



University of Pittsburgh

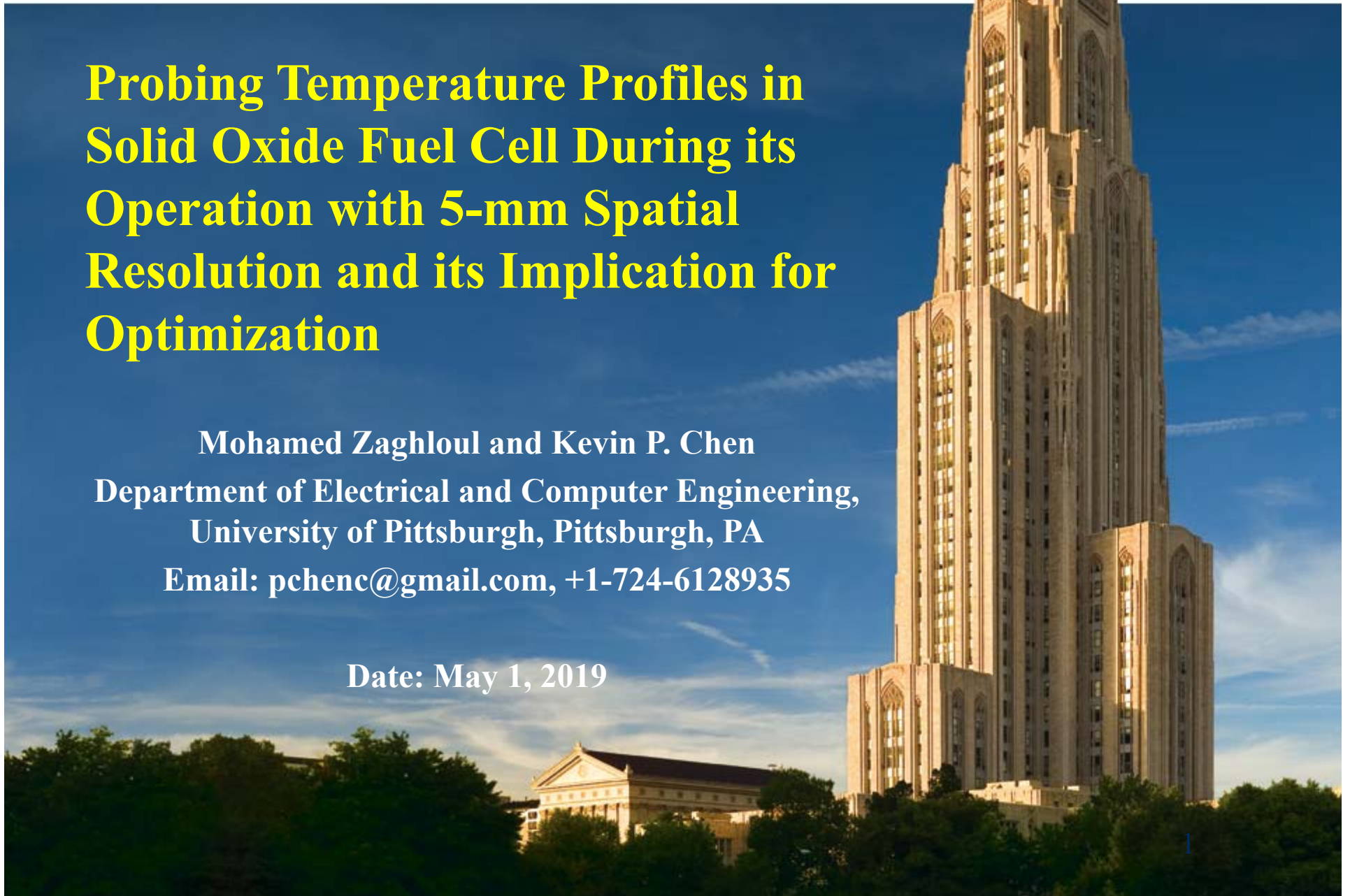
Probing Temperature Profiles in Solid Oxide Fuel Cell During its Operation with 5-mm Spatial Resolution and its Implication for Optimization

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University of Pittsburgh, Pittsburgh, PA

Email: pchenc@gmail.com, +1-724-6128935

Date: May 1, 2019



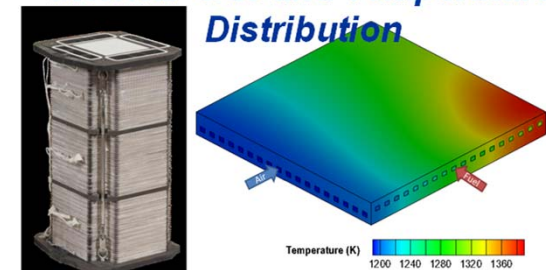


Objective/Vision: Probing High-T Chemistry in SOFC Operation

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

- **Develop high-T stable fiber sensors for**
 - Ultrafast laser direct writing
 - High spatial resolution data enabled big-data analytics
- **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?
- **Energy system optimization**

**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 data gathered by sensor to optimize design, operation, and control of Solid oxide fuel cell energy system.



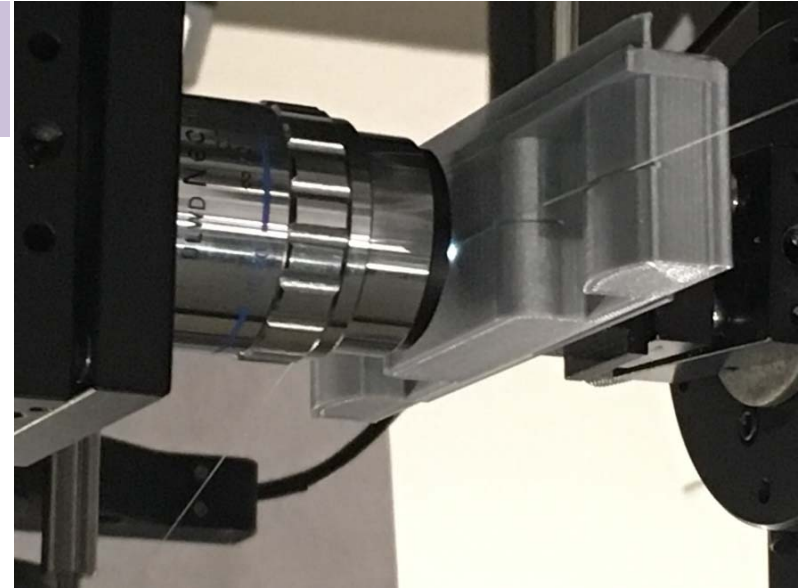
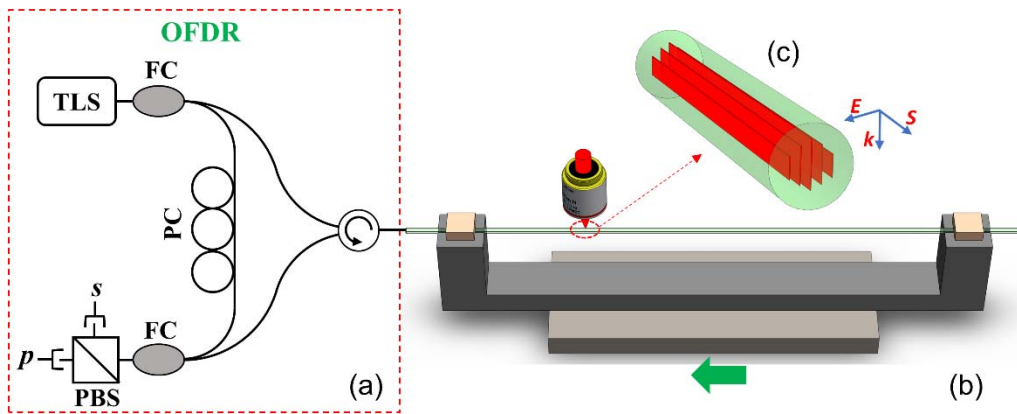
Outlines: Team

- **PI: Kevin Chen – University of Pittsburgh**
 - Graduate Student Researchers: Mohamed Zaghloul, Mohan Wang, Rongtao Cao, Zhaoqiang Peng
 - Research Scientist: Dr. Guanquang Liang
- **Industry Collaborator**
 - Watts Fuel Cell Technology
- **National Lab Collaborator**
 - NETL: 6 fuel cell on-site tests

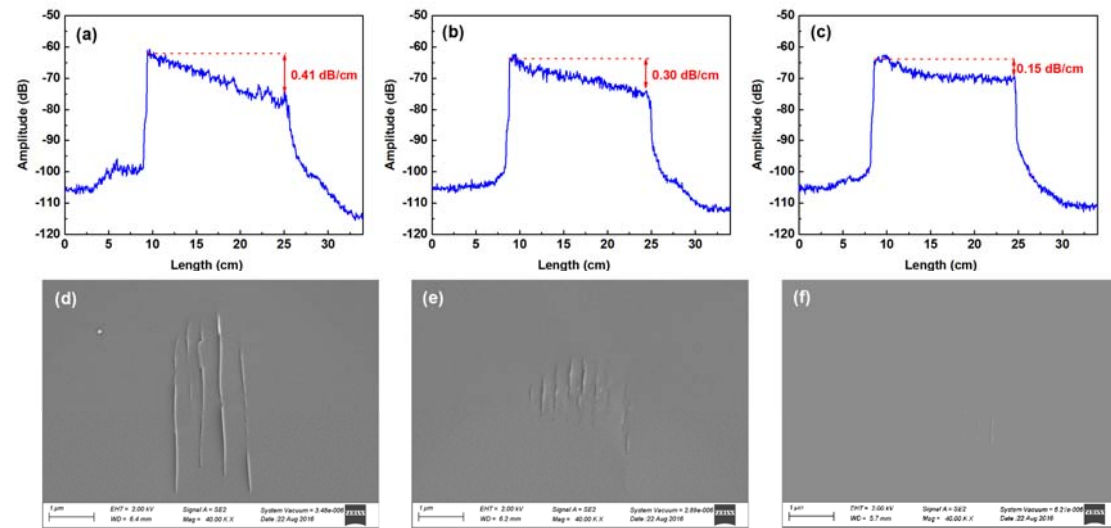


Distributed Sensors for High-T Applications

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



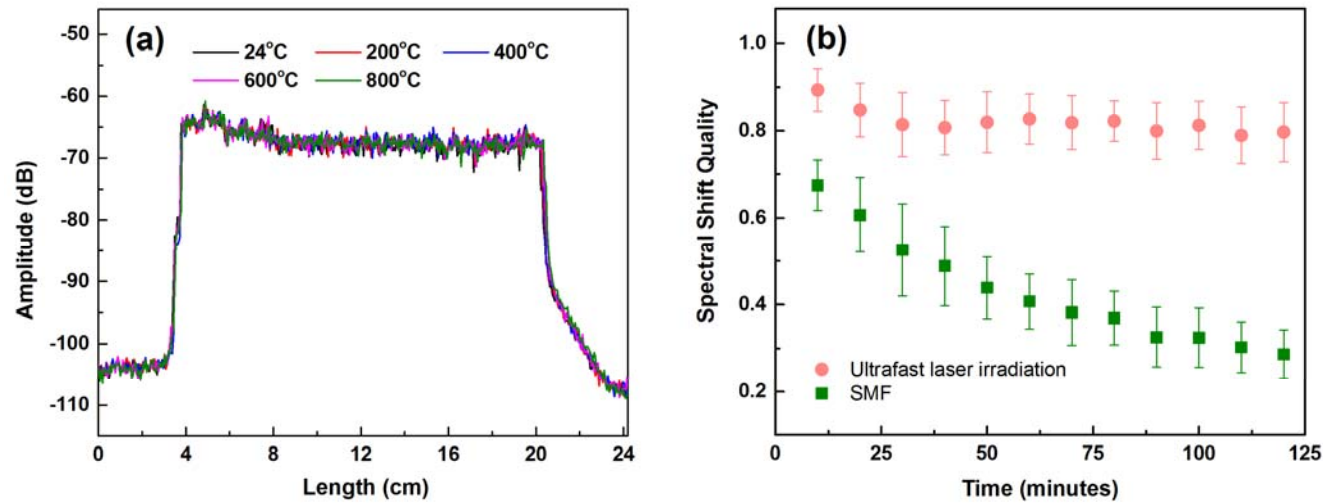
- Temperature measurements can now be performed at 800C with H₂ atmosphere
- Stability verified at 800C



