Novel Functional Sensor Materials R&D for Advanced Fossil Power Generation and Carbon Capture Utilization and Storage

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Materials Scientist / Team Lead

Electrochemical and Magnetic Materials Team

Contributors: Thomas Brown, Congjun Wang, John Baltrus, Andrew Schultz, Michael Buric, Benjamin Chorpening, Joe Tylczak, Xin Su, and Gordon Holcomb

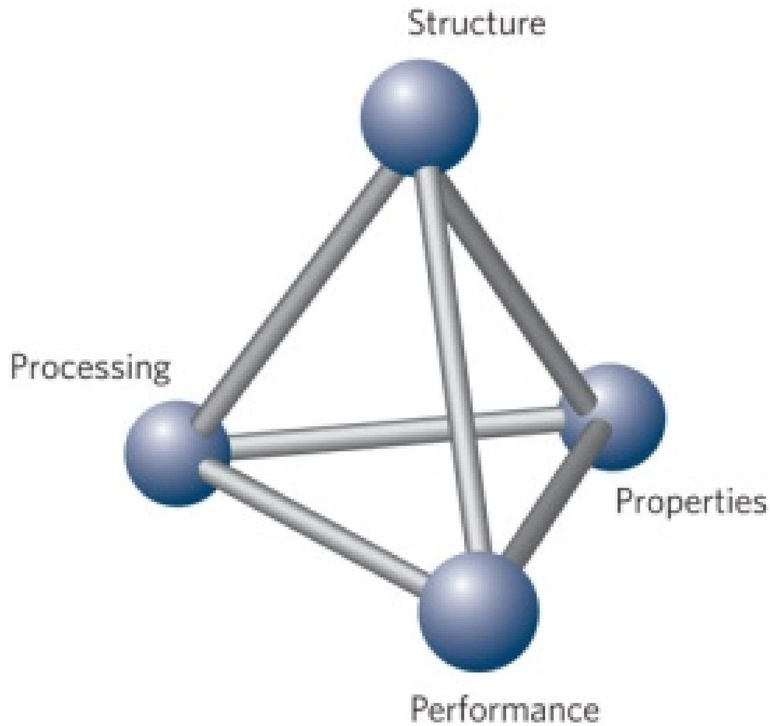
Overview of Presentation

- **Overview of In-House Sensor Materials / Device R&D**
- **Sensor Materials for Power Generation**
- **Sensor Materials for Subsurface Applications**
- **Opportunities for Collaborations with NETL**
- **Summary and Conclusions**

Overview of In-House Sensor Materials / Device R&D

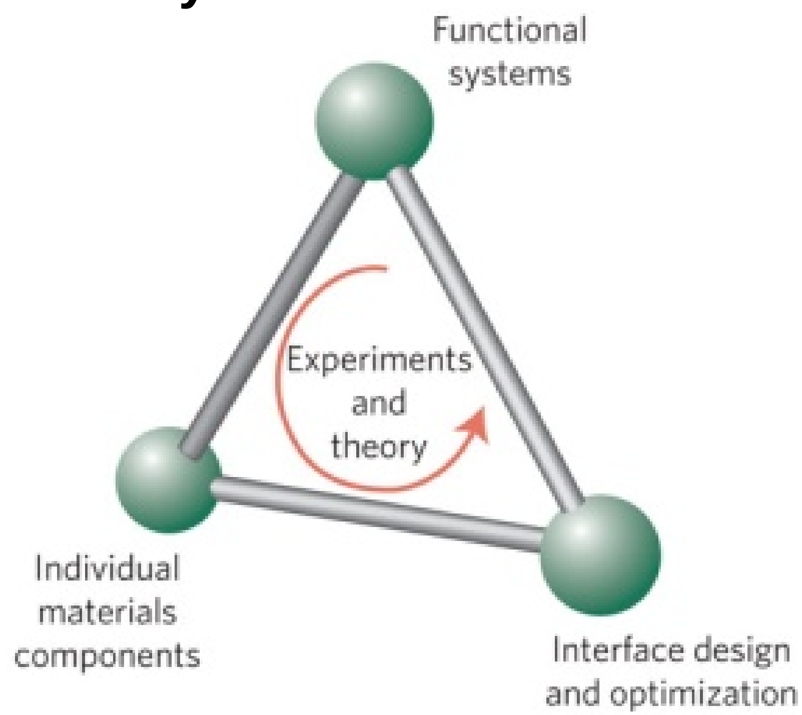
Functional Material Development for Devices

Classic Materials Science Paradigm



Emerging Paradigm

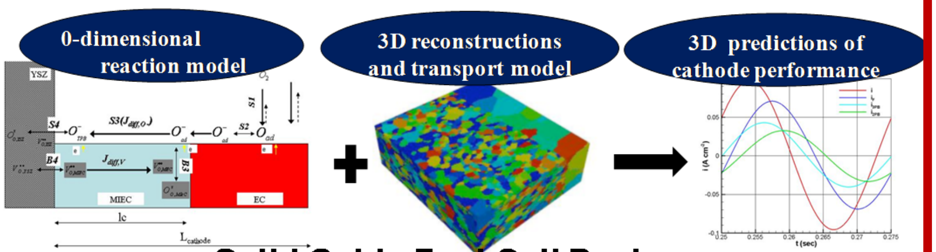
Materials Interface with Functional Systems and Devices



There Are Increasing Opportunities for Providing Unique Value by Engineering at the "Interface" Between Functional Materials and Devices.

Electrochemical and Magnetic Material Team: Recent Efforts

Current Fiscal Year 2015



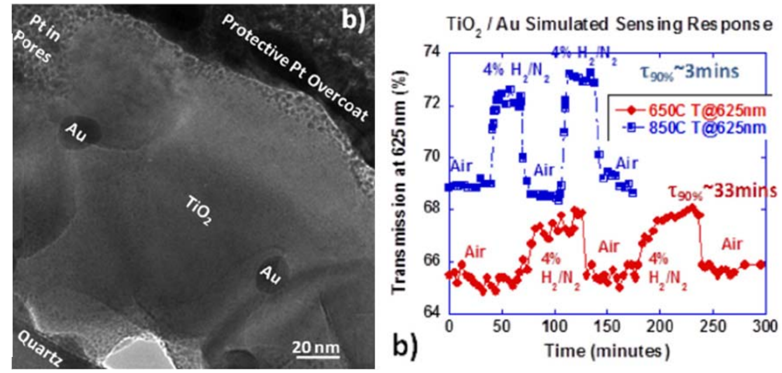
Solid Oxide Fuel Cell Devices

Modeling + Characterization → Optimal Device Performance

Solid Oxide Fuel Cell Materials

Function and Durability
(DOE FE SECA Program)

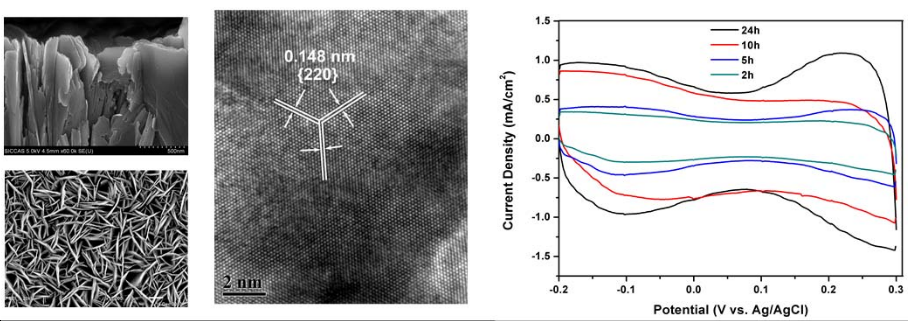
Current Fiscal Year 2015



Sensor Materials

Chemical and Temperature Sensing
(DOE FE Cross-Cutting Program)

Ended Fiscal Year 2014



Energy Storage Materials

(DOE EERE Program)

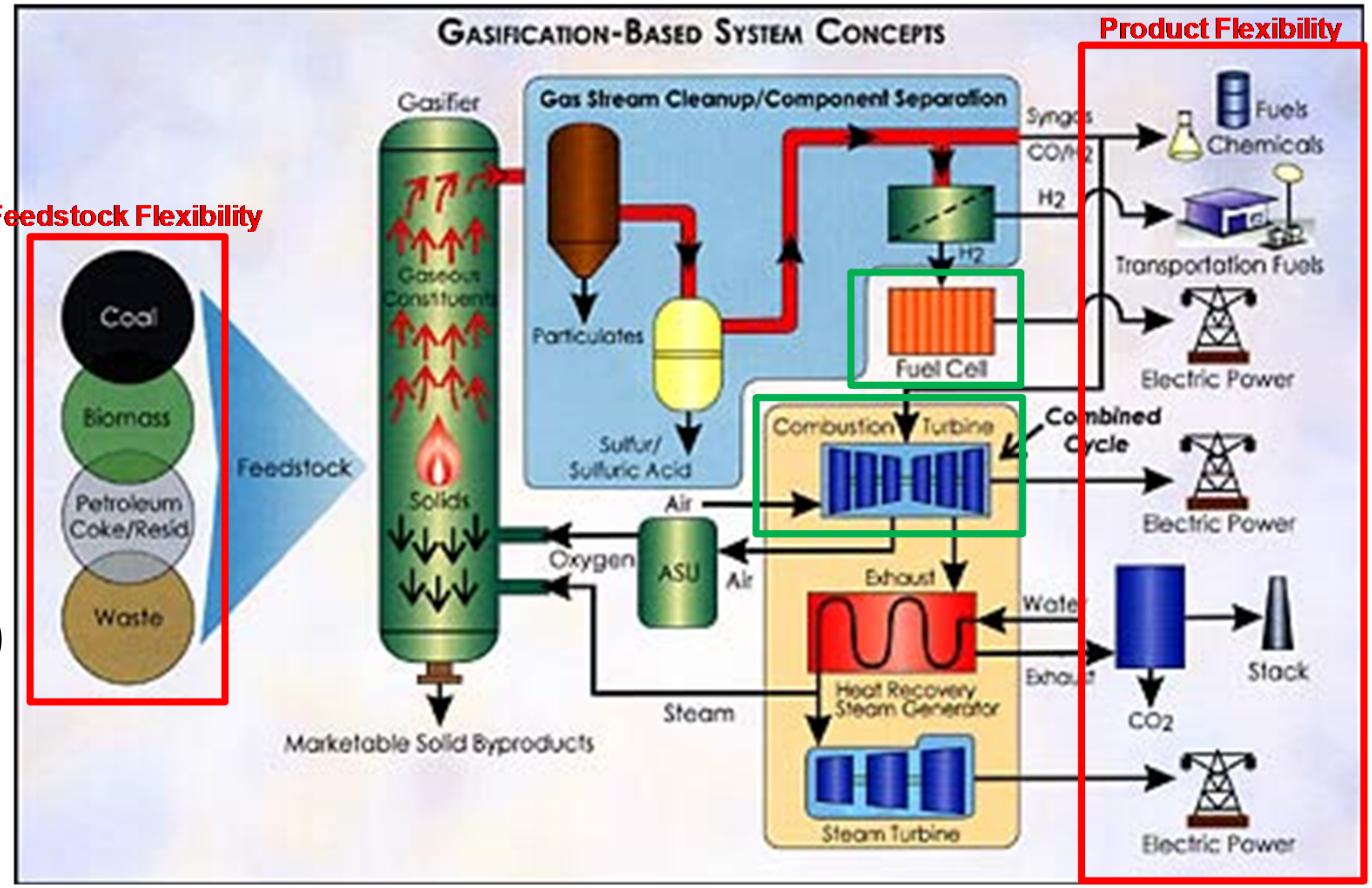
Current Fiscal Year 2015

Soft Magnetic Materials

Inductors and Sensors
(ARPA-E, URS, Others)

Higher Efficiency Fossil-Based Power Generation

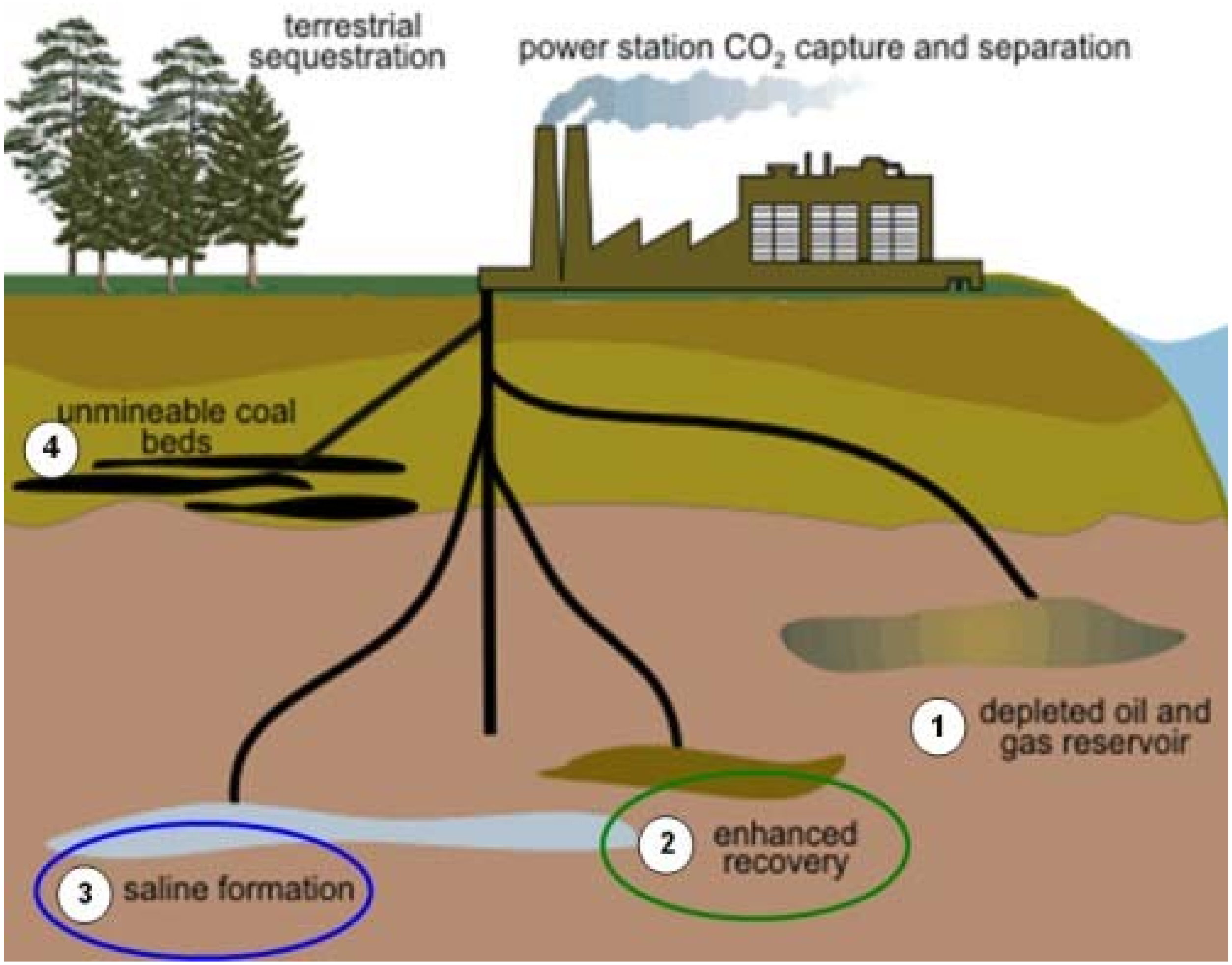
Advanced Fossil-Based Power Generation Involves High Temperature Gas Streams (Coal or Natural Gas)



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

Envisioned Fossil-Based Power Plants of the Future are Highly Complex with a Number of Processes Integrated Into a Large Hybrid System.

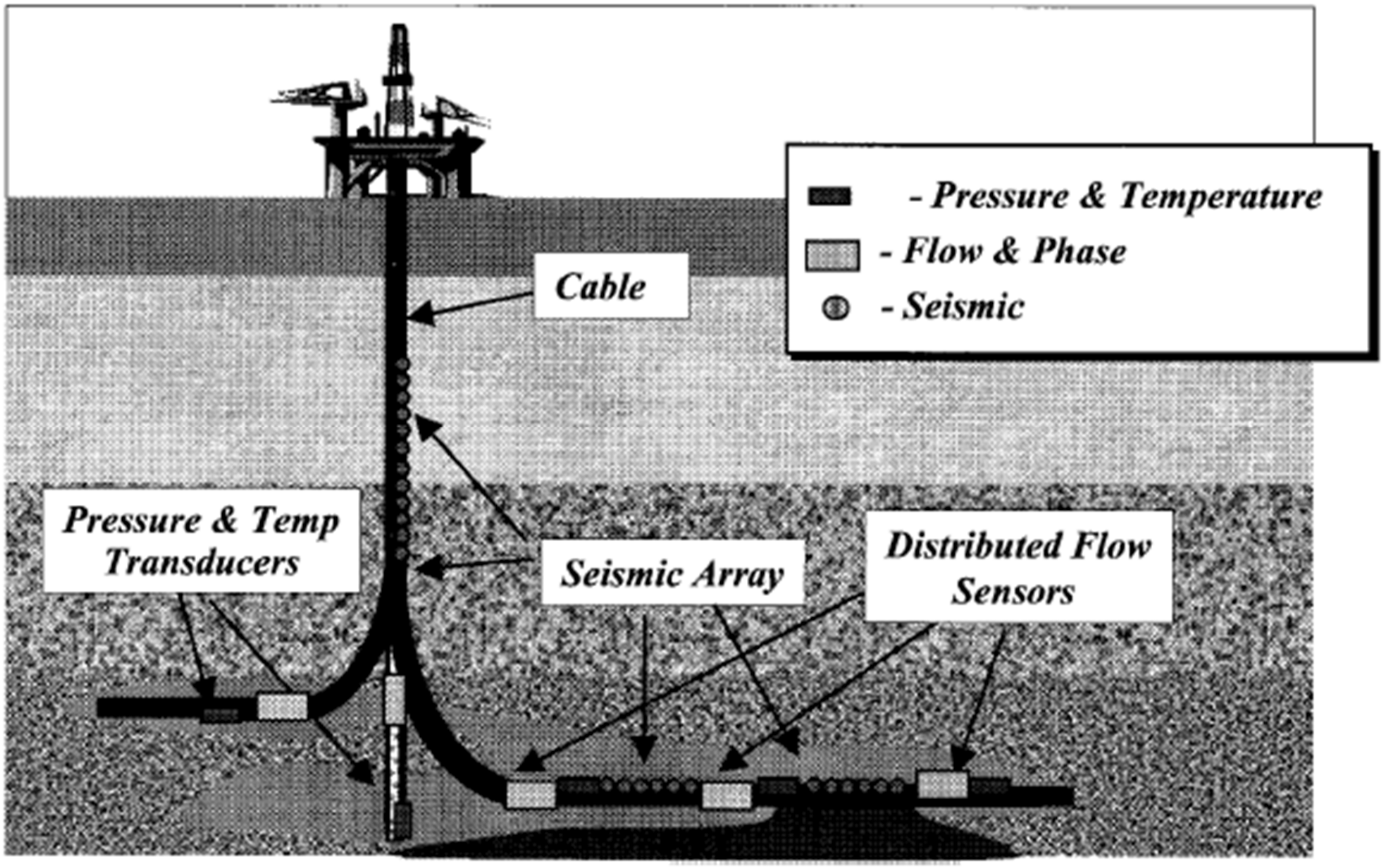
Mitigation of Environmental Impacts of Power Generation



CO_2 Capture and Sequestration is a Primary Technology Currently Under Research and Development to Reduce Environmental Impacts of Greenhouse Gas Production

Economical / Environmentally Responsible Resource Recovery

IEICE TRANS. ELECTRON., VOL.E83–C, NO.3 MARCH 2000



A Number of Parameters are Important to Monitor Throughout a Well-Bore to Ensure Environmentally Responsible and Economical Resource Recovery Including Pressure, Temperature, Flow, Chemistry, Seismic Activity, etc.

