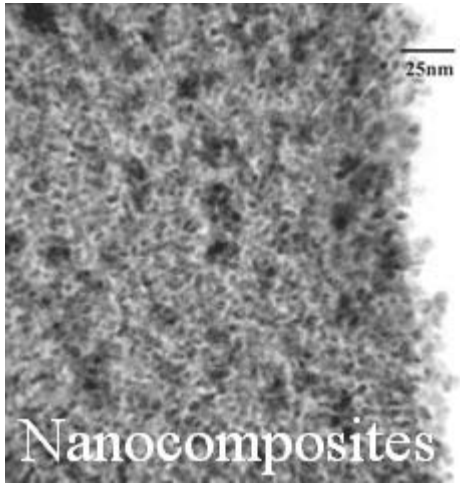

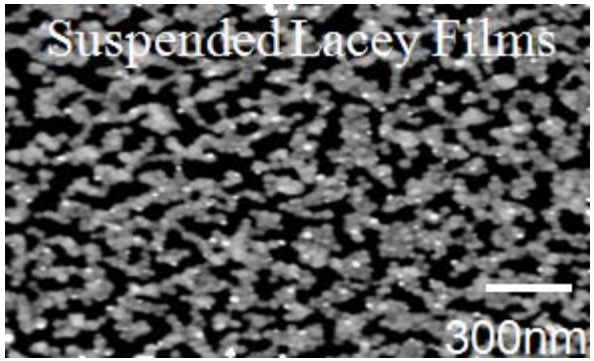

Plasmonic-Based Harsh Environment Compatible Chemical Sensors

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College of NanoScale Science and Engineering
Energy & Environmental Technology Applications Center
University at Albany – SUNY

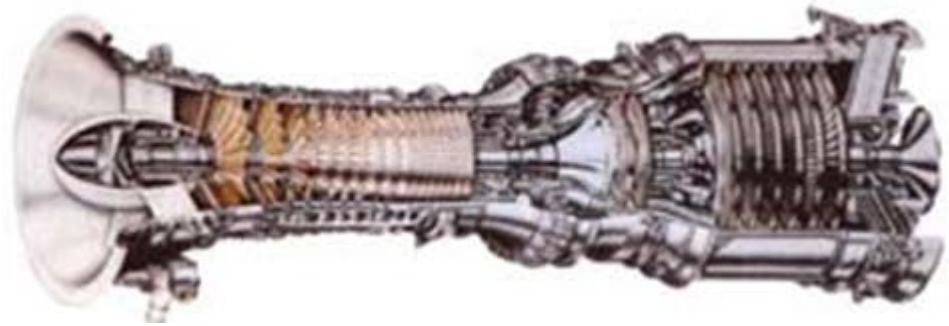
6/2/10

Harsh Environment Chemical Sensors

Need for new sensing technologies to meet the requirements for zero emission energy sources

Overview

- CO, H_2, NO_x, R_xS
- 500-800 C operating environment
- SOFC, Jet engines, turbines
- Optical analysis of SPR Au NPs
- YSZ matrix material

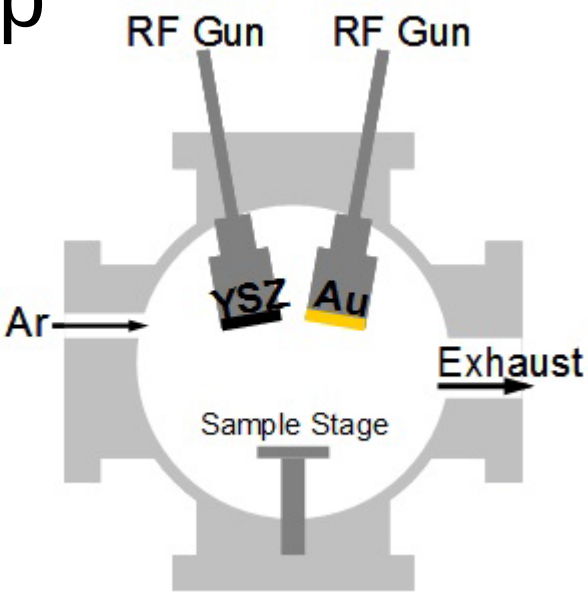


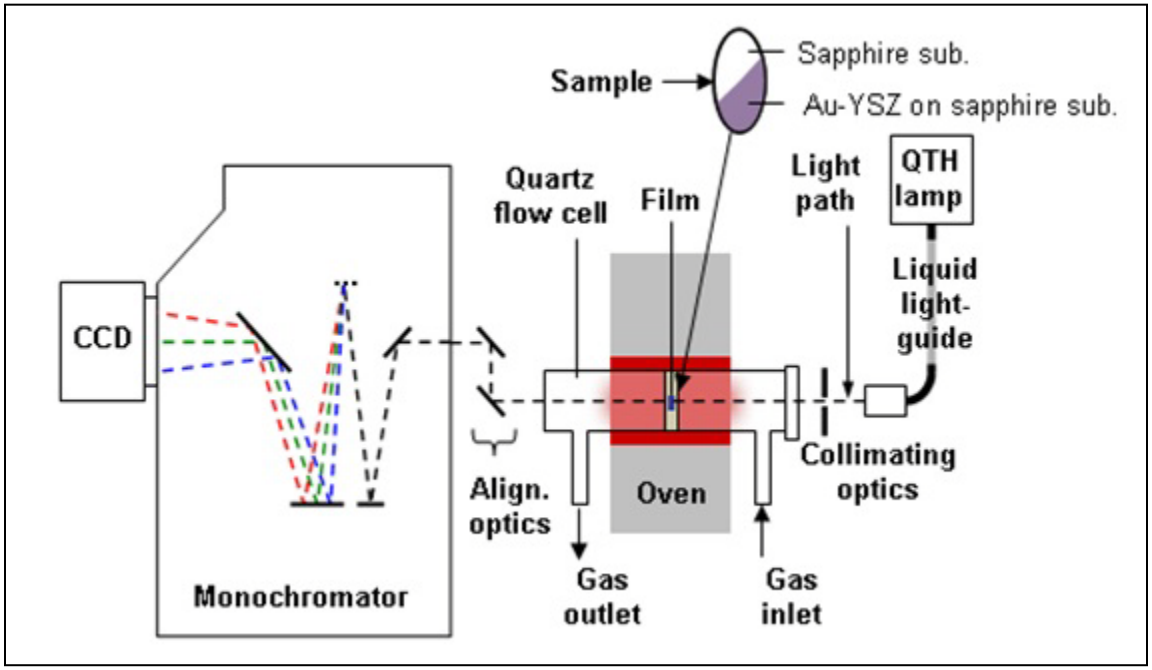
Goals of Research are Two-Fold

1. Develop prototype materials for use in next generation sensing devices
   - ➢ Sensitivity, reliability, selectivity
2. Determine fundamental material properties/reactions/kinetics which govern the sensing mechanism

