University of Pittsburgh

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

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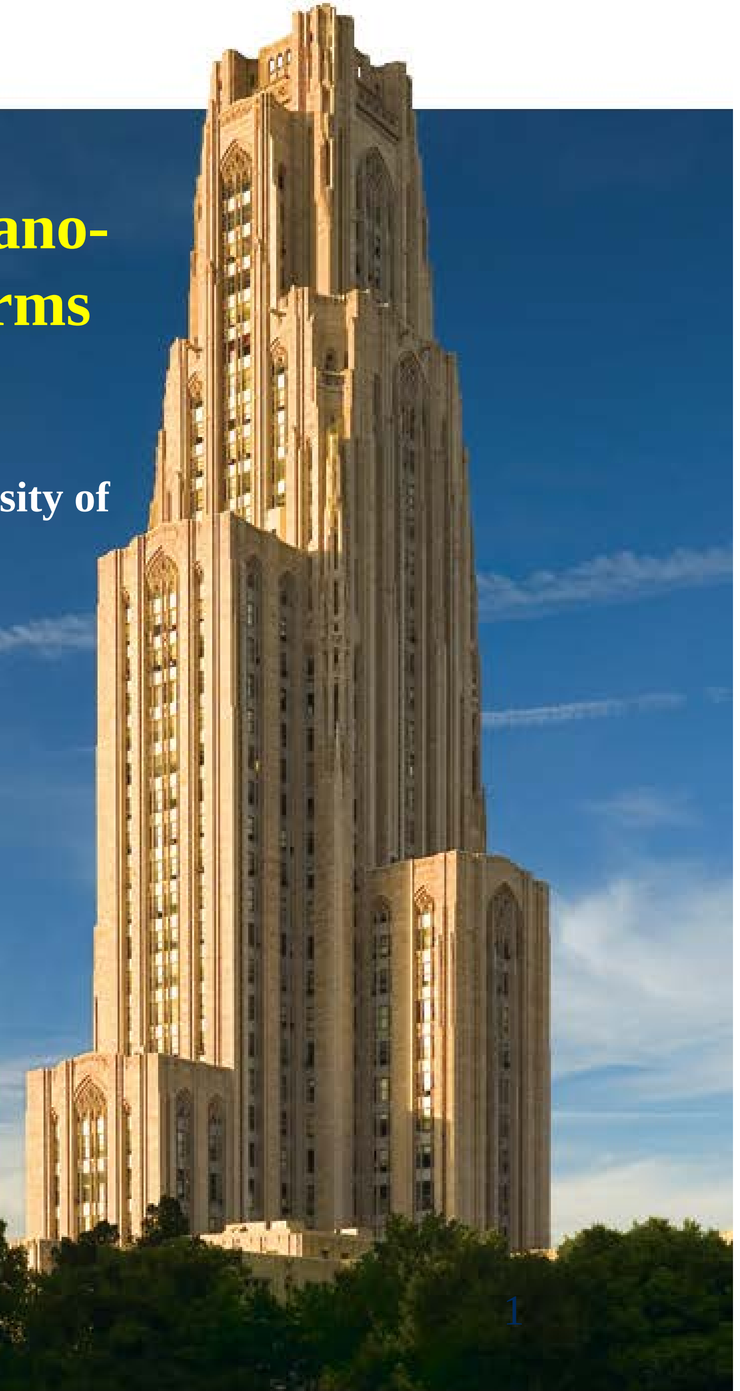
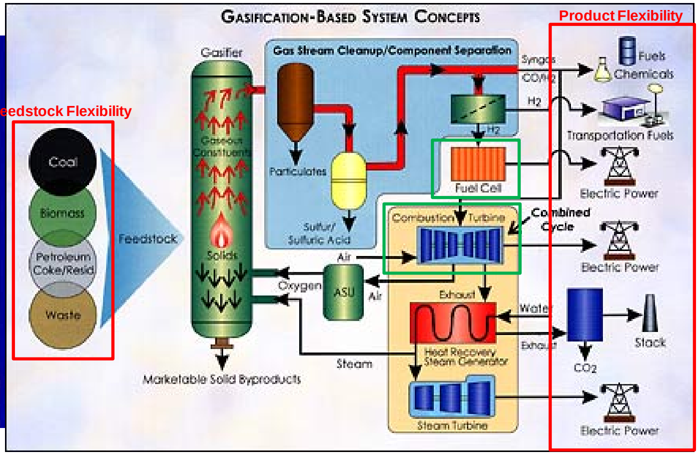
Collaborators

- **NETL scientists**
- **INL, ORNL**
- **Corning**
- **Westinghouse**
- **Watts fuel Cells**
- **A few**



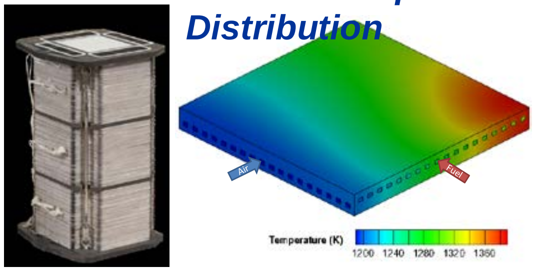
Objective/Vision: Probing High-T Chemistry in SOFC Operation

Develop an integrated sensor solution to perform direct and simultaneous measurements of physical and chemical parameters with 5-mm spatial resolution.



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

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

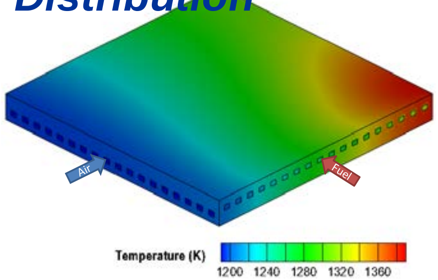
Using high spatial resolution data gathered by sensor to optimize design, operation, and control of energy system.

Distributed Fiber Sensor will be Sensor-of-Choice for AI Driven Power System Optimization and Control

Outlines: A Complicate but Interesting Story

- **Develop high-T stable silica fiber platform**
  - Ultrafast laser direct writing
  - Nano-fabrication of on-fiber nanostructures for high-T measurements
- **Sensor Materials Development and integration**
  - Metal oxide nanostructures
    - Improve high-T stability and chemical reactivities
  - Noble and rare-earth metal doping
  - 3D direct microstructuring
- **Sensor Deployment and Measurement**
  - What do we learn?
  - Comparison with simulation
- **Energy system optimization**

Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution



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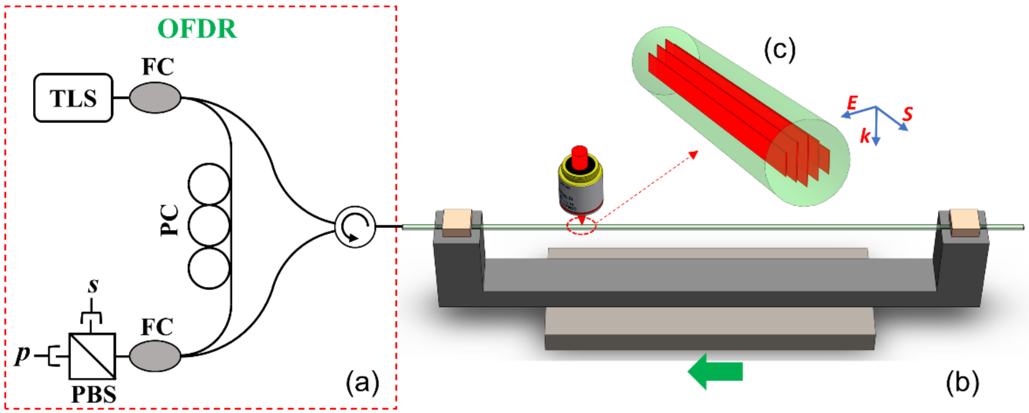
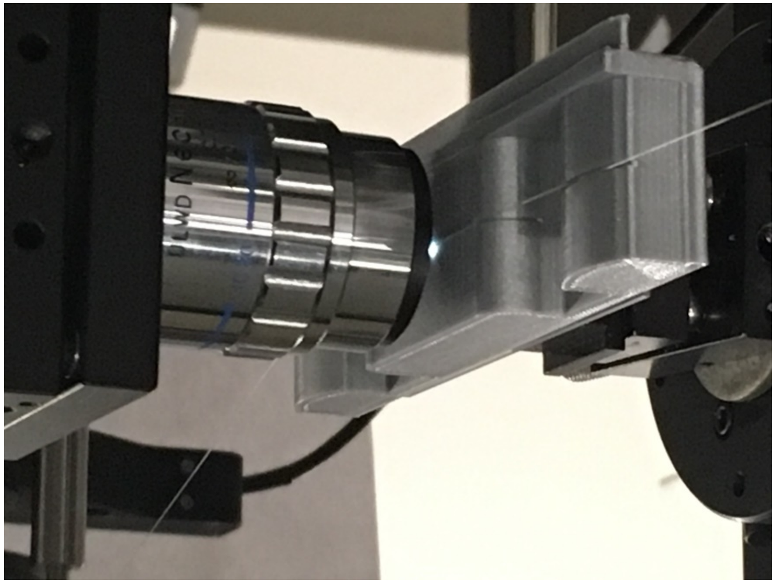
Outlines: Team

- **PI: Kevin Chen – University of Pittsburgh ($400k/3years)**
  - Graduate Student Researchers: Mohamed Bayoumy, Zsolt Poole, Rongtao Cao, Zhaoqiang Peng
  - Research Scientist: Dr. Guanquang Liang
- **Industry Collaborator**
  - Corning Inc.
  - Watts Inc.
  - Westinghouse
  - Smaller corporations
- **National Lab Collaborator**
  - NETL: 6 fuel cell on-site tests
  - ORNL: sensor implementation
  - INL: cross-cutting application of fiber sensors

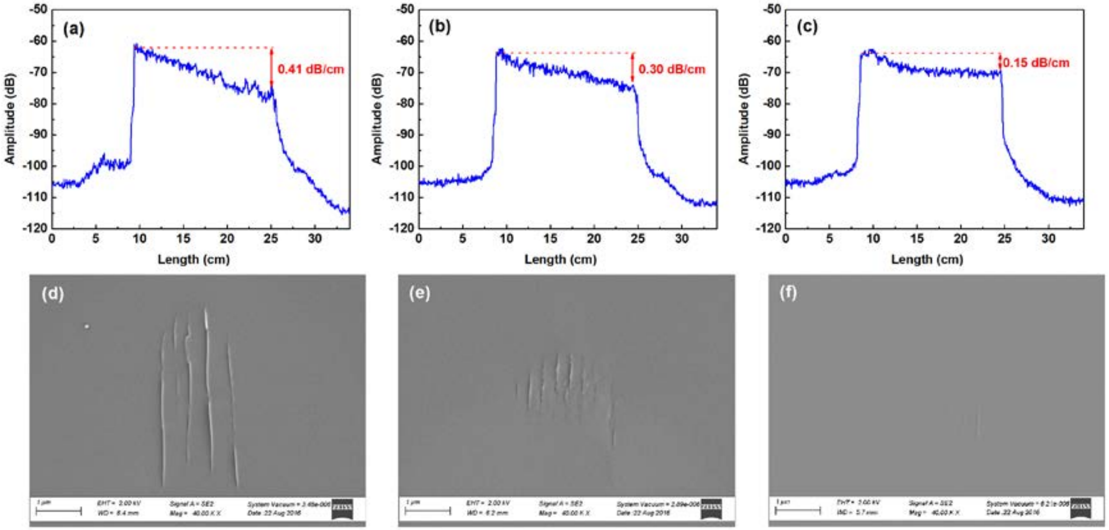
Distributed Sensors for High-T Applications

Ultrafast laser irradiation to enhance T/radiation resilience and measurement accuracy





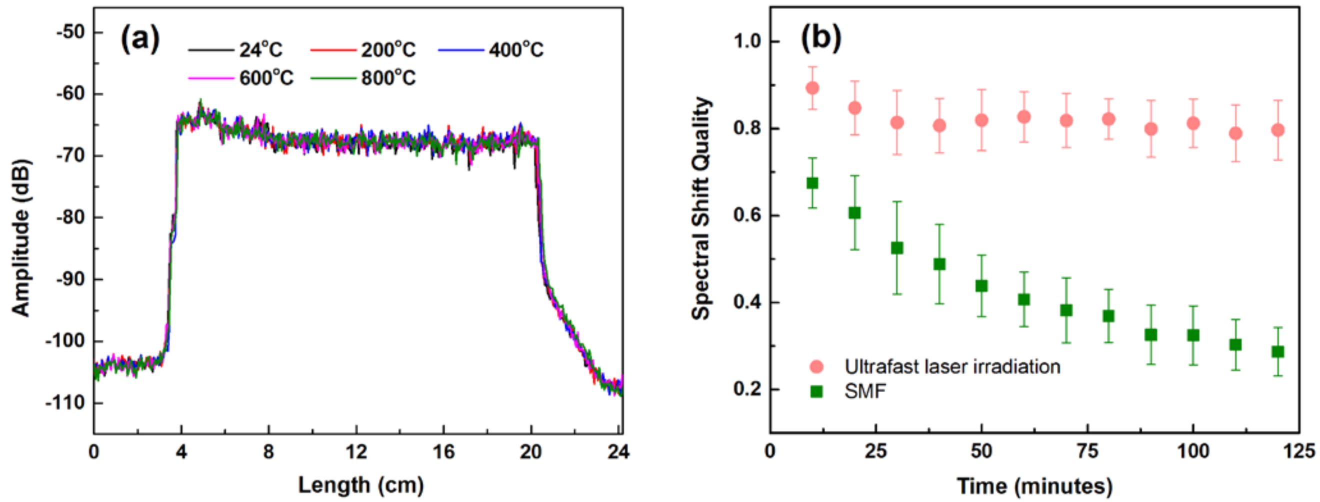
- Temperature measurements can now be performed at 900C with H_2 atmosphere
- Stability verified at 900C