Harsh Environment Sensor Material and Device R&D

	Coal Gasifiers	Combustion Turbines ★	Solid Oxide Fuel Cells ★ (Short Term Focus)	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

Sensor Development for Embedded Sensing in Power Generation

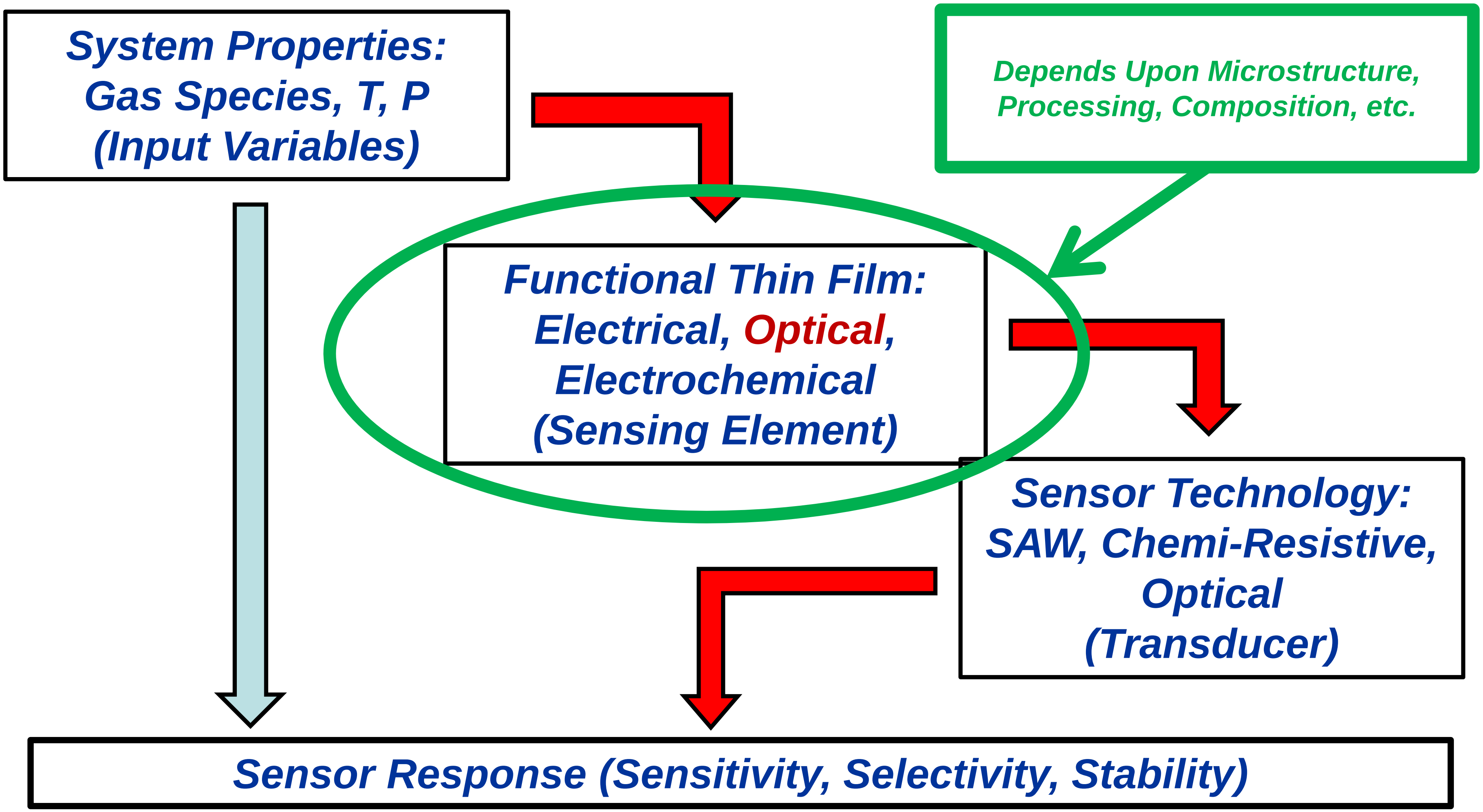
★ **2015 R&D**

★ ***Potential* 2015 and/or 2016 R&D**

Conditions	Downhole Drilling ★	Deep/Ultra-deep ★	Geological CO_2 Sequestration (Vilarrasa et al., 2013) ★
Depth of interest (feet)	1,500–13,500	30,000–40, 000	6,000–7,000
Temperature (K)	Up to 470	Up to 580	Up to 370
Pressure (psi)	Up to over 10,000	Up to 30,000	Up to 3,000
Typical pH	4–8	4–8	2–6

Sensor Development for Embedded Sensing in Subsurface Applications

Thin Film Functional Sensor Layers in Harsh Environment Sensing Applications



Motivation for Looking at Optical Materials

Chemi-resistive materials : the fundamentals are understood

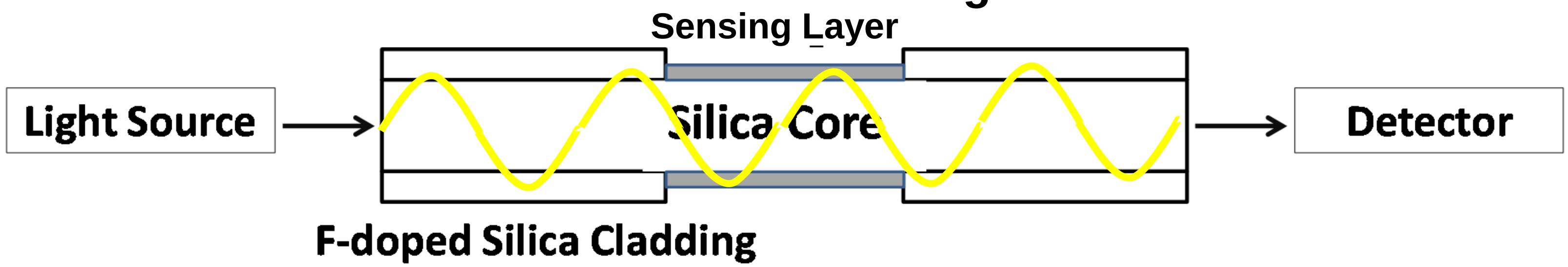
- G. Korotcenkov (2007). Materials Science and Engineering: B **139(1): 1-23**
- Gas Species Interact with Adsorbed Surface Species or Alter Defect Chemistry Changing:

  (1) Free Charge Carrier Concentration, (2) Mobility of Free Carriers

Optical materials : fundamentals are poorly understood

- How Do Refractive Index and Optical Absorption Depend Upon Defect Chemistry or Concentration of Adsorbed Species?
- How Can Materials with Useful Responses Be Optimally Integrated into Optical Sensing Devices?

e.g. Evanescent Wave Sensors



Silica-Based Fibers are Stable up to Temperatures Approaching 900°C

Advanced Functional Sensor Material Project Team
University Partnerships

University of Pittsburgh

Sensor Interrogation Methodologies

Supporting Sensor Material R&D

NETL

Office of Research and Development

VirginiaTech
Invent the Future®

Sensor Device Platform Stability

Project Leadership / Coordination

Sensor Material R&D

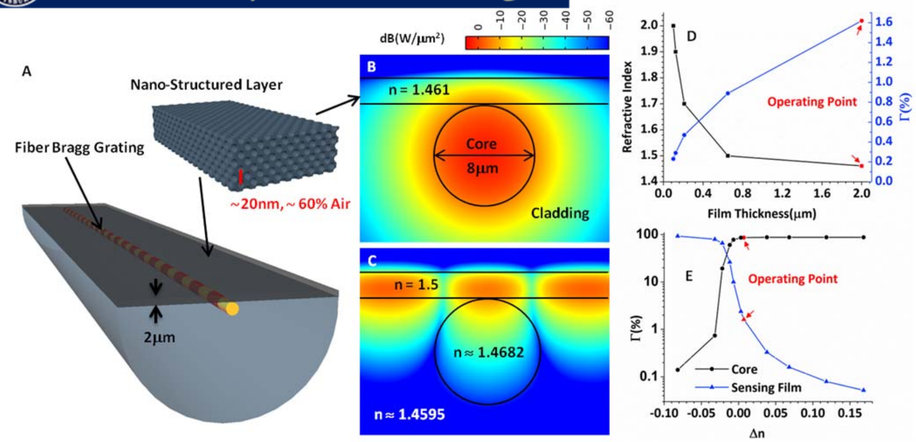
Sensor Packaging and Prototype Development

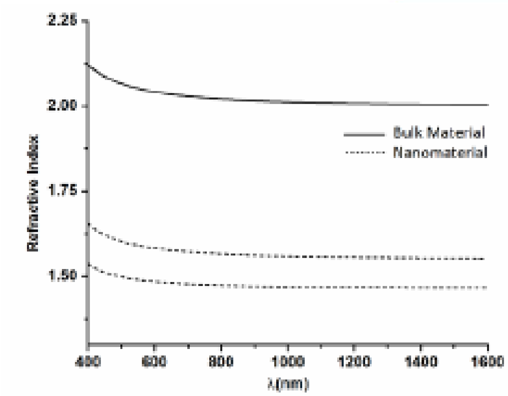
The Project Team is an Interdisciplinary Team Centered within the Office of Research and Development with Strategic University Collaborations to Accelerate and Enhance the Project Outputs.

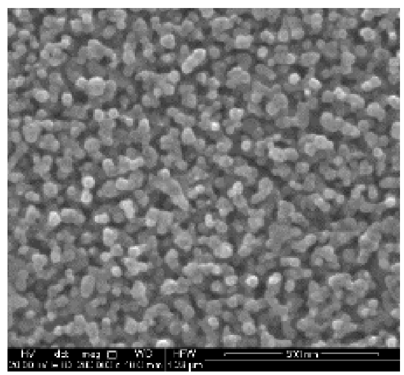
Collaborative Research: Univ. of Pittsburgh

Nanostructuring to Tailor Refractive Index for Device Compatibility

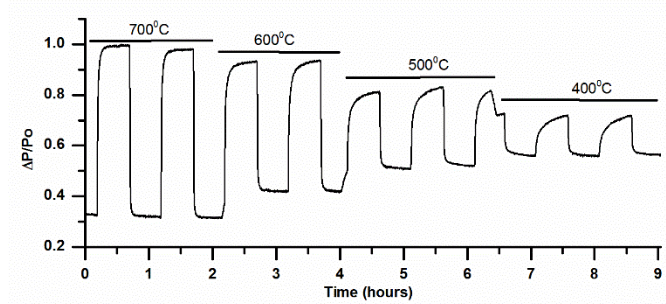
University of Pittsburgh



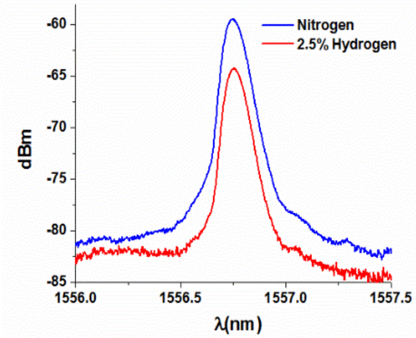




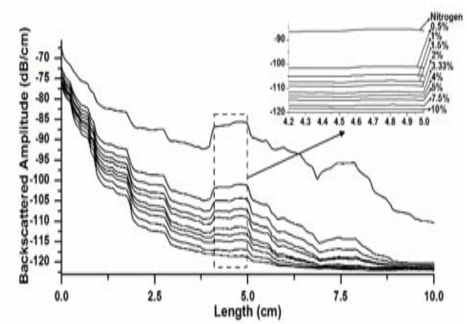
High Temperature Compatible Distributed Sensing Interrogation for Chemical Sensing Applications



Total Transmission



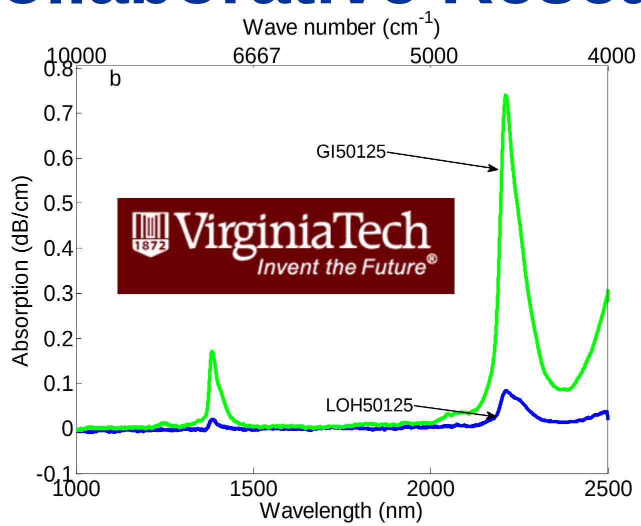
Regenerated FBG's

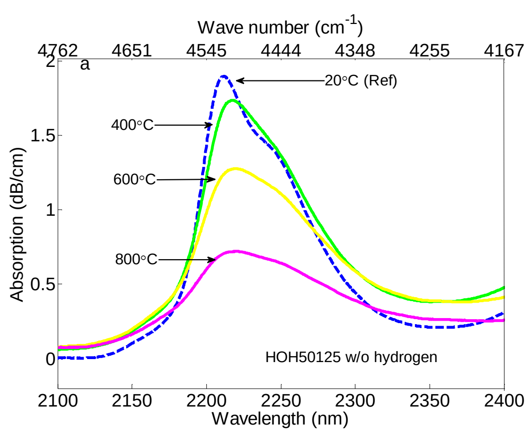


OFDR (Rayleigh Backscattering)

Engineering of Functional Sensing Layer Porosity to Enhance Responses for Thick Film Sensing Layers and Strategies for High Temperature Compatible Distributed Interrogation Have Been Developed.

Collaborative Research: Virginia Polytechnic Univ.





Assignment	Wave number (cm^{-1})	Wavelength (nm)	Description	Reference
$v_1(OH) + v_4(SiO_4)$	4100	2439	Combination fundamental OH stretching and fundamental SiO_4 vibrations	[18], [23]
$v_1(OH) + v_1(SiO_4)$ / $v_{comb,2}$ (OH)	4450	2247	Combination fundamental OH stretching and fundamental SiO_4 vibrations / Asymmetric distribution of silanol vibration due to hydrogen-bond	[18], [23]
$v_4(OH) + v_3(SiO_4)$ / $v_S(SiOH) + v_B(SiOH)$	4520	2212	Combination fundamental OH stretching and fundamental SiO_4 vibrations / Combination fundamental OH stretching and SiOH bending	[18], [17], [23] and [24]
$v_B (H_2O)_I + v_{SS}(H_2O)_I$	5102	1960	Possibly, combination bending and symmetric stretching band of Type I molecular water	[23]
$v_B(H_2O)_I + v_{AS}(H_2O)_I$	5249	1905	Combination bending and stretching of molecular water, or more specifically, bending and asymmetric stretching of Type I molecular water	[23]
v_S(GeOH)	7042	1420	OH stretching vibration bonded to Ge site	[13]
$2v_3$(OH)	7100	1408	First overtone OH stretching	[18]
$2v_2$(OH)	7220	1385	First overtone OH stretching	[18], [17], [13] and [23]
$2v_1$(OH)	7260	1377	First overtone of OH stretching	[18], [17], and [23]
$2v_3(OH) + v_2(SiO_4)$	7380	1355	Combination first overtone OH stretching and fundamental SiO_4 vibration	[18]
$2v_3(OH) + v_1(SiO_4)$	7920	1263	Combination first overtone OH stretching and fundamental SiO_4 vibration	[18]
$2v_1(OH) + v_1(SiO_4)$	8065, 8130	1230, 1240	Combination first overtone OH stretching and fundamental SiO_4 vibration	[18], [17]
$2v(OH) + 2v (SiO_4)$	8889	1125	Combination first overtone OH stretching and first overtone SiO_4 vibration	[17]

Bands at same the wavelength are listed in one row when they were interpreted differently in references

Characteristic Absorption Peaks are Observed for Different Silica-Based Fiber Compositions, Strength Depends Upon Formation of OH-Defects and a Reversible Temperature Dependent Behavior is Observed.

Collaborative Interactions with the Project Team

Collaboration Products Since 2012

7 – Joint Publications (U. Pitt, U. Albany, OSU)

4 – Joint Patent Applications (U. Pitt., Stevens, OSU)

4 - Additional Joint Publications in Preparation (U. Conn., U. Pitt., VA Tech)

Advanced Functional Sensor Material Project Team

Extramural Crosscutting Program Research

University of Pittsburgh

University of Cincinnati

Carnegie Mellon University

VirginiaTech Invent the Future®

Stevens Institute of Technology — The Innovation University®

OSU Oregon State University

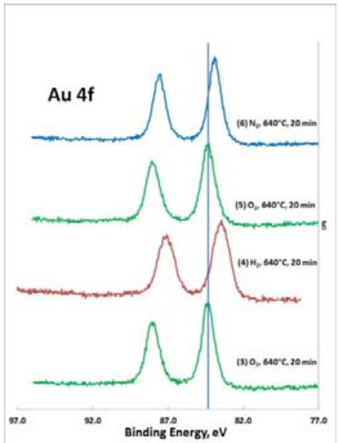
UCONN University of Connecticut

Colleges of Nanoscale Science and Engineering — SUNY Polytechnic Institute

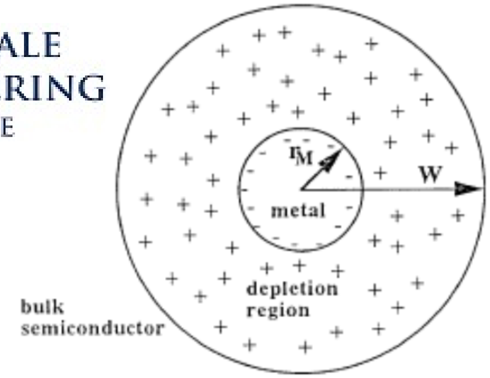
The Team Also Seeks to Establish New Collaborations with Other NETL-Funded Projects and Others to Help Promote the Mission of the Laboratory and the Crosscutting Research Program.