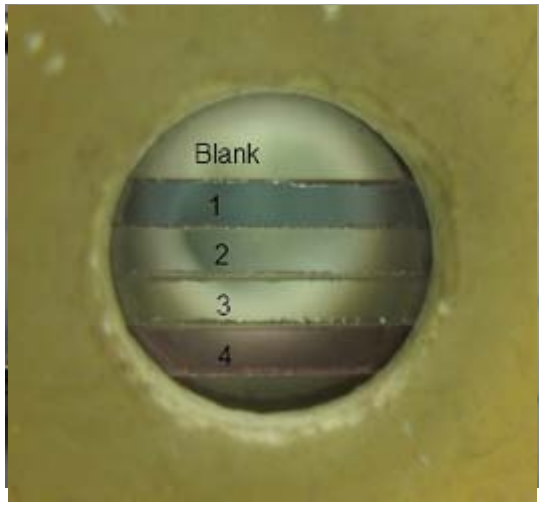
Experimental Setup

- Sample preparation
  - **PVD deposition of 10 at. % Au-YSZ films in 5 mtorr of Ar**
  - **Film thickness is varied by changing deposition time**
  - **Films are annealed at ~ 970 C for 3 hours at 760 torr and ~2000 sccm of Ar**

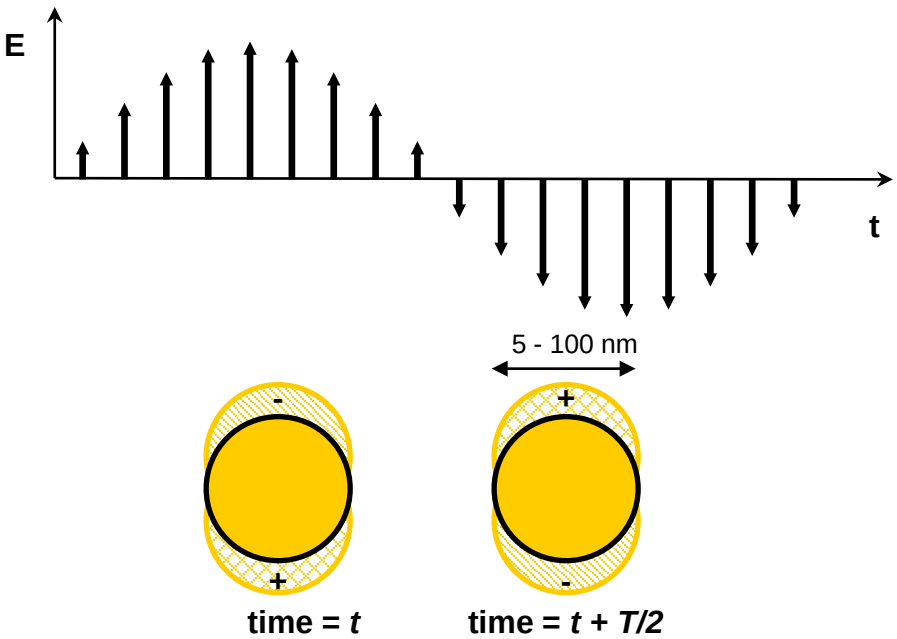


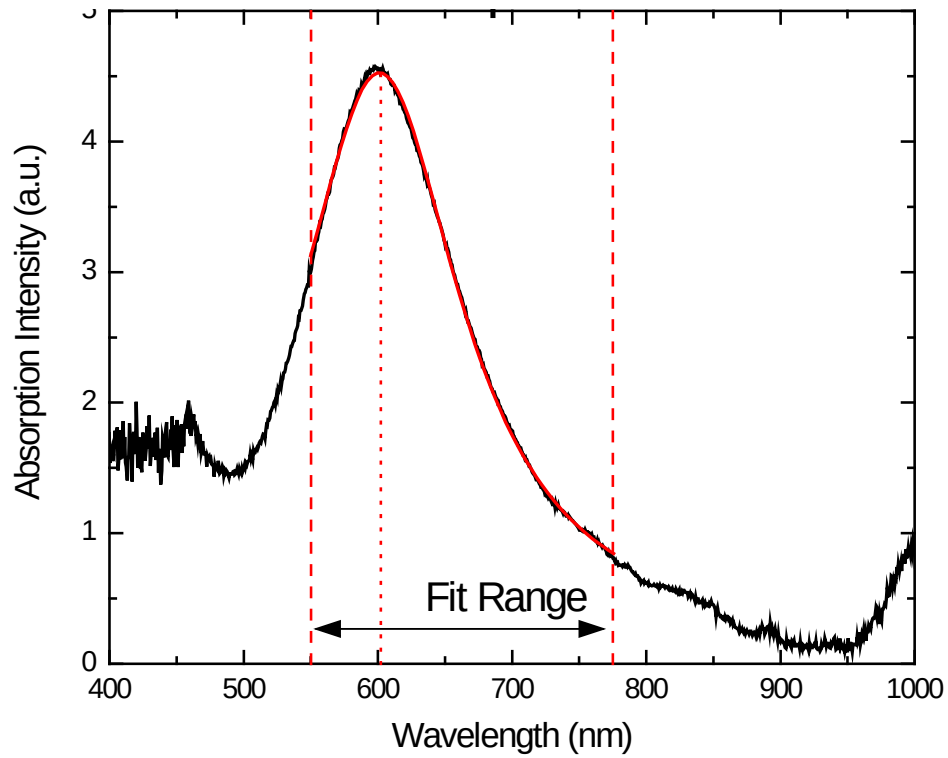


Gas exposure bench



Background - Au Nanoparticles as Optical Beacons For Transduction Events





SPR: Surface Plasmon Resonance

$$\Omega = \sqrt{\frac{Ne^2}{\left(1 + 2\varepsilon_m + \chi^{ib}(\Omega)\right) m_e \varepsilon_0}}$$

Ω - SPR Frequency

N - free electron density

m_e - electron mass

ε_0 - permittivity of free space

ε_m - matrix (YSZ) dielectric constant

$\chi^{ib}(\Omega)$ - Interband trans. dielectric const.