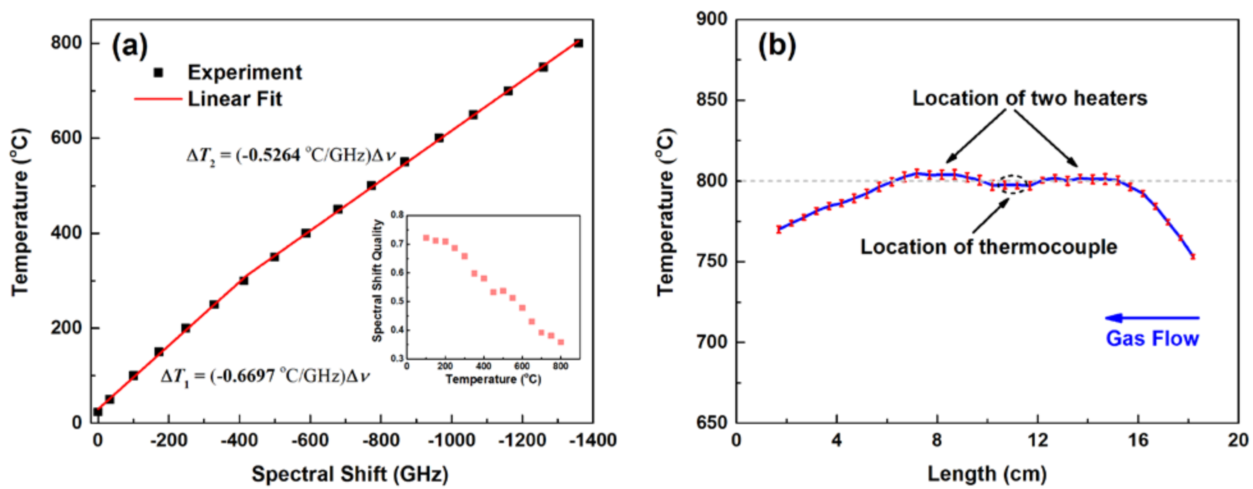
U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Distributed Sensors for Energy Applications

Temperature Resilience from the RT to 800C

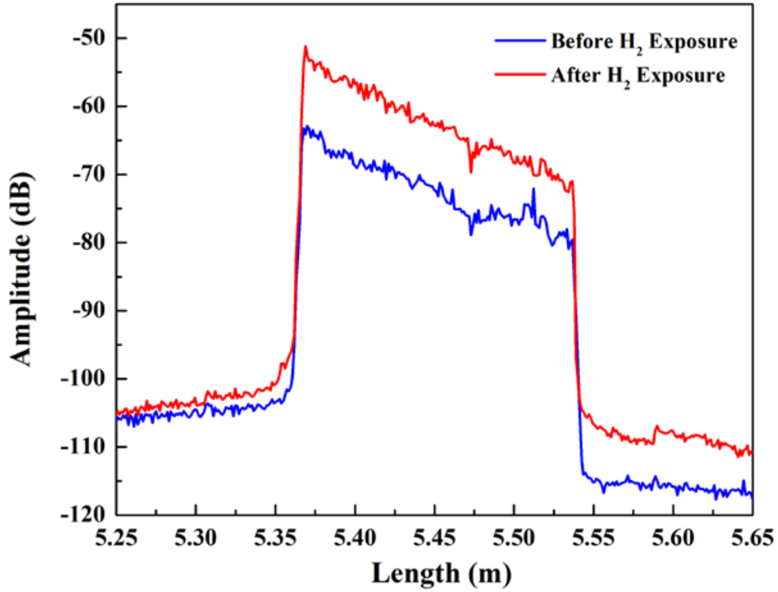


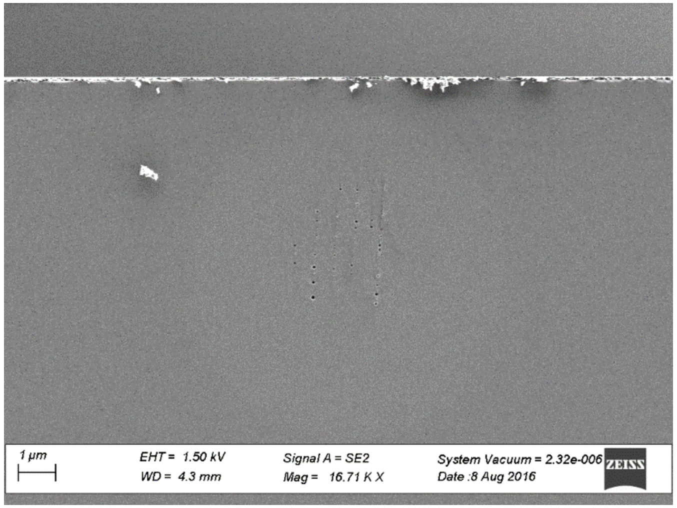
Measurement Repeatability better than 4C from the RT to 800C



Increasing Rayleigh scattering stability

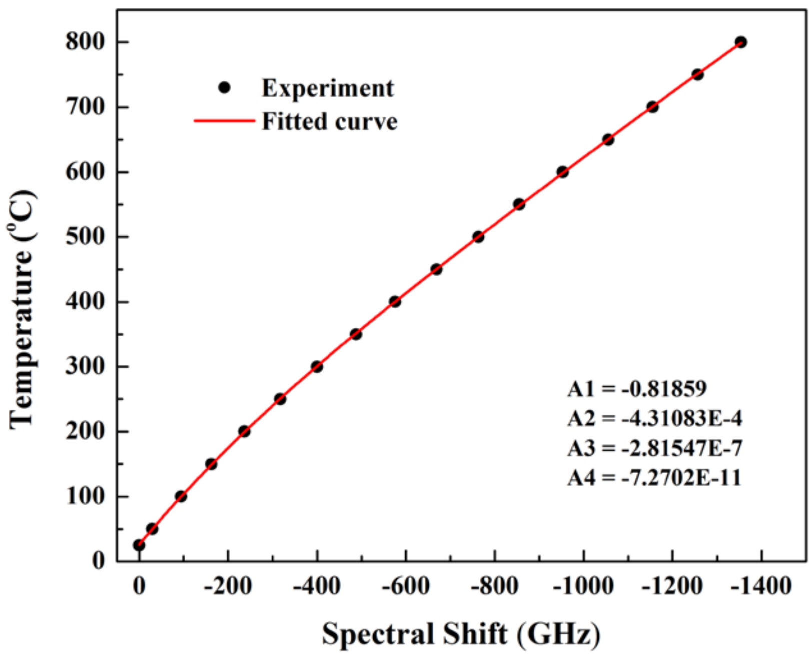
- Hydrogen exposure still increases loss and scattering
- H2 induced scattering is now less than irradiation-induced scattering
- Cross-correlation is more effective with increased scattering features that do not change with temperature

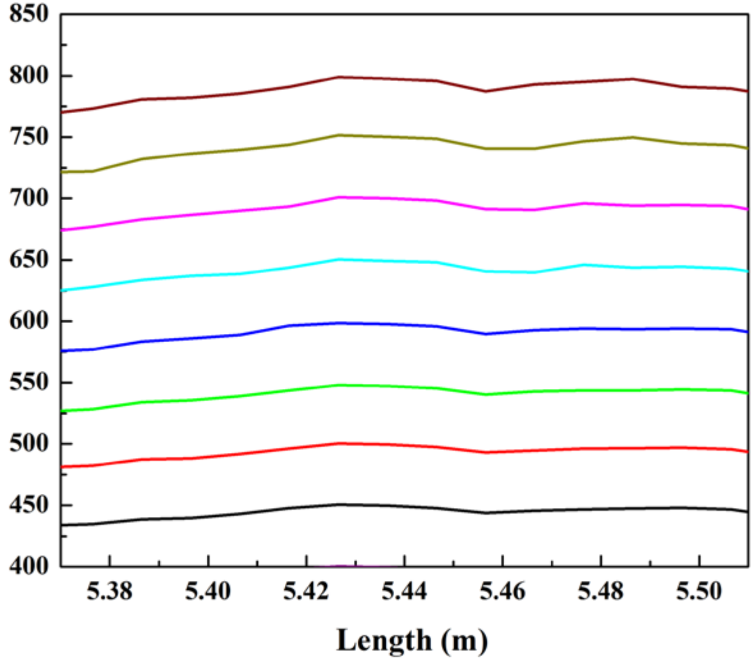




Temperature coefficients determined to 800C

- Temperature can now be measured at 800C with H_2 atmosphere
- Stability verified for ~19 hours at 800C
- 4C accuracy with heat/reheat

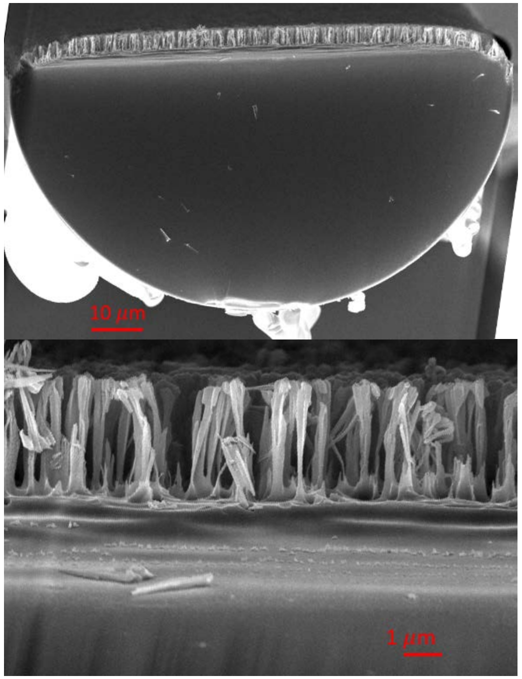




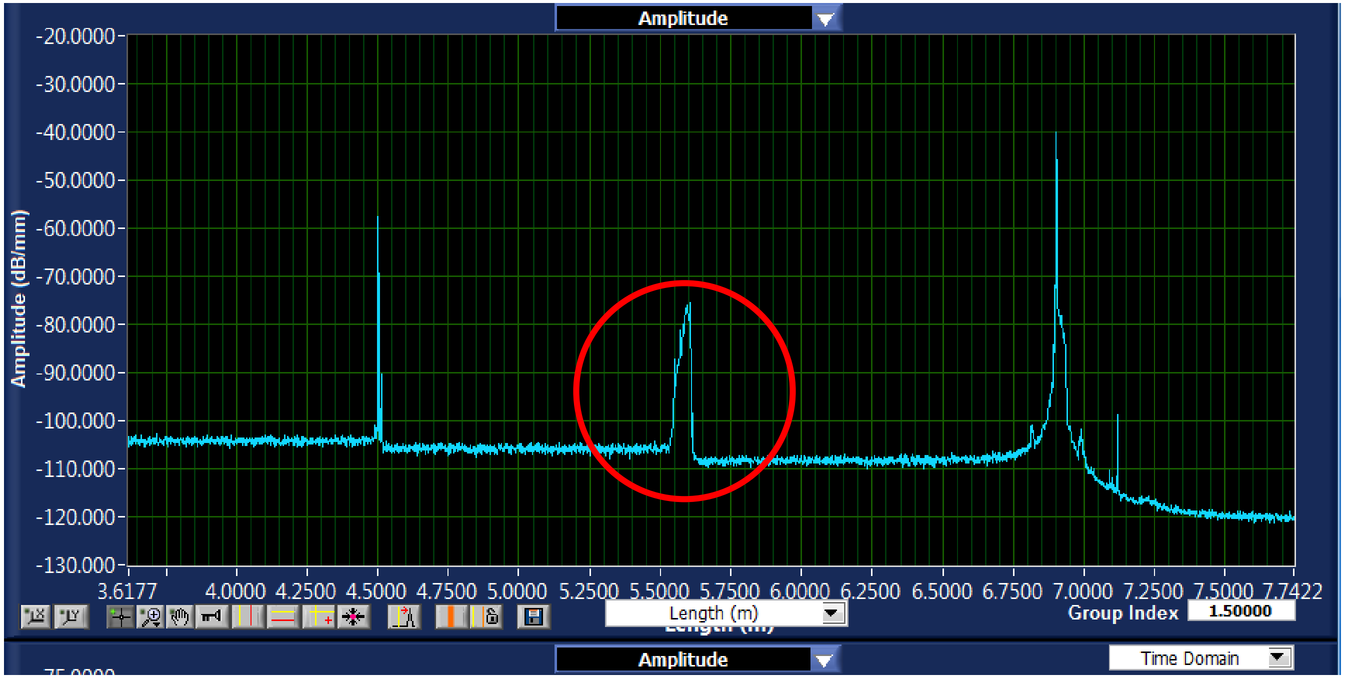
RIE on D-shaped fiber, Coating, Rayleigh

- **Equipment: The Trion Phantom III LT RIE (Reactive Ion Etching)**
- **RIE Gas: CHF_3 and O_2**
- **Power 100-300 W**

Nano-grass (height: 4.7 µm)