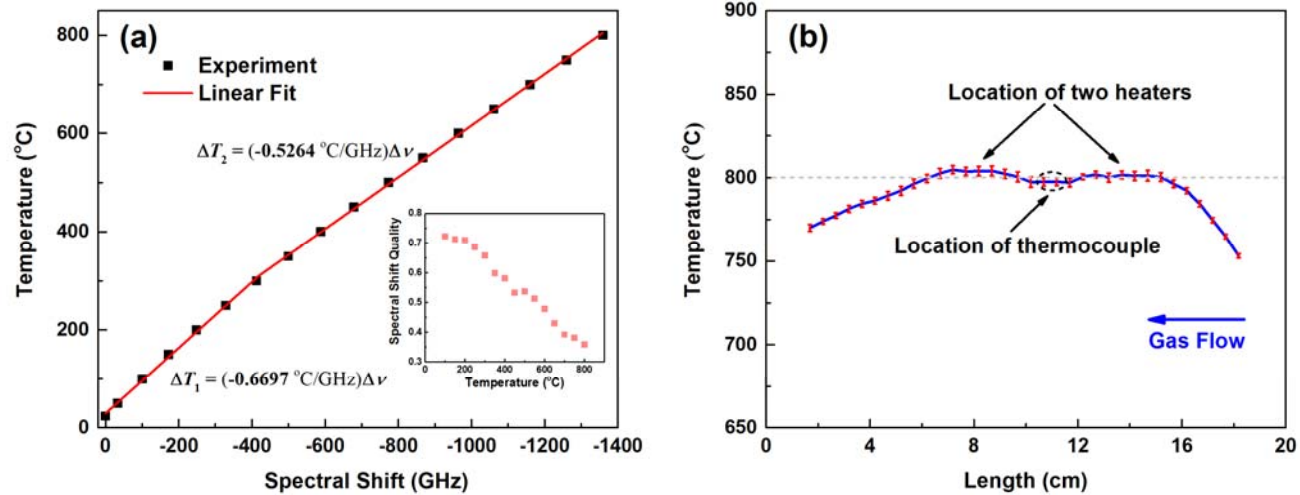


Distributed Sensors for Energy Applications

Temperature Resilience from the RT to 800C



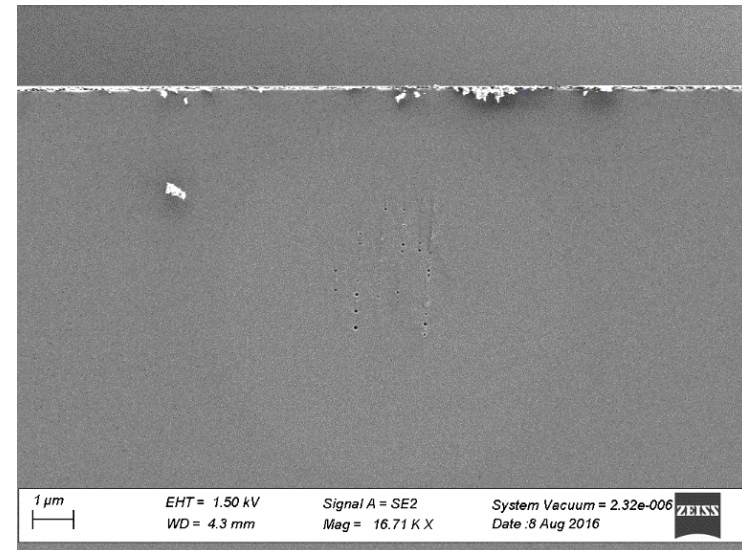
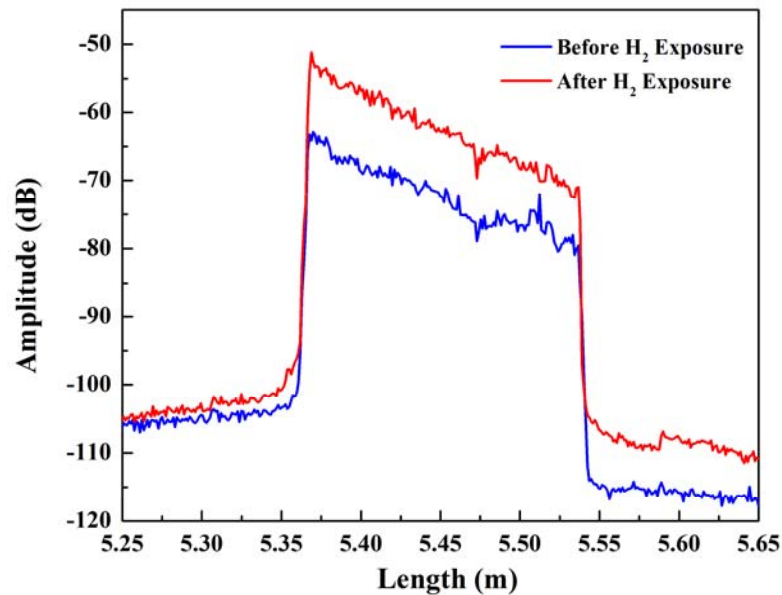
Measurement Repeatability better than 4C from the RT to 800C





Increasing Rayleigh Scattering Stability

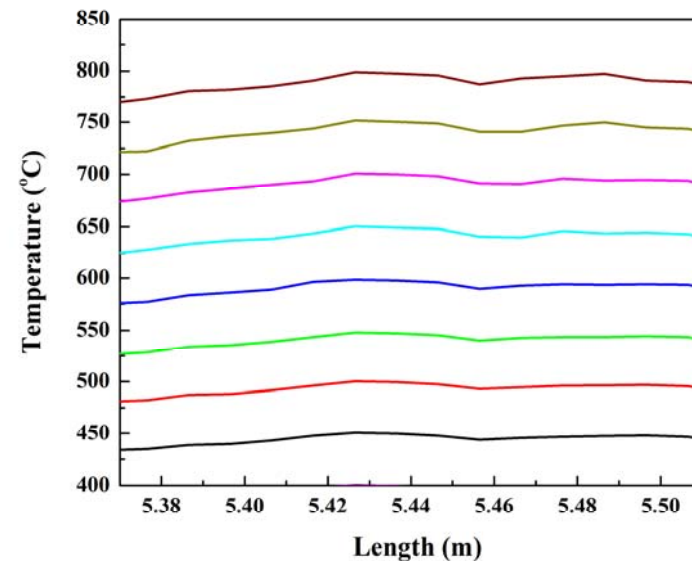
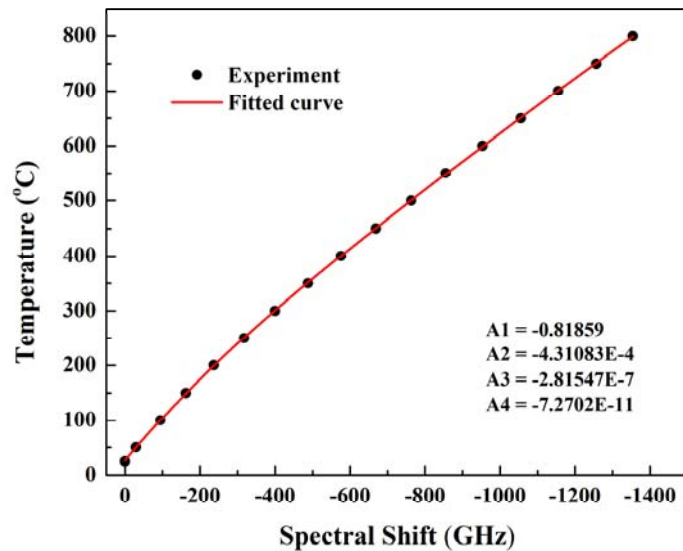
- H₂ exposure still increases loss and scattering.
- H₂ induced scattering is now less than irradiation-induced scattering.
- Cross-correlation is more effective with increased scattering features that do not change with temperature.





Temperature coefficients determined to 800 C

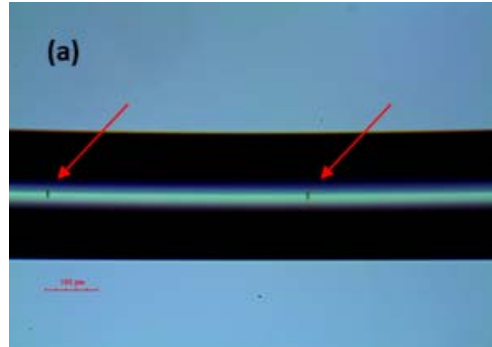
- Temperature can now be measured at 800 C with H₂ atmosphere.
- Stability verified for ~19 hours at 800 C.
- 4 C accuracy with heat/reheat.