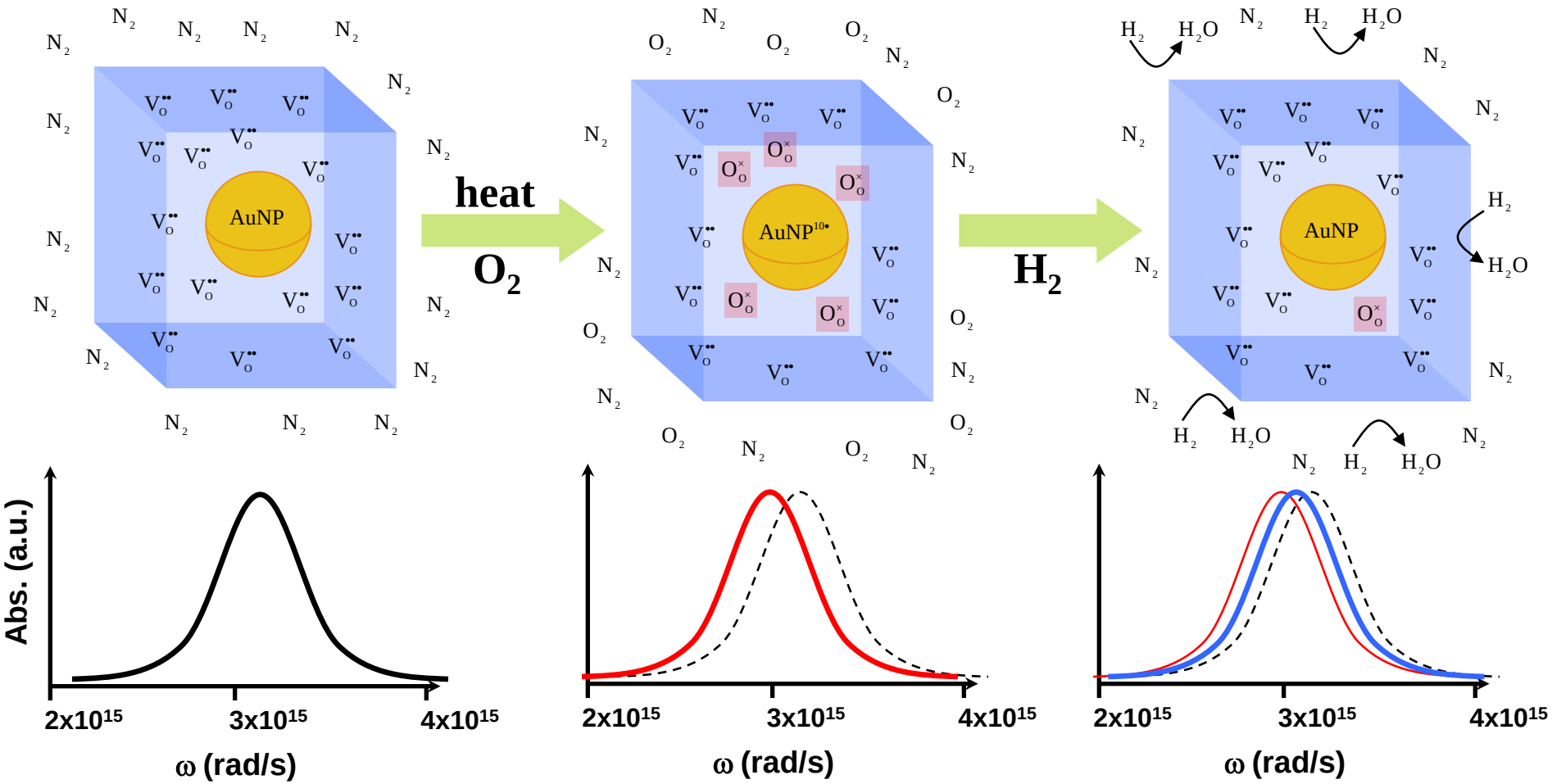
Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer, Berlin, 1995

H_2 Studies

Volume cell of one AuNP and corresponding YSZ matrix in inert gas

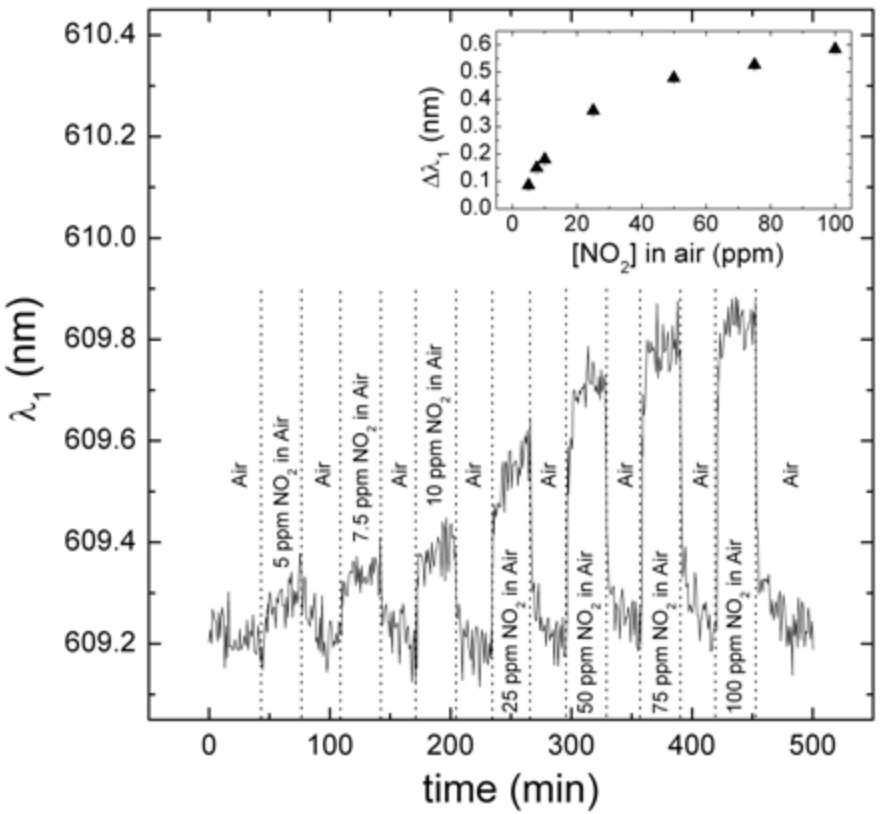
Same volume cell exposed to a AuNP oxidizing gas