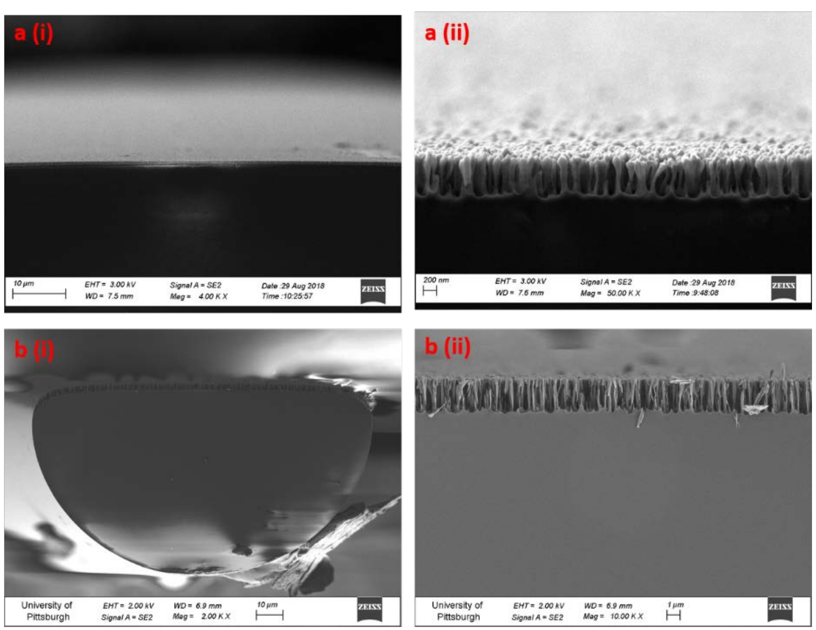
D-fiber with nano-grass Rayleigh scattering

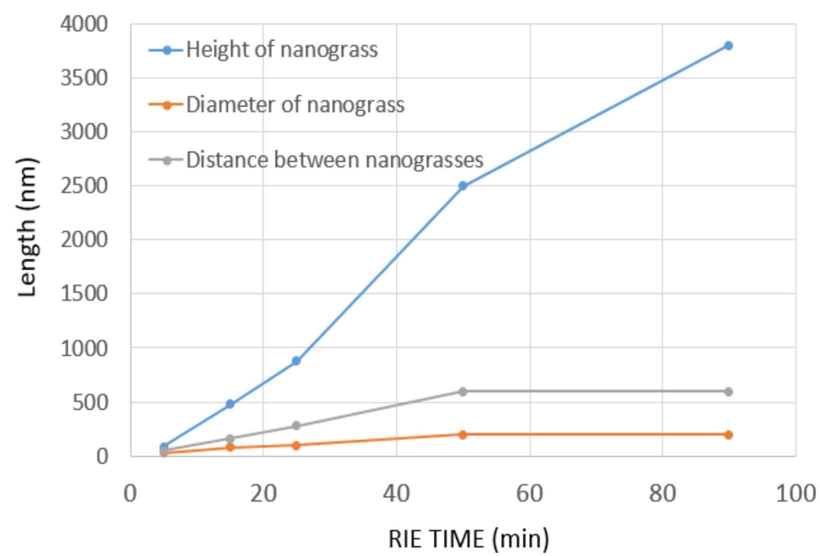


Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

2. Distributed Hydrogen Sensor Based on Nano-grass at High Temperature

- **Challenges:**
  - Avoid metal oxide sensing film collapses at high temperature
  - Improve chemical sensor performance
- **Our Sensor:**
  - Introduced Nano-grass textured optical fiber

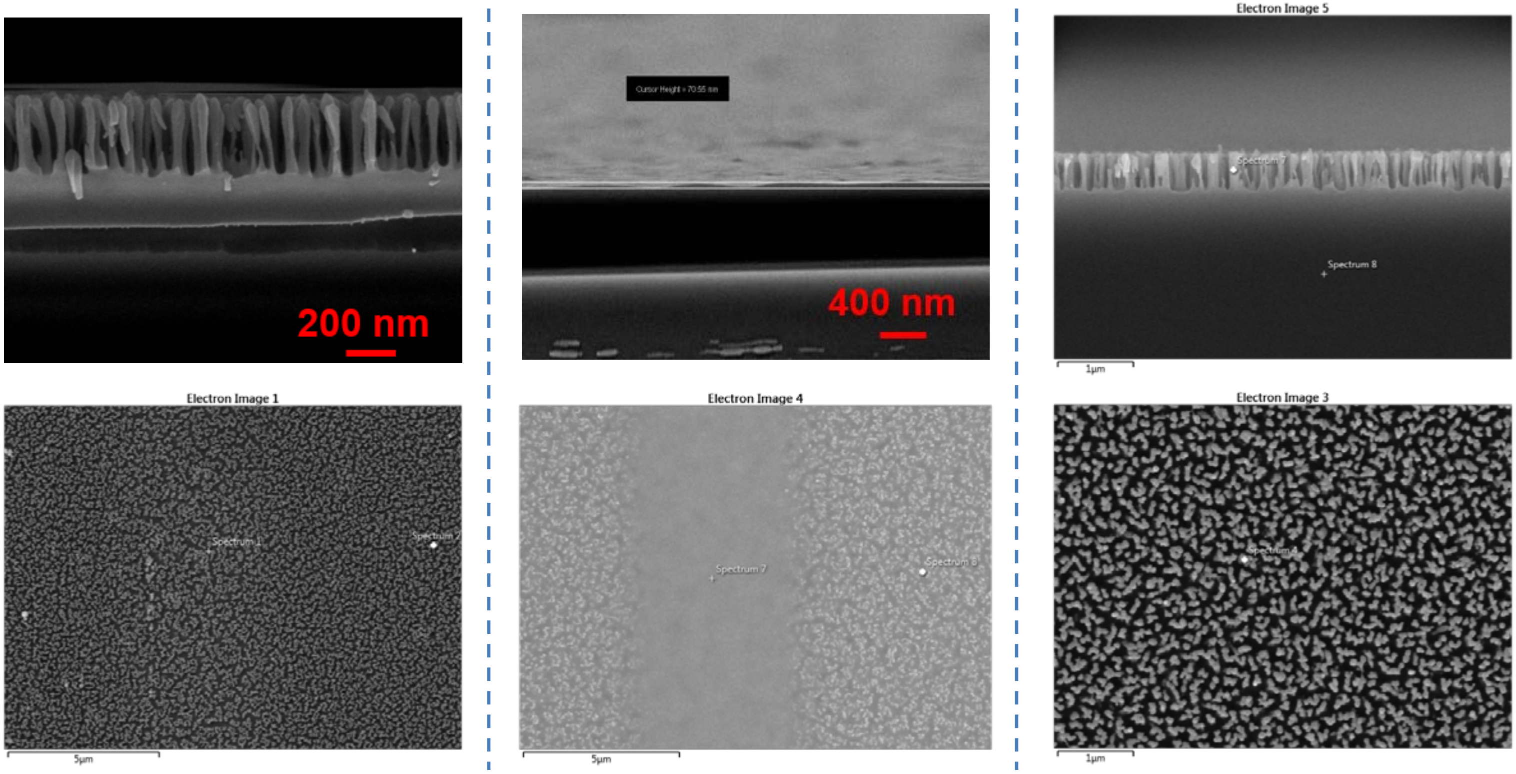




3. Metal Oxide (HfO_2) Protected Nanostructure

- **Challenges:**
  - Nano-grass "melting" on top of the fiber core at high temperature
  - Introduce HfO_2 coating to solve the problem

600 °C | 800 °C | 800 °C *with* HfO_2



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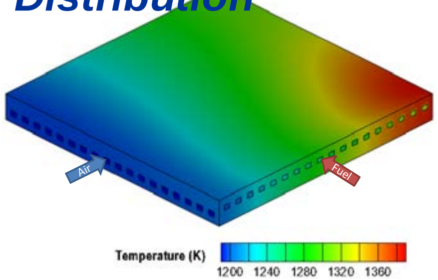

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Objective- Sensing Materials: Tailoring the Refractive Indices and Chemical Responsivity

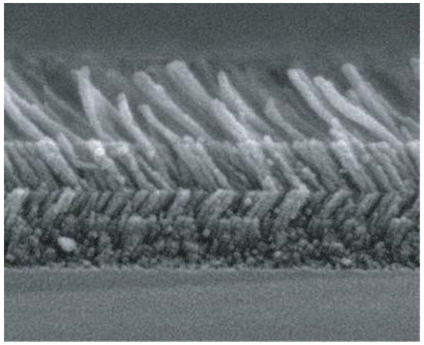
Requirement:

- 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?

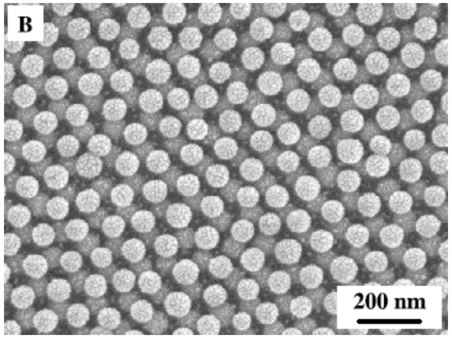
- Doping, sputtering
- Cost, not flexible



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

Colloidal Templating?

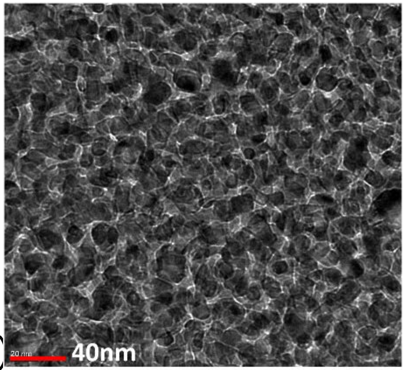
- <50-nm
- Structure limited
- Limit tuning of porosity



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

Block Copolymer Templating?

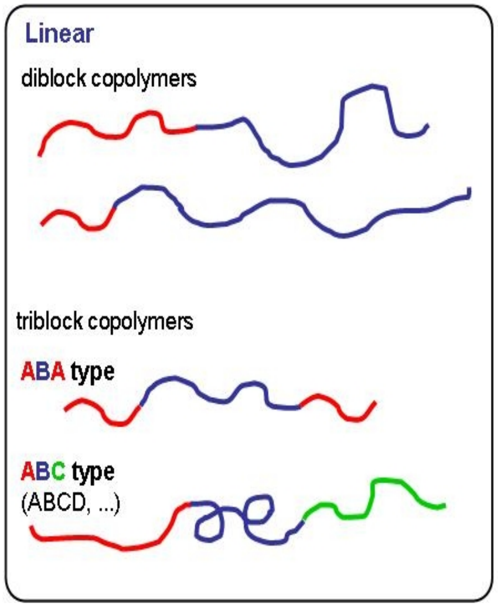
- ✓ alcohol soluble
- ✓ 5nm to 100nm
- ✓ Flexible structures
- ✓ Wide tuning of porosity



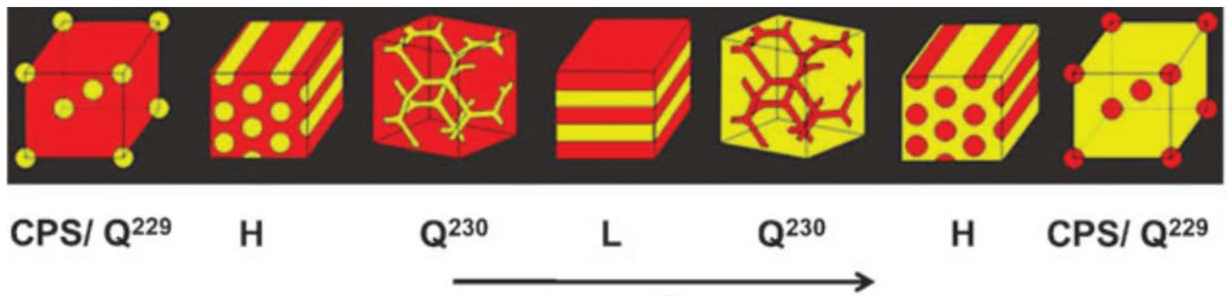
Sensing Materials: Co-Polymer Templating by F-127

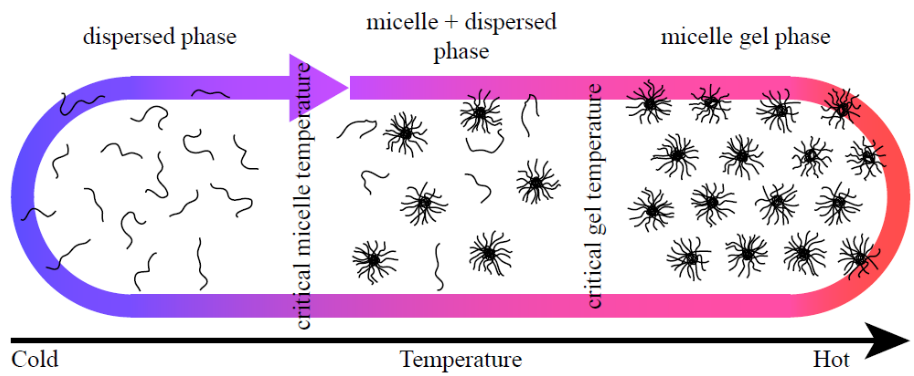
F127 Pluronic

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

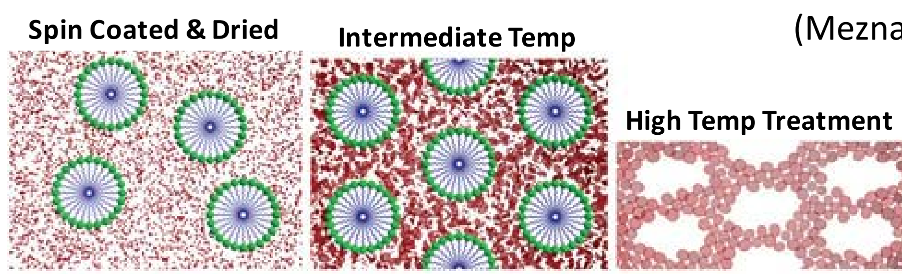


(Orilall, 2011)