Collaborative Research Effort: U. Albany (SUNY)

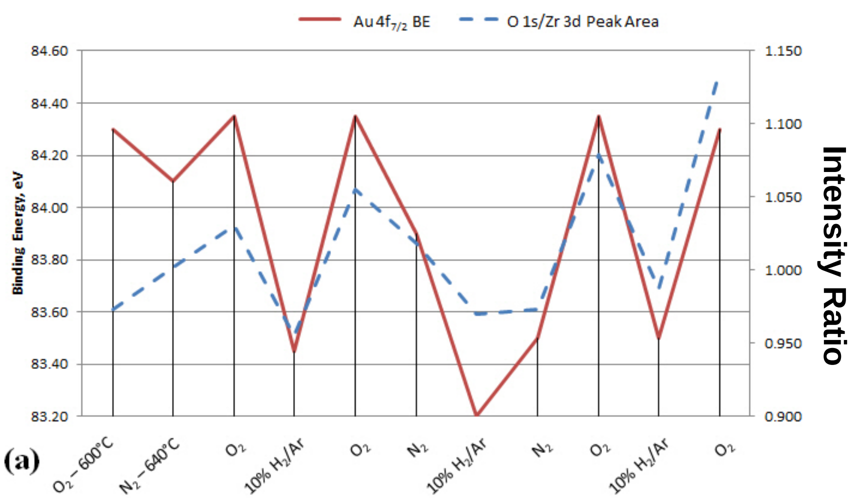
Au-YSZ/Si

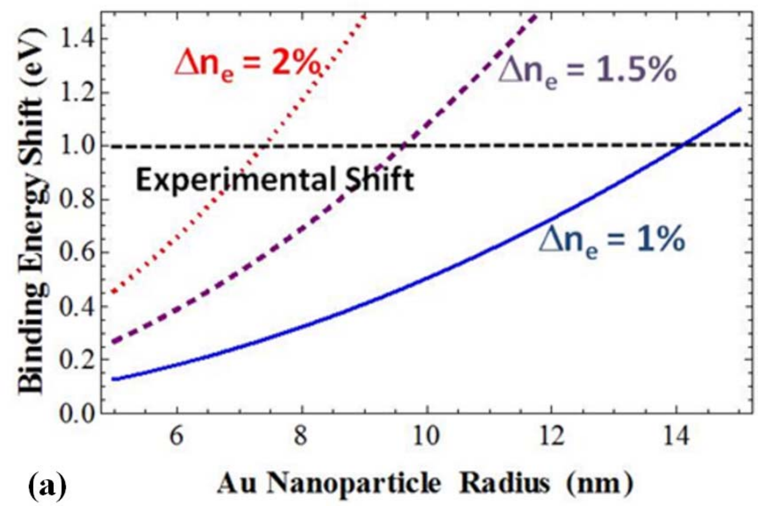


COLLEGES OF NANOSCALE SCIENCE AND ENGINEERING
SUNY POLYTECHNIC INSTITUTE



(T. Ioannides & X.E. Verykios, J. Catal. ***1996****, 161, 560-569.)*



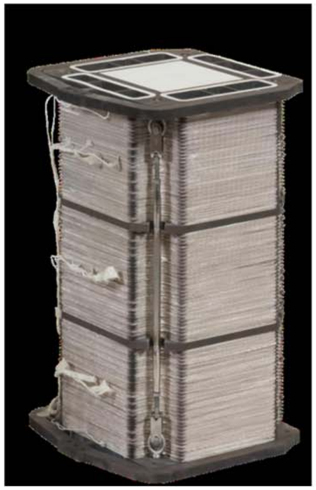


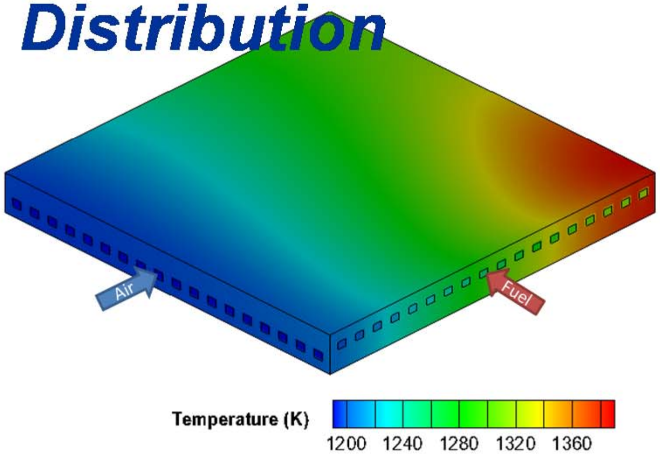
Estimates of Binding Energy Shifts Associated with Electronic Charge Transfer for this System Based on Metal / Semiconductor Contact Theory are of the Correct Order of Magnitude → Mechanistic Understanding of Optical Response.

Sensor Materials for Power Generation

In-House Efforts Have Targeted Embedded Sensing

Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution





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

Spatial Distribution in Temperature and Fuel Gas Composition

Incompatible with Traditional Sensing Technologies

1) At Limits of High Temperature Electrical Insulation
2) Limited Access Space
3) Only Single-Point, Single-Parameter Sensing

Stable Sensors Capable of Embedding in Harsh Environments Would Enable Unprecedented Access to New Process Information.

Key Thrusts:

(1) Stable Sensing Devices, (2) Compatible with Distributed Interrogation

Sensing Materials Classes Investigated

Binary Semiconductor Metal Oxides: SnO_2, TiO_2, ZnO

→ High Temperature Stable Variants Show Weak Optical Responses

→ Link Between Resistive Changes and Optical are Weak

→ Temperature Dependent Band-Gap Useful for Temperature Sensing

Au-Nanoparticle Incorporated Oxides: Au-TiO_2, Au-SiO_2

→ Shifts of the Au LSPR Absorption Peak (Reducing vs. Oxidizing)

→ Damping and Shifting of the Au LSPR Absorption Peak (Temperature)

→ Multi-Parameter Monitoring Possible (Gas and Temperature)

Doped Semiconductor Metal Oxides: Al-Doped ZnO, Nb-Doped TiO_2

→ Enhanced Optical Responses Due to Free Carrier Contribution

→ Enhanced Chemical Sensitivity of Band-Edge Due to Burstein-Moss Shift

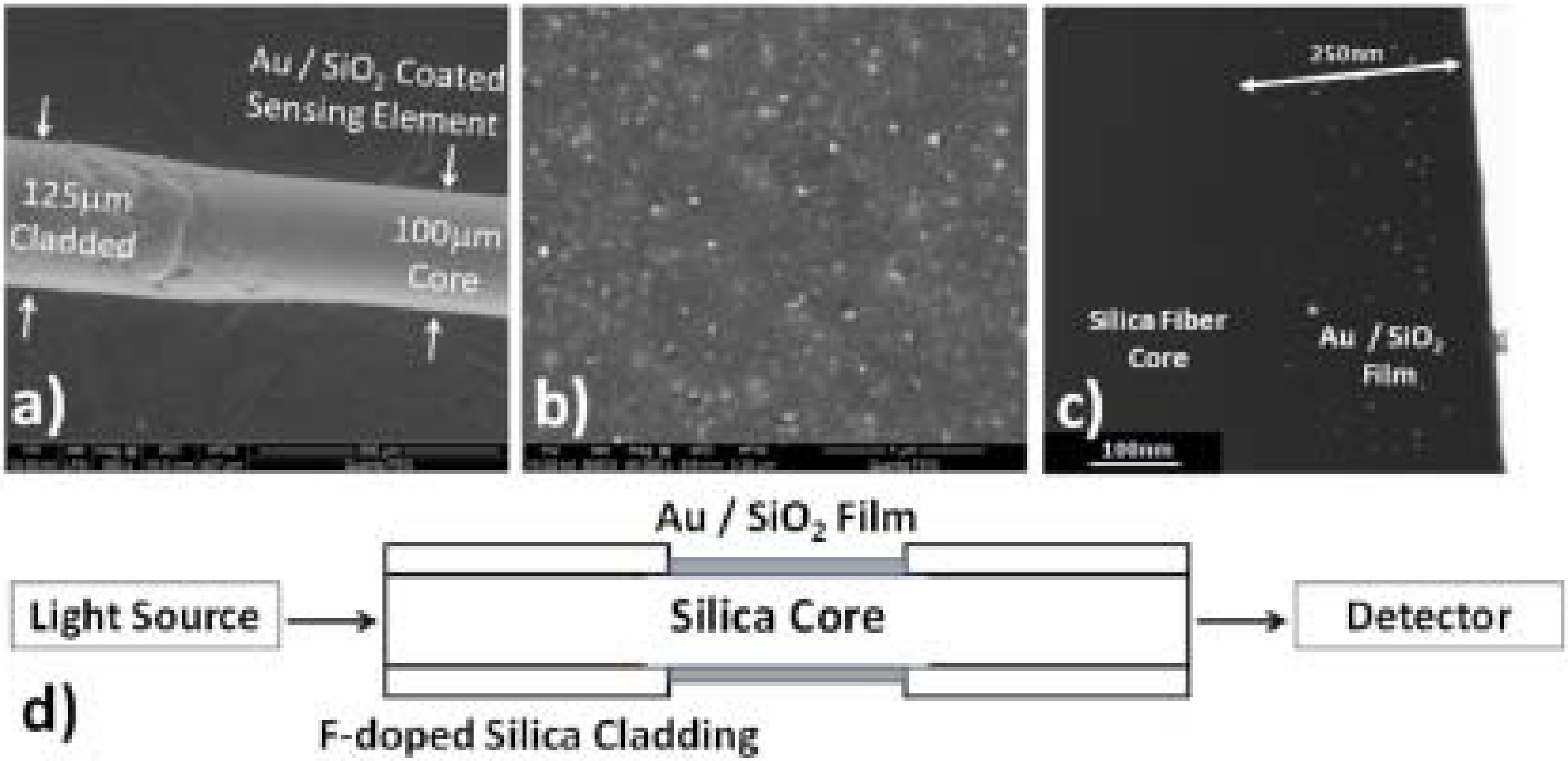
Perovskite Based Oxides: $SrTiO_3$, La-Doped $SrTiO_3$

→ Stable Under SOFC Operational Conditions, Response up to 100% H_2

Example Sensing Material Class #1:

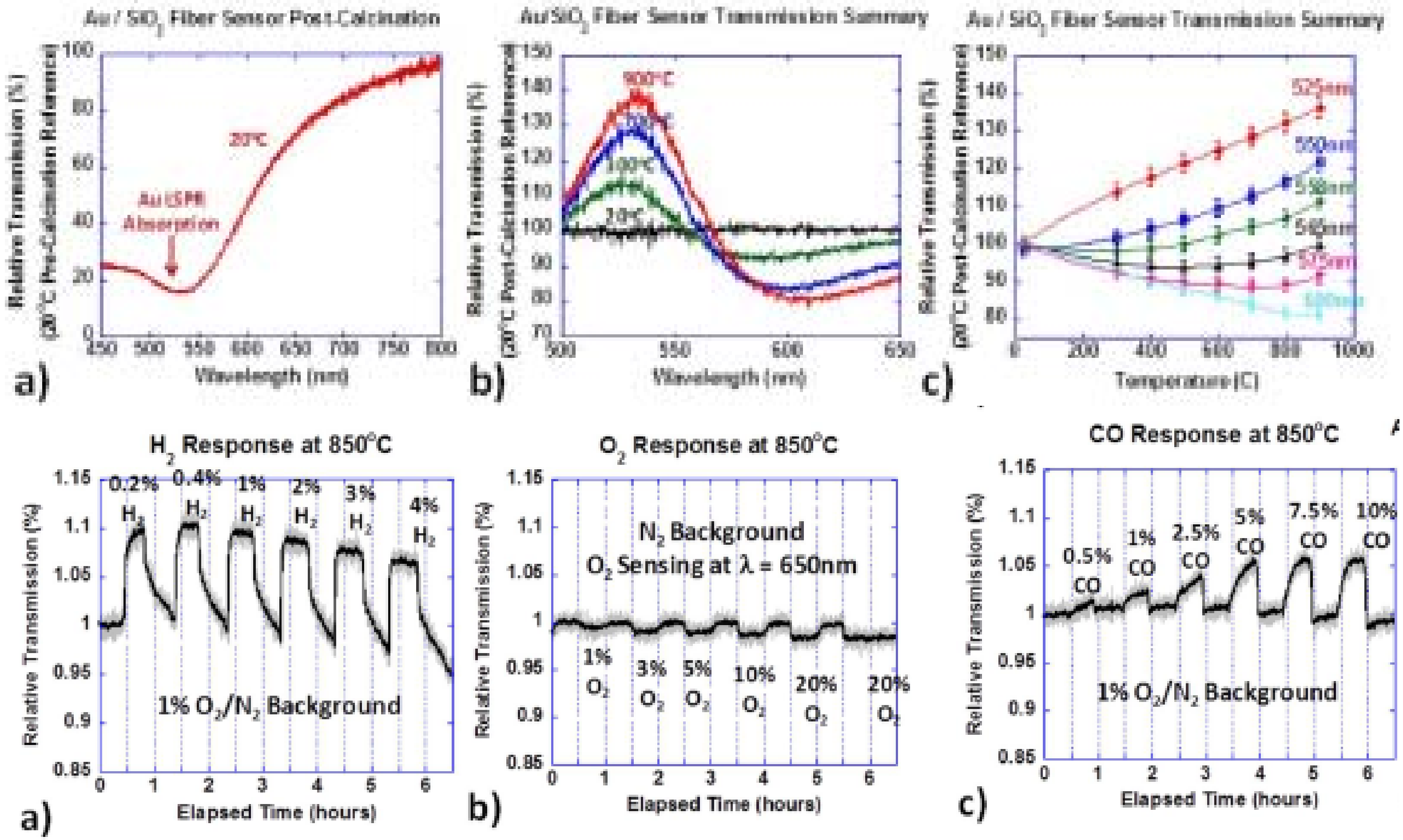
Plasmonic Au-Nanoparticle Incorporated Oxides (e.g. Au / SiO_2)

Demonstration of Fabricated Prototype Sensor



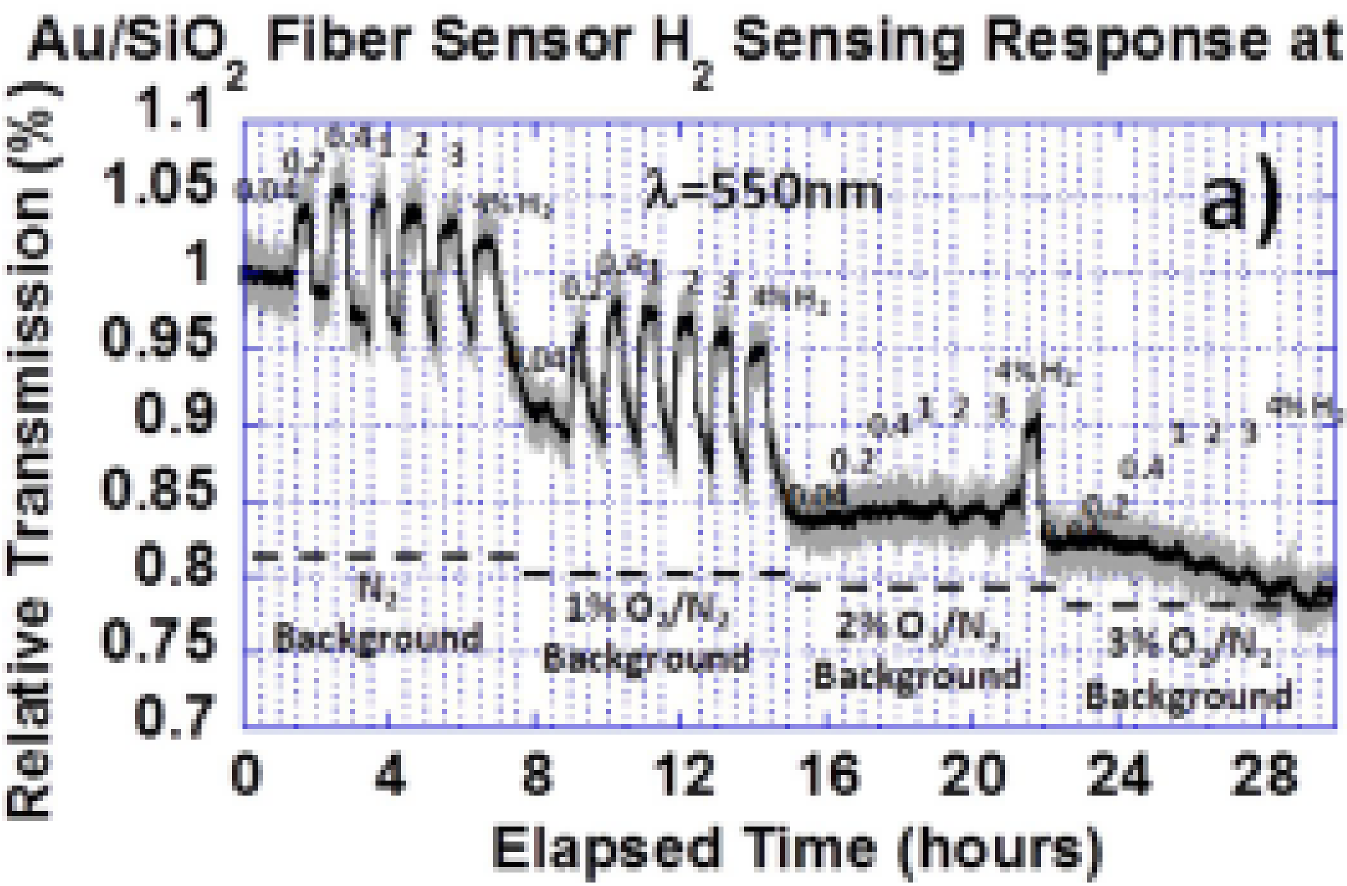
Sensor Elements Have Been Fabricated Based upon the Au / SiO_2 System to Explore High Temp. Plasmonic Sensing Exploiting Au LSPR Absorption Modifications.