Volume cell then exposed to a AuNP reducing gas



- YSZ is an oxygen ion conductor above ~350°C

An assumption with the current model is that the dielectric function is constant

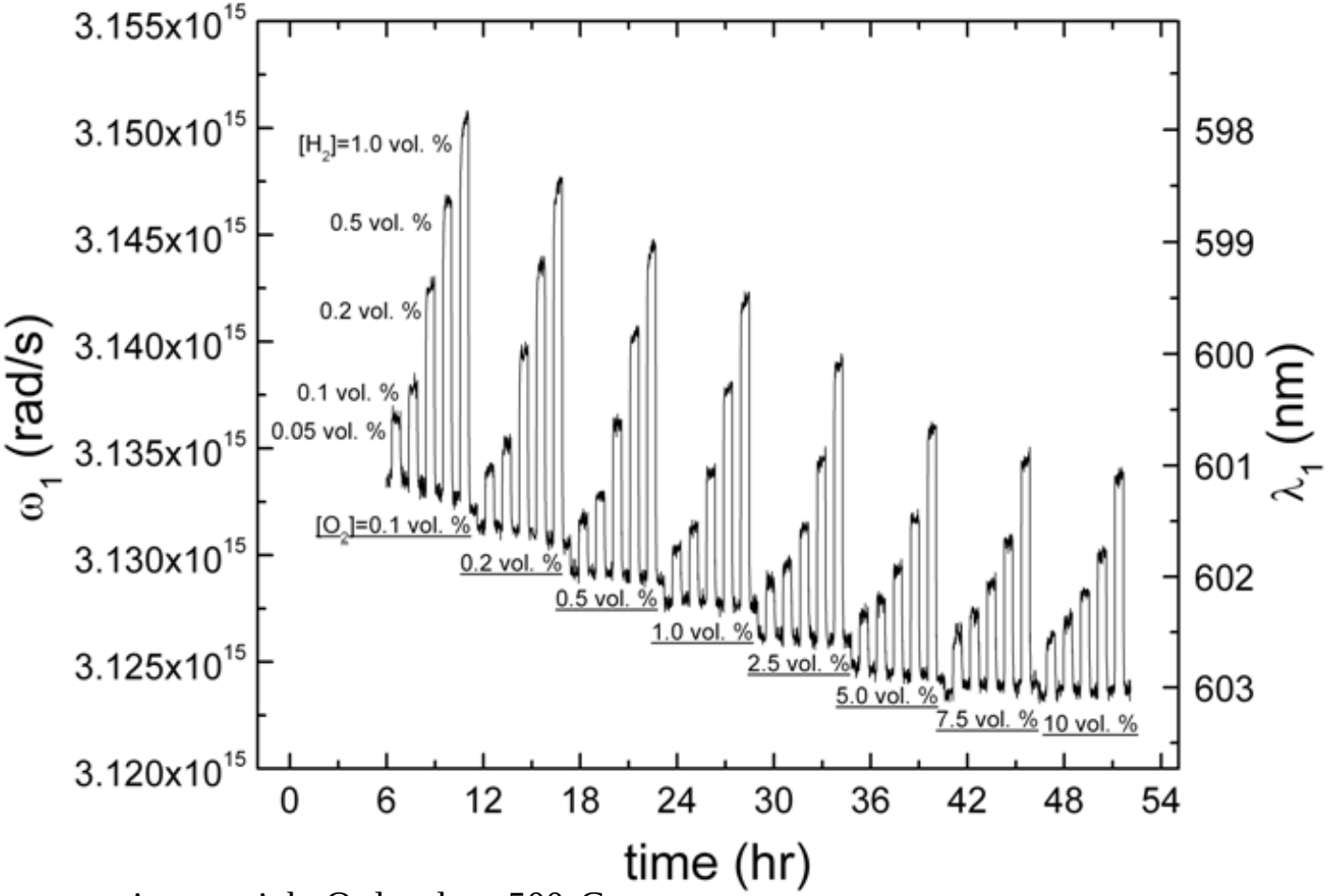


$$\Omega = \sqrt{\frac{Ne^2}{\left(1 + 2\varepsilon_m + \chi^{ib}(\Omega)\right) m_e \varepsilon_0}}$$

- Filling oxygen vacancies likely increases polarizability of material
- *Dielectric function should increase as well*
- $\uparrow\varepsilon_m$ will cause red shift in SPR
- Coincides with $\downarrow$N on filling oxygen vacancies

Deconvolution of ΔN and $\Delta\varepsilon_m$ requires in-situ measurement of ε_m which is of interest

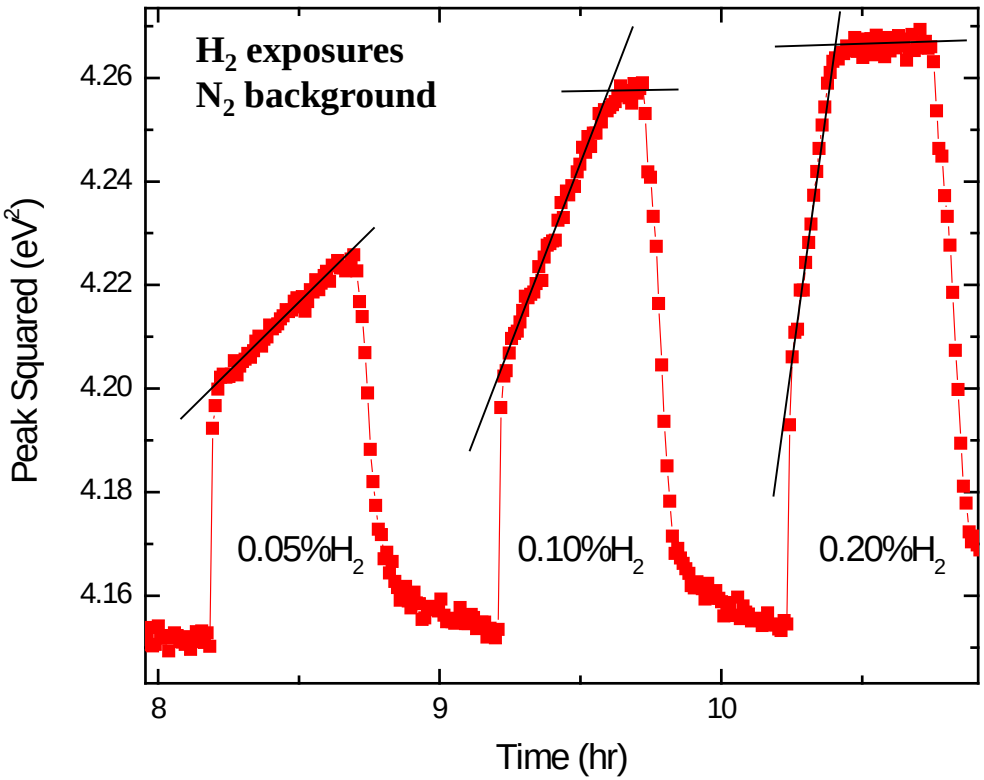
Experimental Results: H_2/O_2 Titration



- Five H_2 Concentrations at eight O_2 levels at 500 C
- Signal change used to examine electrochemical charge transfer between AuNPs and diffusing oxygen ions
- Stable over long periods

Rogers, P. H.; Sirinakis, G.; Carpenter, M. A. *J. Phys. Chem. C* 2008, *112*, 6749

