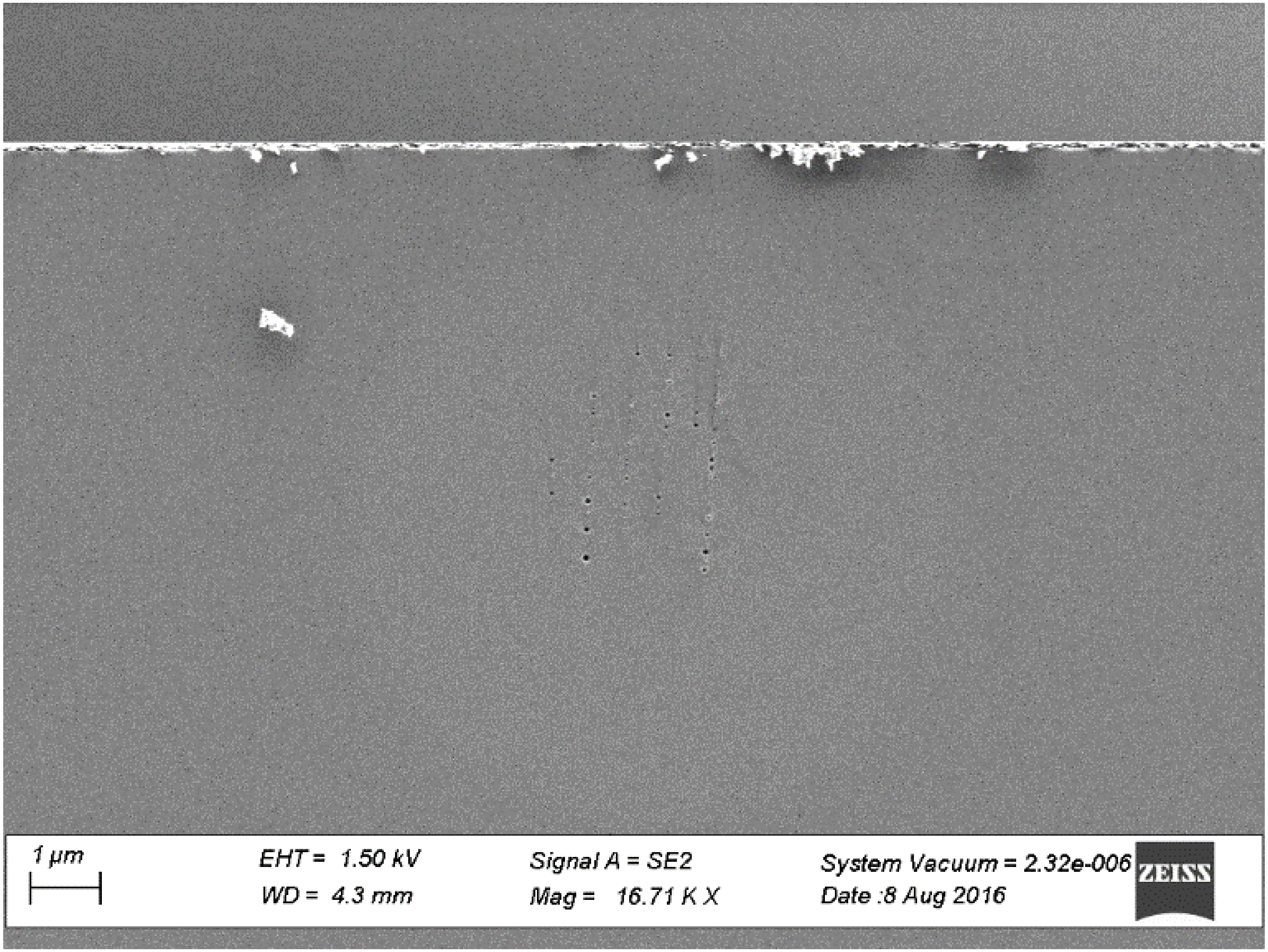






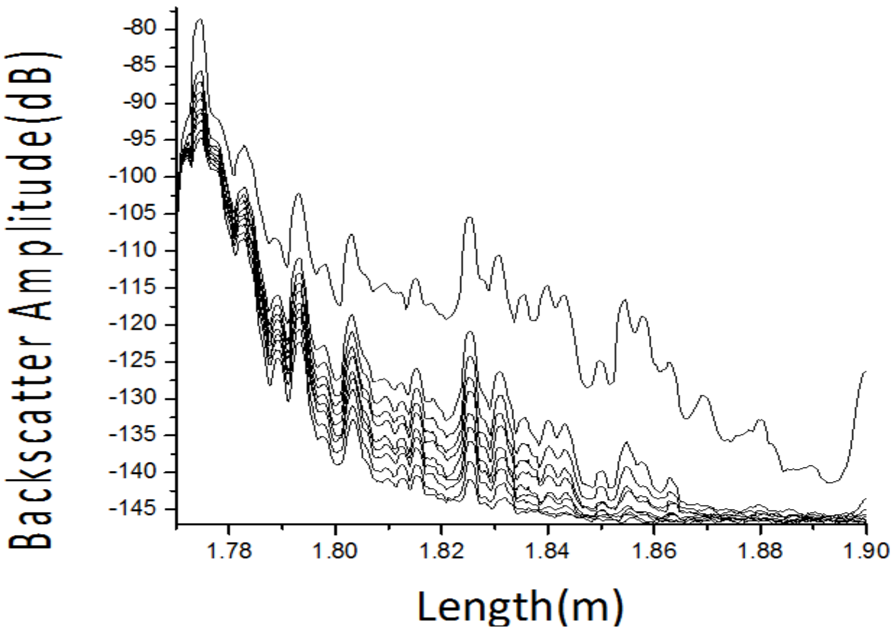


Nanograting Change after H2 exposure