(Meznarich, 2012, p. 107)



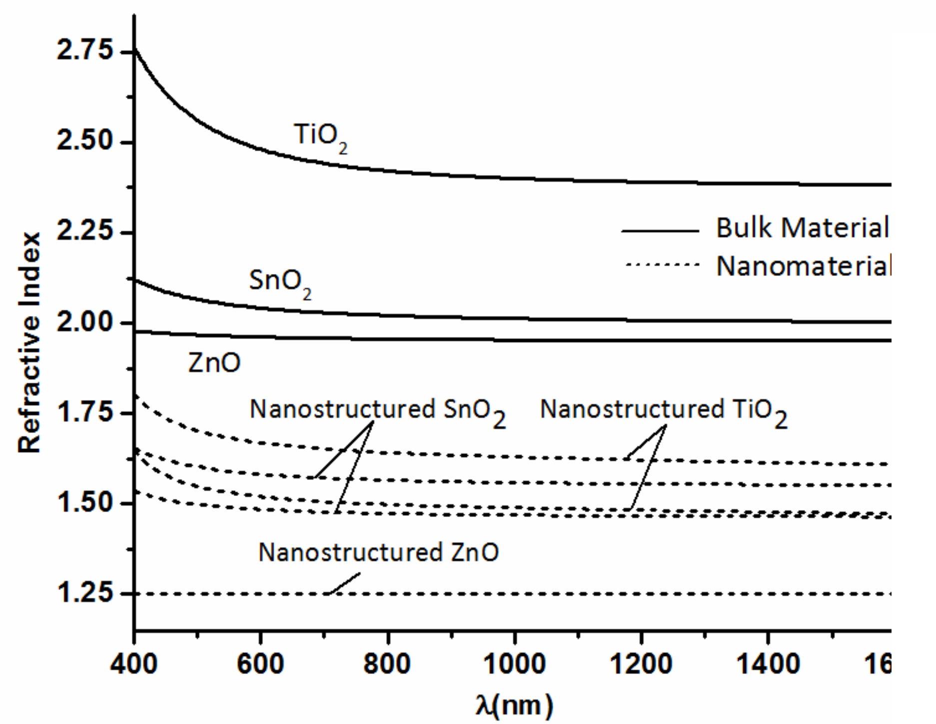
(Shao, 2010)

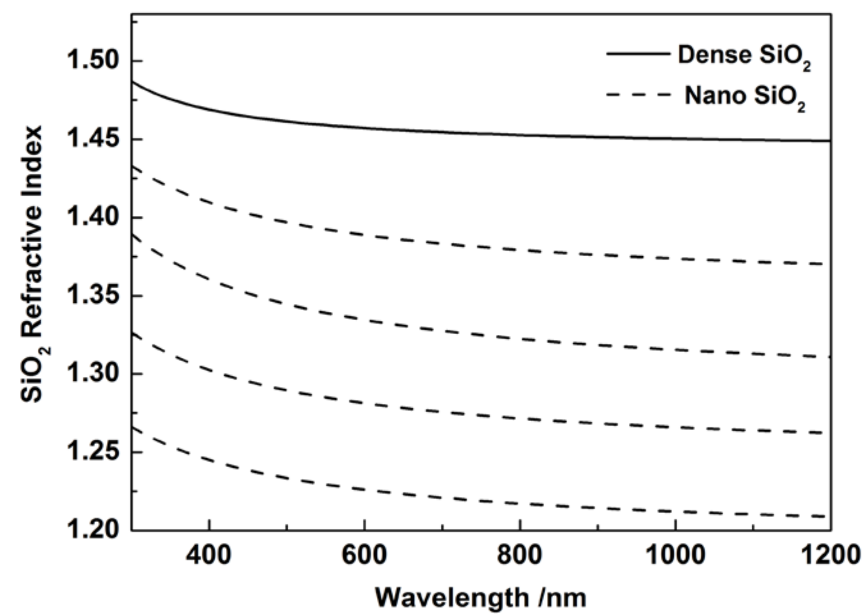
Metal Oxides and Their Dopant Variants

- 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

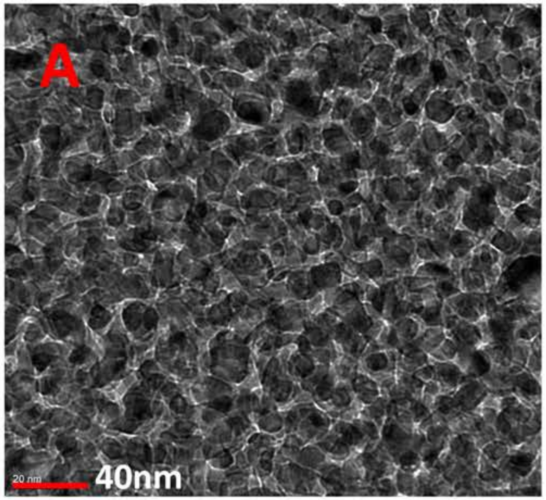
- **TiO_2: Δn~ 1.4 to 2.5**
- **SnO_2: Δn~ 1.4 to 2.1**
- **ZnO: Δn~ 1.25 to 2.0**
- **SiO_2: Δn~ 1.2 to 1.45**