Hydrogen Spillover Kinetics: Plasmonics Study



$$\Omega = \sqrt{\frac{Ne^2}{\left(1+2\varepsilon_m+\chi^{ib}(\Omega)\right)m_e\varepsilon_0}}$$

$$\downarrow$$

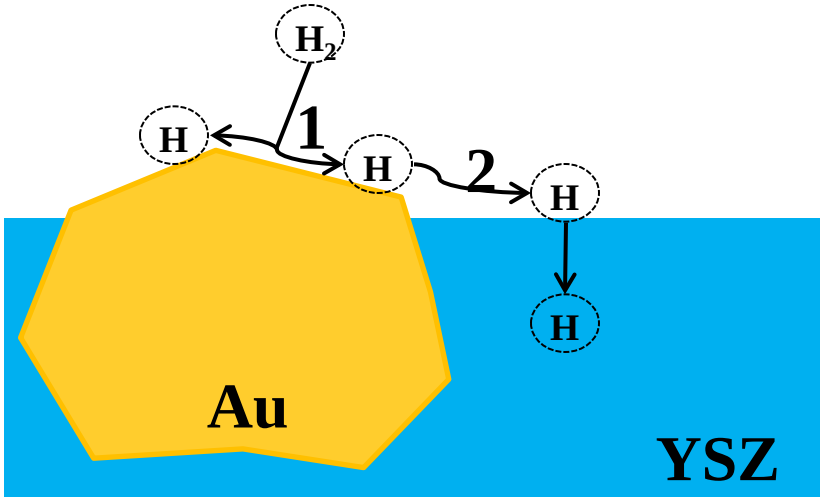
$$\frac{d\Omega^2}{dt} = C\cdot\frac{dN}{dt}$$

$$\downarrow$$

- **Measure of the reaction rate**
- **Dependent on H_2 partial pressure**

Understanding the reaction pathway can lead to better gas selectivity by design

Hydrogen Spillover Reactions



$$(1) \quad \frac{1}{2}H_2^{(g)} + S \leftrightarrow H^{(ad)}$$

$$(2) \quad H^{(ad)} \leftrightarrow H^{(inc)}$$

$$r_2 \propto P_{H_2}^{1/2}$$

Example of Similar Work: Au on TiO_2 [1]

- H_2 dissociative adsorption on Au
- H spillover to TiO_2 forming shallow trap states
- Probed by FTIR

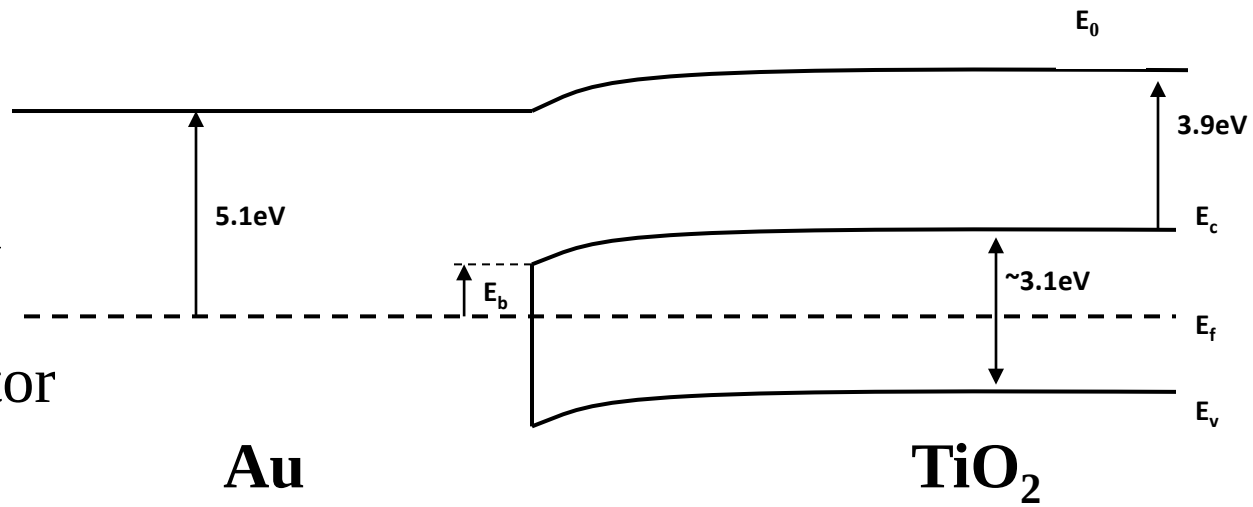
- YSZ: wide band gap, less likely to form trap states

[1] D.A. Panayotov and J.T. Yates Jr, "Spectroscopic Detection of Hydrogen Atom Spillover from Au Nanoparticles Supported on TiO2: Use of Conduction Band Electrons," 2007.