Demonstration of Fabricated Prototype Sensor



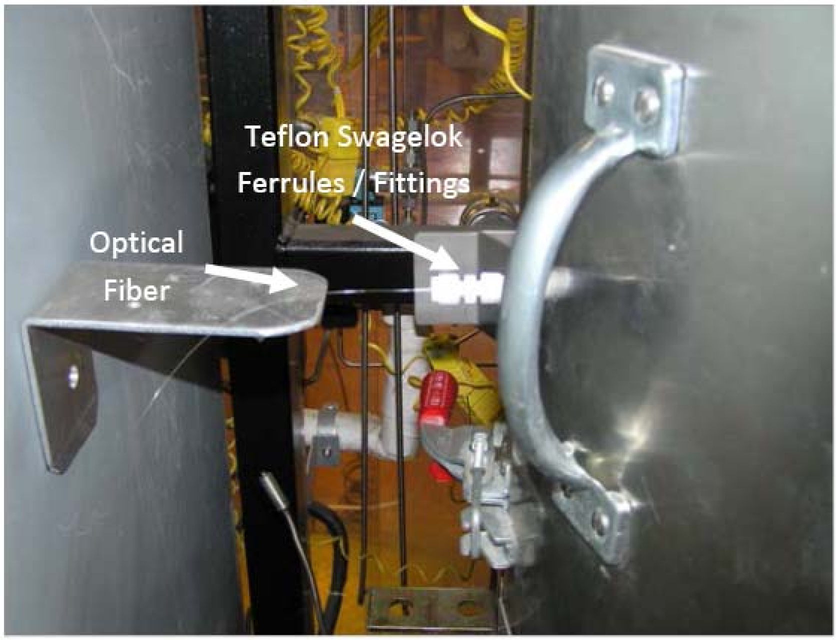
Responses to Both Chemical Composition and Temperature Are Observed at Unique Wavelengths Due to Unique Responses of Au Absorption to Free Carrier Density / Temperature.

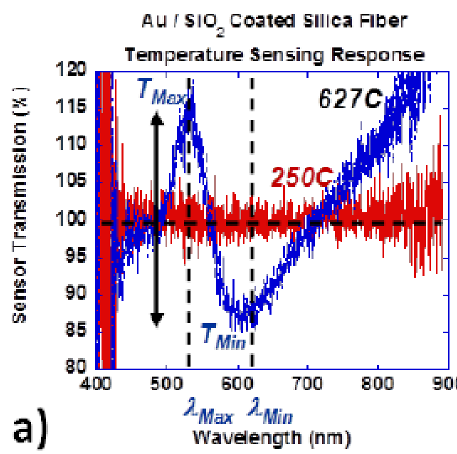
Fabricated Sensor Results

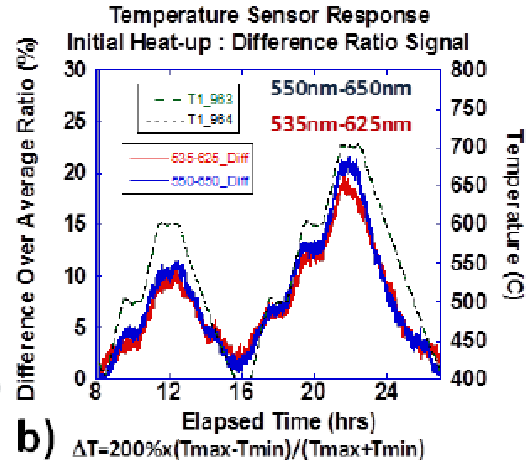


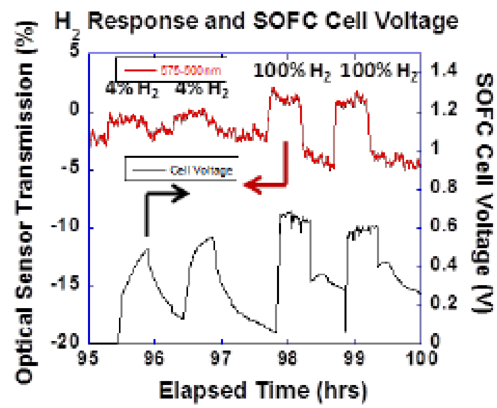
Optical Fiber Stability at Such Extreme Temperatures is a Concern, Particularly in H_2 Containing Atmospheres. This is Why the VA Tech. Effort Plays a Critical Role in the Program.

Fabricated Sensor Results : Testing in SOFC





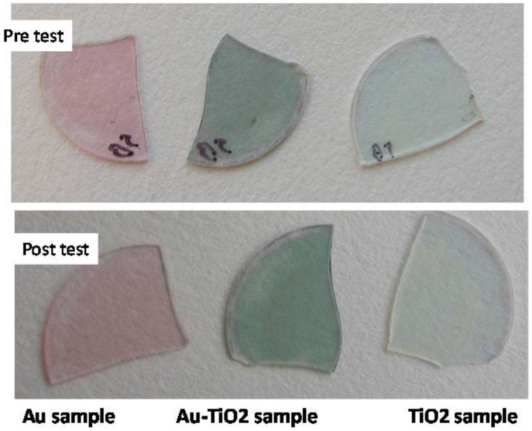




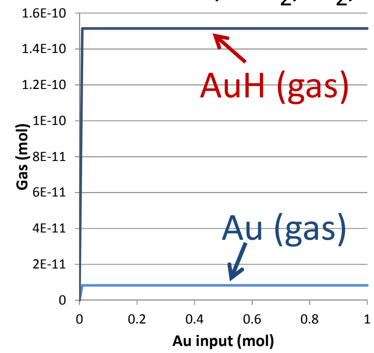
T=750ºC

We Have Successfully Demonstrated Embedded Temperature and H_2 Responses in an Operational SOFC Although More Work is Required to Better Understand Stability at Visible Wavelengths.

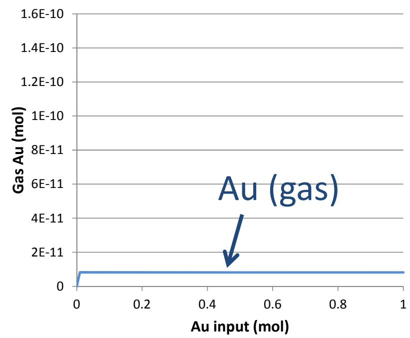
Long-Term Exposure Testing of Sensor Materials



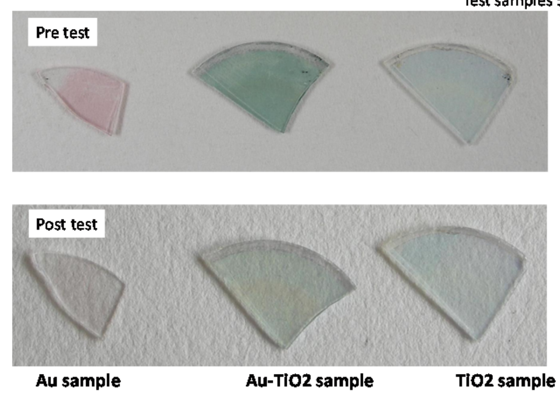
T=800 °C,
Gas mix: CO, CO_2, H_2, N_2



T=800 °C, air



Test samples 5b1



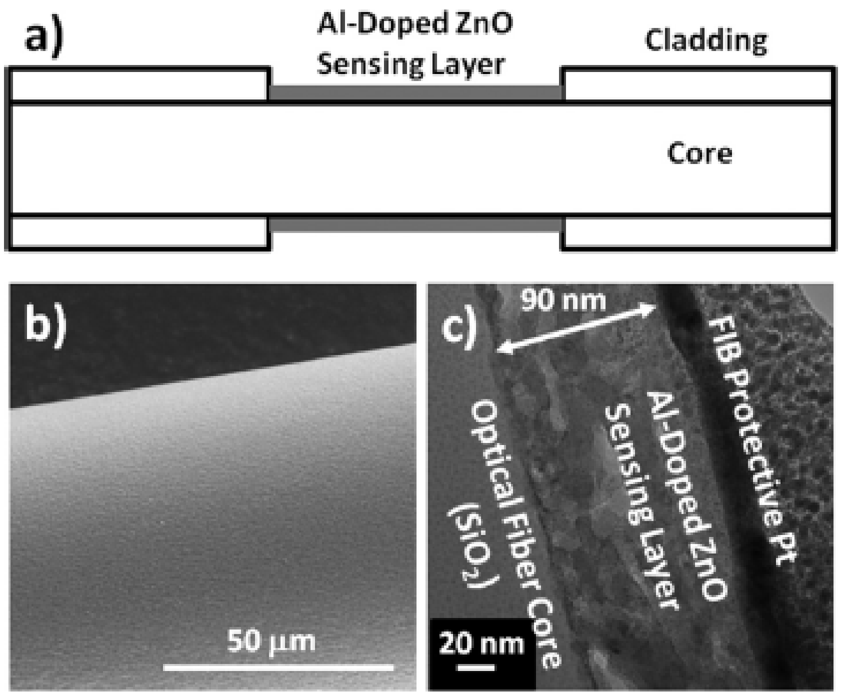
Reactive Evaporation of Noble Metals Such as Ag, Pd, and Au is Increasingly Being Observed at High Temperatures Depending Upon the Specific Gas Atmosphere in Question.

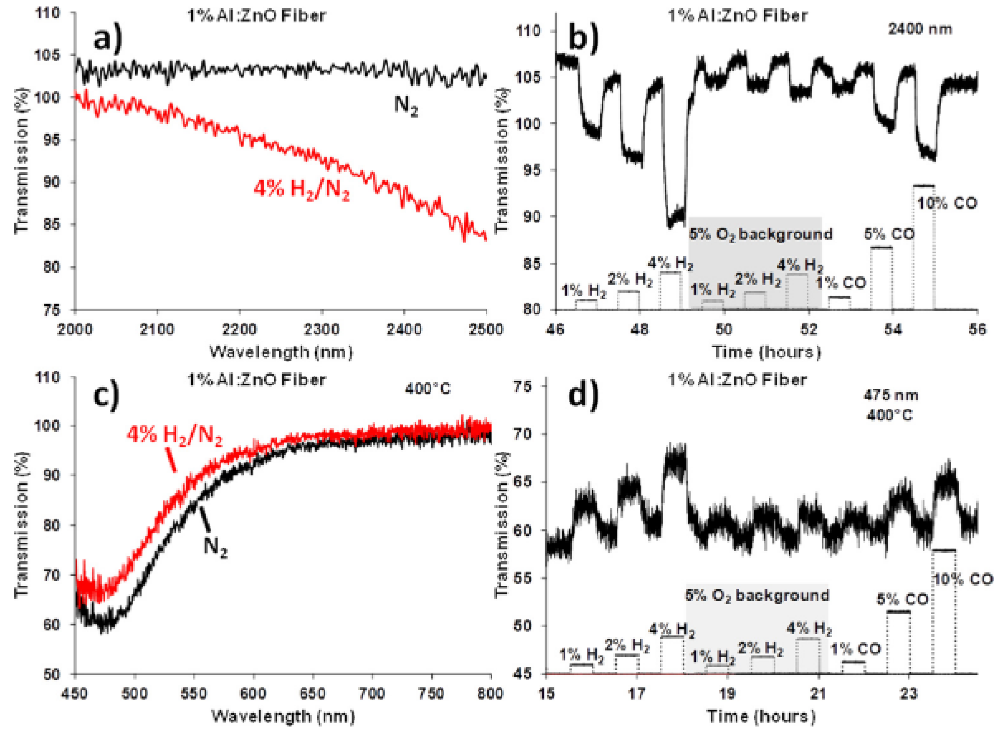
Exploration of Alternative Materials Systems is Needed…

Example Sensing Material Class #2:

High Electronic Conductivity Metal Oxides (e.g. Al-Doped ZnO and La-Doped $SrTiO_3$)

Fabricated Sensors Based on Al-Doped ZnO



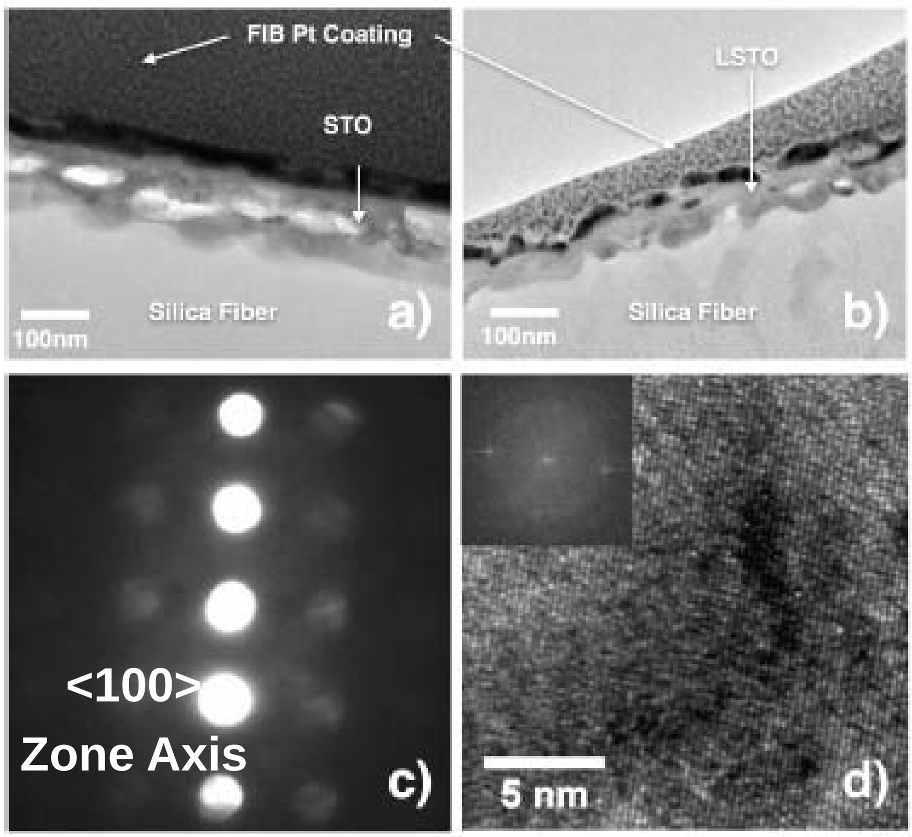


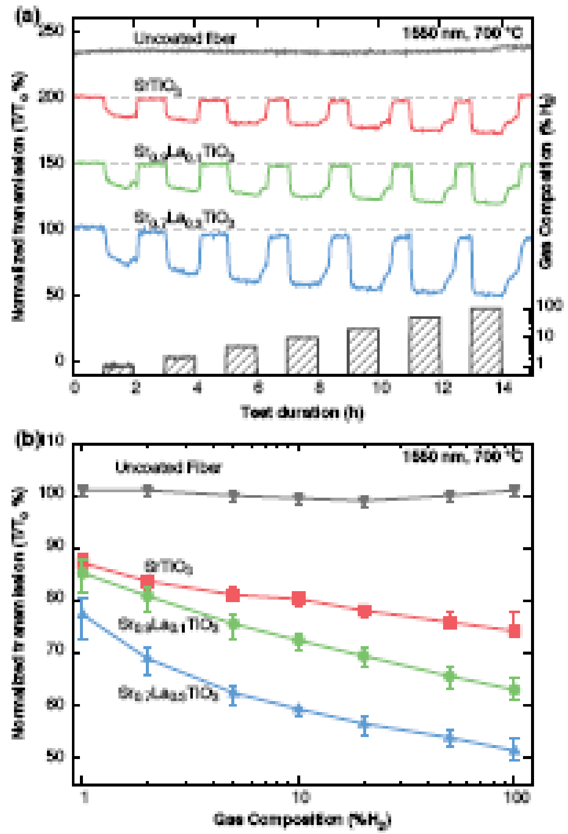
Attractive High Temperature and Broadband Near-IR Sensing Responses Observed for Al-Doped ZnO Thin Films.

Fabricated Sensors Show Promising Results in Near-IR and UV / Visible Wavelength Ranges Due to Free Carrier / "Burstein-Moss" Effects.

Higher Temperature Stable Oxides are Showing Great Promise

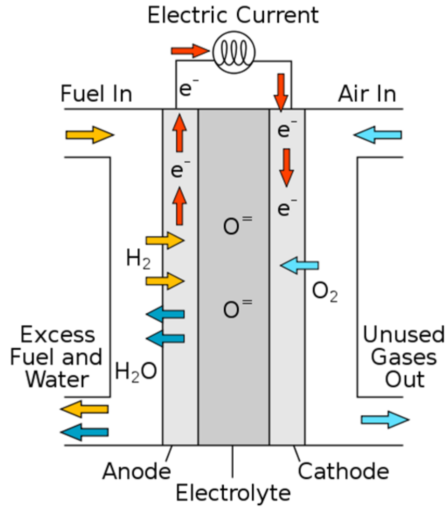
La-Doped $SrTiO_3$ Based Sensor Materials

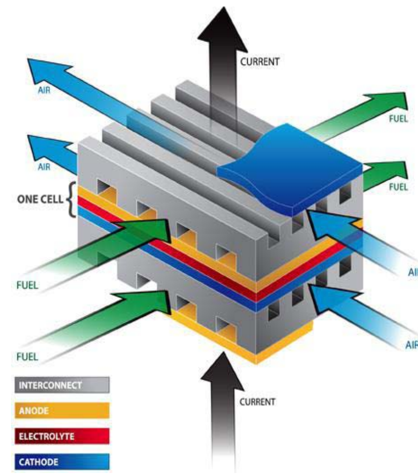




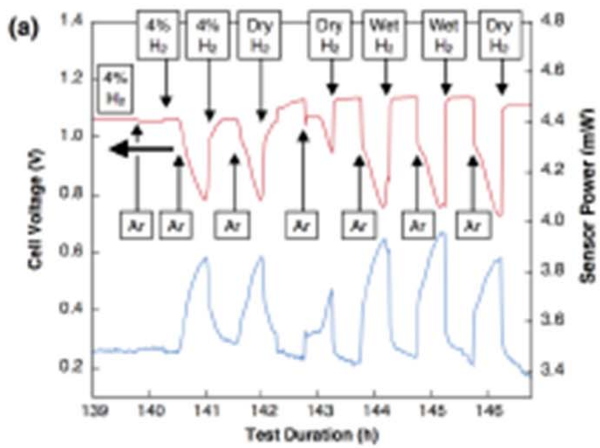
Structure and Response of Fabricated Sensors Based Upon Doped Perovskite Oxides.