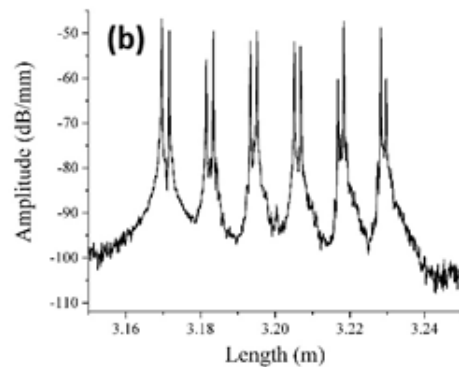


Distributed Inline FP sensors Enabled by fs-laser direct writing

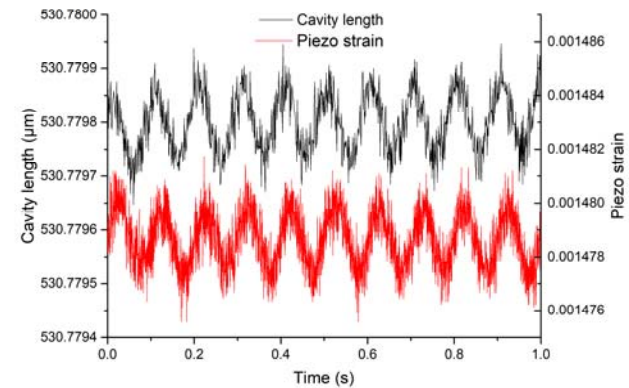
Inline FP created by fs-laser



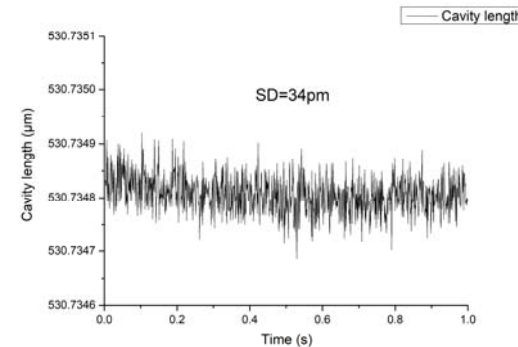
Six pairs of FP sensors



Vibration measurements



Dynamic strain resolution



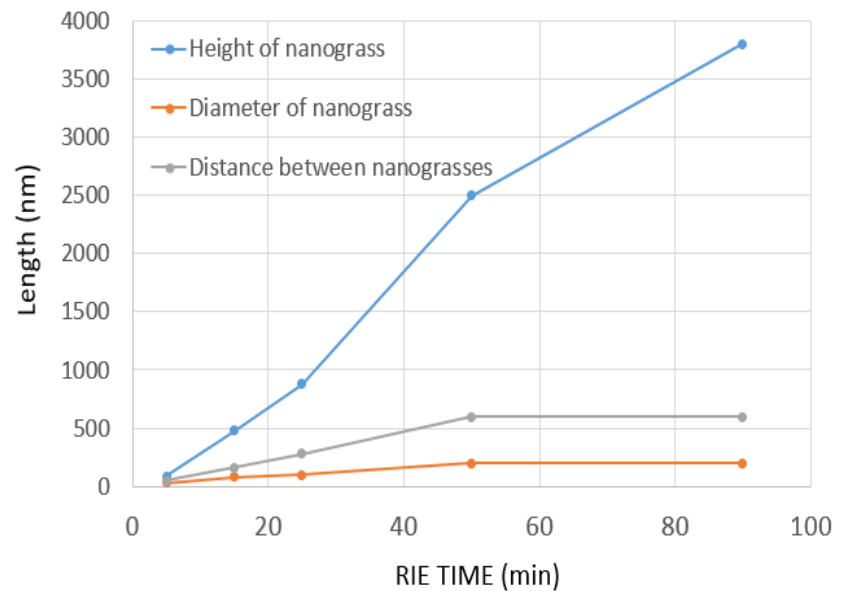
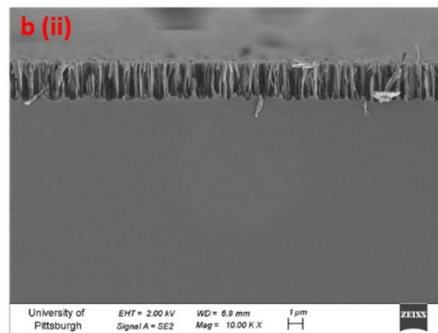
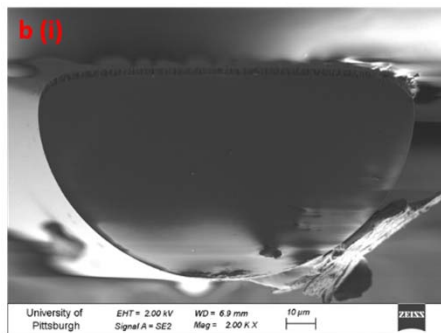
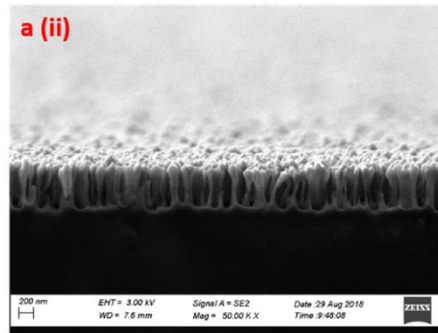
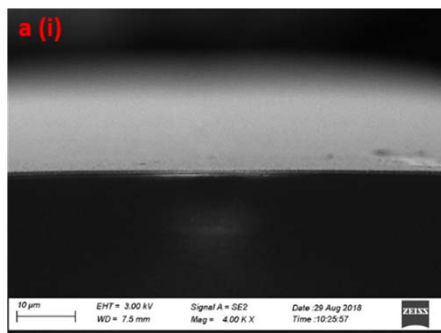
- 6 inline FP cavities inscribed in one fibers
- Cavities length 600 μm to 1000 μm
- Target temperature 400-900 C
- Capable of performing static temperatures and dynamic vibration measurements
- Inscribing in two types of fibers (RAL and F-doped core)
- Distributed temperature measurements



Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

Distributed Hydrogen Sensor Based on Nano-grass at High Temperature

- **Challenges:**
 - Avoid metal oxide sensing film collapses at high temperature
 - Remain similar sensory performance
- **Our Sensor:**
 - Introduced Nano-grass textured optical fiber

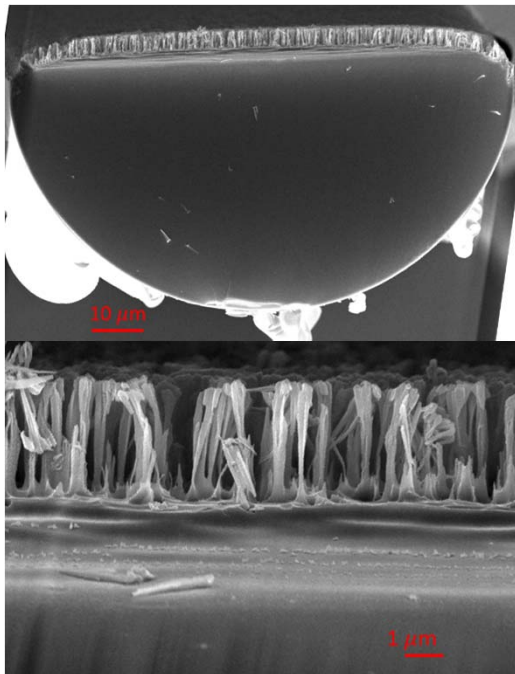




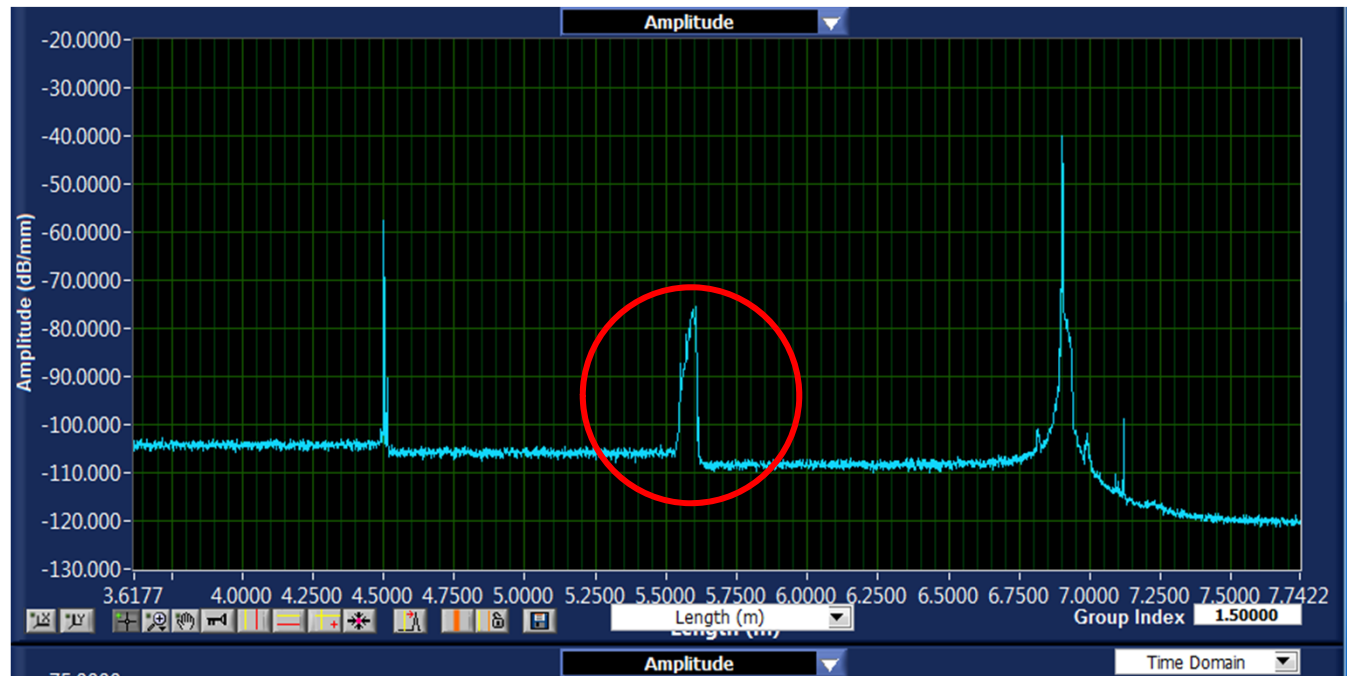
RIE on D-shaped fiber, Coating, Rayleigh

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

Nano-grass (height: $4.7 \mu\text{m}$)



D-fiber with nano-grass Rayleigh scattering





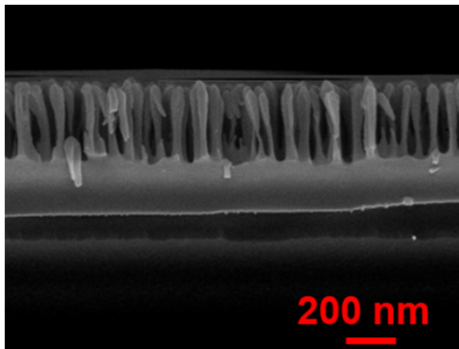
Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

Metal Oxide (HfO_2) Protected Nanostructure

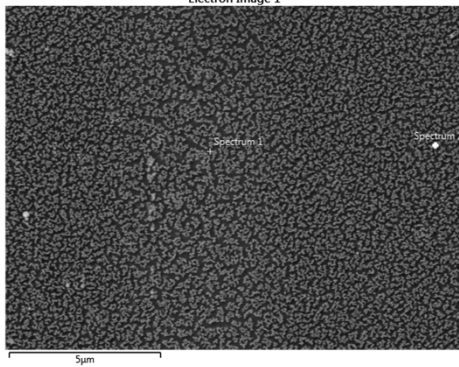
- **Challenges:**

- Nano-grass “melting” on top of the fiber core at high temperature
- Introduce HfO_2 coating to solve the problem

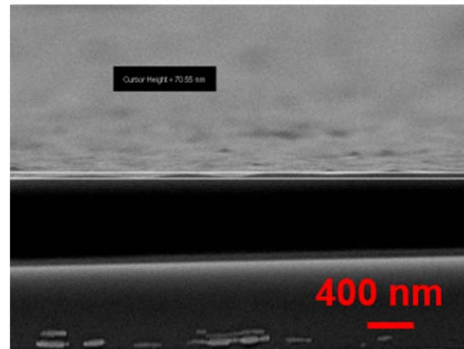
600 °C



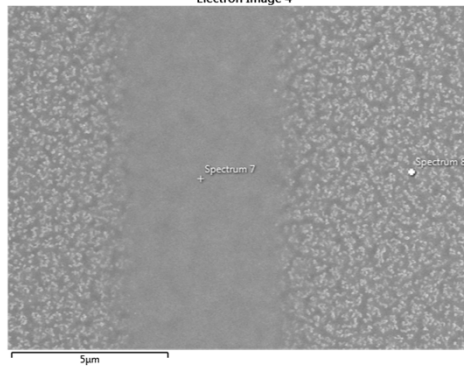
Electron Image 1



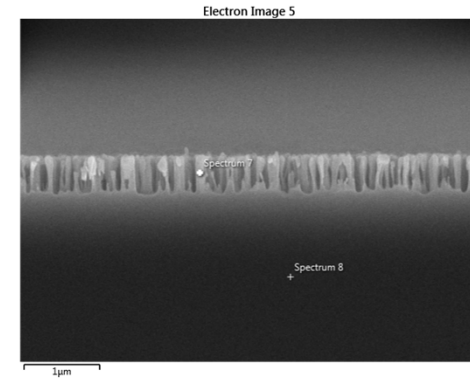
800 °C



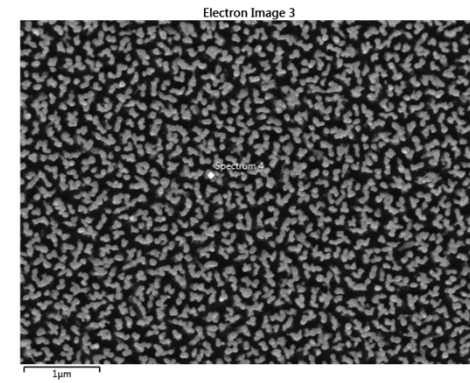
Electron Image 4



800 °C with HfO_2



Electron Image 5



Electron Image 3



Objective Sensing Materials: Tailoring the Refractive Indices and Chemical Responsivity