Au/Metal Oxide Band Diagrams: Comparing TiO_2 with YSZ

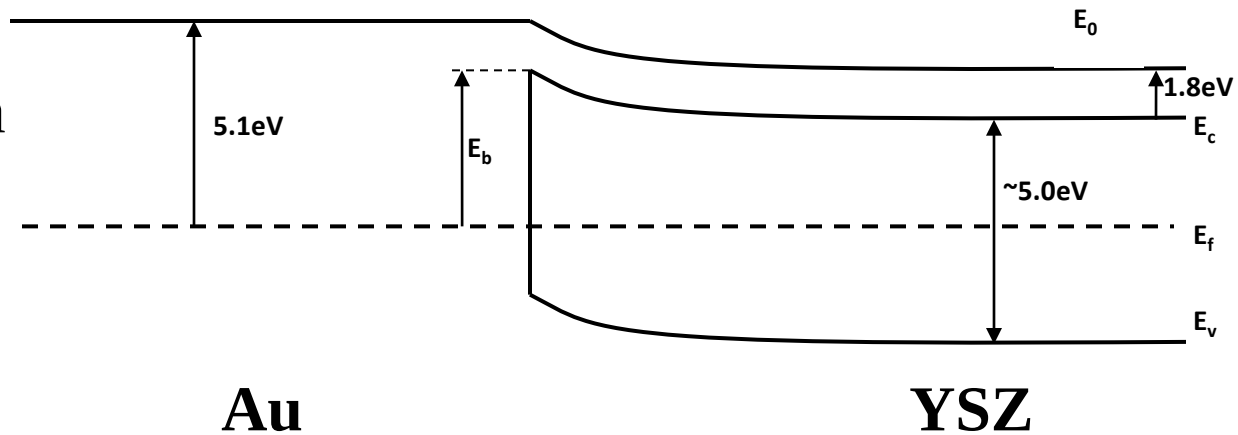
Au/TiO_2

Ti Stable Oxidation States: 4+, 3+, 2+
n-type semiconductor



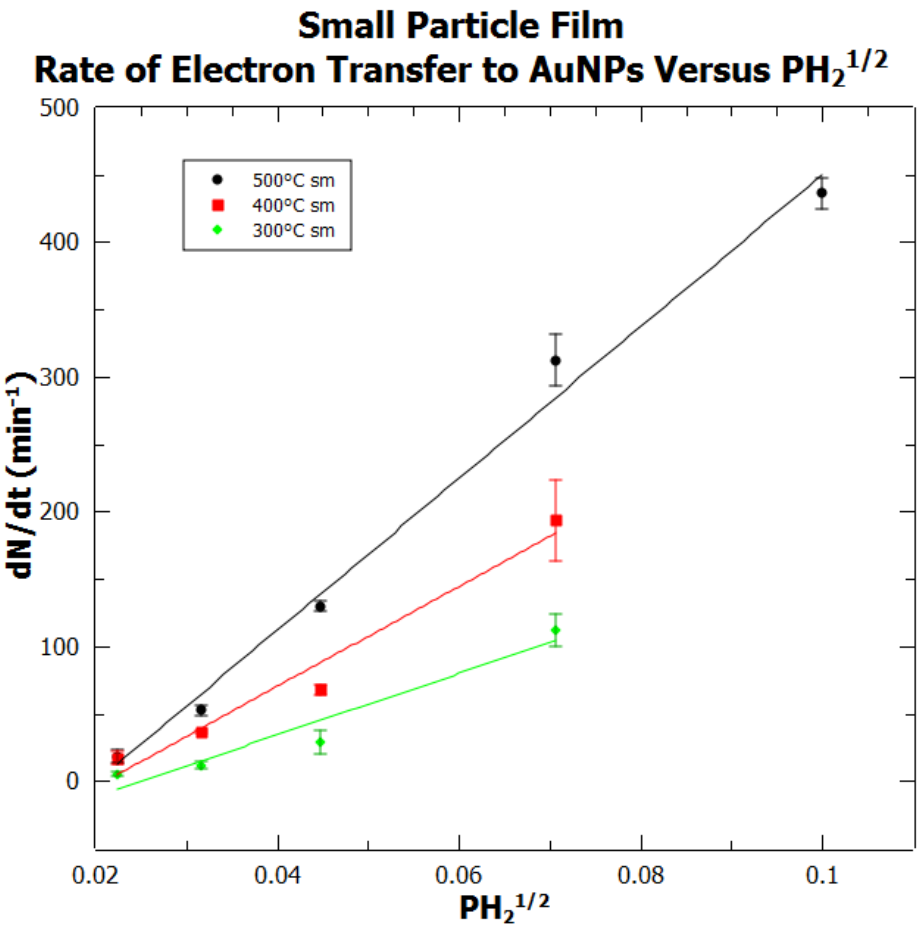
Au/ZrO_2

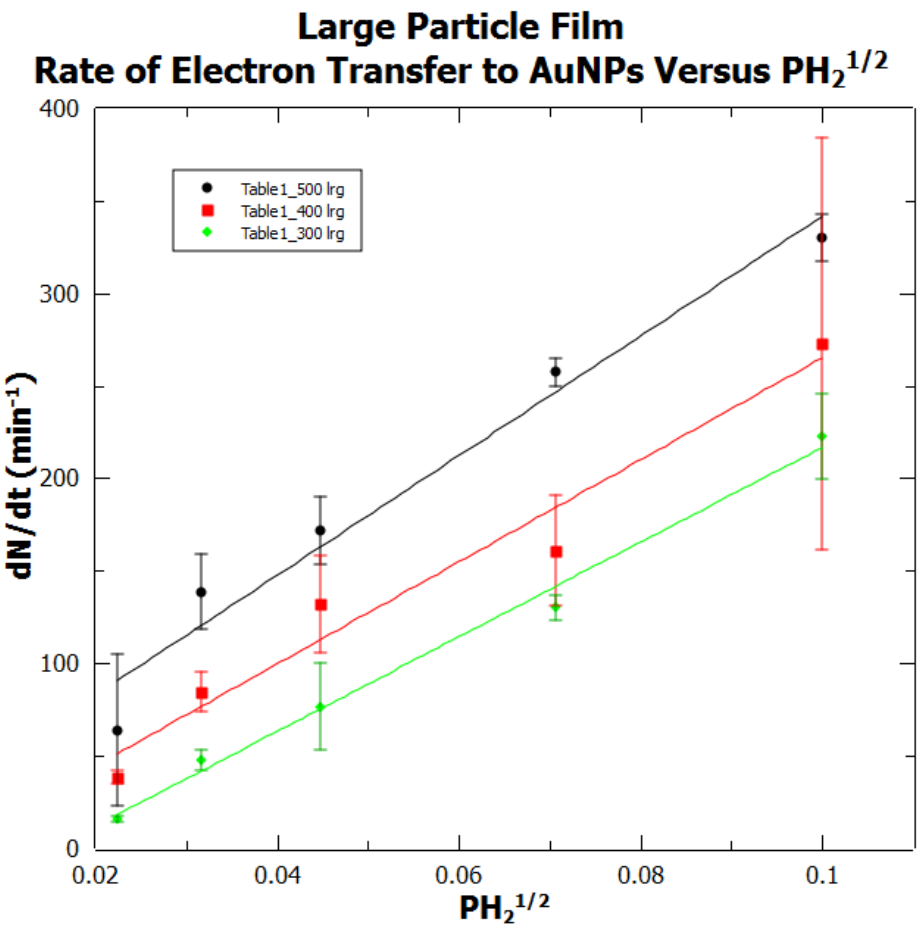
Zr Stable Oxidation States: 4+
Wide band gap insulating oxide



Manzoli, Chiorino, Boccuzzi, Surf. Sci., 532-535, 377 (2003)