Experimental Measurements in Operational SOFCs

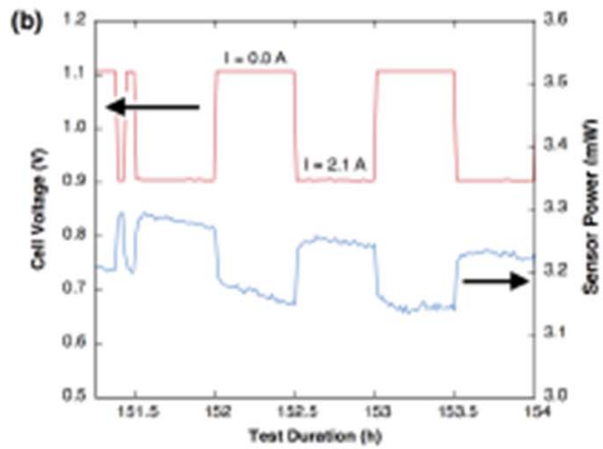




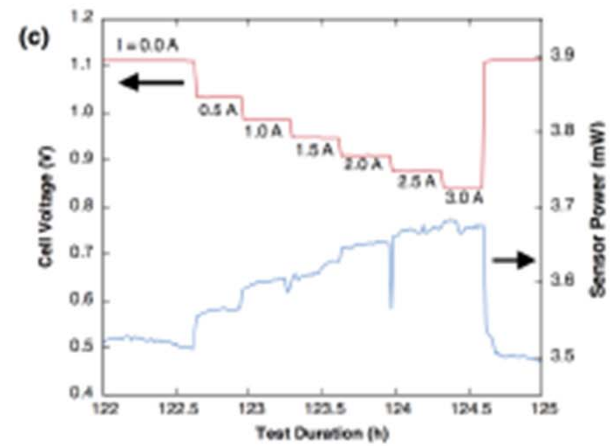
Fuel Gas Stream Variations



Fuel Utilization

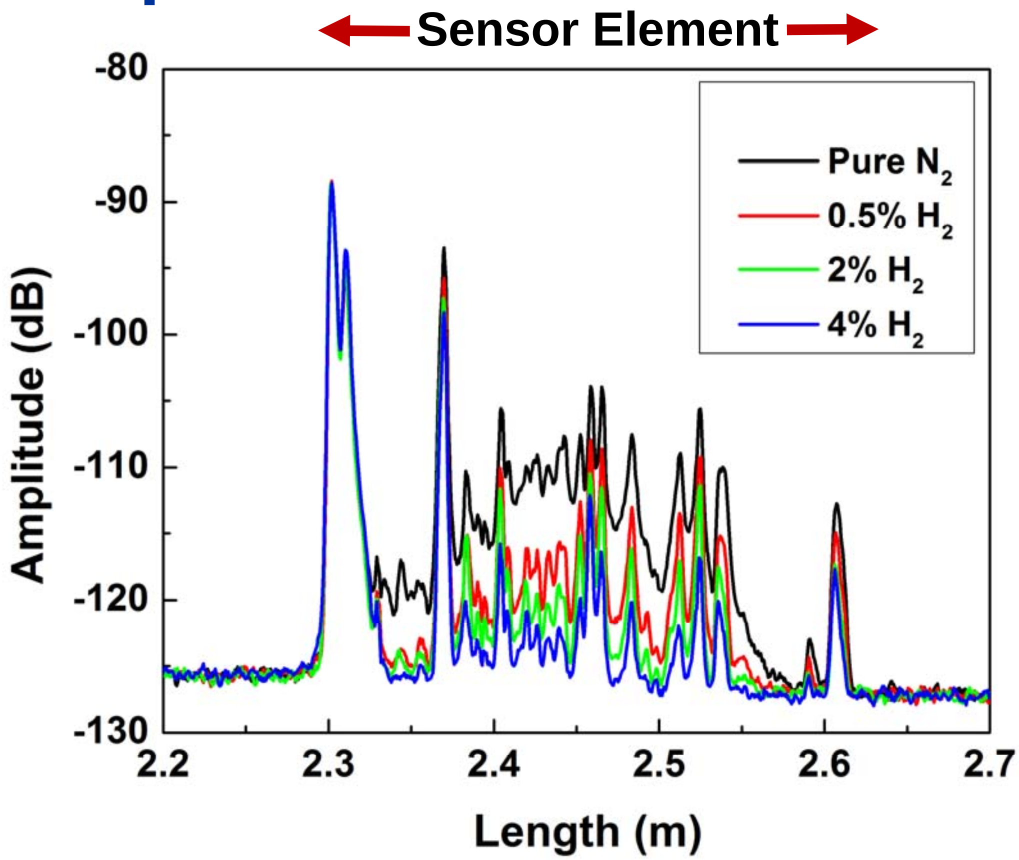


Fuel Utilization

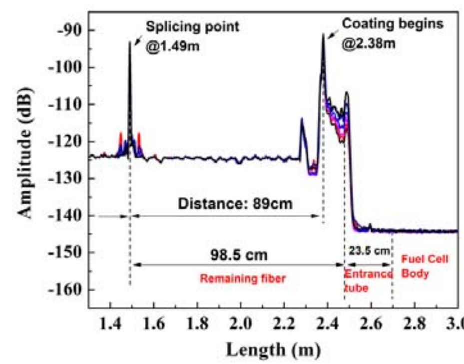


Fabricated Sensors Have Undergone Testing Under Operational Solid Oxide Fuel Cell Conditions.

Experimental Measurements in Operational SOFCs



Optical Backscattering Reflectometry Based Distributed Interrogation.



University of Pittsburgh

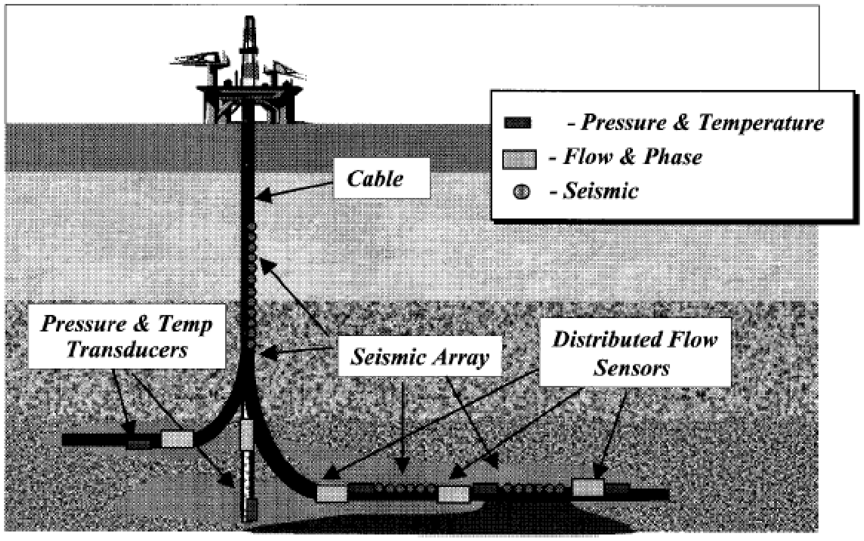
Pursuing the Holy Grail : High Temperature, Embedded, Distributed Information About Chemical Composition in Real-Time.

Early Results are Highly Encouraging… But the Physics of High Temperature Distributed Interrogation Needs More Understanding.

Sensor Materials for Subsurface Applications

Downhole pH and Chemical Sensing Applications

Pressure, Temperature, and Flow Sensors are Commercially Available



Importance of Downhole pH Sensors:

- **Oil & gas production**
- **Corrosion and Scaling : Functions of Brine Chemistry & Well-Bore Conditions**
  - pH is Single Most Important Chemical Parameter Predicting Corrosion and Scaling
  - Scaling Removal for a Single Well Can Be as Large as **$2.5million**[1]
- **pH Helps to Characterize Formation, e.g. Transition Zones**
- **pH Can Be an Indicator of Chemical Composition *in* Some Down Hole Environments**

$$pH = pK_1 + Log([CO_2] - 0.0449\alpha P_{CO2})/0.0449\alpha P_{CO2}$$

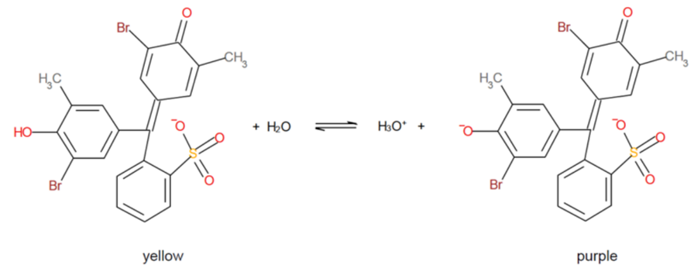
Apparent Acid Constant — ***Total Conc. Of Carbonates and Free CO_2*** — ***CO_2 Partial Pressure (bar)*** — ***Bunsen Abs. Coeff.***

Commercial Distributed Temperature and Pressure Sensors Exist. (Schlumberger, Haliburton, Baker Hughes, and Others)

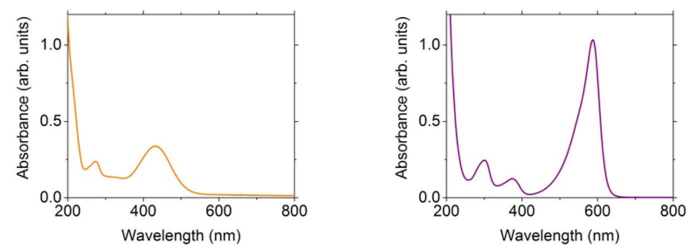
Chemical Sensing Technologies are Relatively Under-Developed Despite The Importance and Potential Economic / Environmental Impact

Traditional Optical Based pH Sensing

Indicator	Low pH color	Transition pH range	High pH color
Gentian violet (Methyl violet 10B)	yellow	0.0–2.0	blue-violet
Malachite green (first transition)	yellow	0.0–2.0	green
Malachite green (second transition)	green	11.6–14	colorless
Thymol blue (first transition)	red	1.2–2.8	yellow
Thymol blue (second transition)	yellow	8.0–9.6	blue
Methyl yellow	red	2.9–4.0	yellow
Bromophenol blue	yellow	3.0–4.6	purple
Congo red	blue-violet	3.0–5.0	red
Methyl orange	red	3.1–4.4	yellow
Screened methyl orange (first transition)	red	0.0–3.2	grey
Screened methyl orange (second transition)	grey	3.2–4.2	green
Bromocresol green	yellow	3.8–5.4	blue
Methyl red	red	4.4–6.2	yellow
Azolitmin	red	4.5–8.3	blue
Bromocresol purple	yellow	5.2–6.8	purple
Bromothymol blue	yellow	6.0–7.6	blue
Phenol red	yellow	6.4–8.0	red
Neutral red	red	6.8–8.0	yellow
Naphtholphthalein	colorless to reddish	7.3–8.7	greenish to blue
Cresol Red	yellow	7.2–8.8	reddish-purple
Cresolphthalein	colorless	8.2–9.8	red
Phenolphthalein	colorless	8.3–10.0	fuchsia
Thymolphthalein	colorless	9.3–10.5	blue
Alizarine Yellow R	yellow	10.2–12.0	red



Bromocresol purple



$$A_x = [HA]\epsilon^x_{HA} + [A^-]\epsilon^x_{A^-}$$
$$A_y = [HA]\epsilon^y_{HA} + [A^-]\epsilon^y_{A^-}$$

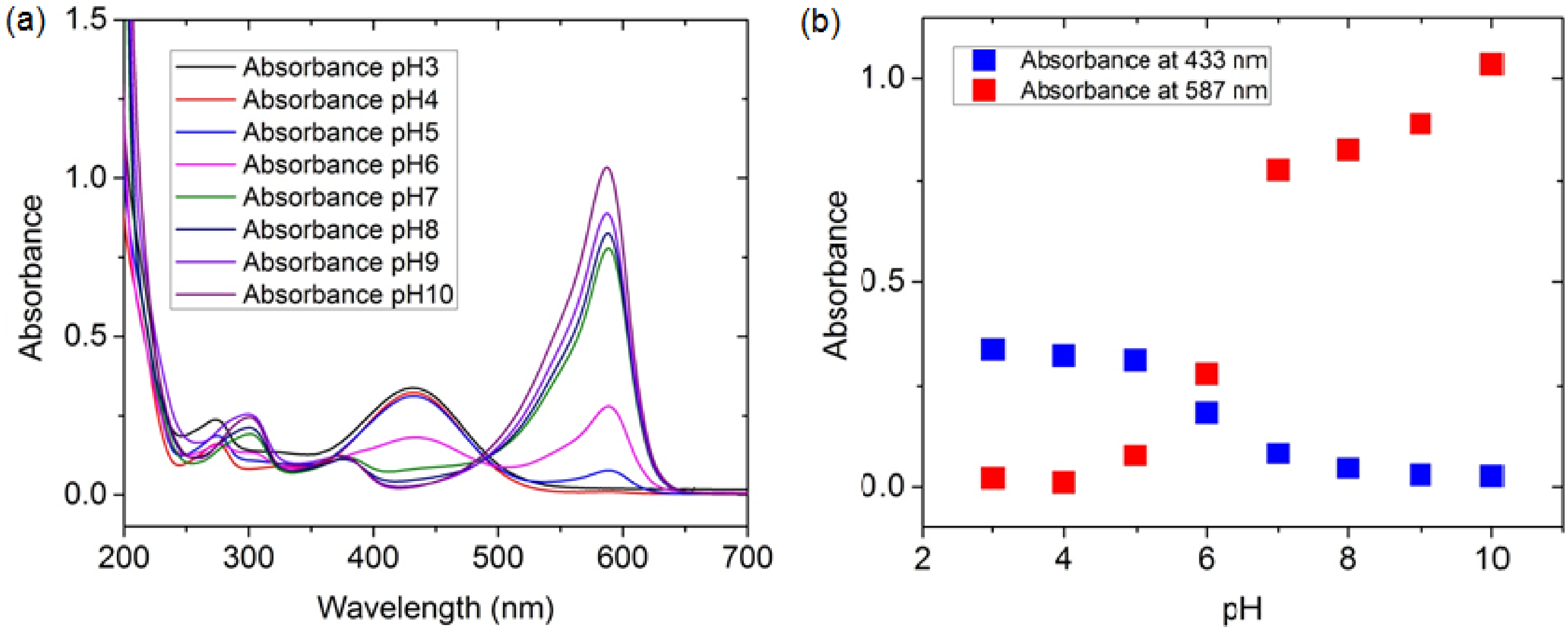
$$K_a = \frac{[A^-][H^+]}{[HA]} \quad pK_a = -\log_{10} K_a$$

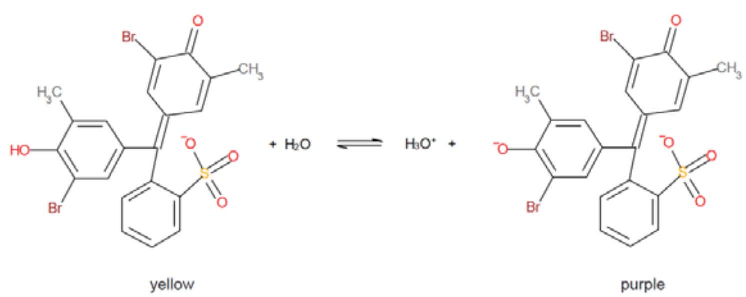
$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

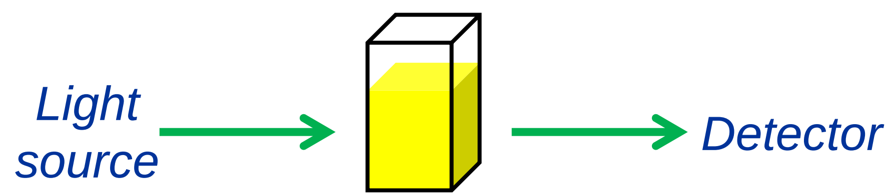
wikipedia.org; quantum.esu.edu/~scady/Experiments/KaIndicator.pdf

Conventional optical fiber based pH sensors utilize organic pH indicators.

Traditional Optical Based pH Sensing

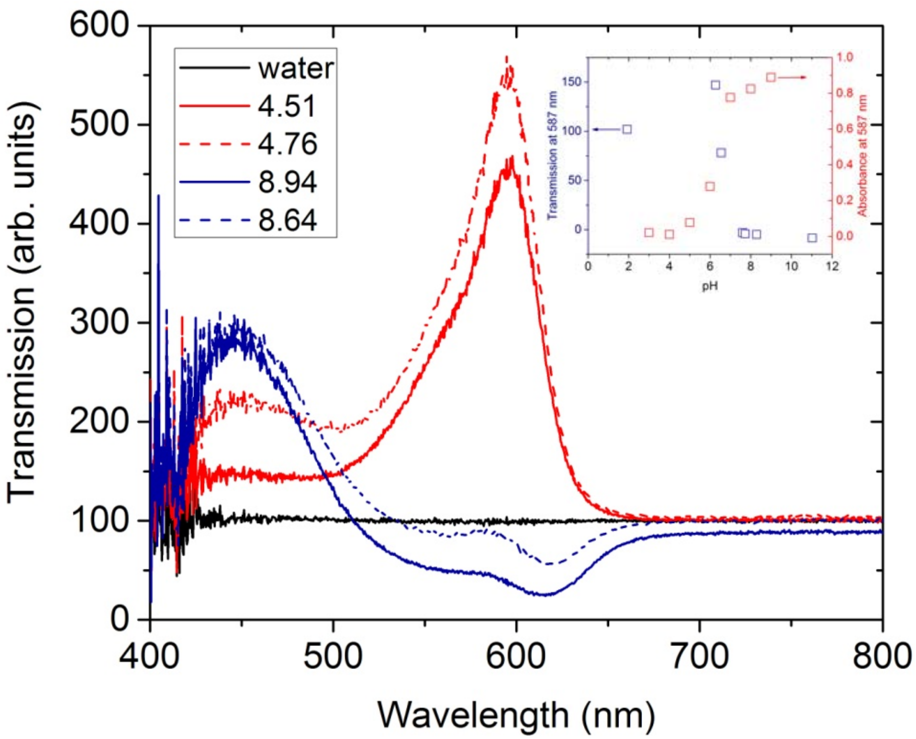


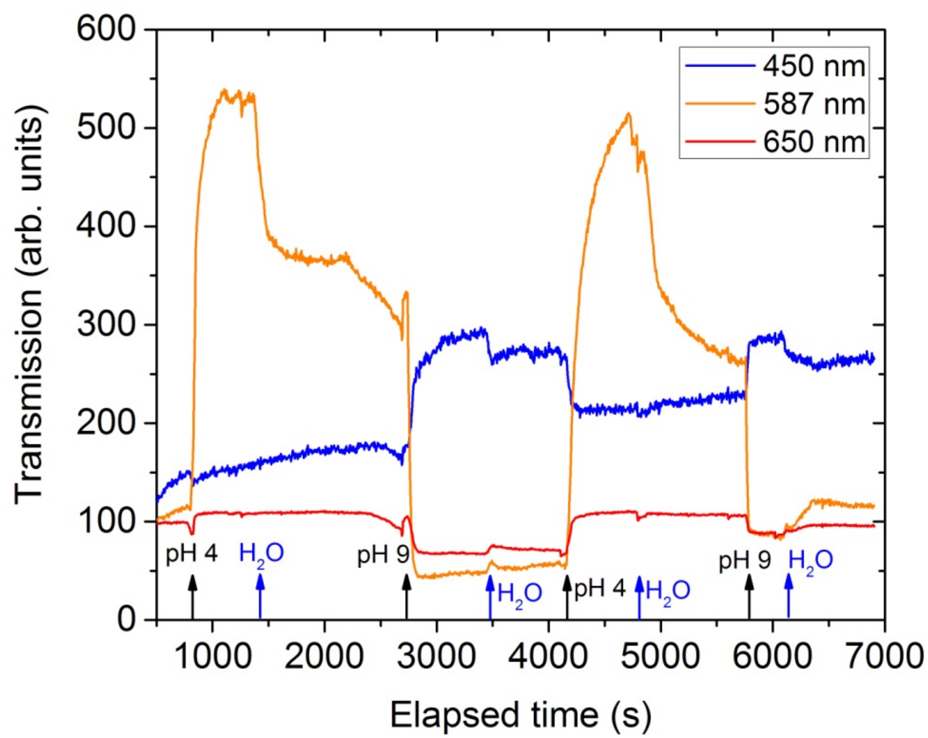


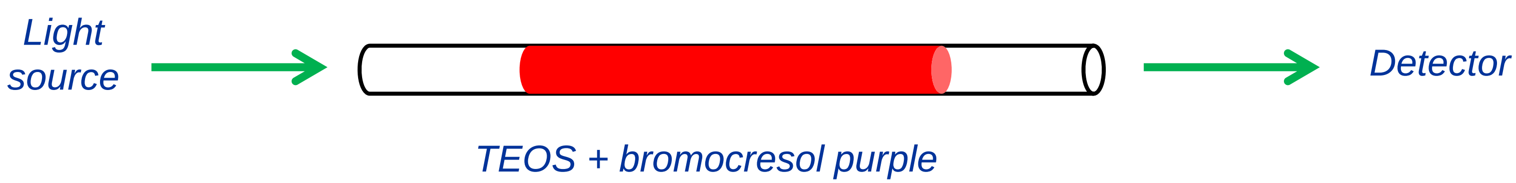


Example: Bromocresol purple dispersed in solution as a pH indicator.