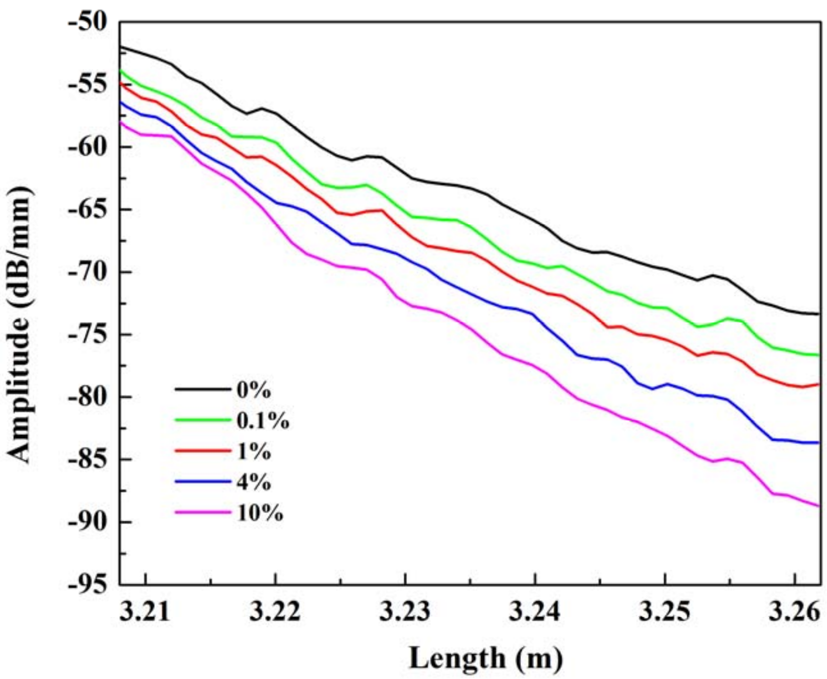


Now… Distributed H2 Measurement Again…

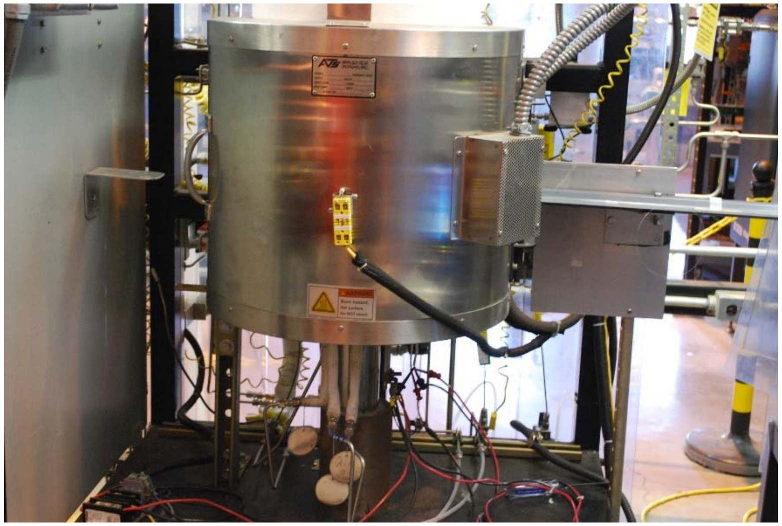
Before… (700C)