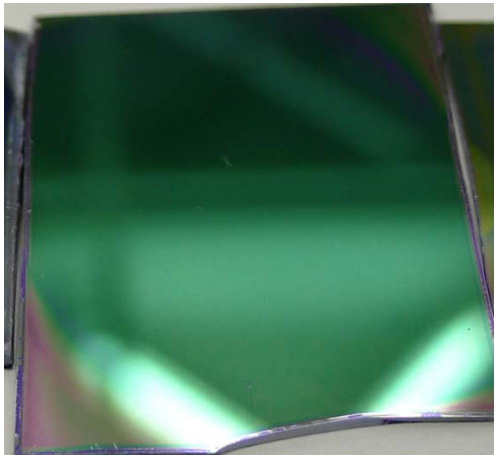




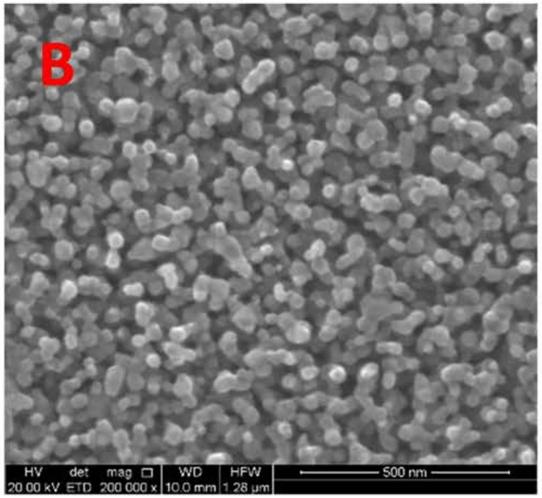
Metal Oxides and Their Dopant Variants

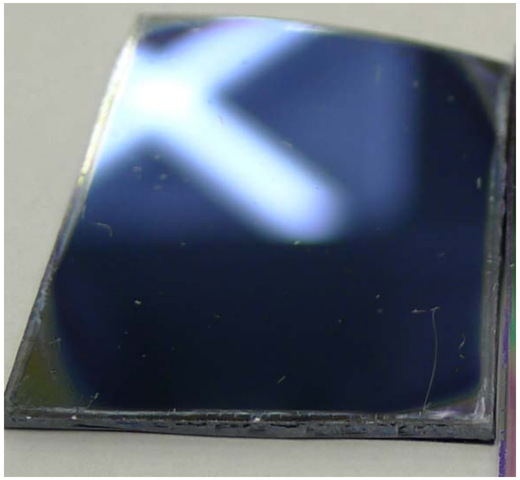
TEM of TiO_2



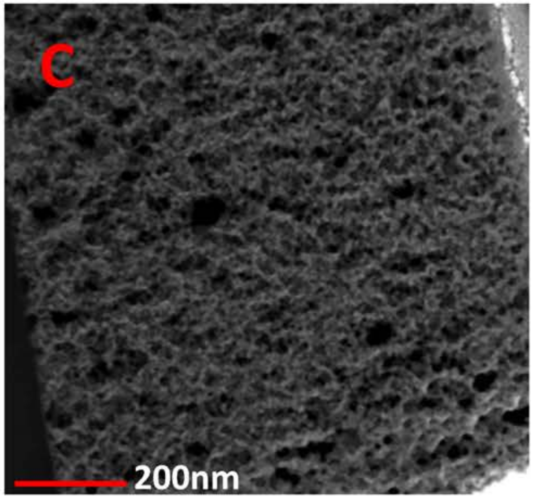


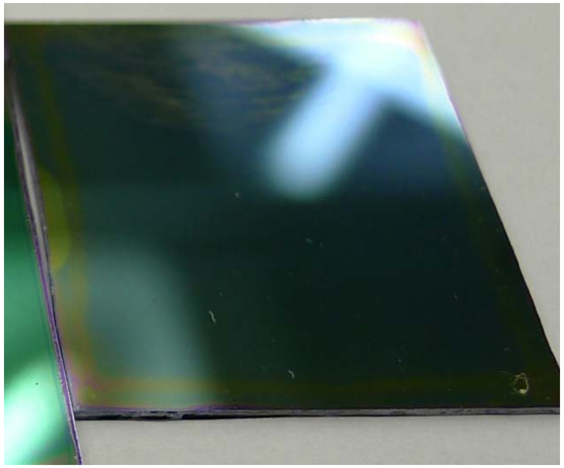
SEM of ZnO





SEM of SnO_2

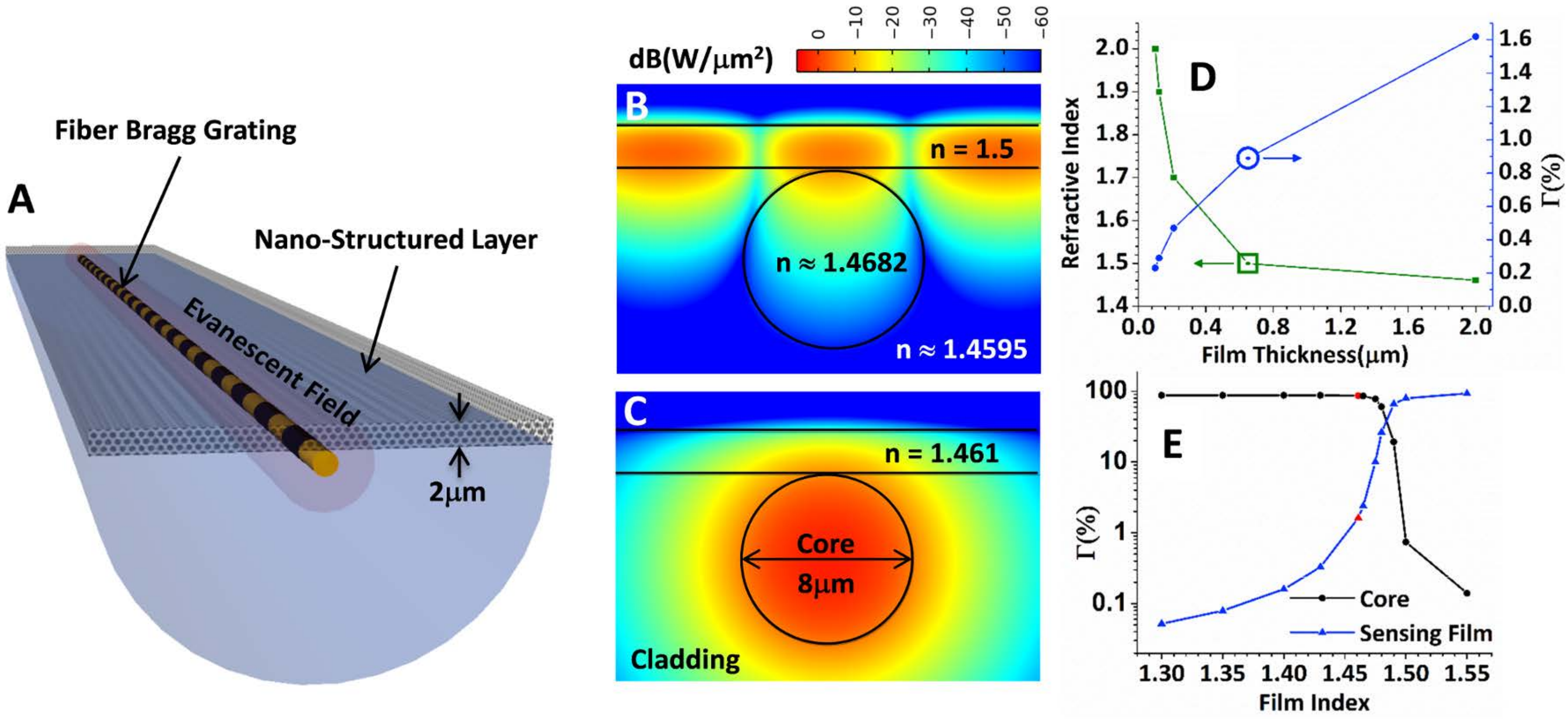




Optical Sensing: Metal Oxide on Optical Fiber Platform

In the evanescent wave configuration

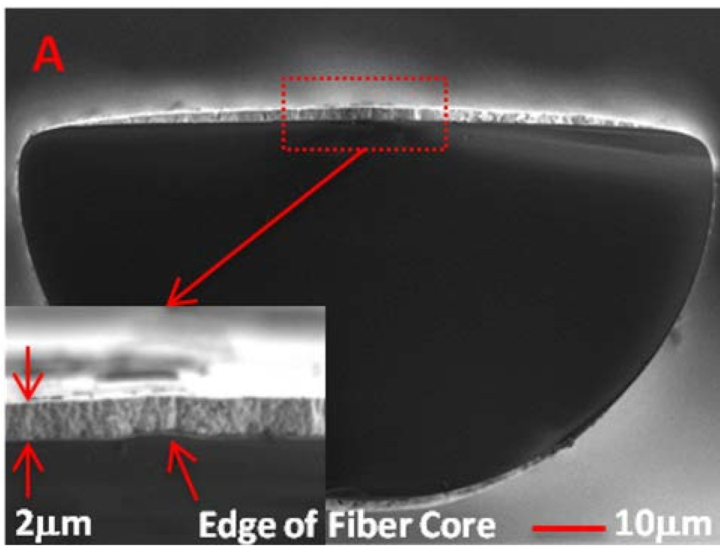
Refractive Index Matching is Critical

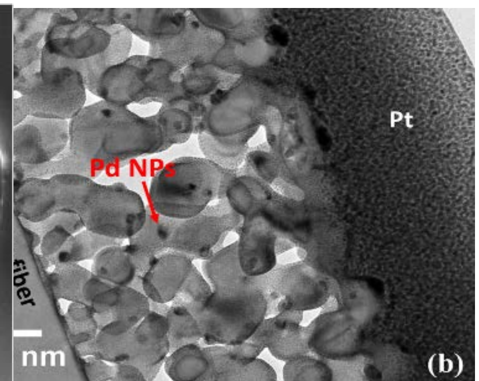


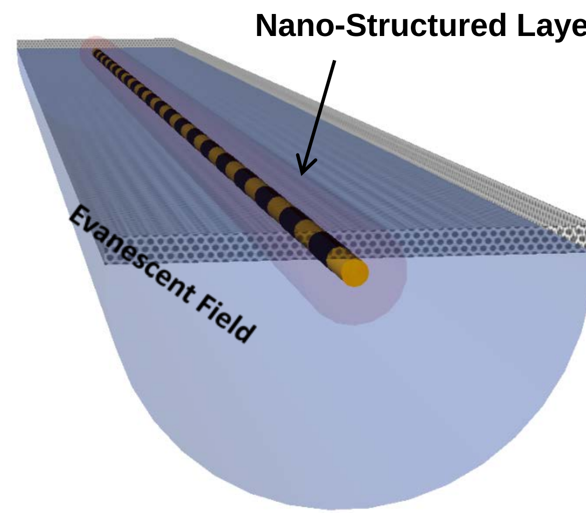
Finite Element Simulation of the Power Distribution of the Fundamental Mode

Metal Oxides Enabled Chemical Sensors

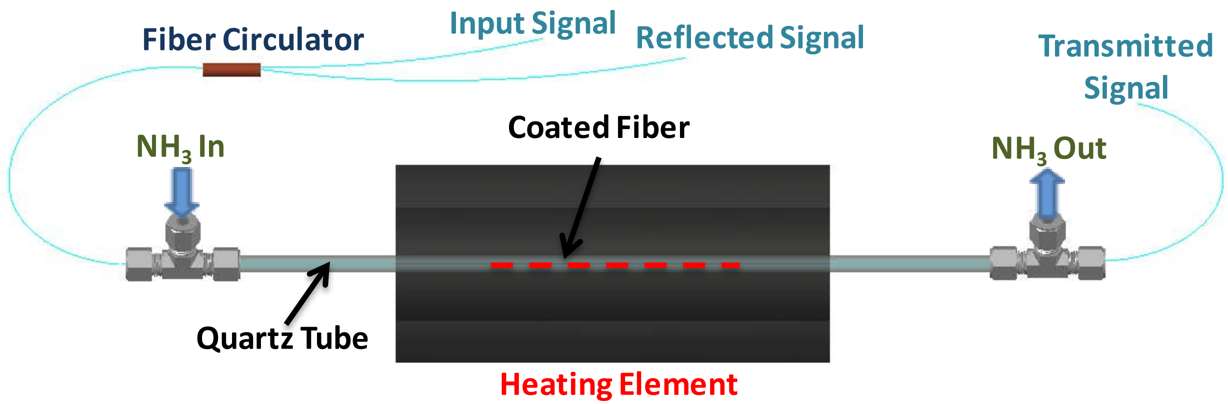
- Nano-Engineered metal oxide sensory film
  - Porosity control for refractive index matching
  - Rare-earth or noble metal dopants for specificity
  - Pd-TiO2
- Sensor can operate >700C
- No electrical components in target environment

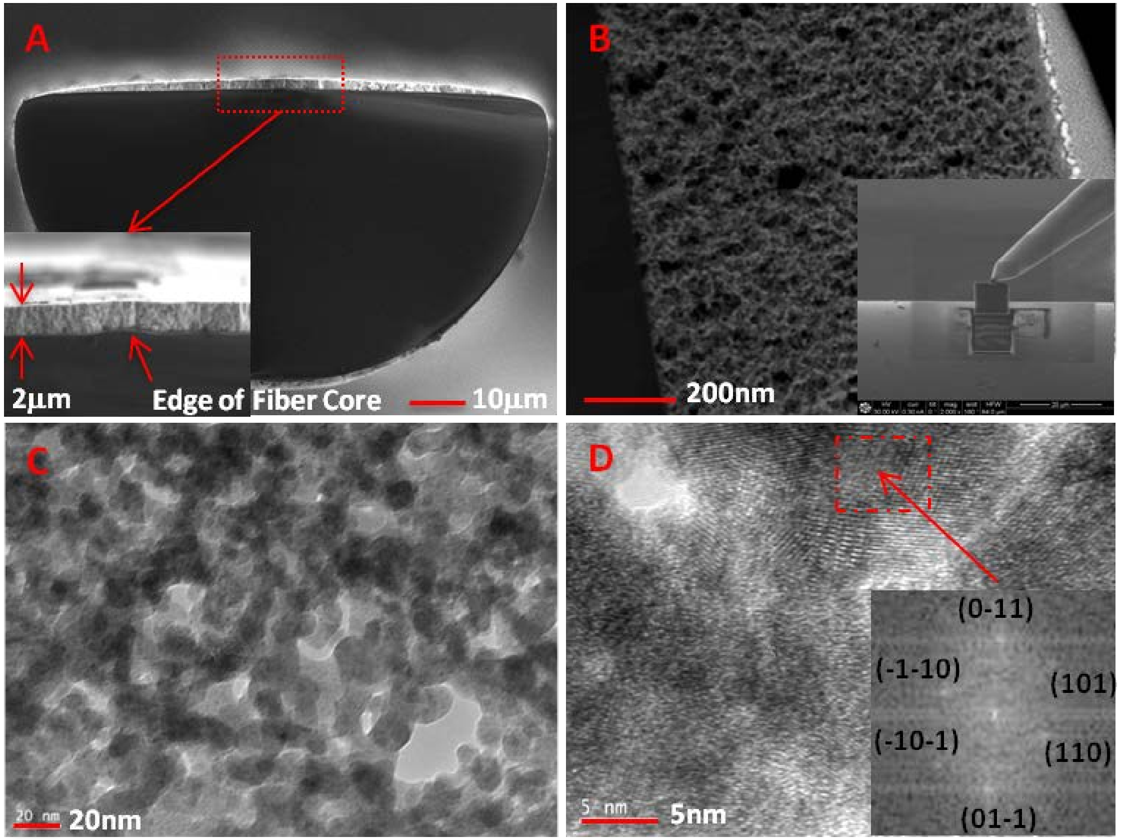






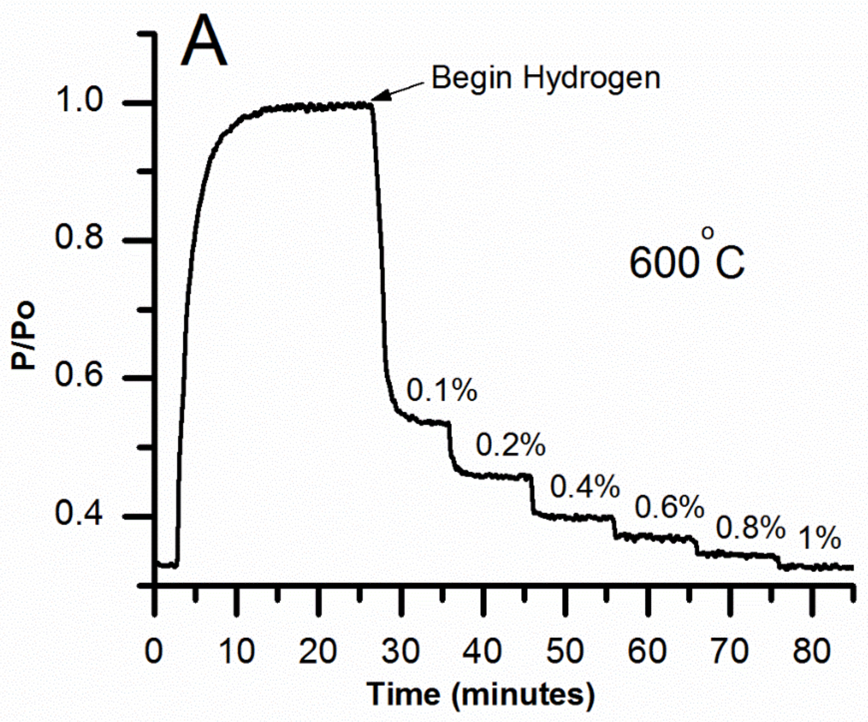
High-Temperature Chemical Sensor on D-shaped Optical Fiber

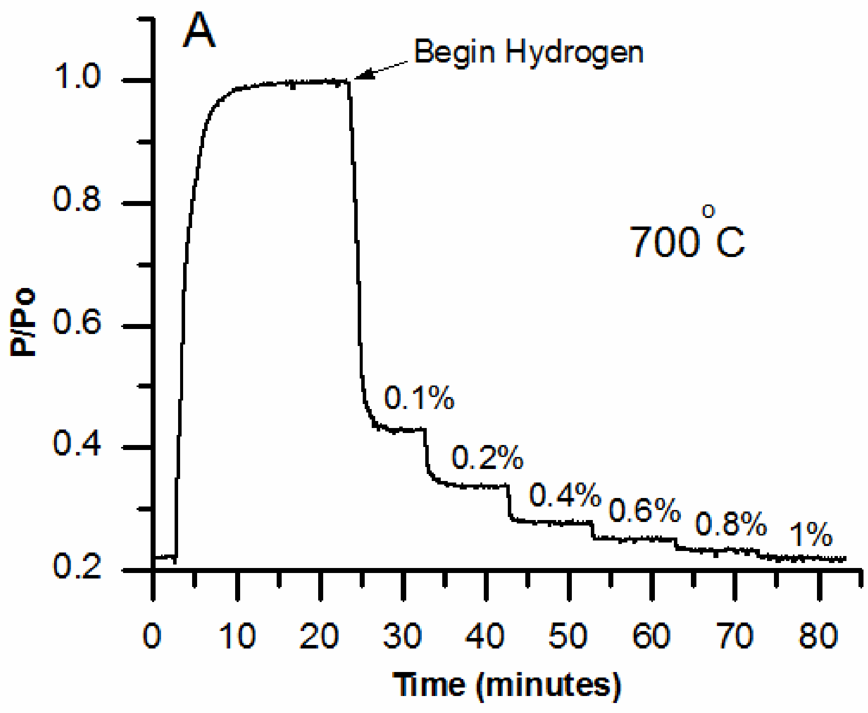




Fiber Optic Hydrogen Sensor at 700C

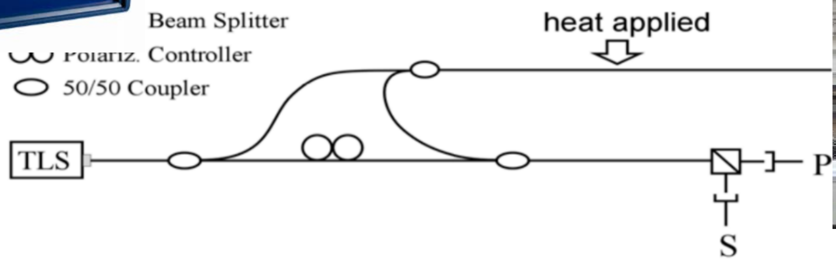
Optical Transmission vs. Hydrogen Concentrations