Traditional Optical Based pH Sensing







pH Indicators Can Also Be Embedded within a Sol-Gel Matrix Such as Silica and Integrated with a Fiber Optic Based Sensing Platform

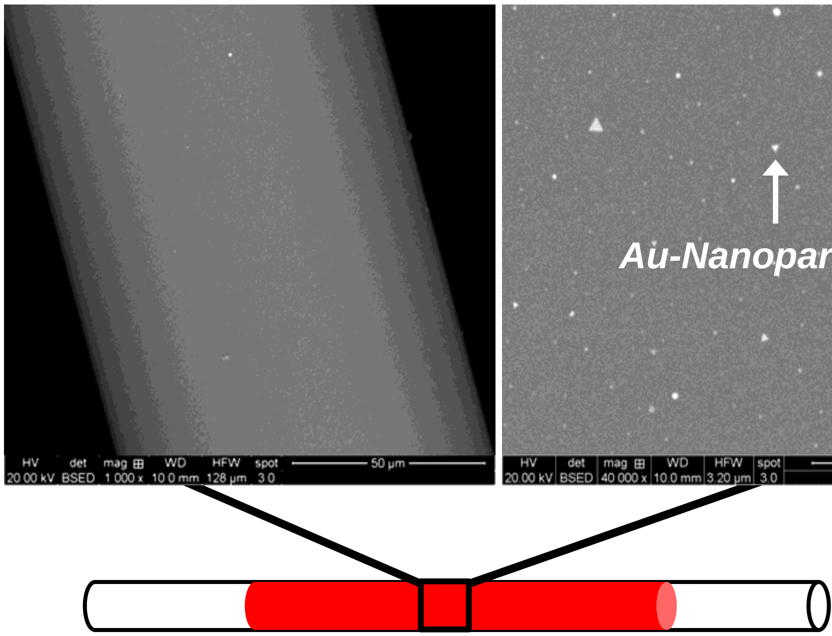
Temperature Instability of Optical-Based pH Sensors

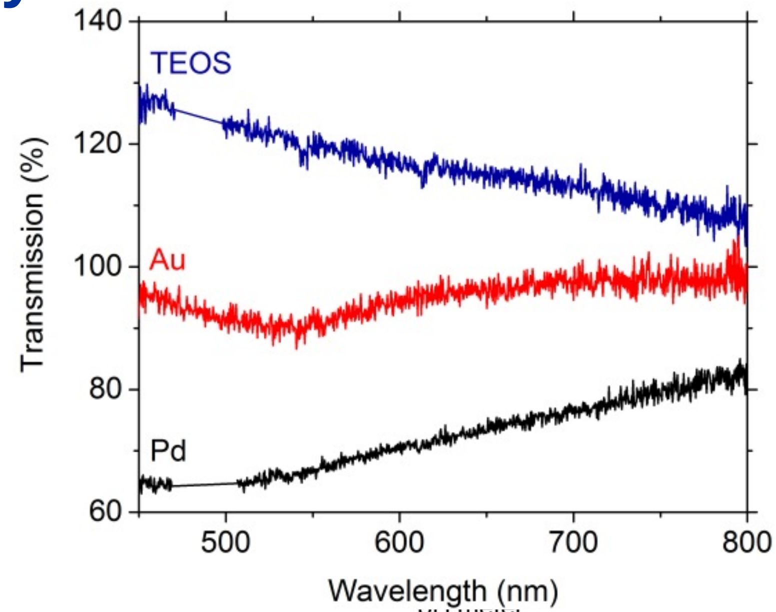
Traditional Optical-Based pH Indicators Have Inherent Temperature Limitations that Create a Challenge for the Most Aggressive Conditions.

Sensing Material	Thermal Stability	Chemical Stability	pH Responsive Range	Reported Research
Dye	low (up to ~ 100 °C)	low – moderate	0 – 14	very well studied and have been investigated for down-hole sensing
pH responsive polymer	moderate (a few hundred °C possible)	moderate – high	2 – 13	some reports and not aware of down-hole sensing application
Au nanoparticles	high (up to 1000 °C)	high	2 – 12*	a few reports on using pH sensitive molecules/polymer to enable optical response from Au
Oxides	high (up to 1000 °C or more)	high	?	?

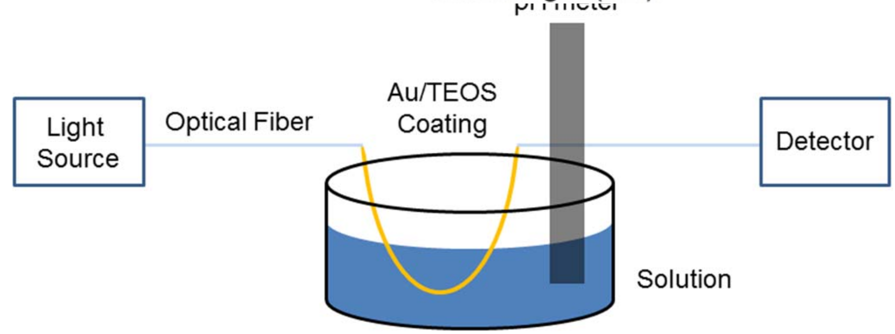
How Can we Exploit Optical Properties of Inherently Stable Materials for the Purpose of Optical pH Sensing in Extreme Temperature Applications?

Nanocomposite Metal-Nanoparticle Incorporated Silica Based Sensing Layers





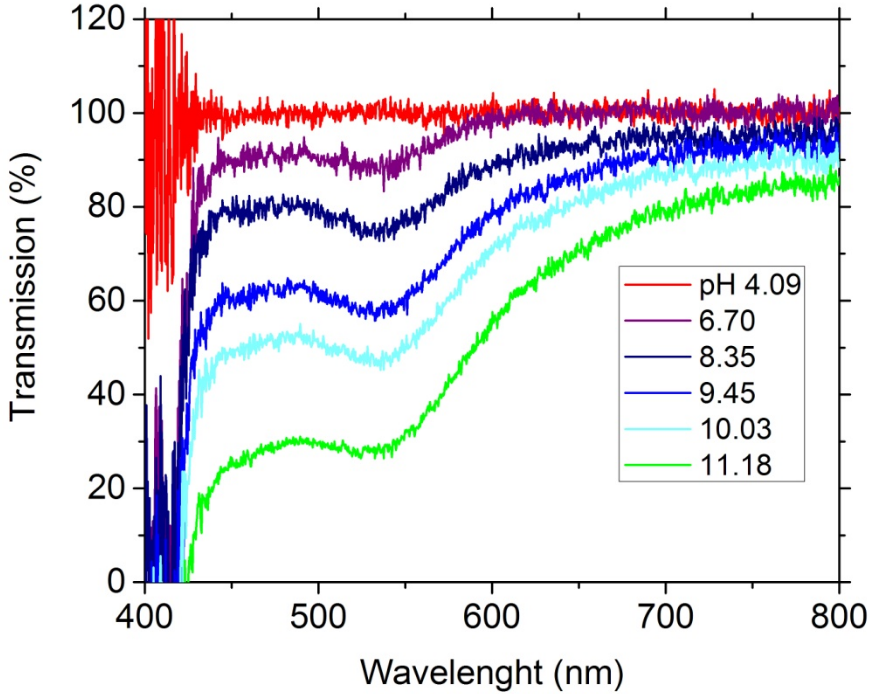
TEOS + $HAuCl_4$ ($PdCl_2$)
200 °C ~ 600 °C

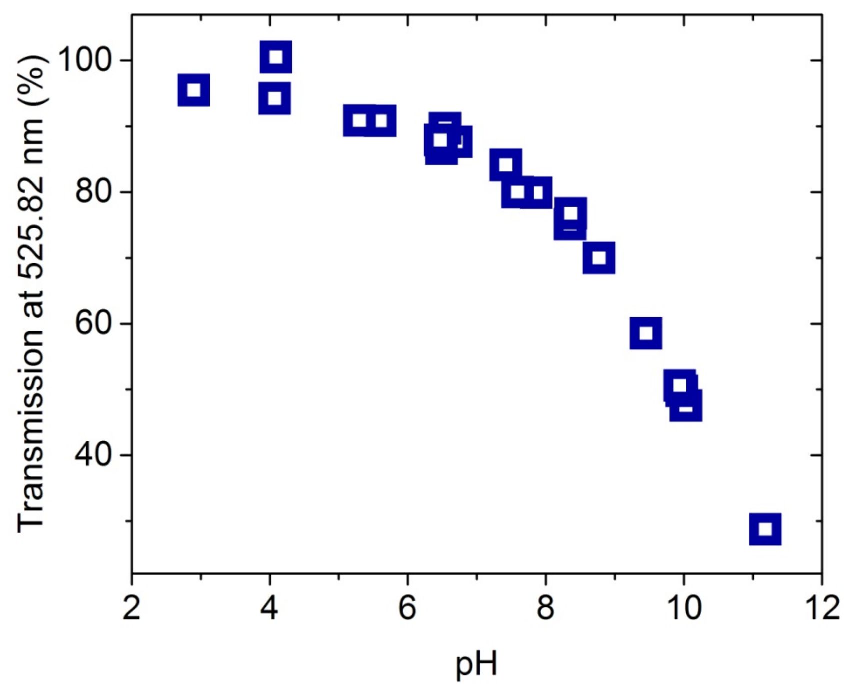


Incorporation of Metal Nanoparticles Into an Organic or Inorganic Matrix Provides a Unique Optical Absorption Feature Characteristic of the Nanoparticles in Question.

Nanocomposite Metal-Nanoparticle Incorporated Silica Based Sensing Layers

Au-Nanoparticles



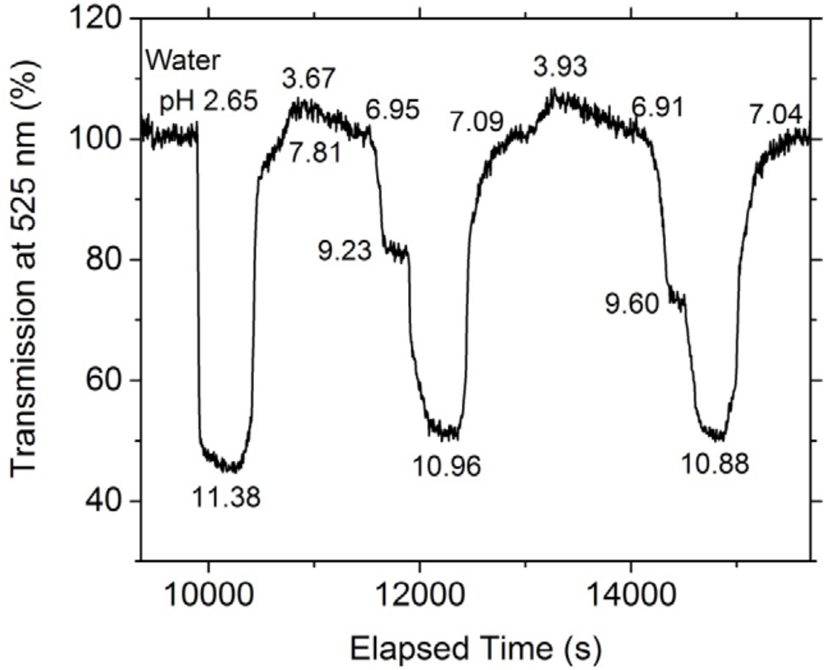


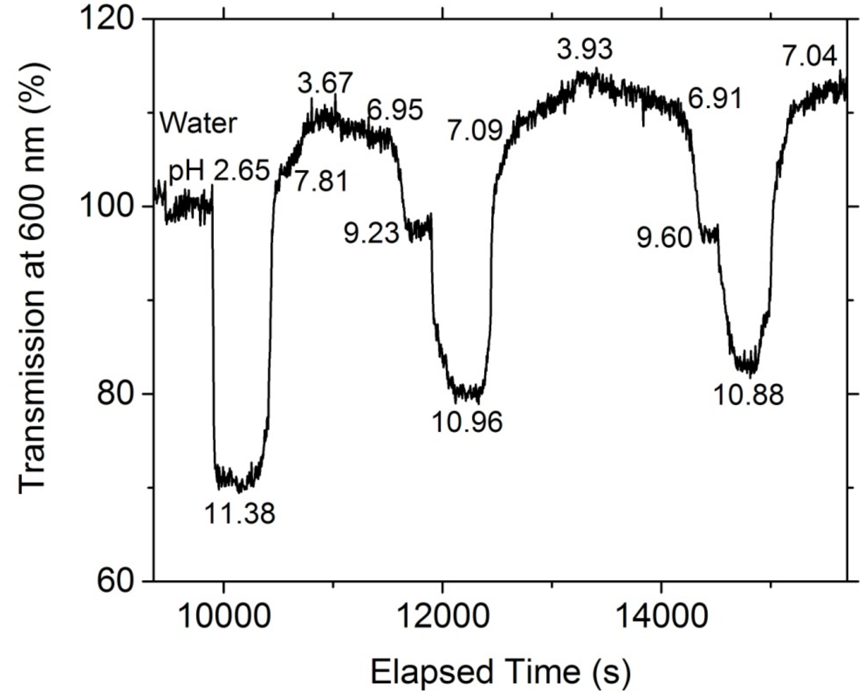
Higher pH Solutions "Amplify" the Inherent Absorption Associated with the Plasmonic Au-Nanoparticles.

A Strong Shift in the Au LSPR Absorption Peak Wavelength Cannot Be Resolved, Suggests it is Not a Pure LSPR Shift Due to Refractive Index.

Nanocomposite Metal-Nanoparticle Incorporated Silica Based Sensing Layers

Au-Nanoparticles



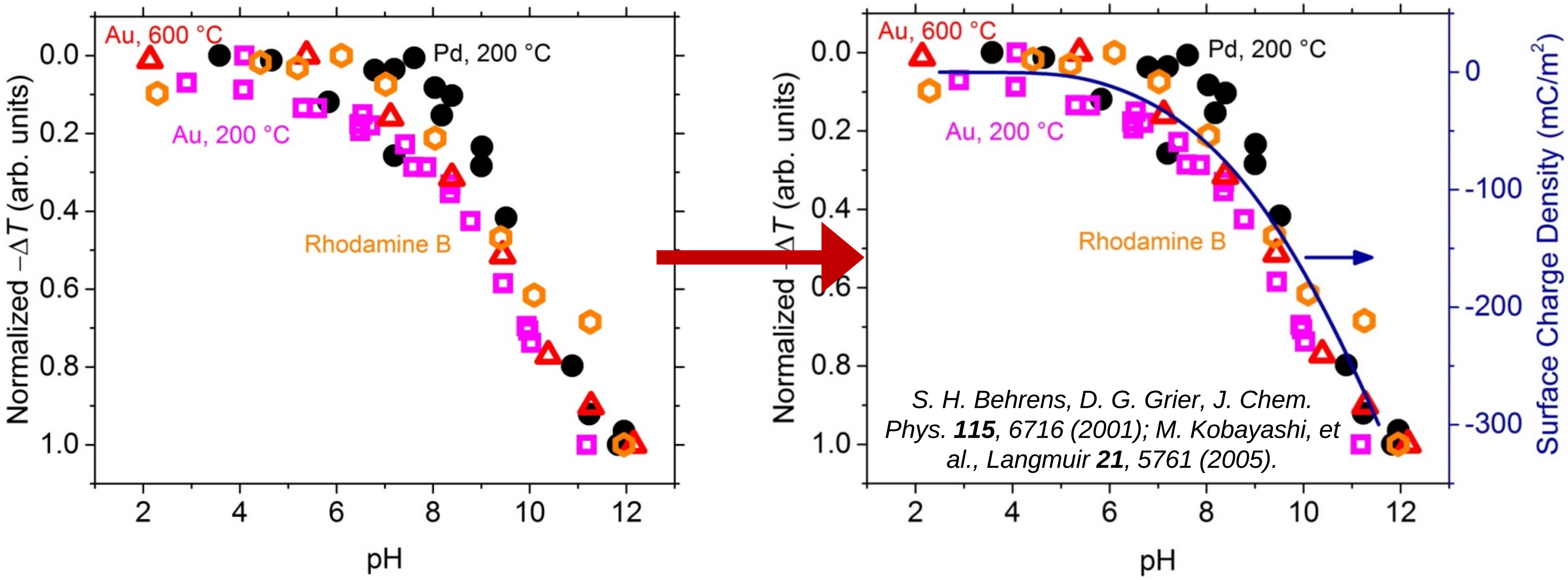


The Optical Absorption Response Appears Rapid, Robust, and Reversible as pH is Varied from Acidic to Basic.

What is the Mechanism Responsible for the Optical pH Response?