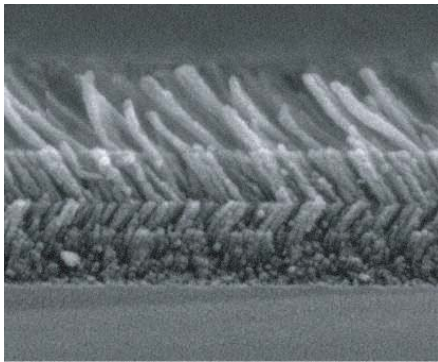
Requirements:

- 3D Geometry (reduces unwanted anisotropy)
- $\Lambda \ll \lambda$ (reduce optical scattering loss)
- Processing on arbitrary shapes (fiber...)
- **Wide tunability of refractive indices ($\Delta n > 1.5$)**
- **Reactive to a wide array of gas species**
- **Low cost**
- **High temperature stability**

Options

Semiconductor Processing?

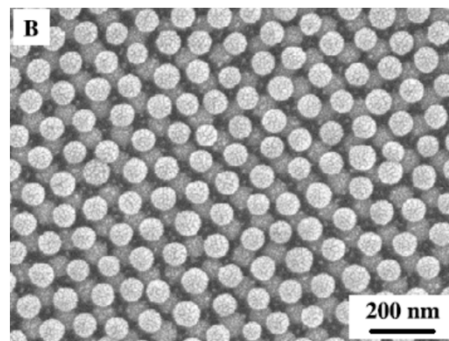
- ❖ Doping, sputtering
- ❖ Cost, not flexible



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

Colloidal Templating?

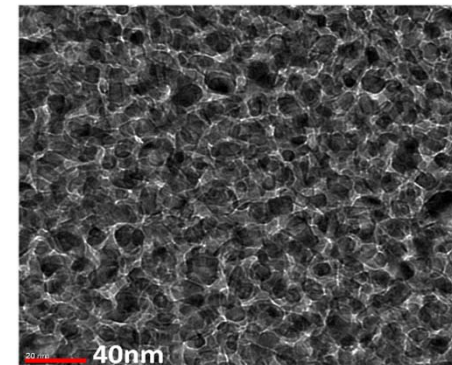
- < 50 nm
- Structure limited
- Limit tuning of porosity



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

Block Copolymer Templating?

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

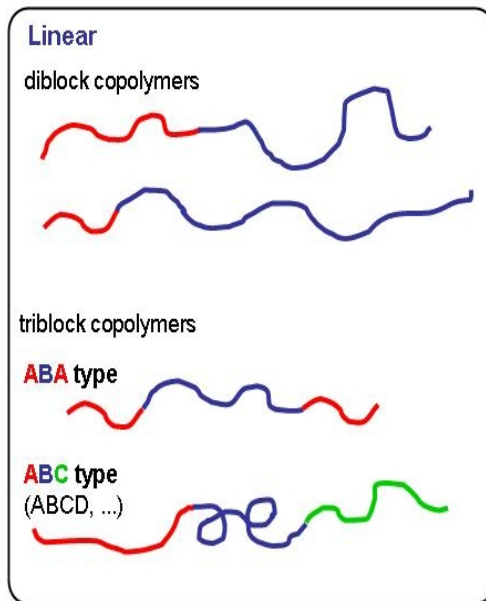




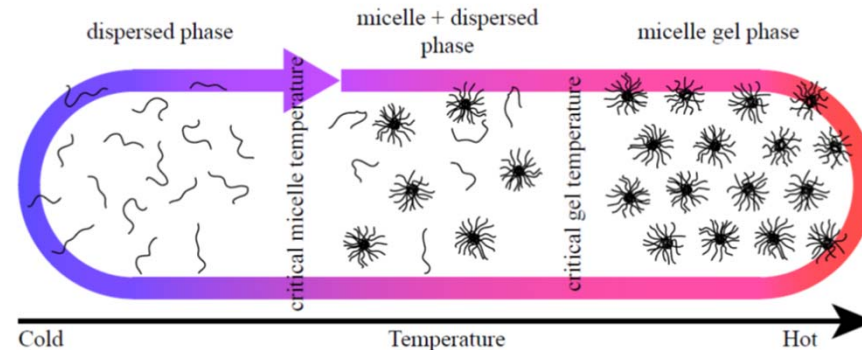
Sensing Materials: Co-Polymer Templating by F-127

F-127 Pluronic

- A triblock copolymer
- Highly compatible with the preferred solvents (alcohol)
- Has better higher temperature stability



(Orilall, 2011)



(Mezmarich, 2012, p. 107)



(Shao, 2010)

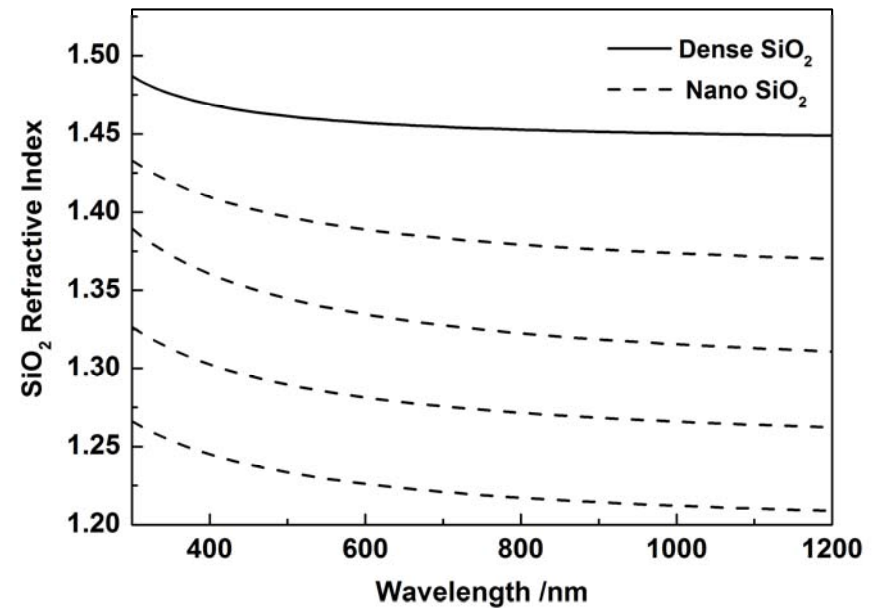
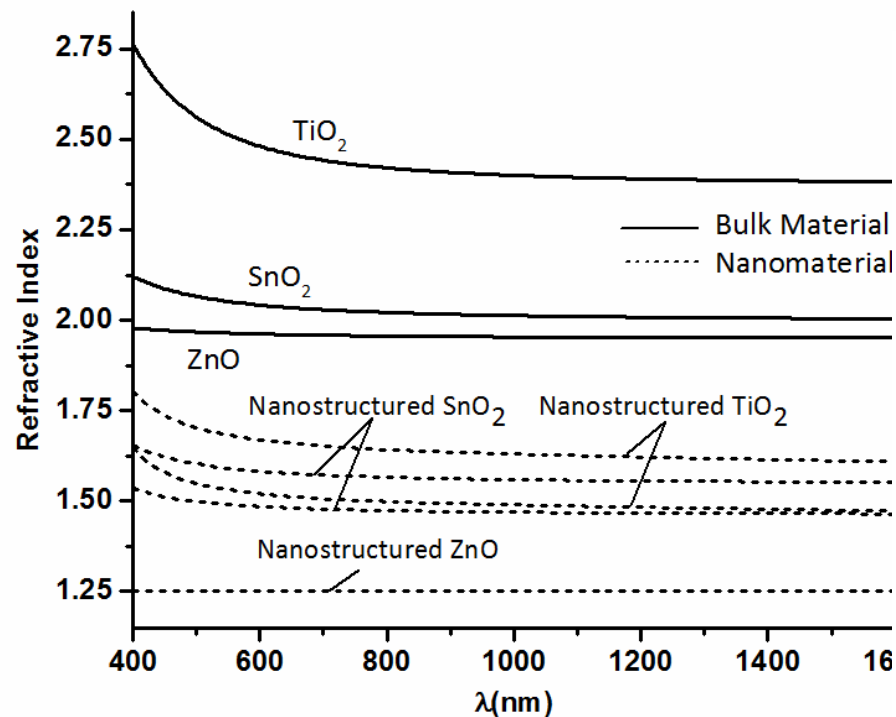


Metal Oxides and Their Dopant Variants

- Metal Source: SnCl_4 , TiCl_4 , and $\text{Zn}(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2$
- Si Source: Tetraethyl Orthosilicate
- Solvent: Ethanol
- Block Copolymer: Pluronic F-127
- Stabilizer: HCl for most, NH_4OH for Zn

Controlling Refractive Indices

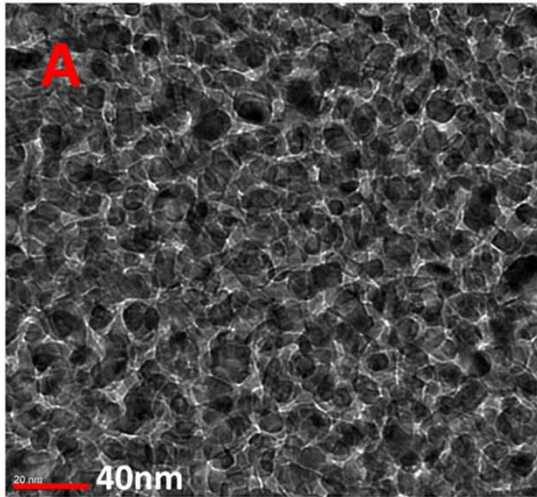
- TiO_2 : $\Delta n \sim 1.4$ to 2.5
- SnO_2 : $\Delta n \sim 1.4$ to 2.1
- ZnO : $\Delta n \sim 1.25$ to 2.0
- SiO_2 : $\Delta n \sim 1.2$ to 1.45