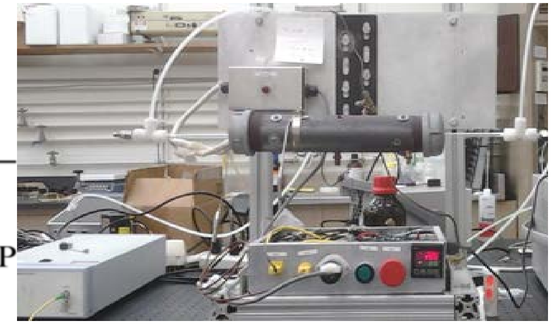


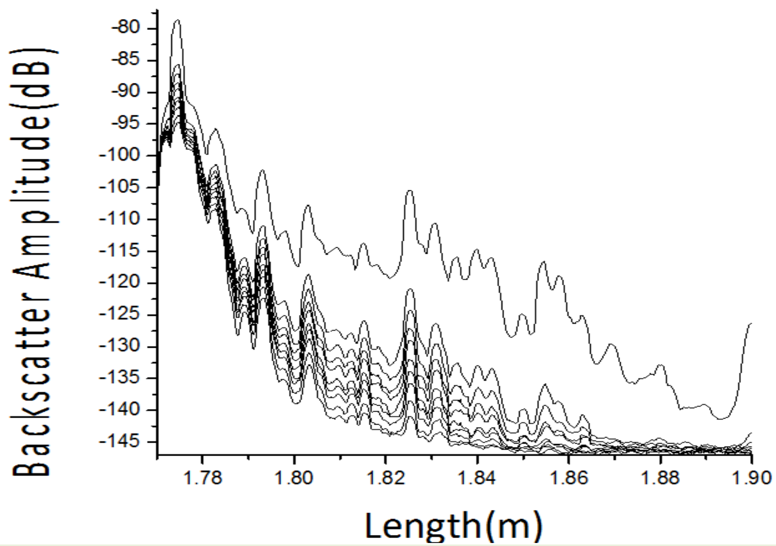


Exposed to various concentrations of hydrogen in nitrogen, recovered with nitrogen
Ideal for hydrogen driven energy conversion systems

Distributed H2 Measurements (Distributed Loss)







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 …

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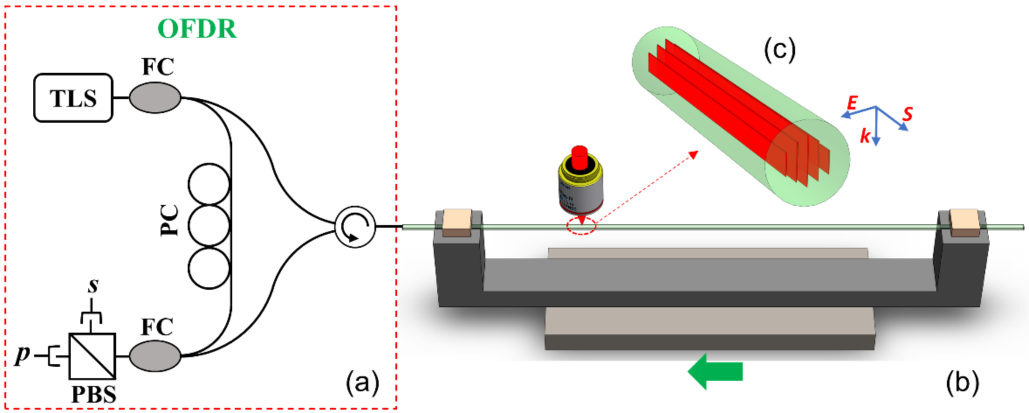
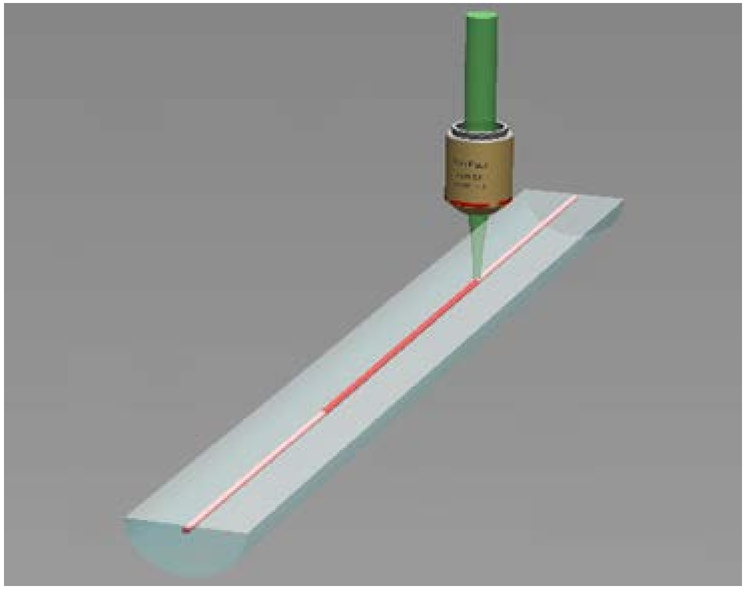
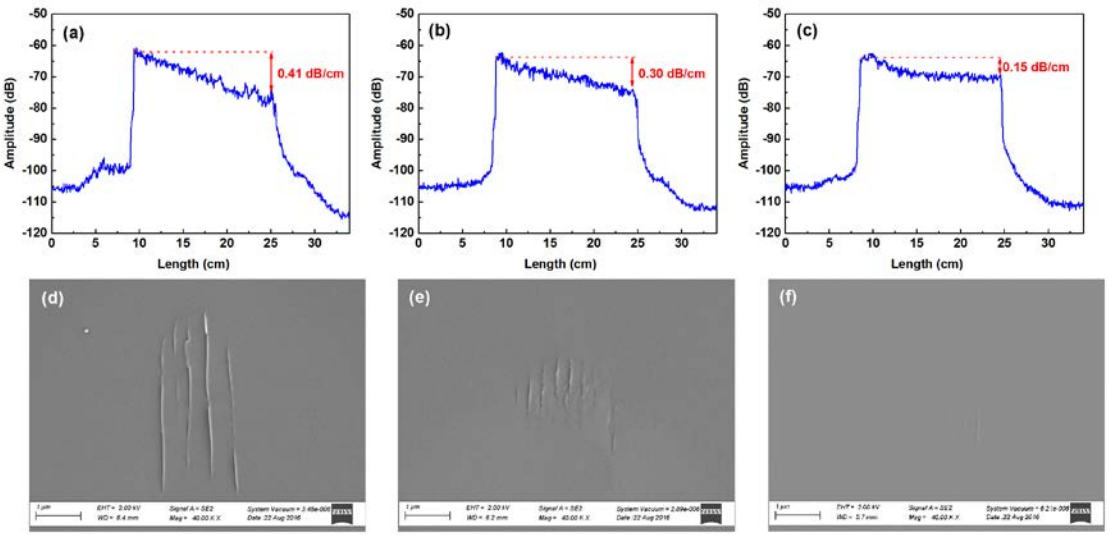
Ultrafast laser irradiation to enhance T/radiation resilience and measurement accuracy







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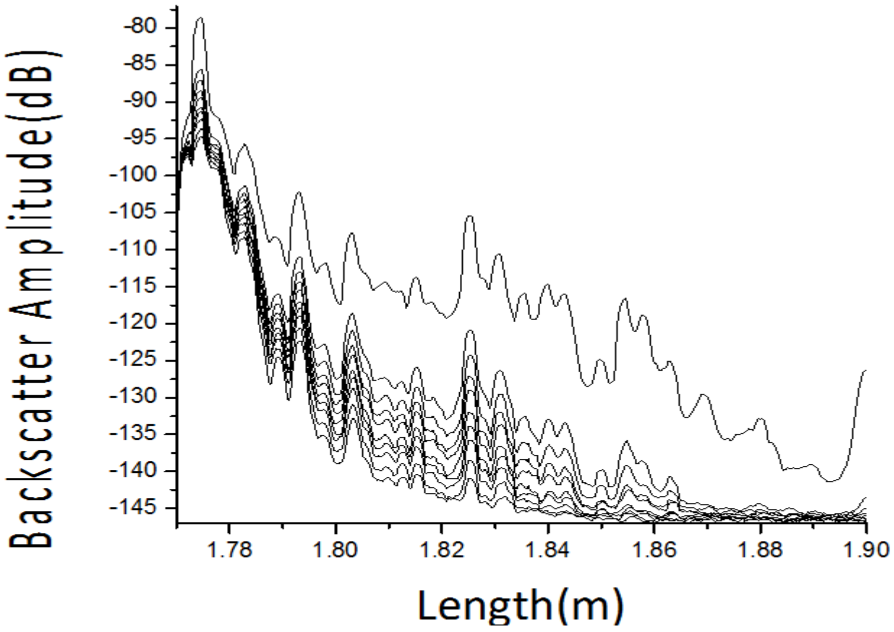
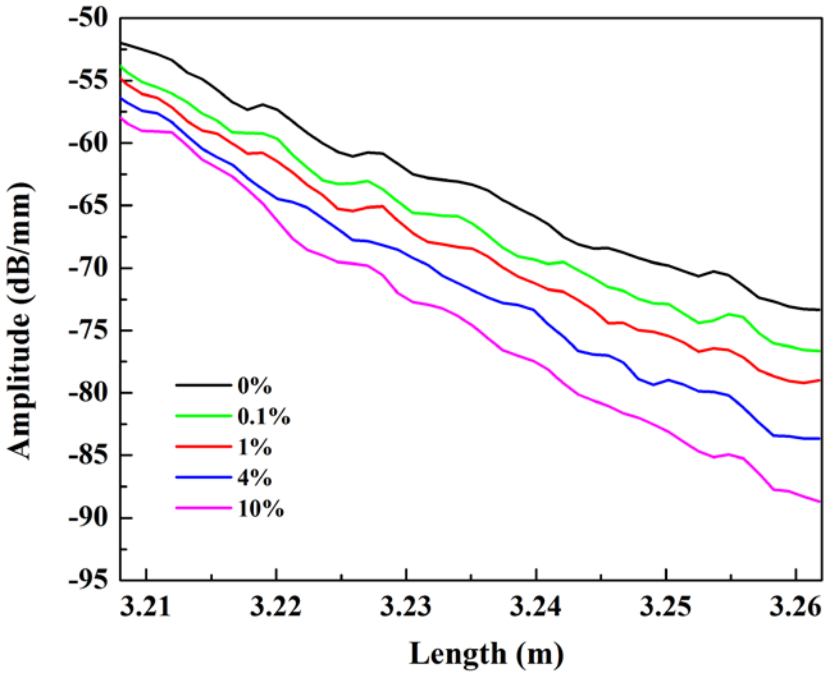
- Stability verified at 800C

Now… Distributed H2 Measurement Again…

Before… (700C)



After… (750C)

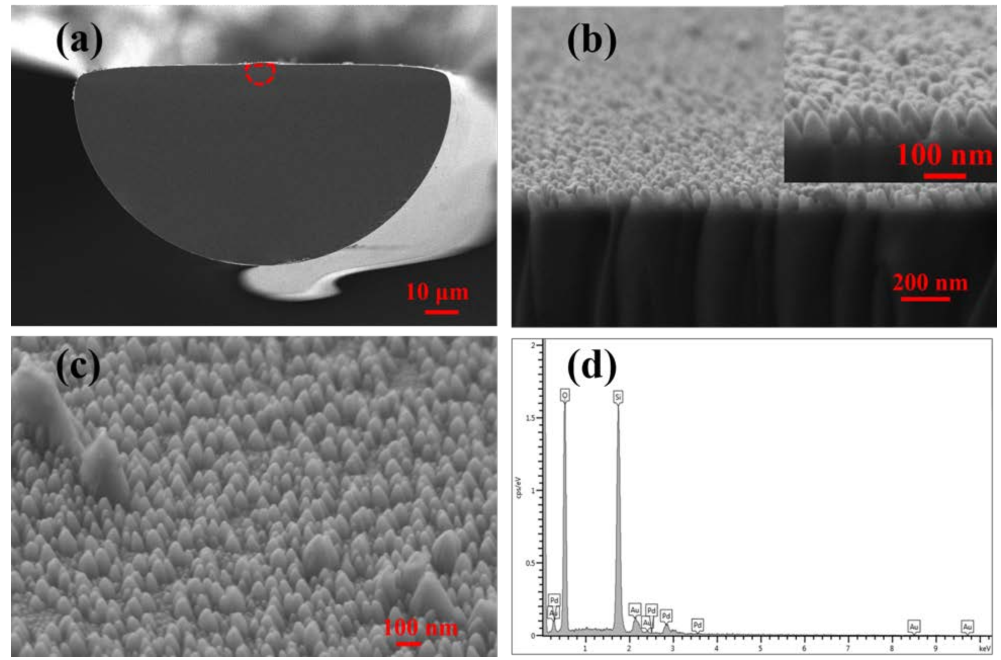


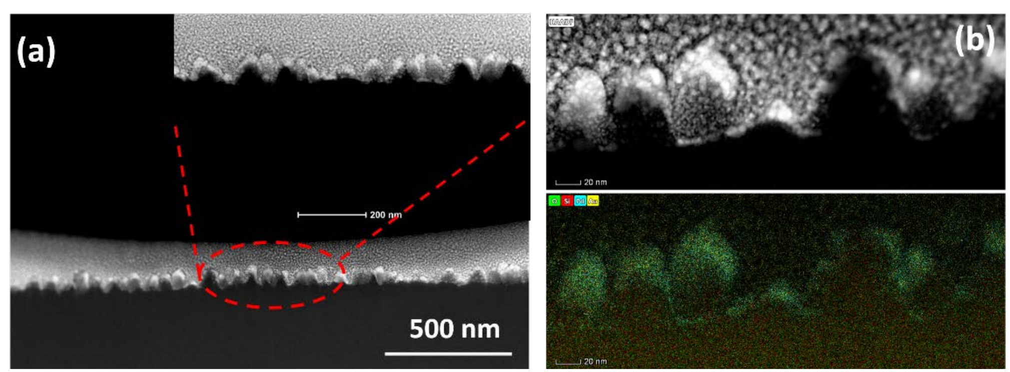
Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

1. Hydrogen Sensor Based on Nano-cone

- **Requirement:**
  - Fast sensory speed
  - Repeatable response
  - Continuous monitoring