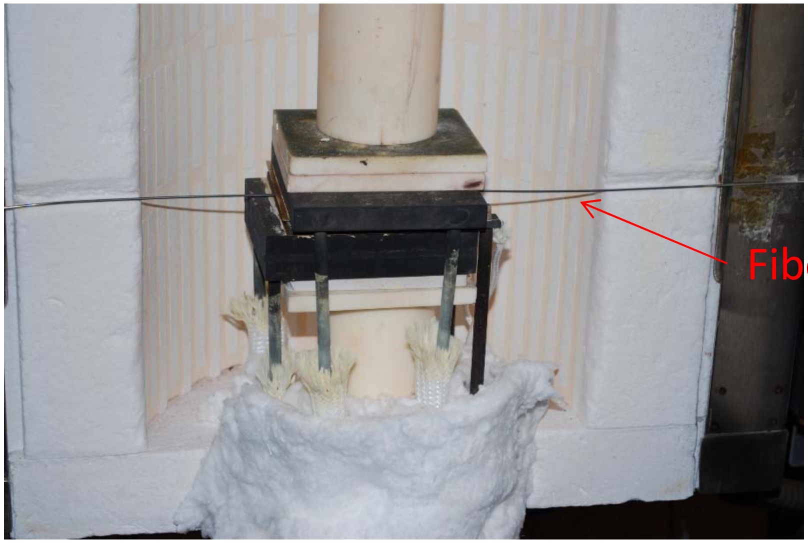


After… (750C)



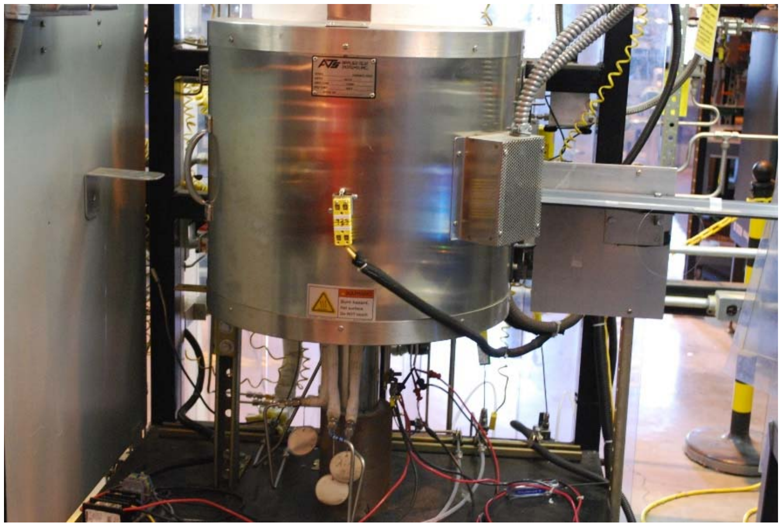
Current Status

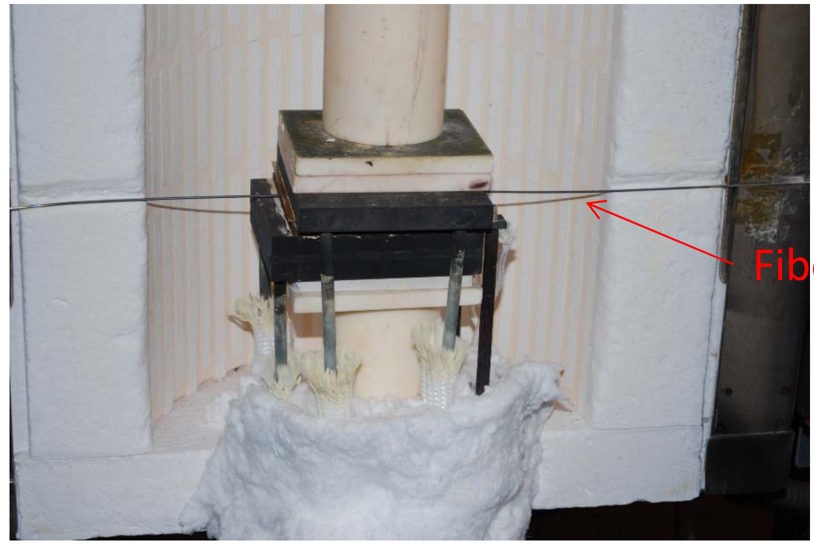




- It is possible that distributed T and Chemical sensing can be achieved with 4-mm and 1-mm spatial resolution using a single fiber.
- This sensing scheme can be used to probe other fuel cell chemistry and other energy chemistry at high temperature (<700C)