Characteristic “pH Dependence” of Optical Sensing Responses Regardless of “Indicator”

“Universal Response”

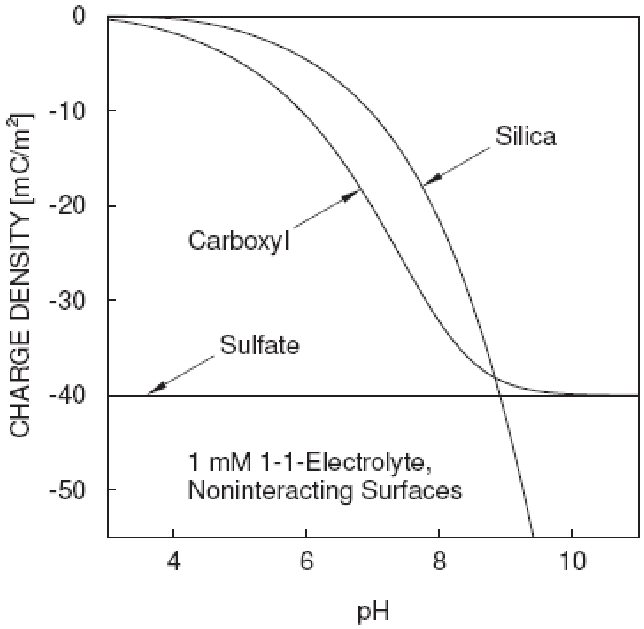


Even Organic, Non-pH Sensitive Organic Dyes Show a Similar Qualitative Response as Au and Pd!

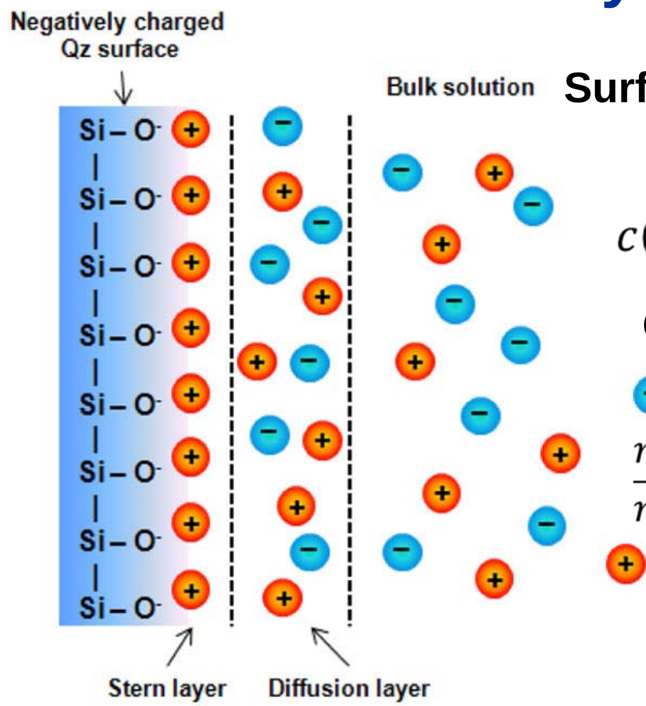
Could Refractive Index Impacts on Waveguiding Conditions Be Responsible for the Observed Responses?

Correlation of Response with Surface Charge Density of Silica Suggests Surfaces are Playing a Critical Role.

Surface Charging + Electrochemical Double Layer Formation



Surface Charging Behavior is "Tunable"



Adsorption of Cations Near the Charged Silica Surface

Surface Concentration Variation

$$c(z) = c_{\mathrm{bulk}} e^{-\frac{e\psi(z)}{kT}}$$

Clausius-Mossoti Relation

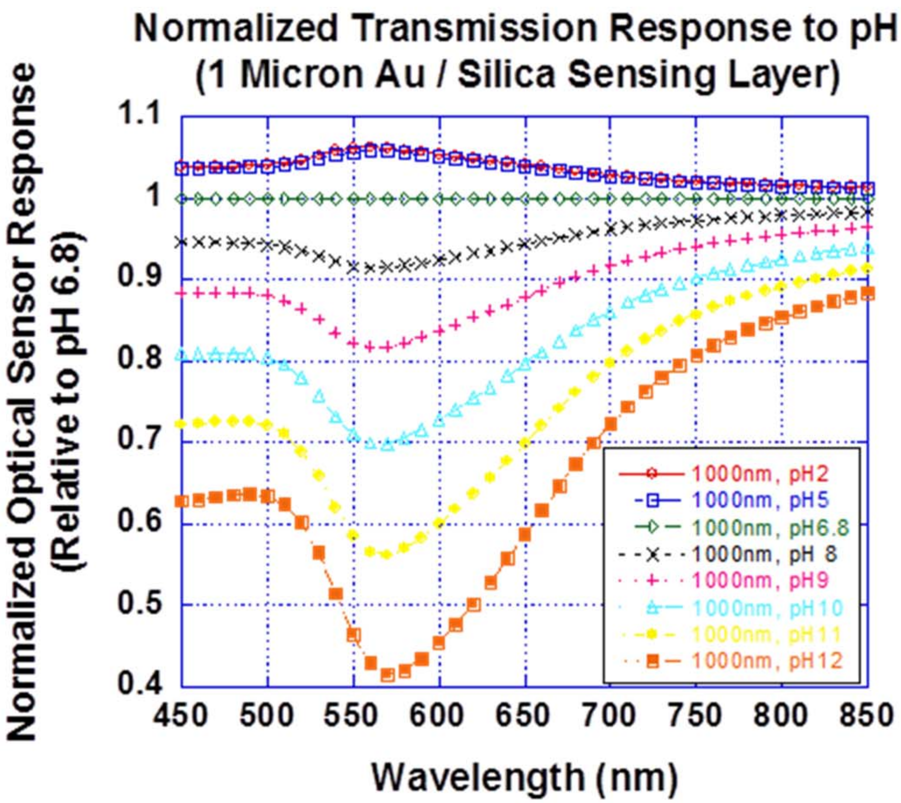
$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum_i (N_i \alpha_i)$$

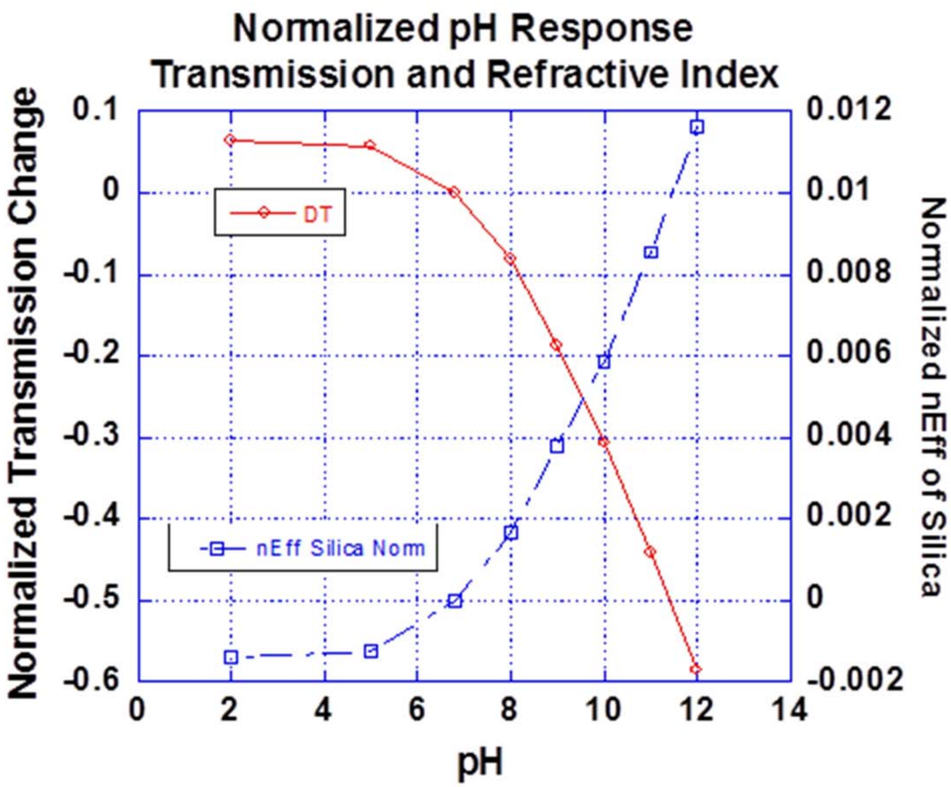
One Can Hypothesize that the Surface Layer Refractive Index Has a Monotonic (Linear?) Dependence on Surface Charge Density.

For "Porous" Layers This May Translate into a "Bulk" Index Modification.

J. Rayss, G. Sudolski, Sens. Actuators B ***87****, 397 (2002).* **Suggested "Increase in Electron Density" Increases Silica Refractive Index**

Waveguide Modeling of a Au / TEOS Sensing Layer

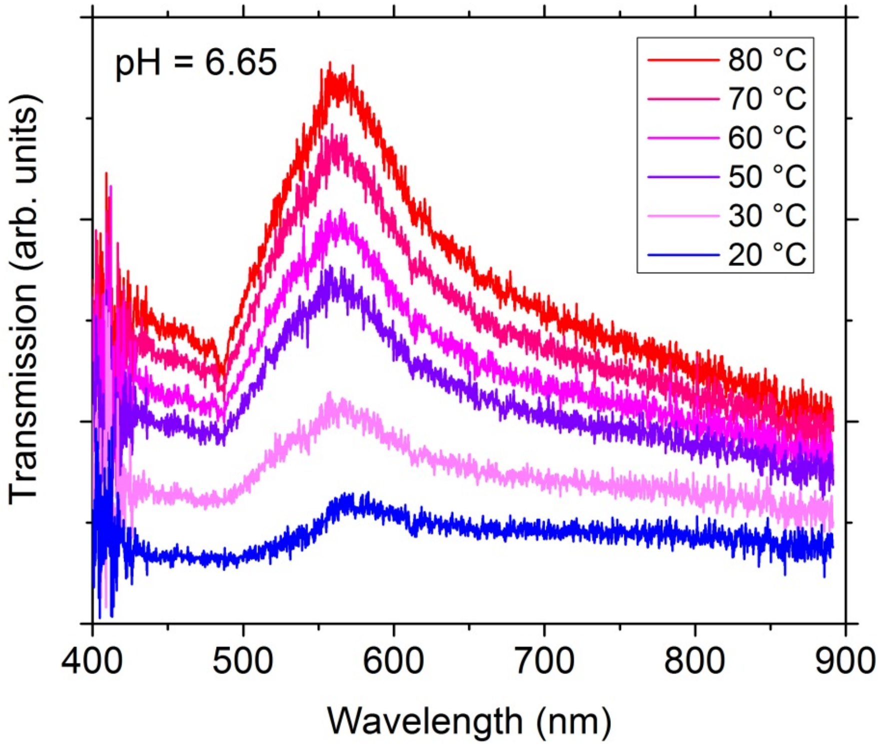


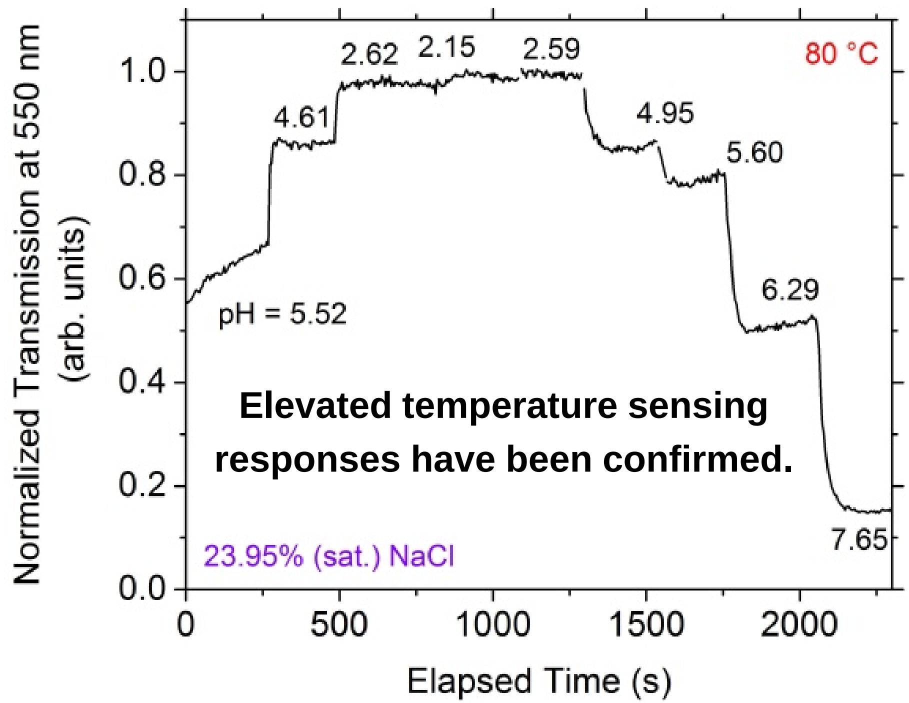


1 μm sensing layer, varying pH (left) and normalized transmission change and effective silica index vs. pH (right)

Linearity between the transmission and effective refractive index of the matrix layer is consistent with experimental results.

Elevated Temperature Measurements : Au / TEOS Sensor

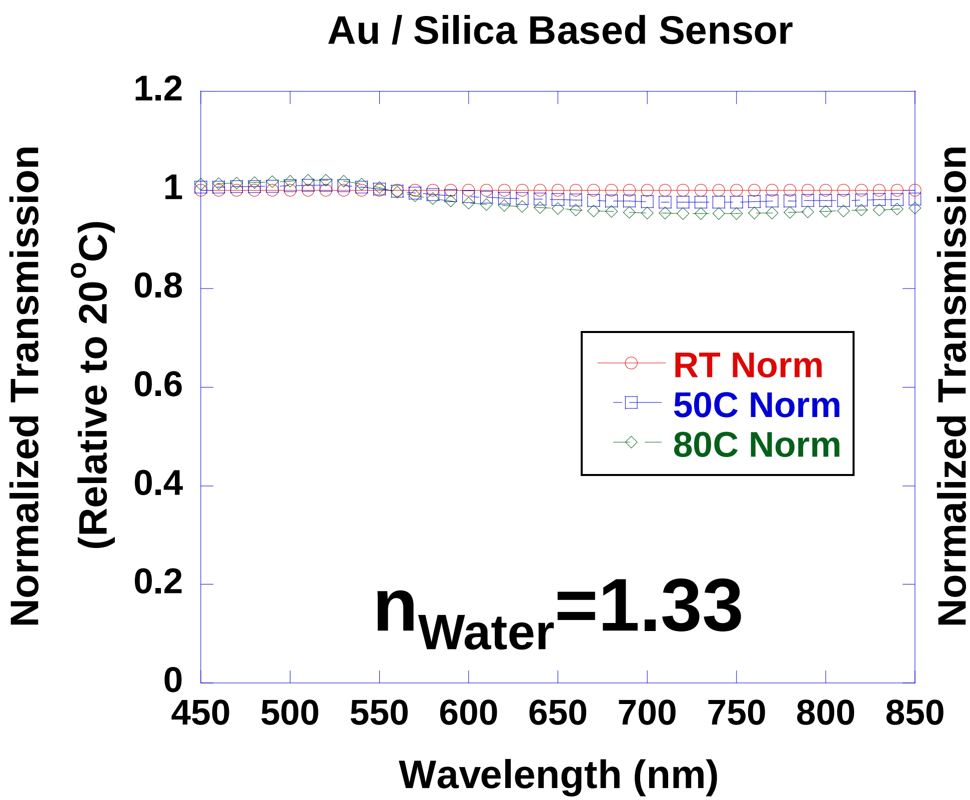


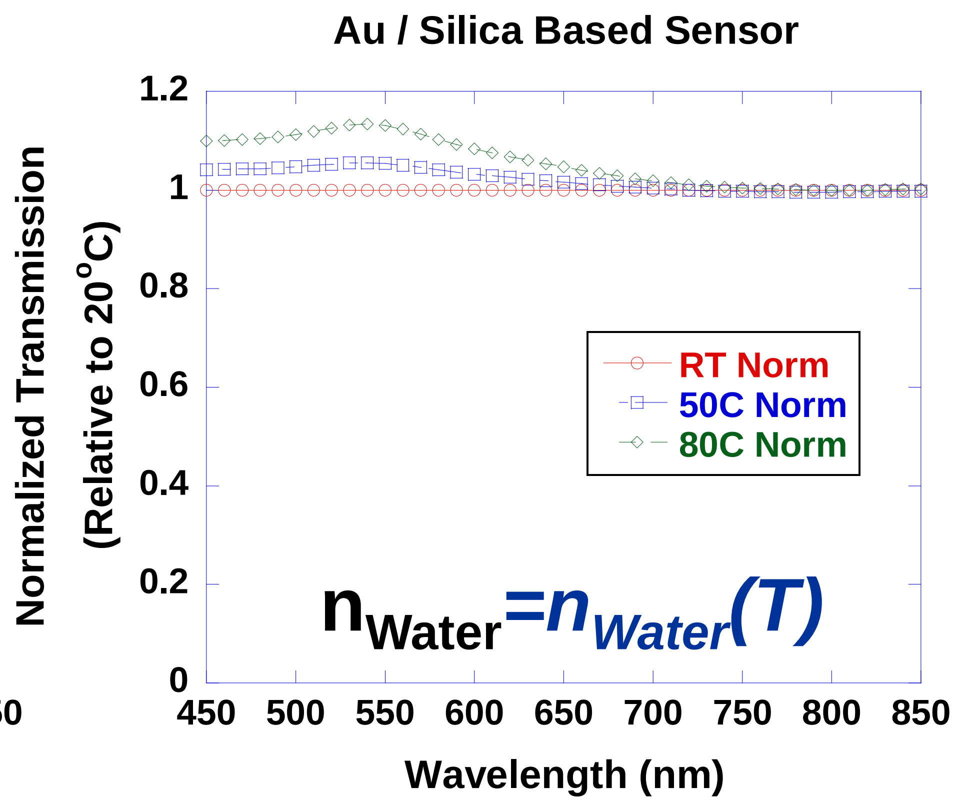


As temperature is increased up to 80^{o}C for fixed pH, a unique temperature dependence of the Au / TEOS sensor is observed.

We currently believe that the observed dependence is related to a relatively large temperature dependence of optical constants of water.