- **Our Sensor:**
  - Au/Pd atomic ratio = 1.2
  - Densely packed nano-cones
  - Average cone size < 100 nm
  - Operates from RT – 600C

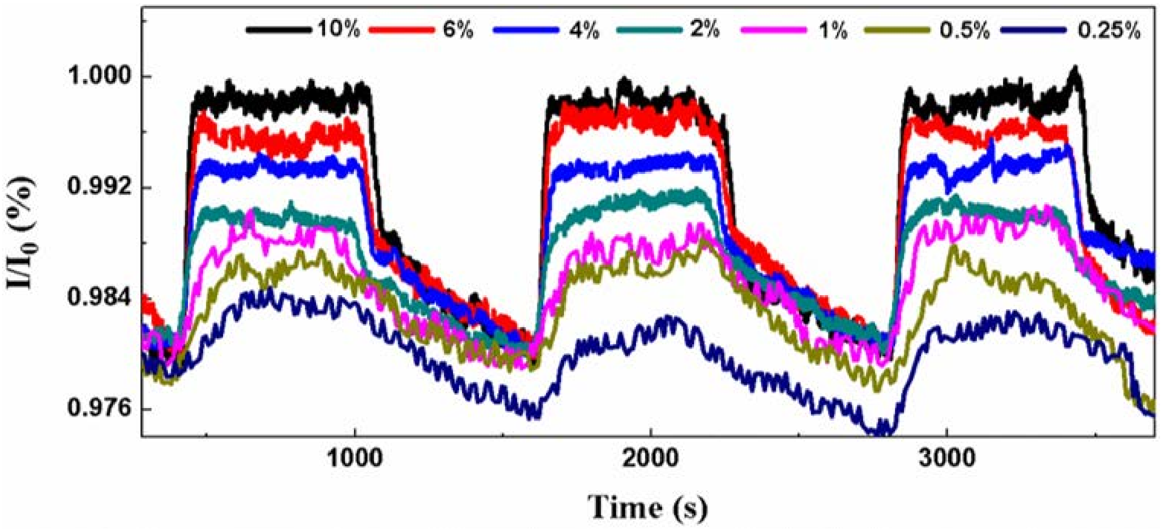


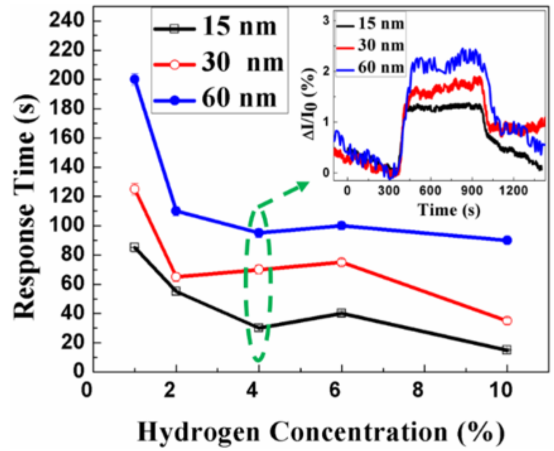


Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

1. Hydrogen Sensor Based on Nano-cone: Room Temperature Results

- **Results:**
  - Reversible response
  - Thinner alloy film, better response

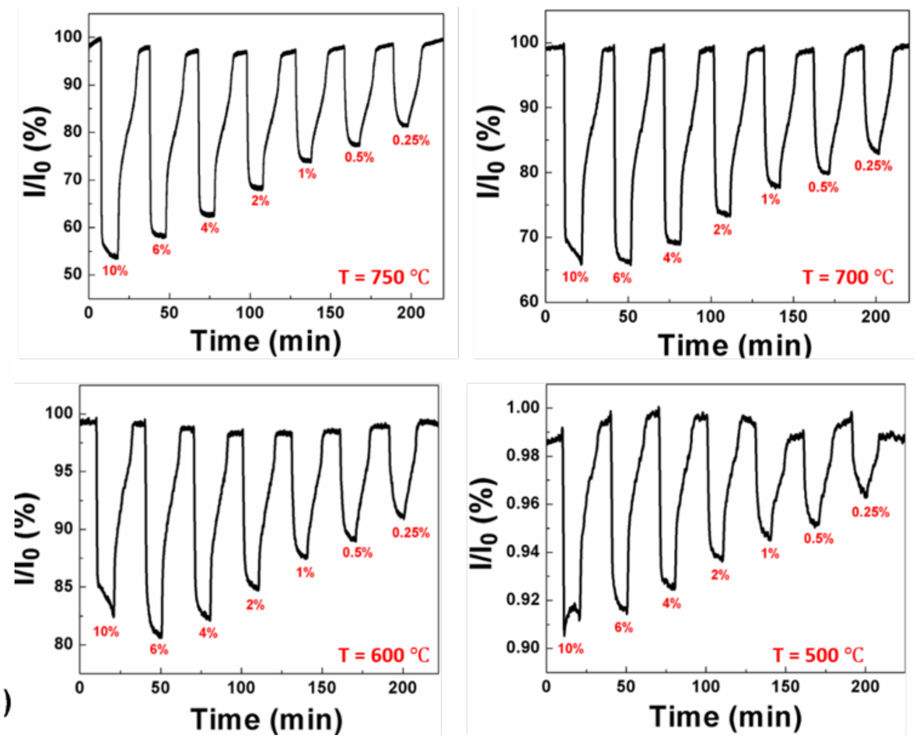


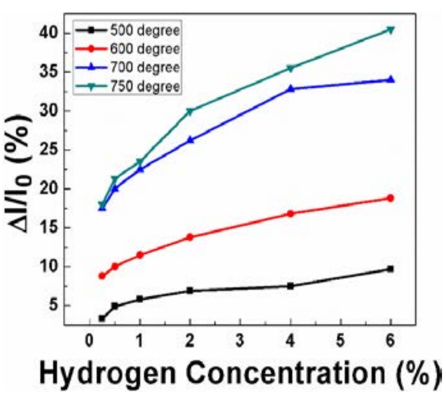


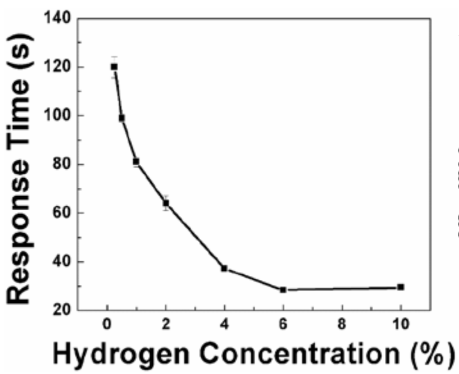
Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

2. Distributed Hydrogen Sensor Based on Metal Oxide

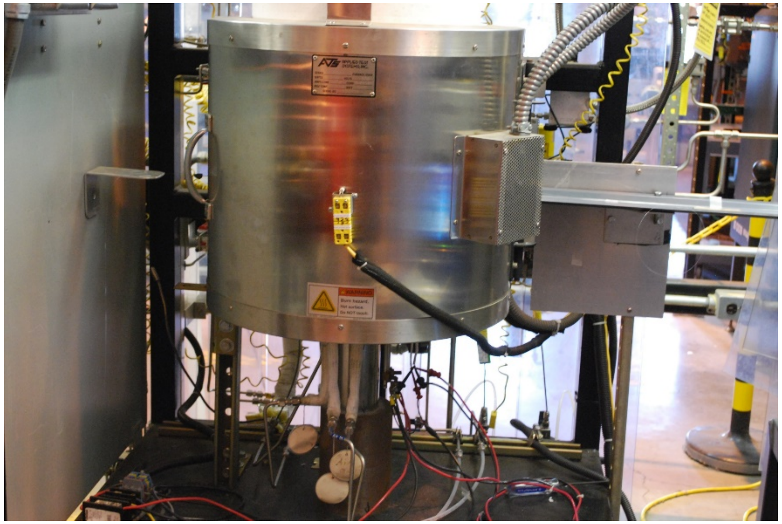
- **Results:**
  - Higher T, more stable response
  - High T, more significant response





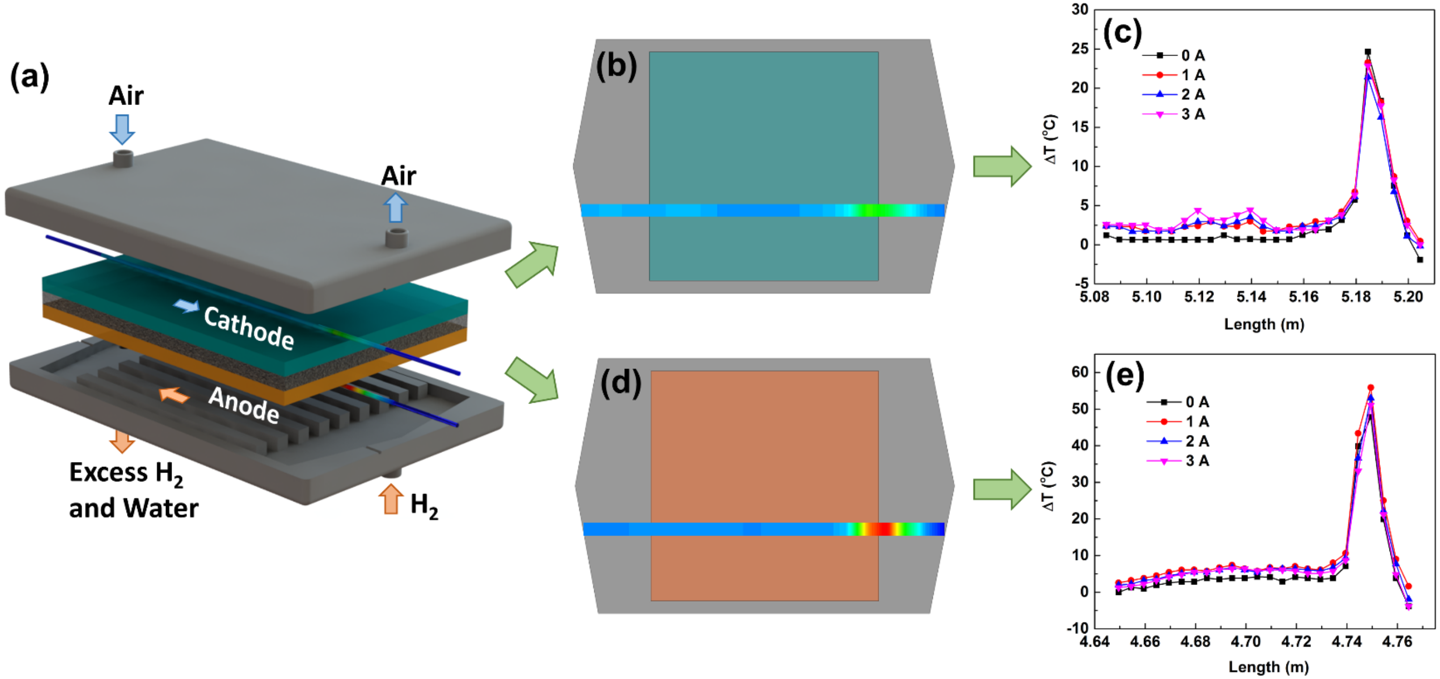


Fuel Cell Tests



- 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)

Distributed T measurement in SOFC



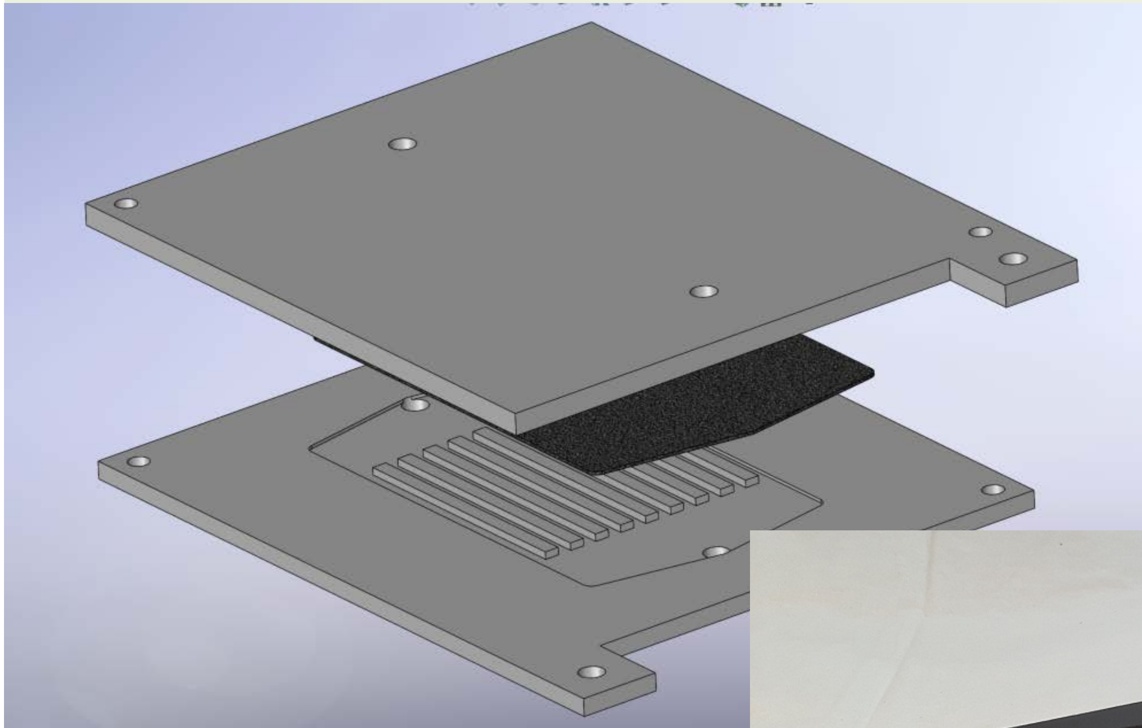
Temperature in cathode and anode were measured respectively