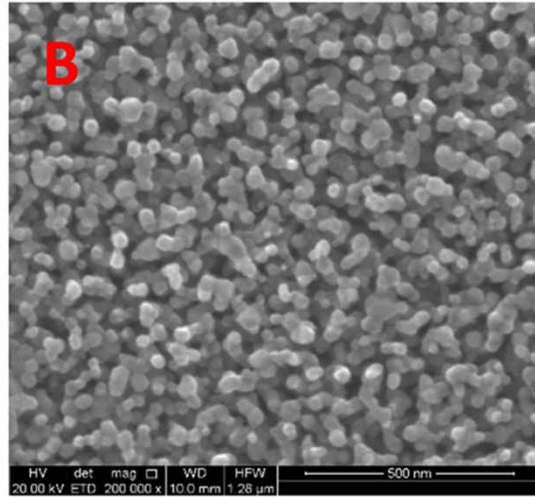


Metal Oxides and Their Dopant Variants

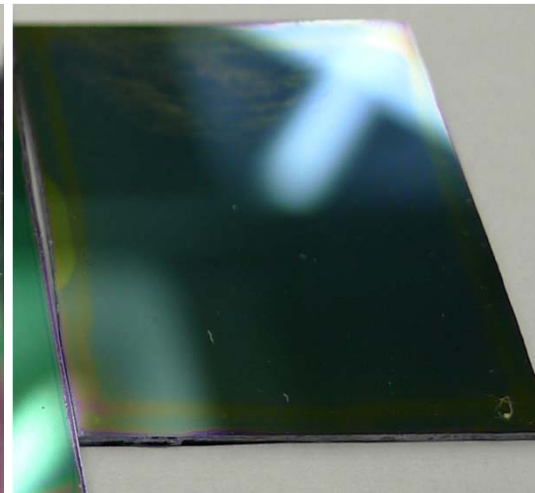
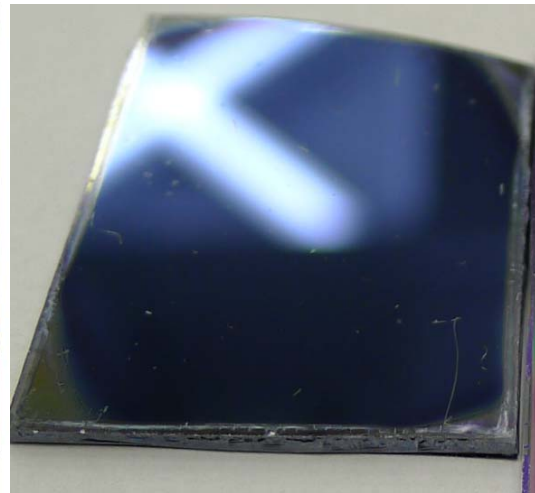
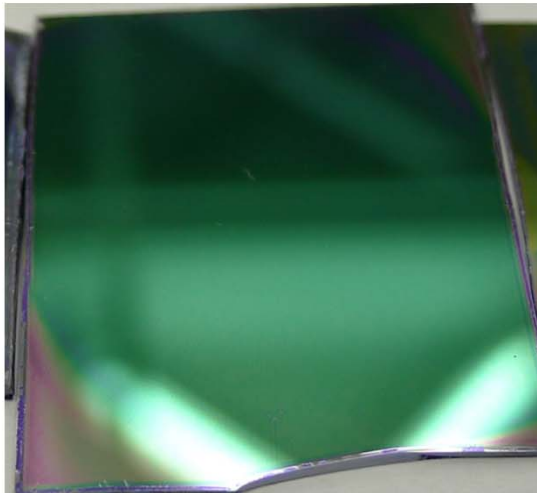
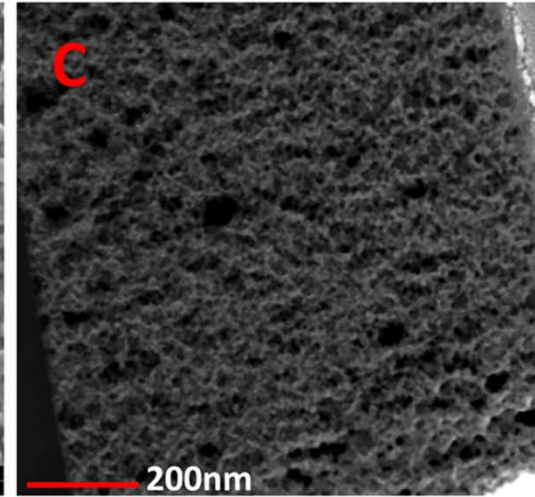
TEM of TiO₂



SEM of ZnO



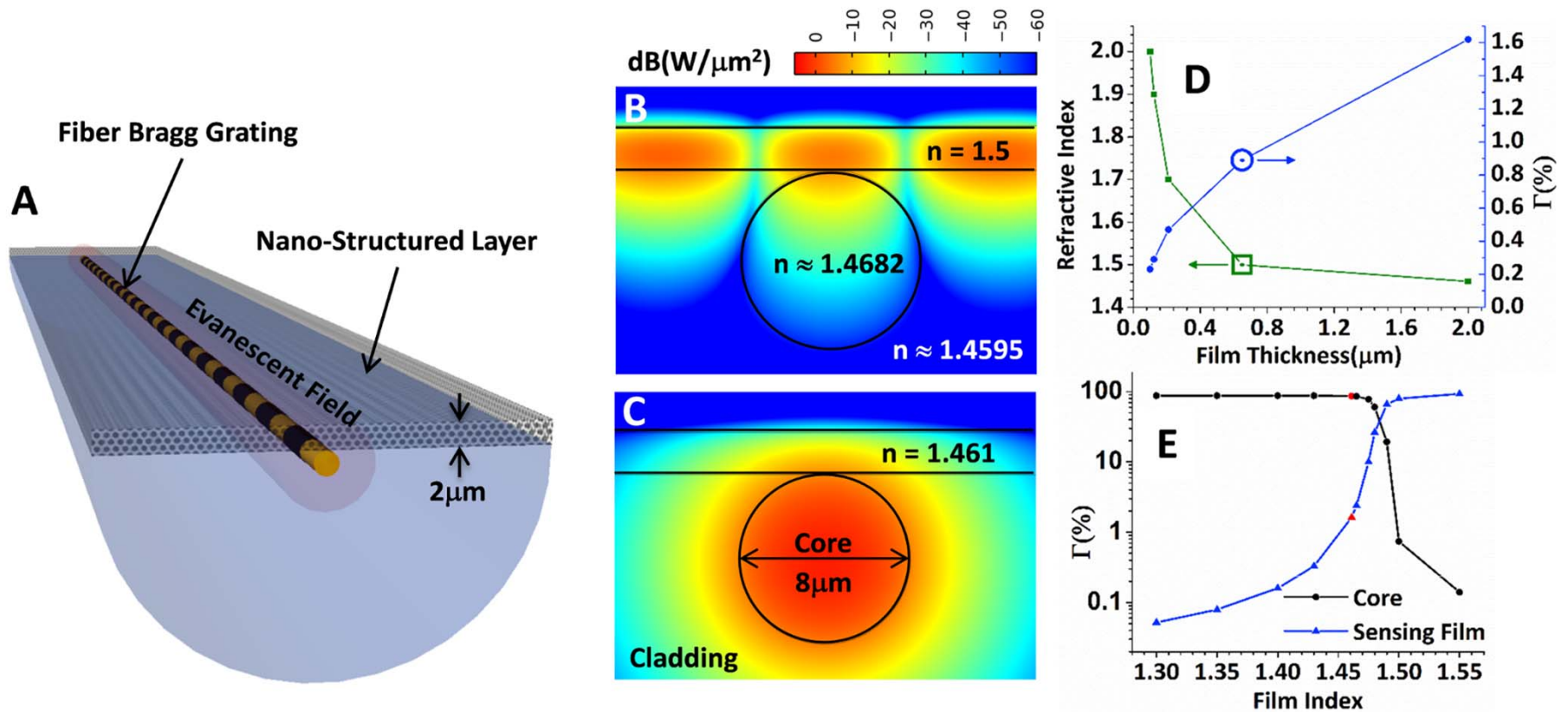
SEM of SnO₂





Metal Oxide on Optical Fiber Platform

In the evanescent wave configuration
Refractive Index Matching is Critical

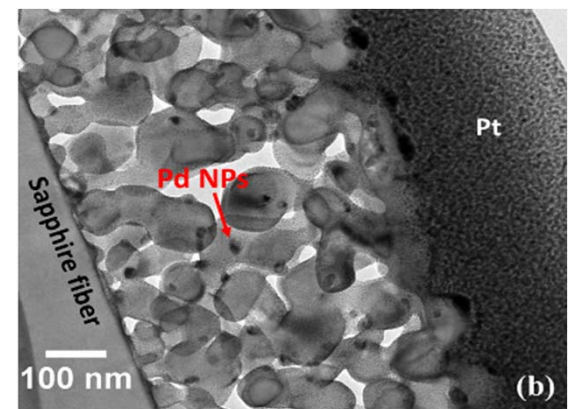
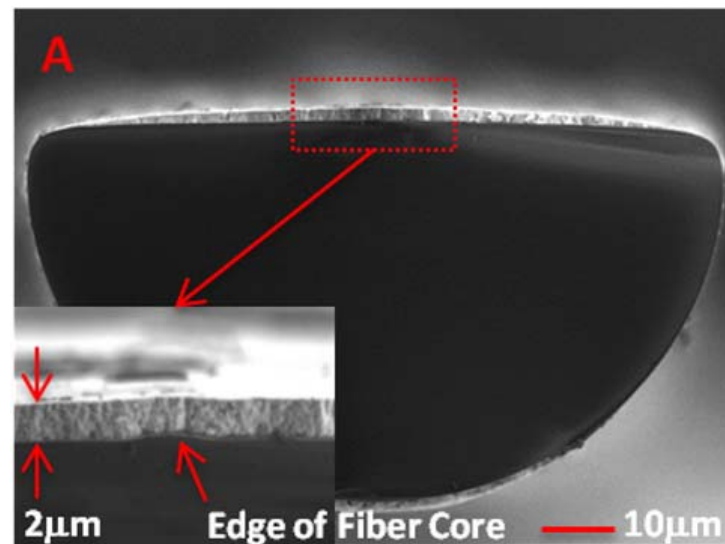
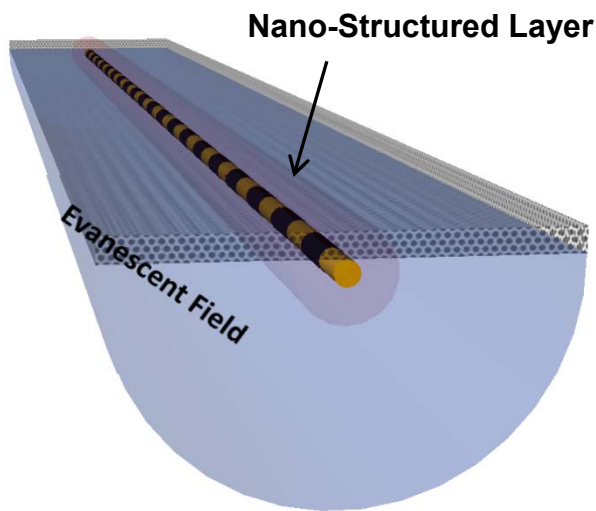