Current Status





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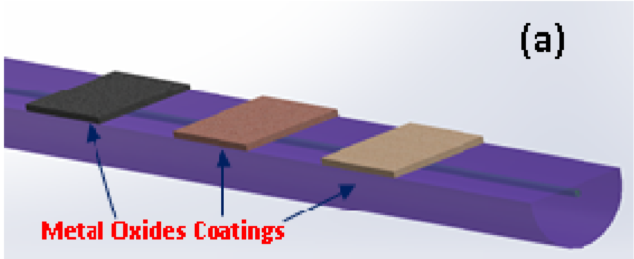
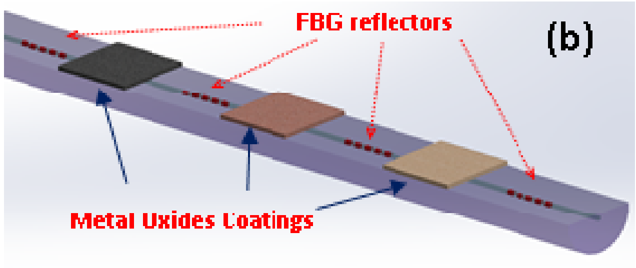
Schedule

	Year 1			Year 2			Year 3		
	4	8	12	16	20	24	28	32	36
Task I: Metal Oxide Syntheses & Analyses									
Subtask 1.1: Syntheses of transition metal oxides	■	■	■	■					
Subtask 1.2: Control and characterize optical and microstructural properties of metal oxides.	■	■	■	■					
Subtask 1.3: Syntheses of dopant variants of transition metal oxides.	■	■	■	■					
Subtask 1.4: Study metal oxides properties changes vs temperatures from 400 to 900°C		■	■	■					
Task 2: Metal Oxide On-Fiber Integration and Tests									
Subtask 2.1: Establish experimental setup for sensor configuration I, II, and III	■	■	■						
Subtask 2.2: Perform gas sensing tests using on sapphire fiber platforms			■	■	■	■			
Subtask 2.3: Perform gas sensing tests using on silica fiber platforms			■	■	■	■			
Subtask 2.4: Perform TEM/SEM and other nanostructure analyses on metal oxide coating on both silica & sapphire fibers				■	■	■			
Task 3: Distributed and Multi-Species Gas Sensing									
Subtask 3.1: Using Rayleigh OFDR to perform distributed H_2 gas sensing test in realistic fuel gas streams.						■	■	■	
Subtask 3.2: Integrate 4 optimized metal oxides on one D-shaped fibers for multi-species gas sensing using the OFDR							■	■	■
Subtask 3.3a: Fabricate FBG array in D-shaped fibers							■	■	■
Subtask 3.3b: Integrate 4 optimized metal oxides on one D-shaped fibers for multi-species gas sensing using FBGs as in-fiber reflectors							■	■	■

Milestones

- **Go beyond hydrogen**





	Year 1			Year 2			Year 3		
	4	8	12	16	20	24	28	32	36
Milestone 1: Successful fabrications of metal oxides and their dopant variants				■					
Milestone 2: High-temperature gas sensing testing setup successfully established for H_2, SO_2, NO_x, and nature gases			■						
Milestone 3: Successful tests of gas sensing characteristics of all transition metal and their dopant variants on both silica and sapphire fiber platforms from 400 to 900°C						■			
Milestone 4: Successful demonstrations of distributed hydrogen sensing in fuel gas streams and in solid oxide fuel cells to achieve 1-cm spatial resolution at temperature >700°C.								■	
Milestone 5: Successful demonstrations of real-time multi-species fuel gas measurements and real-time gas composition analysis using one fiber at high temperatures from 400 to 900°C									■

Thank you!

Questions?

Collaboration Welcomed!

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