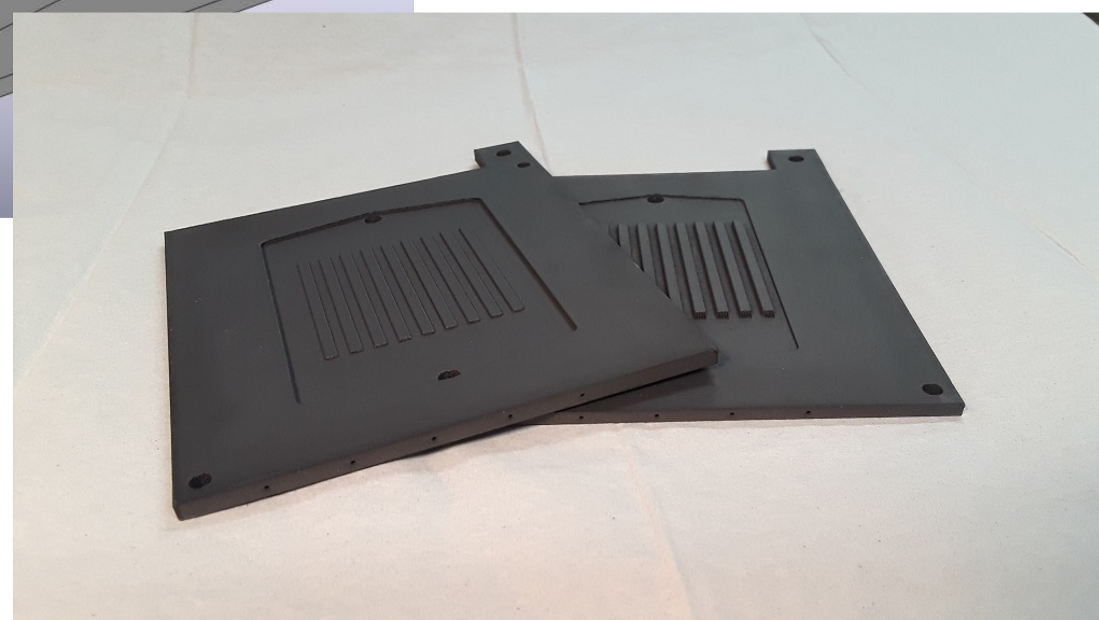
- 100% hydrogen fuel, current load 0 ~ 3 A.
- Temperature increase when fuel gas turned on

  Anode : ~55 ^{o}C, Cathode: ~ 25^{o}C
- Temperature change with different current loads < 5^{o}C

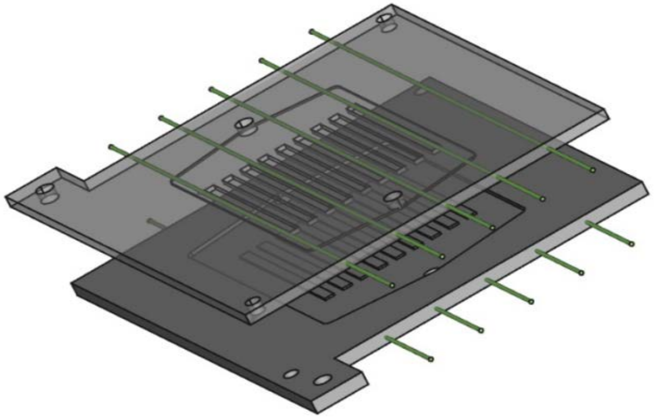
Sensor-Enabled Design Optimization

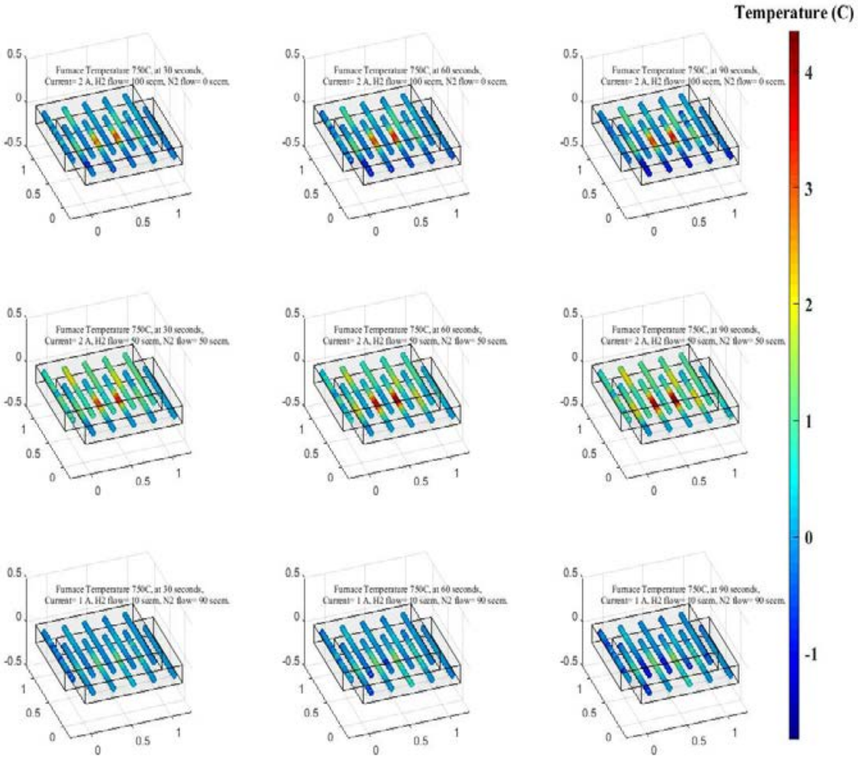
- **Current Fuel Cell Plates: only consider electrical properties**





- Configuration optimization to improve gas fuel (then chemical reaction) to improve the T/Chemical reactor profile in fuel cell.

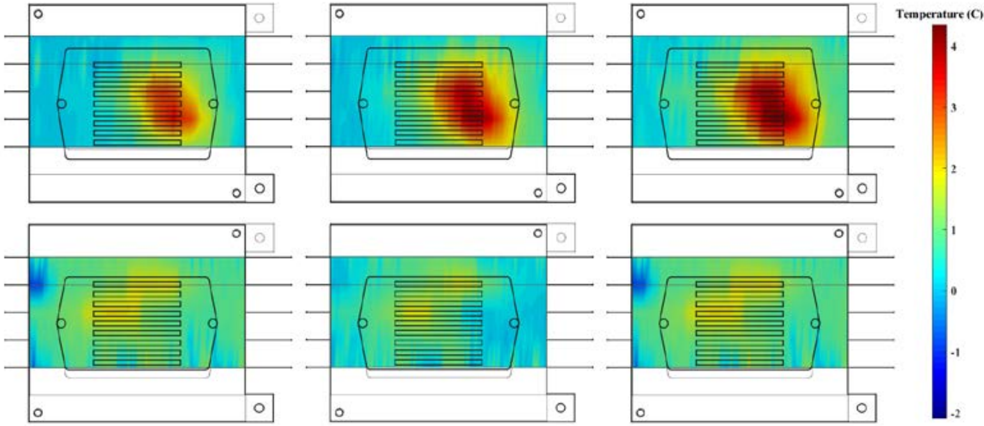




Sensor-Enabled Design Optimization

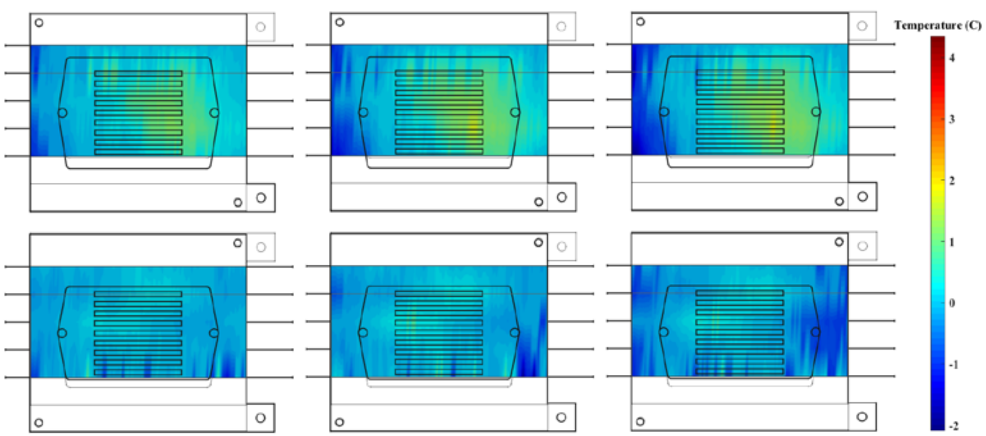
50 sccm H_2 flow, 750C

30s **60s** **90s**



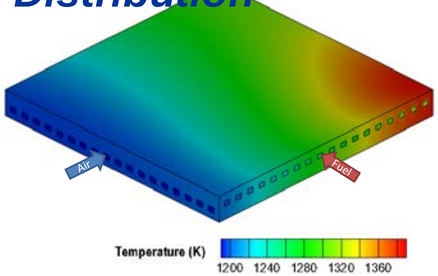
50 sccm N_2 flow, 750C

30s **60s** **90s**



Experiments and Simulation are VERY DIFFERENT….

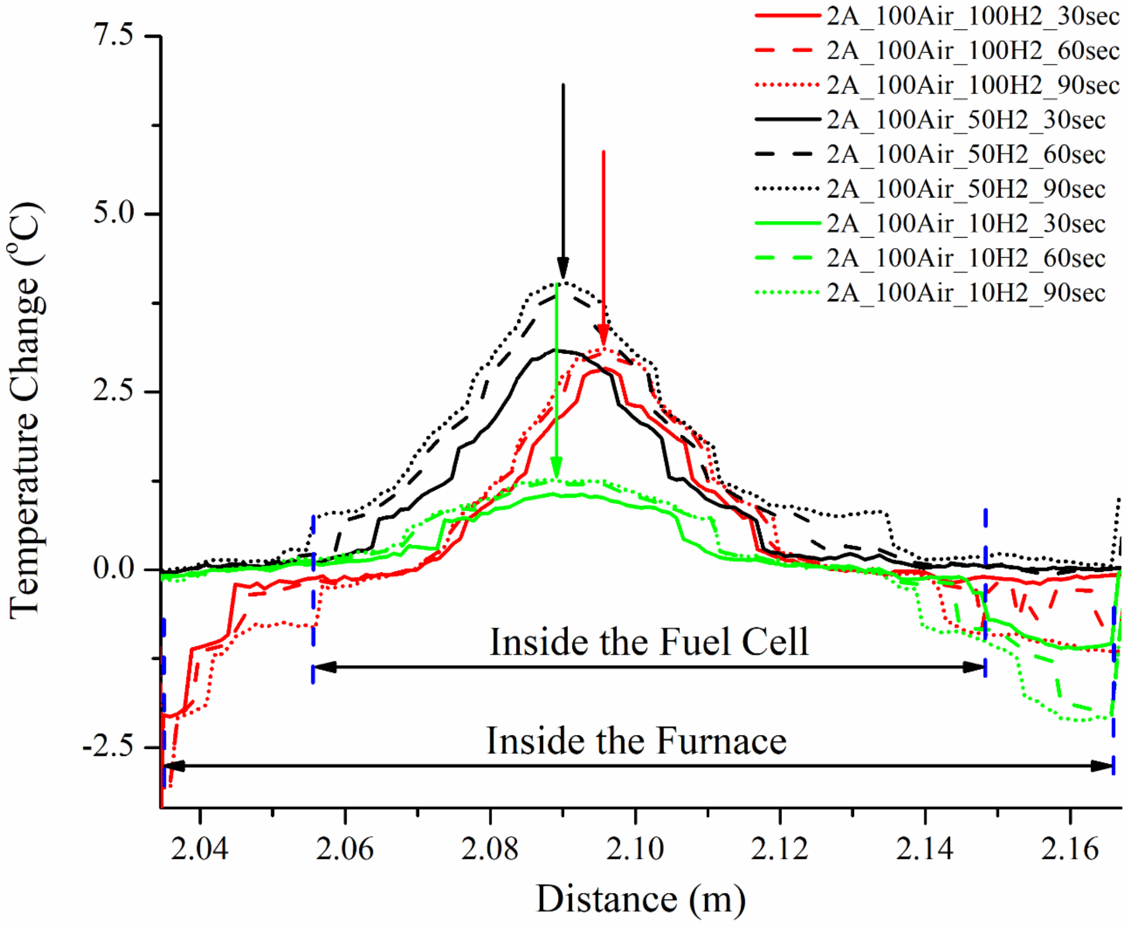
Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution



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

Sensor-Enabled Design Optimization

The peak of the temperature bump appears closer to the H_2 gas inlet, and shifts closer to the inlet as the H_2 flow rate is reduced.



Summary

- **Fiber sensors will play greater roles in energy industry especially in cross-cutting areas.**
- **Innovation in optical fiber Sensor is a truly integrated and looping efforts from fiber, to manufacturing, to deployment, to design optimization, and back .**
- **Interdisciplinary collaboration essential.**

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Thank you!

Questions?

Collaboration Welcomed!

Kevin P. Chen

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