Finite Element Simulation of the Power Distribution of the Fundamental Mode



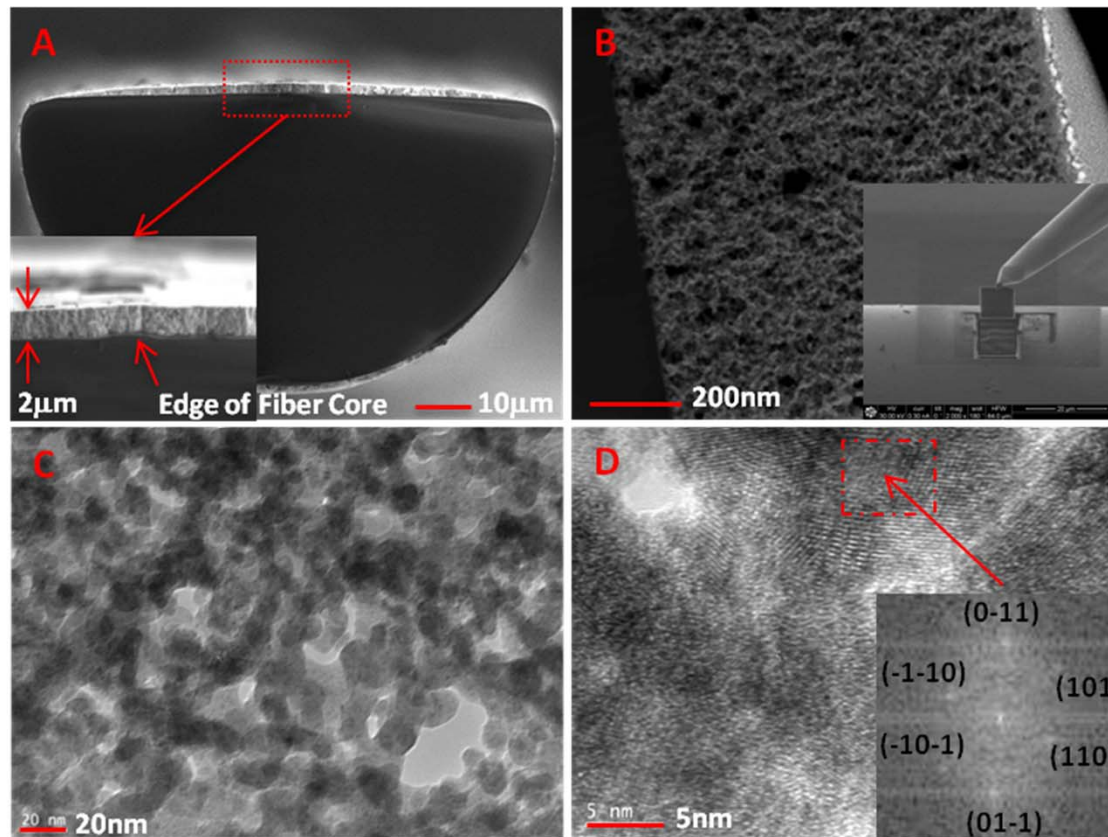
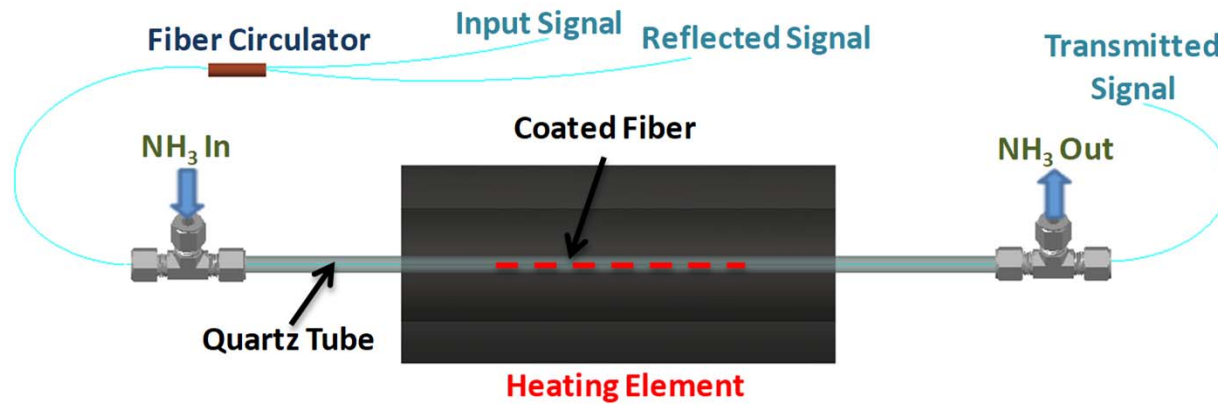
Metal Oxides Enabled Chemical Sensors

- 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





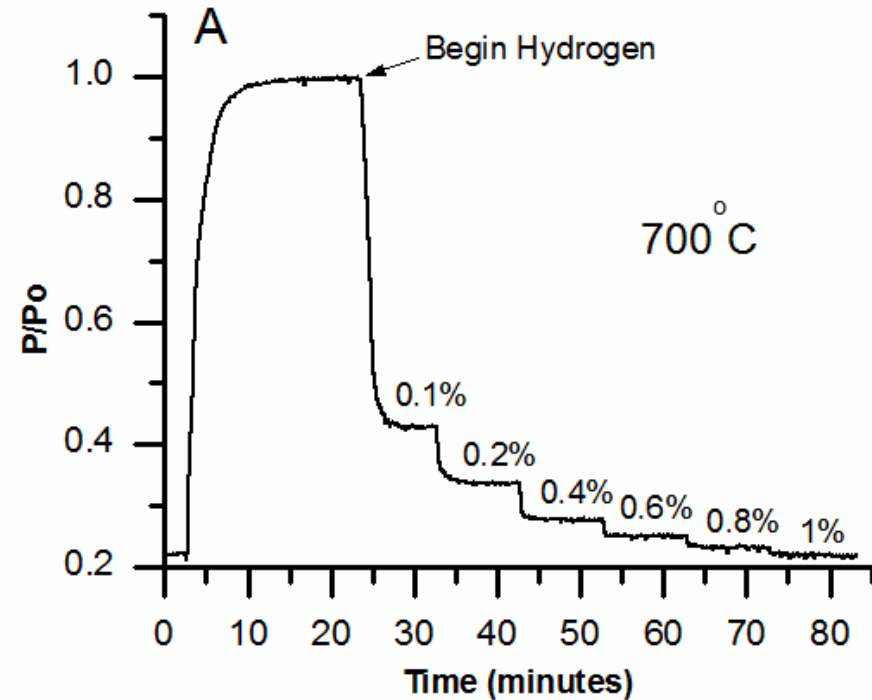
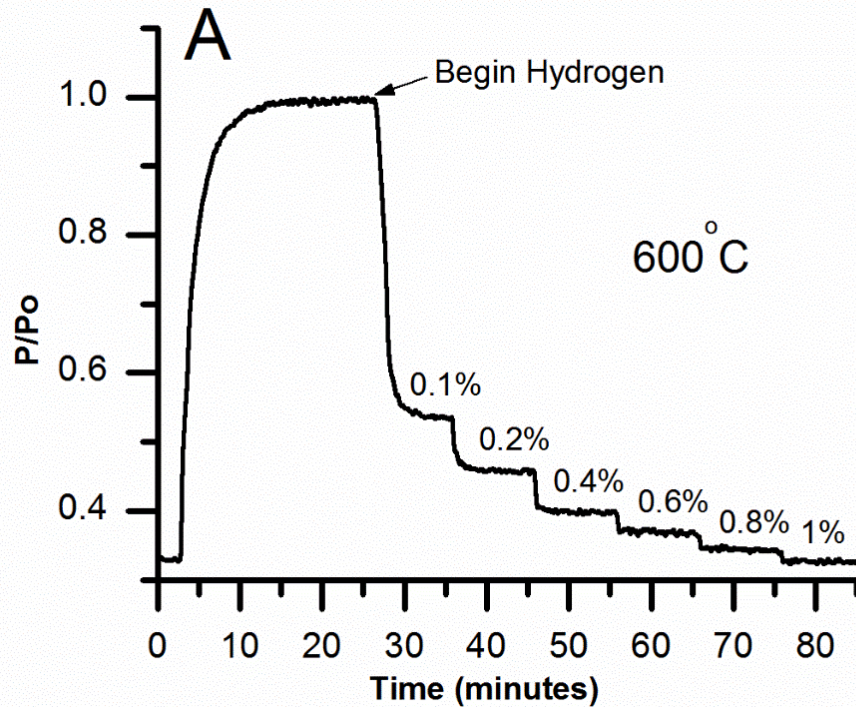
High-Temperature Chemical Sensor on D-shaped Optical Fiber





Fiber Optic Hydrogen Sensor at 700C

Optical Transmission vs. Hydrogen Concentrations



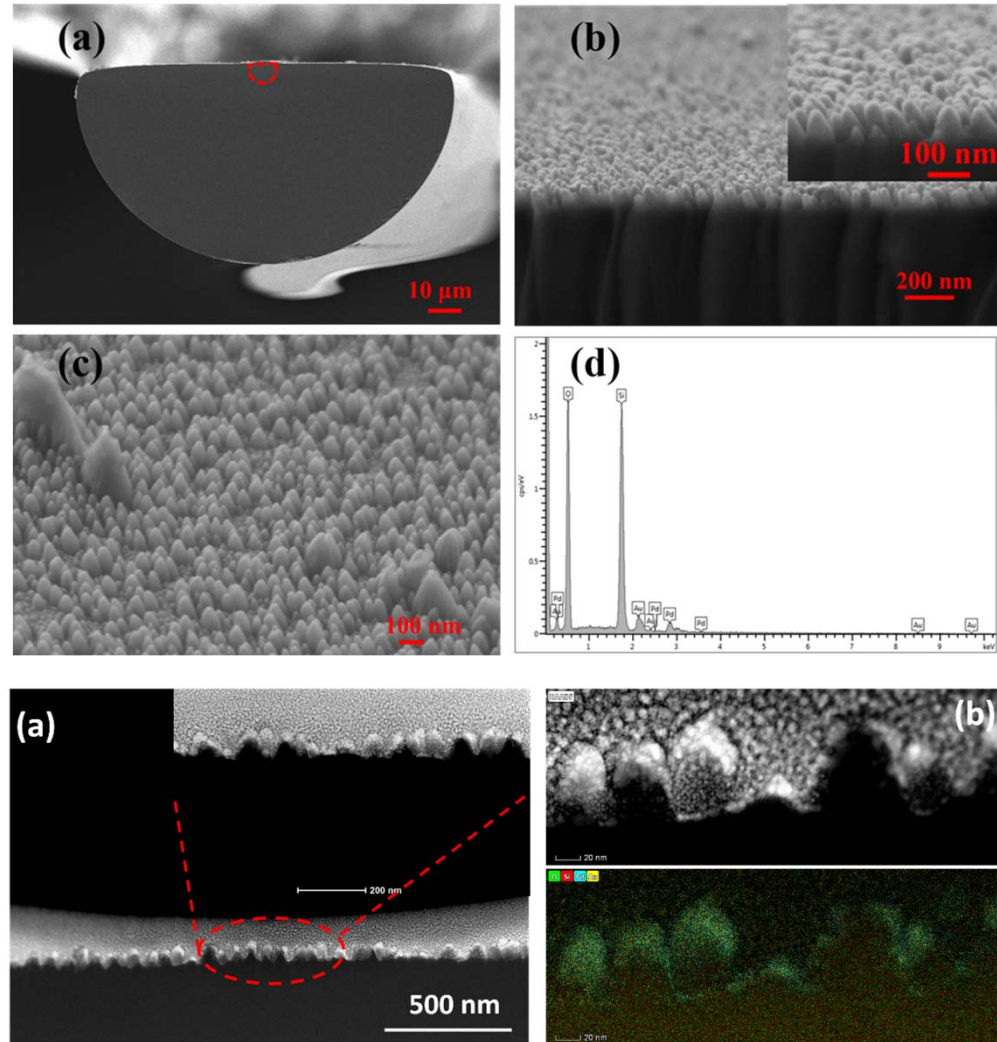
Exposed to various concentrations of hydrogen in nitrogen, recovered with nitrogen
Ideal for hydrogen driven energy conversion systems



Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

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 – 600 C

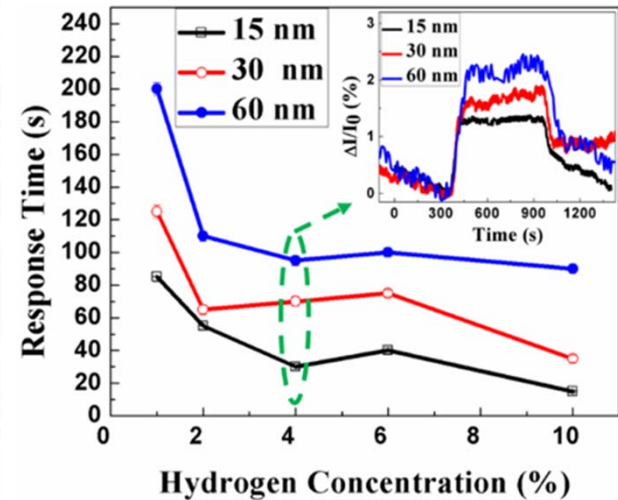
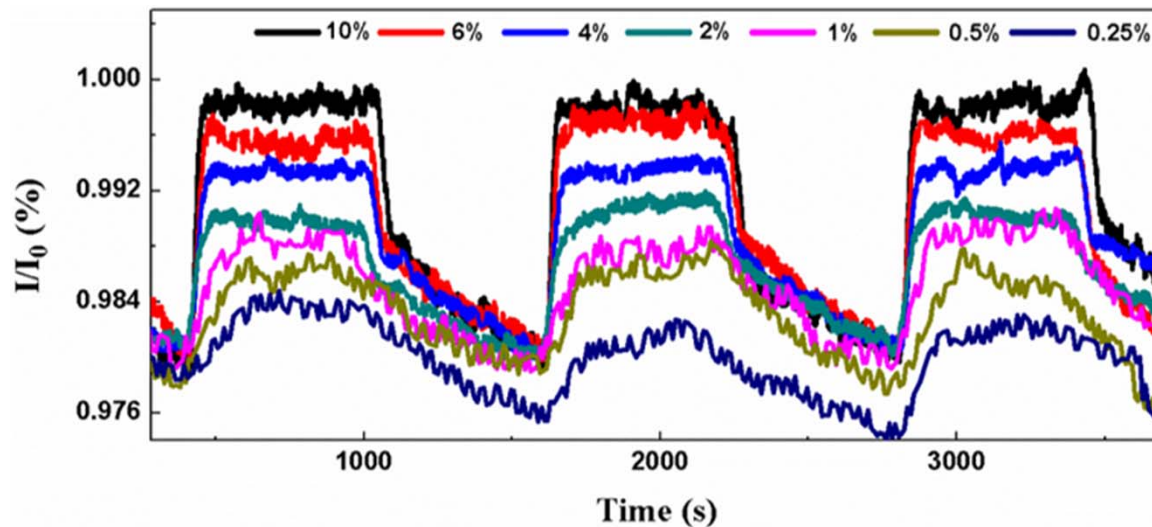




Hydrogen Sensing Based on Nanostructure-textured Optical Fiber

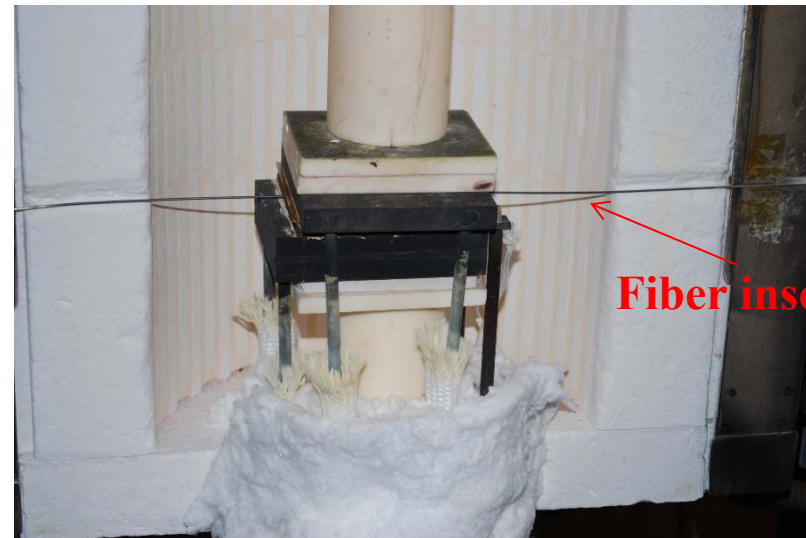
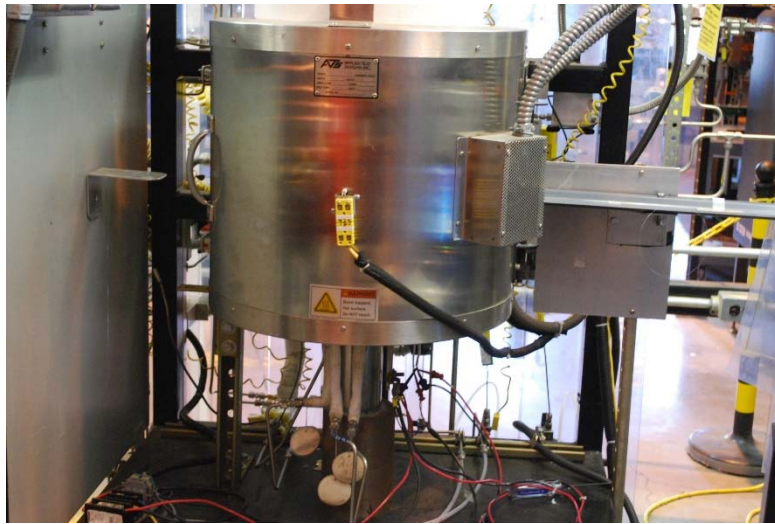
1. Hydrogen Sensor Based on Nano-cone: Room Temperature Results

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





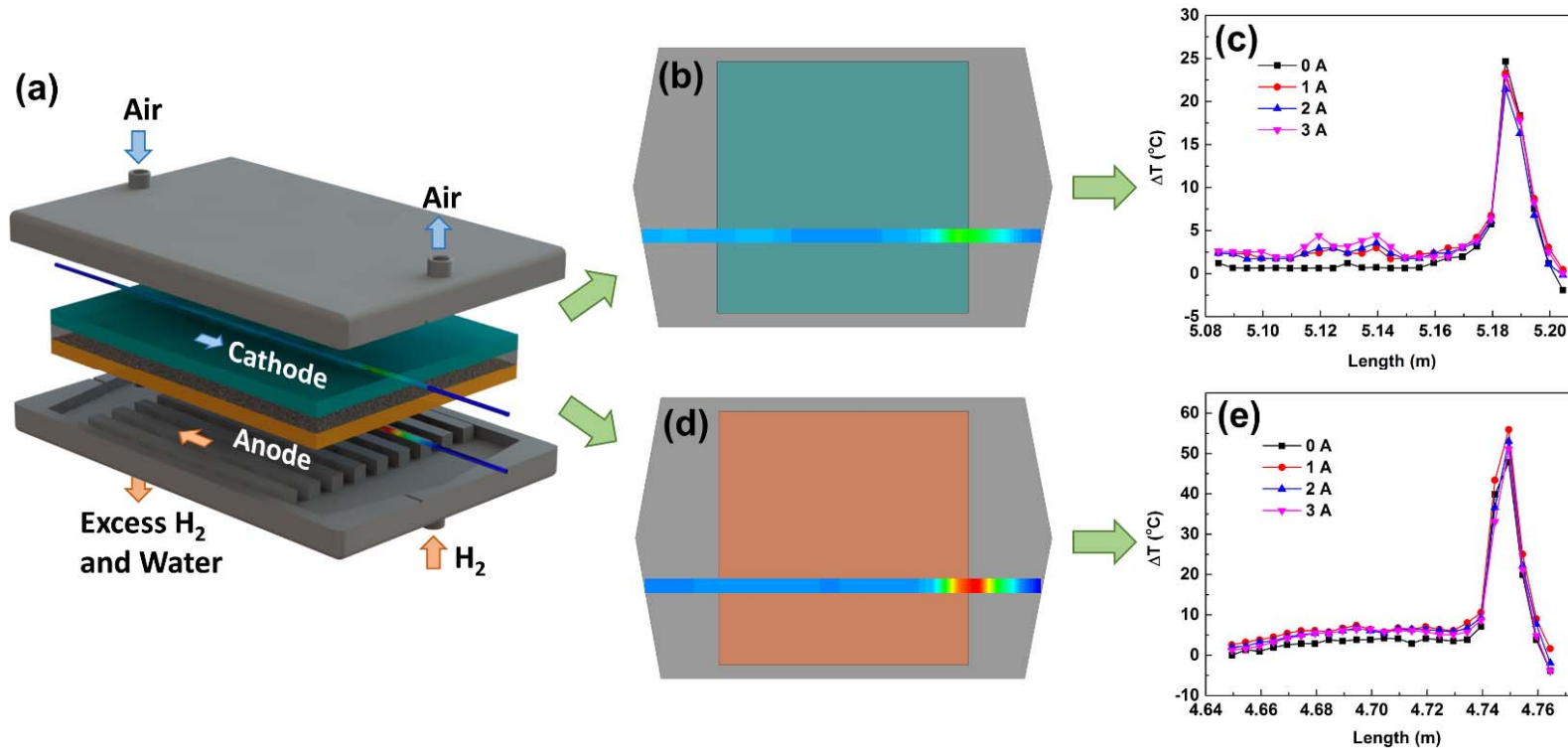
Fuel Cell Tests



- 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 ($<700\text{C}$)



Distributed T measurement in SOFC



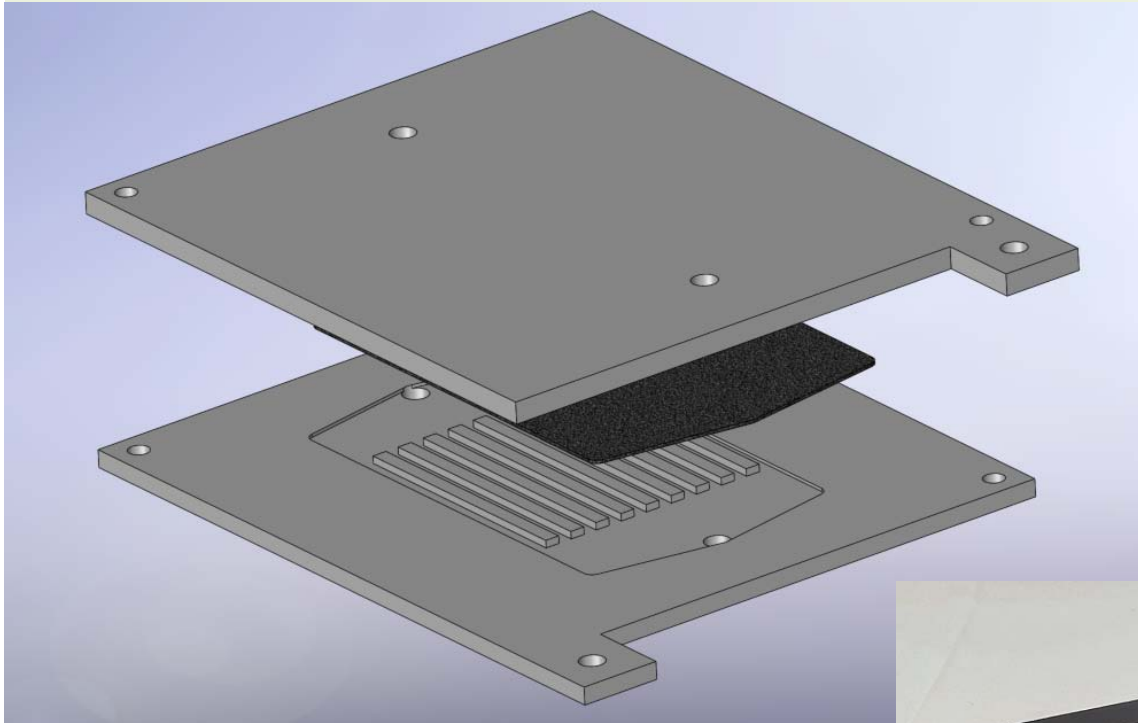
Temperature in cathode and anode were measured respectively