Elevated Temperature Waveguide Modeling : Au / TEOS



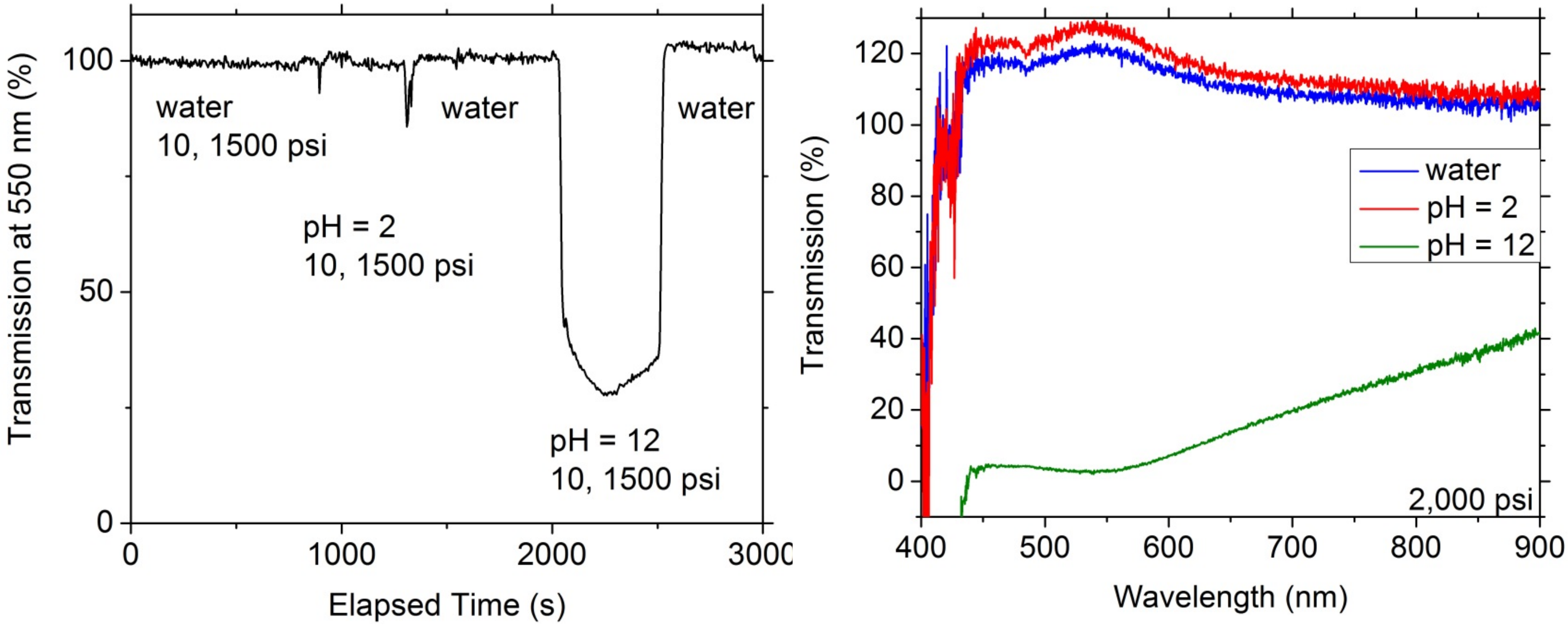


Dominated by $n_{Au}(T)$ Dominated by $n_{Water}(T)$

1 micron thick sensing layer, with and without accounting for the temperature dependence of the refractive index of water.

The results are only consistent with observations when the water temperature dependence is properly accounted for.

Elevated Pressure Measurements : Au / TEOS Sensor

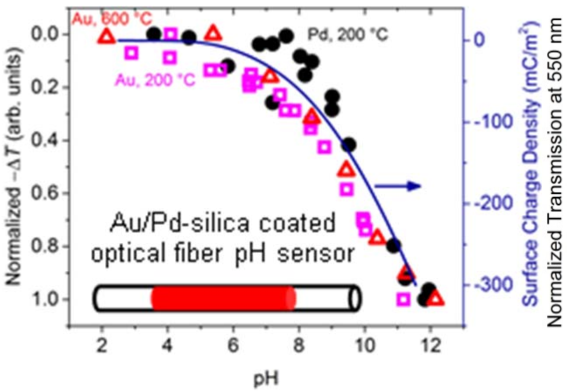


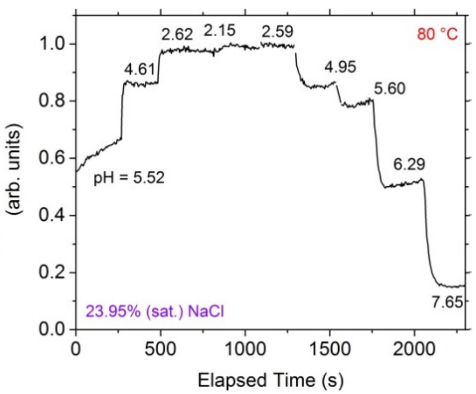
High pressure testing has only recently been initiated. Early results do not show a strong pressure dependence of transmission at fixed pH.

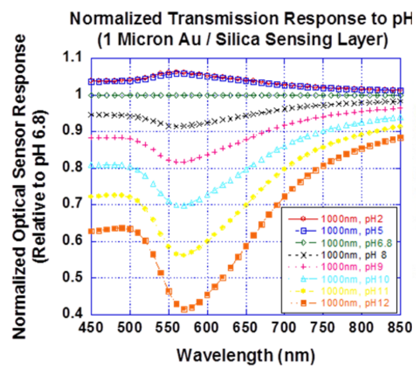
The sensing response also appears to be qualitatively the same as for ambient pressure applications. Work is on-going to better quantify the pressure impacts on pH sensing response in these materials.

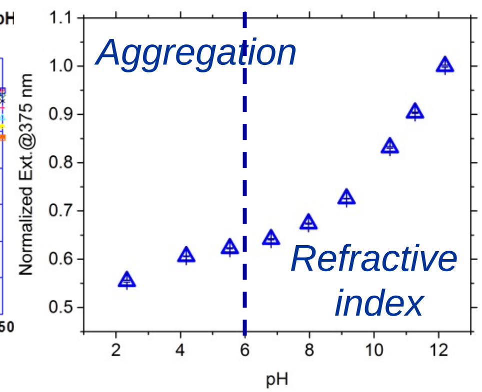
Overall Summary and Future pH Sensing Work

Robust Optical pH Response in Several Materials Described
Current Information Suggests Silica Refractive Index is the Likely Mechanism
→ pH Dependent Surface Charging Plays an Important Role

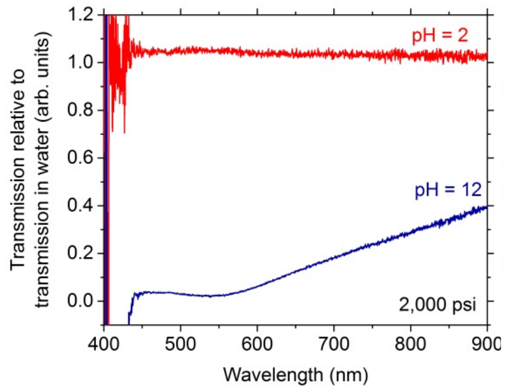


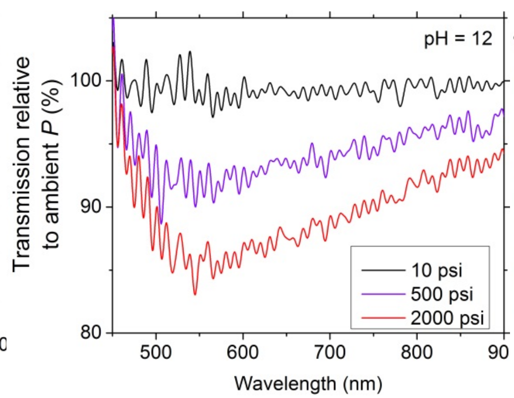


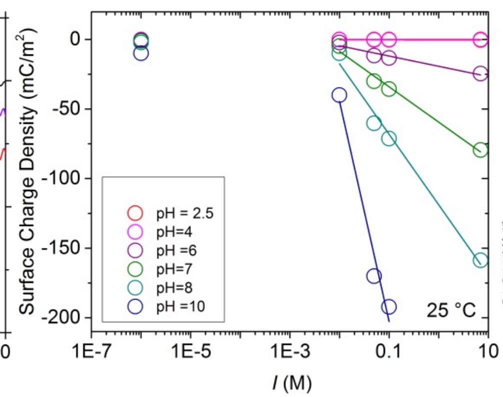


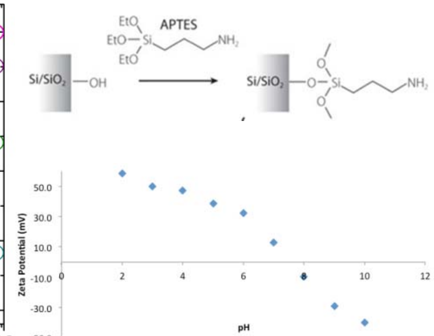


Testing high temperature/pressure performance, development of calibration strategy, and new materials/functionalization for enhanced performance









Expansion of Subsurface Sensing Activity Moving Forward

Expanding pH Sensing Activities to Higher Pressure and Temperature Environments, and Exploring New Functional Sensing Materials

Expanding Beyond pH to Other Chemical Parameters of Direct Relevance:

1) *CO_2 Measurement (CO_2 Migration in Geological Formations)*
2) *CH_4 Measurement (Wellbore Monitoring, Leak Detection)*

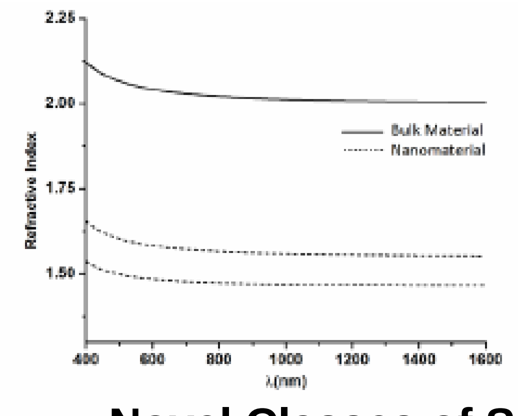
Conditions	Downhole Drilling	Deep/Ultra-deep	Geological CO_2 Sequestration (Vilarrasa et al., 2013)
Depth of interest (feet)	1,500–13,500	30,000–40, 000	6,000–7,000
Temperature (K)	Up to 470	Up to 580	Up to 370
Pressure (psi)	Up to over 10,000	Up to 30,000	Up to 3,000
Typical pH	4–8	4–8	2–6

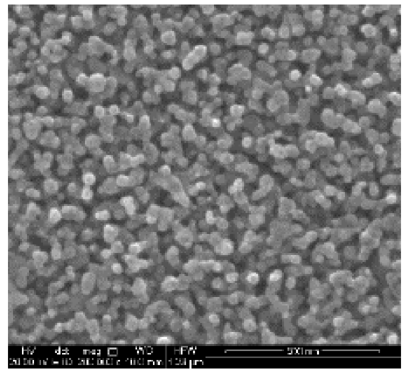
Sensor Development for Embedded Sensing in Subsurface Applications

Opportunities to Collaborate with the In-House Sensor Material and Device R&D Team

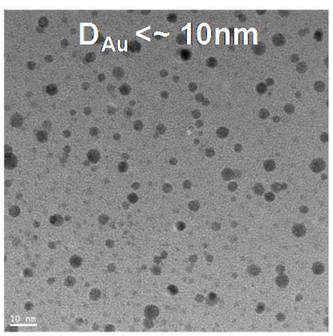
Licensing Opportunities for In-House Sensor Related Patents

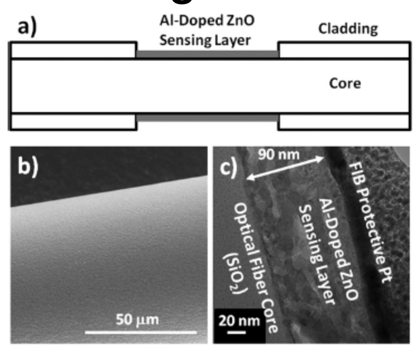
Nanostructuring to Tailor Refractive Index for Device Compatibility





Novel Classes of Sensing Materials





Sensor Material Approaches for Harsh Environment Sensing

Novel Sensor Applications in a Solid Oxide Fuel Cell Environment

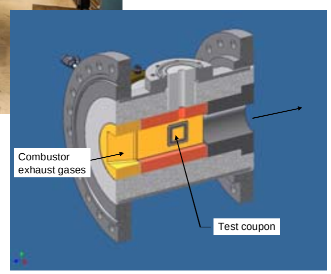
A significant patent portfolio has been established by the in-house research team and collaborators, licensing and technology development partnership opportunities exist.

We are Seeking to Build Stronger Industrial Collaborations and Relationships.

Sensors Testing Opportunity at NETL

NETL currently has two (2) facilities available to support sensors testing.

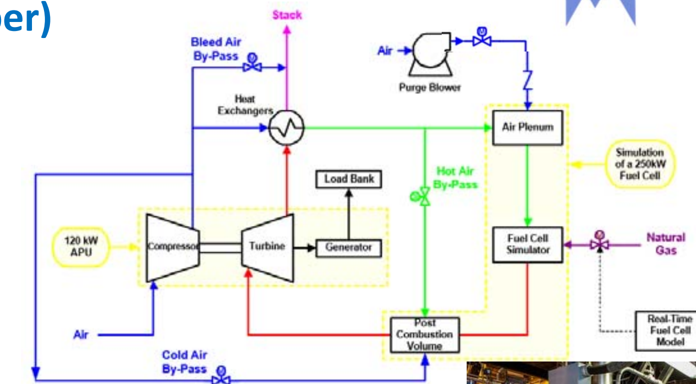
High-Pressure Combustion Facility (Aerothermal Rig)



- Simulates hot gas path of a turbine
- Natural gas or hydrogen fuel
- Capable of 2 lb/s air flow @ 10atm
- Temperature: up to 1300°C
- Optically-accessible combustor and test sections

NETL is currently identifying more facilities and working to streamline internal approval process.

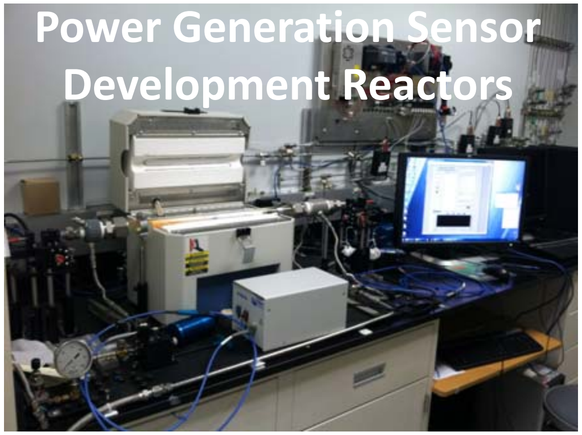
Hybrid Performance Facility (Hyper)



- 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
- 100+ process variables measured including rotational speed (1,200Hz; 40,500 rpm), air/fuel flow, temperature (turbine: 637°C; SOFC: 1133°C), pressure (up to 260kPa), etc.

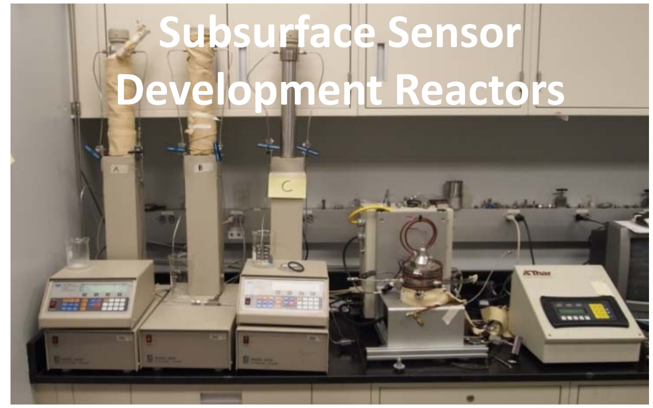
Opportunities for Collaborative Technology Development w/ NETL

NETL has a number of well equipped laboratories for in-house sensor and sensor material research and development activities.



High temperature reaction chambers with automated gas flows and temperature control.

- H_2, CH_4, CO, CO_2, N_2, O_2
- 2 Ambient pressure reactors, up to 1000°C
- 1 Pressurized reactor, up to 900psi, 850°C
- Electrical and optical access for various instrumentation, probes, and devices



Intermediate temperature and elevated pressure reaction chambers with automated gas /fluid flows.

- CH_4, CO_2, N_2, O_2
- 1 Intermediate pressure reactor, up to 3500psi and 150 or 350°C (depending on vessel)
- 1 High pressure reactor, up to 10000psi and 350°C (in construction)
- Probe access

NETL also has significant expertise and facilities for materials development and characterization, applied spectroscopy for sensing and diagnostics, and sensor device fabrication.

Conclusions and Summaries

- **Needs Exist for Harsh Environment Sensors**
  - Power Generation Applications (Combustion, SOFCs, Turbines)
  - Subsurface Environments (CO_2 Sequestration, Unconventional Oil & Gas)
- **Advanced Materials Enable Harsh Environment Compatible Sensors**
  - Particular Focus / Needs for Optical Materials
  - Electrical, Electrochemical, and Even Magnetic Materials are Also of Interest
- **Power Generation Sensors**
  - Early Focus on SOFC Applications as a Demonstration Platform
  - Planned Expansion to Other Power Generation Technologies
- **Subsurface Environment Sensors**
  - Early Focus on pH (Corrosion, Scaling, Key Parameter for Geochemistry)
  - Planned Expansion to CO_2, CH_4, Elevated Temperatures, Elevated Pressures
- **Opportunity Exist for Collaborative Technology Development**
  - Licensing of Developed IP
  - Collaborative Research Activities and Joint Proposals
  - Sensor Demonstration and Testing at Pilot Scale Facilities

Acknowledgements and Funding Sources

- **Sydni Credle, Barbara Carney, Jessica Mullen, Robie Lewis, Steven Seachman, Susan Maley, Robert Romanosky (the Crosscutting Research Program Management Team)**
  - Direct Funding Support Through the Crosscutting Research Program
  - Opportunities to Integrate and Collaborate with the Crosscutting Program

- **Alexandra Hakala, Christina Lopano, Angela Goodman, Kirk Gerdes, Shiwoo Lee**
  - Direct Funding Support Through Unconventional Oil & Gas and CO_2 Storage Programs
  - Collaborations and Demonstrations in Realistic Environments (e.g. SOFC)

- **Michael Carpenter, Kevin Chen, Gary Pickrell, Anbo Wang, Puxian Gao, Junhang Dong, Henry Du, Alan Wang, and Chih-Hung Chang (and their teams)**
  - Collaborations on NETL-Funded Extramural Programs
  - Development of New Future R&D Concepts and Joint Proposal Activities
  - Collaborative Joint Mentoring of Students

Come Speak to Me About Potential Collaborations with the NETL In-House Research Team to Promote the Crosscutting Research Program and the NETL Mission.

We are Seeking to Build Stronger Industrial Collaborations and Relationships.