- 100% hydrogen fuel, current load 0 ~ 3 A.
- Temperature increase when fuel gas turned on
Anode : ~55 °C, Cathode: ~ 25°C
- Temperature change with different current loads < 5°C



Sensor-Enabled Design Optimization

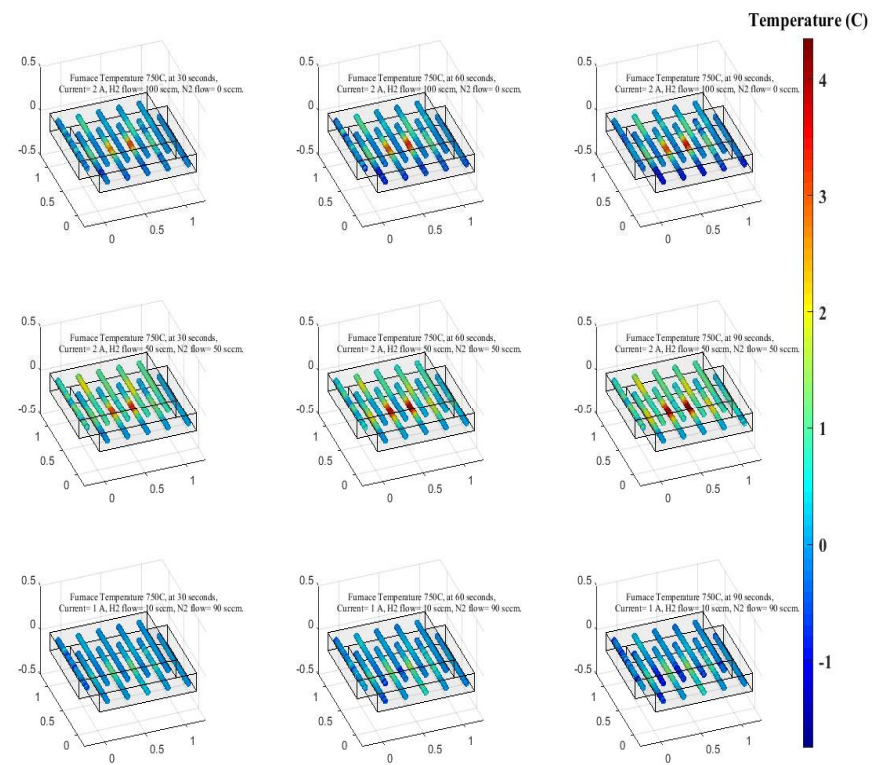
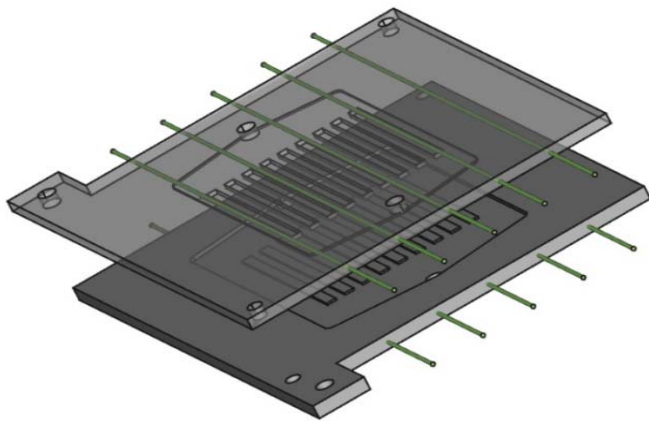
- **Current Fuel Cell Plates: only consider electrical properties**





Sensor-Enabled Design Optimization

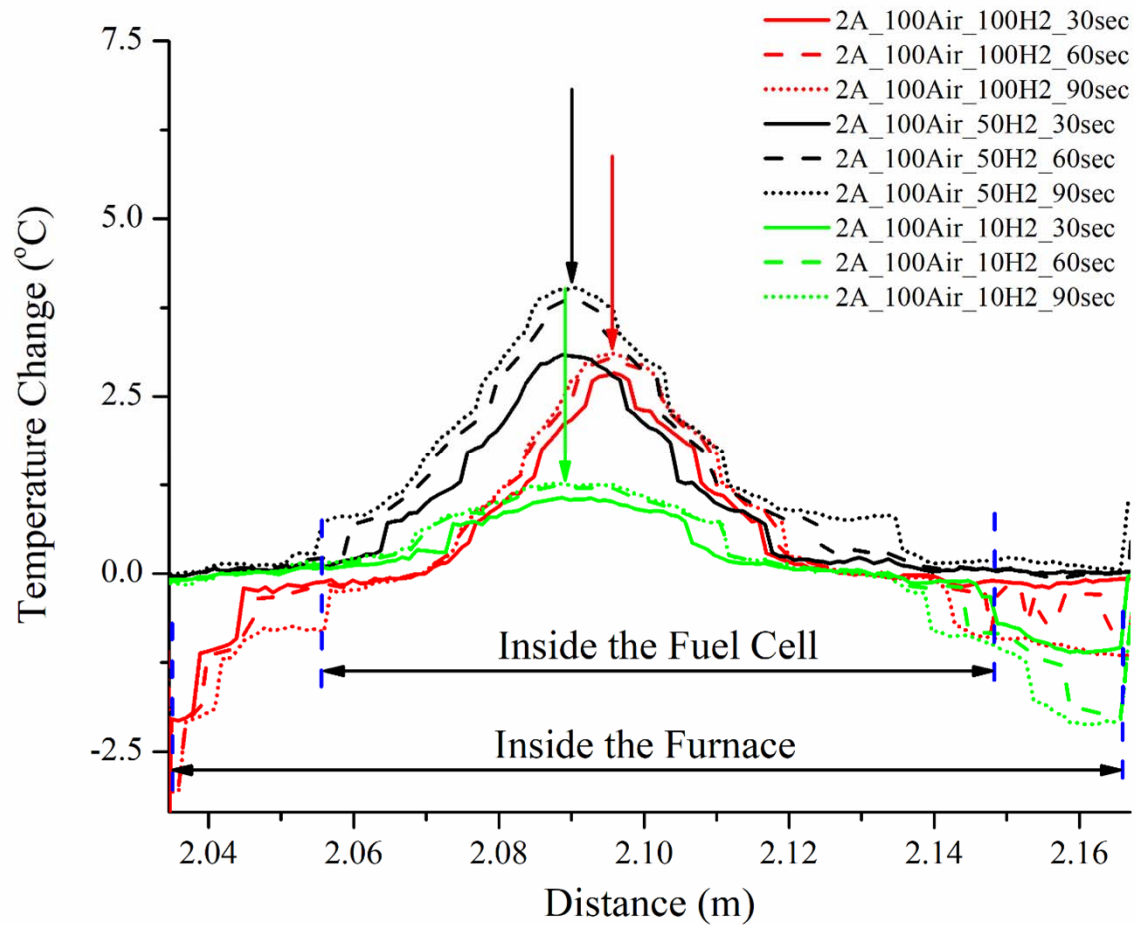
- Configuration optimization to improve gas fuel (then chemical reaction) to improve the T/Chemical reactor profile in fuel cell.





Sensor-Enabled Design Optimization

The peak of the temperature bump appears closer to the H₂ gas inlet, and shifts closer to the inlet as the H₂ flow rate is reduced.





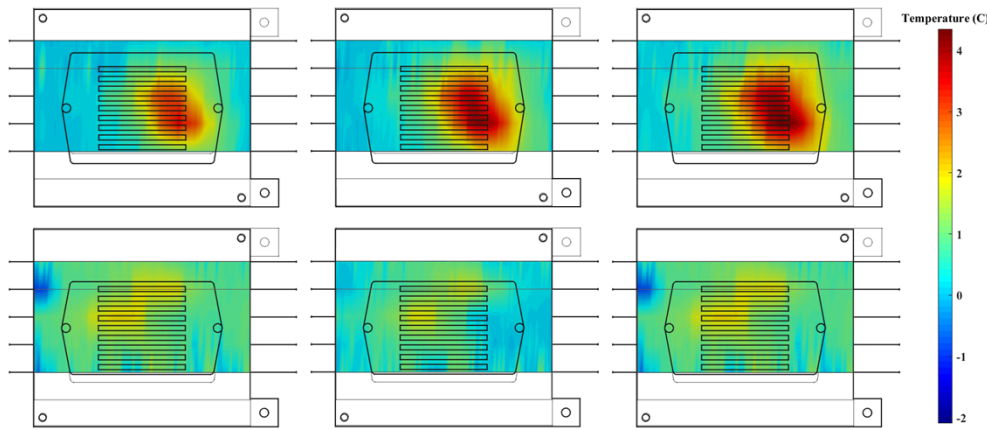
Sensor-Enabled Design Optimization

2 A, 50 sccm H₂ flow, 750C

30s

60s

90s

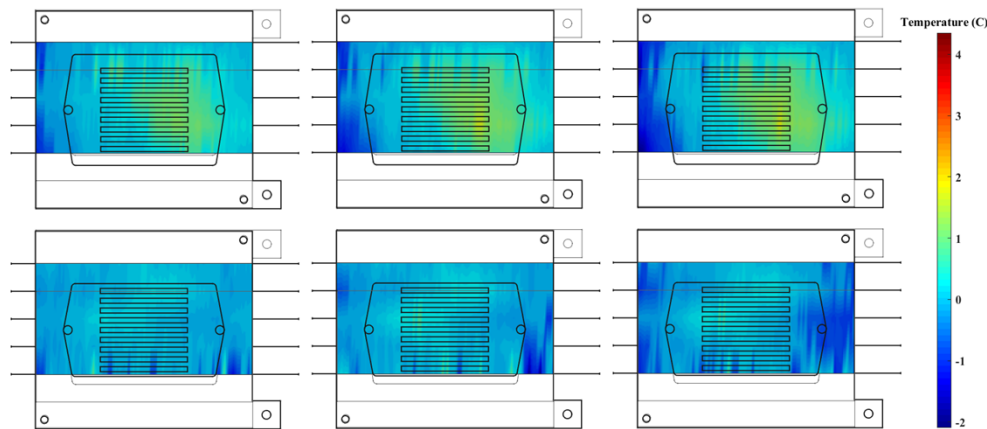


1 A, 50 sccm H₂ flow, 750C

30s

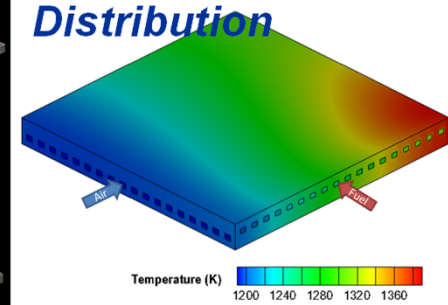
60s

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*



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.**

Contact:

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Thank you!

Questions?

Collaboration Welcomed!

Kevin P. Chen

Email: pec9@pitt.edu