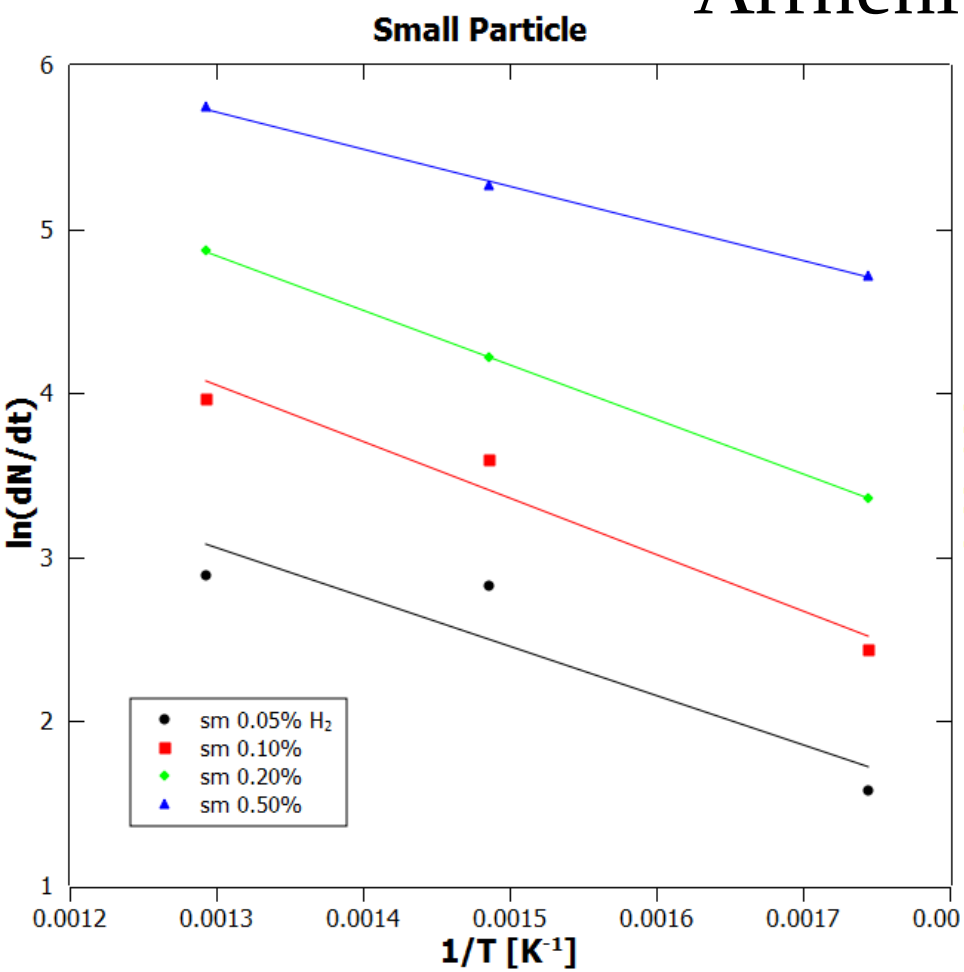
Reaction Rate Versus $P_{H_2}^{1/2}$

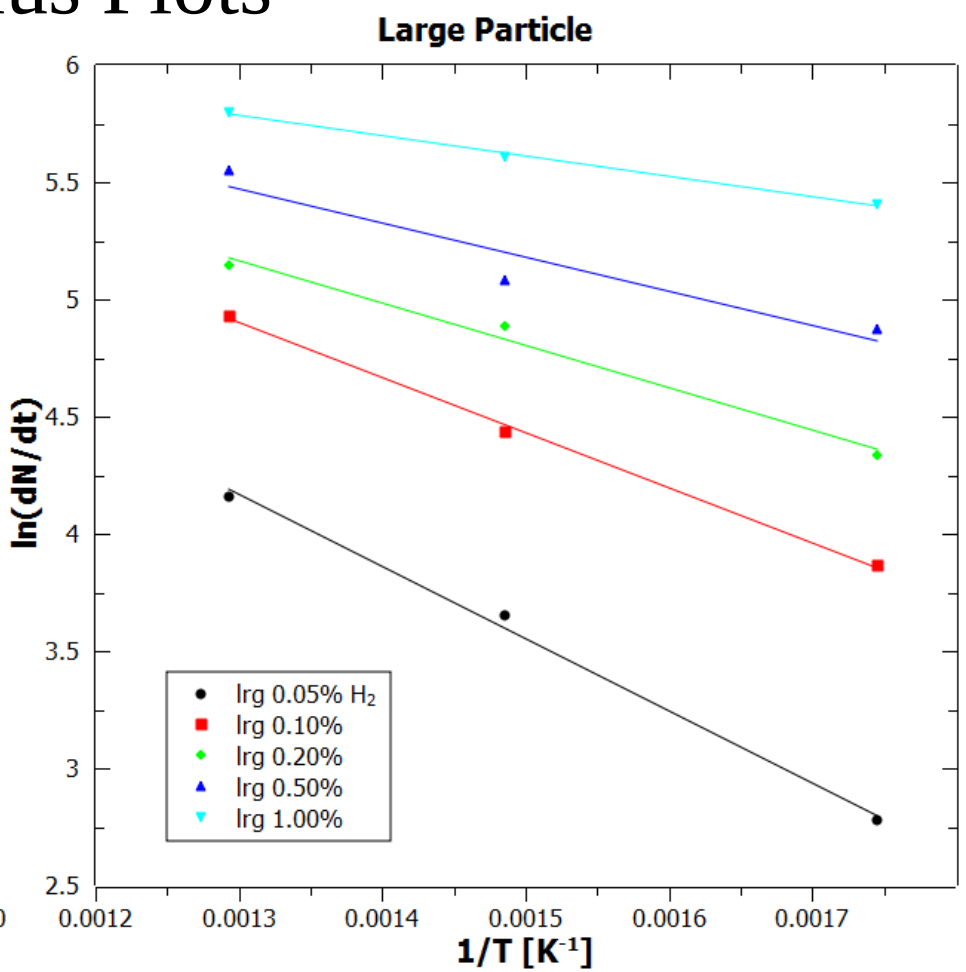




$$rate \propto P_{H_2}^{1/2}$$

Arrhenius Plots



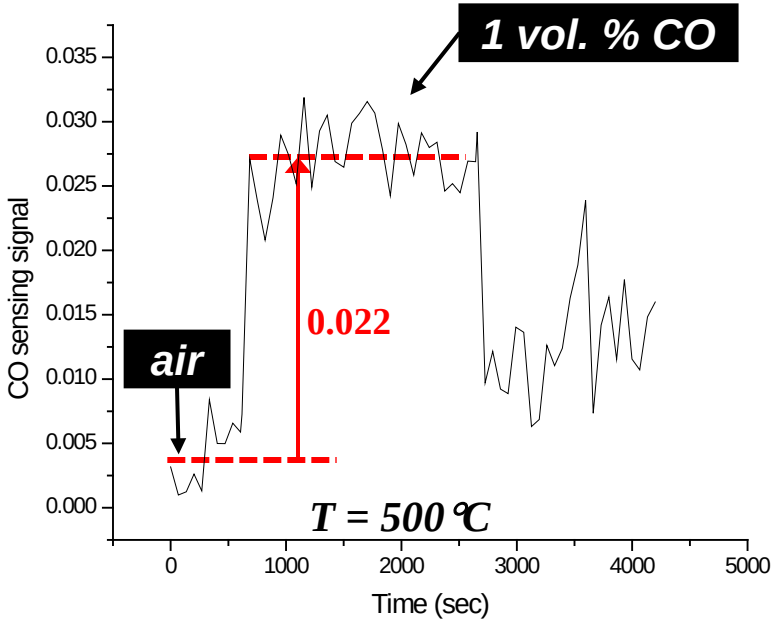


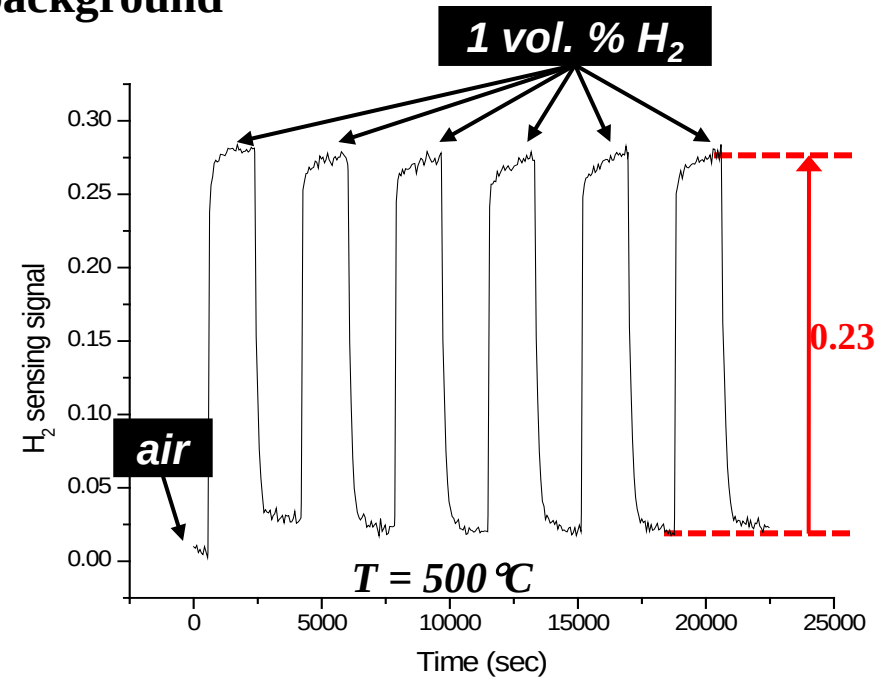
Average E_a for both films is ~0.2 eV

$$\ln\left(\frac{dN}{dt}\right) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$$

Selectivity Demonstration

- **Single Au-YSZ nanocomposite**
- **~25nm Au nanoparticles**
- **Exposed to 1% CO or Hydrogen in air background**



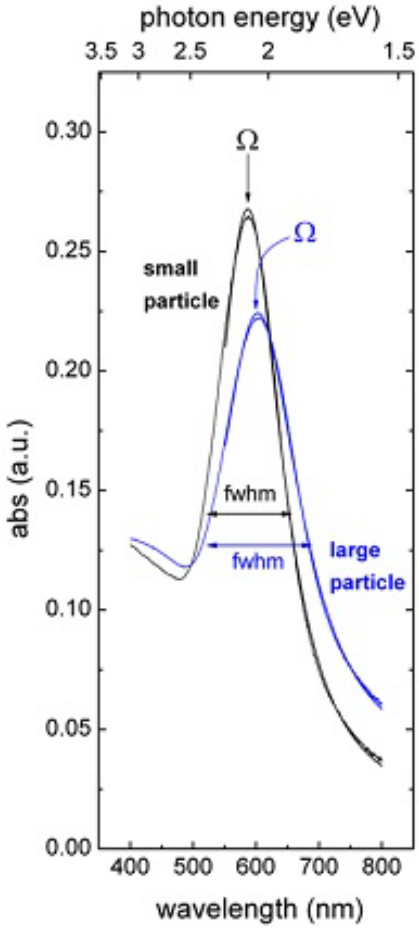


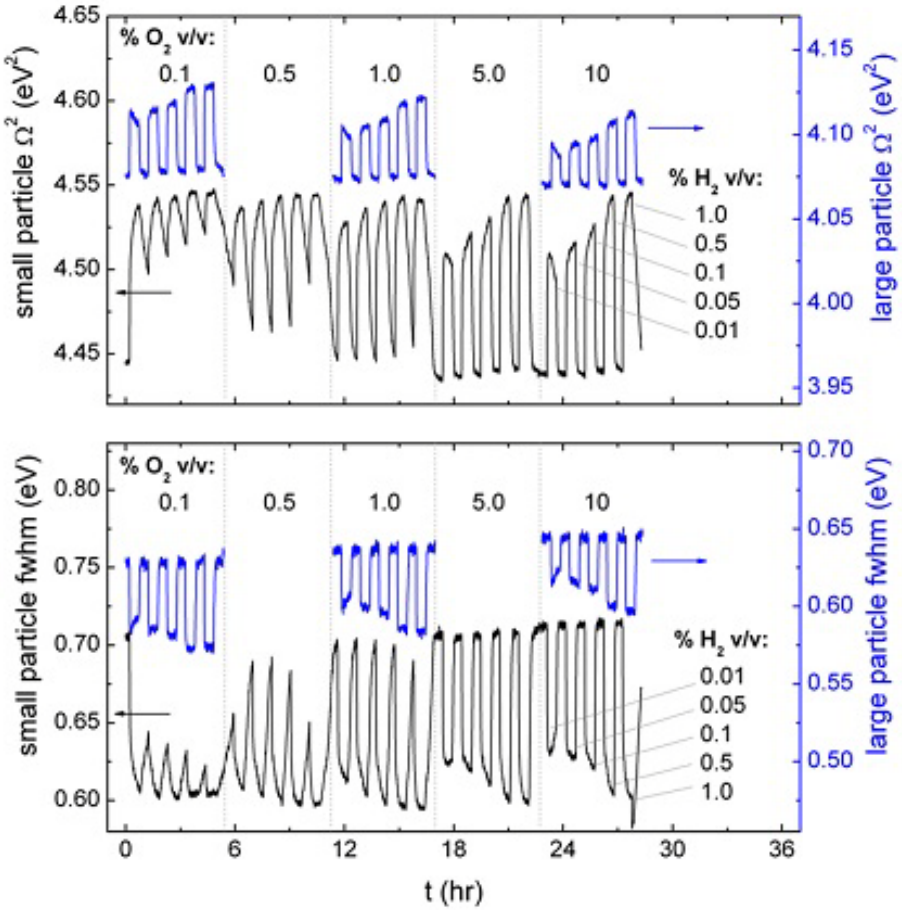
More than 10x signal change for H_2

Selectivity is induced through control of the resulting Au nanoparticle size as CO preferentially reacts with smaller Au nanoparticles

Particle Size Effects: Further Investigation

- **Small particle: 8nm**
- **Large particle: 18nm**
- **Small particles indeed more sensitive, however time response is also dependent on matrix material characteristics**





Rogers, P.H., Carpenter, M.A., Accepted J. Phys. Chem. C, as of May 2010

Mechanistic Details – surface and core reactions

Oxygen Reactions

$$O'_{(s)} \xleftrightarrow{k_1} \frac{1}{2}O_{2(g)} + V^{\times}_{(s)} + e'_{AuNP}$$

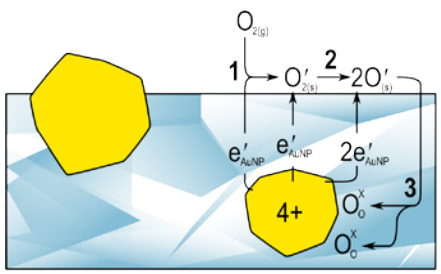
$$AuNP^{\bullet} + e'_{AuNP} \xleftrightarrow{k_2} AuNP$$

Surface

$$O^{\times}_{O} \xleftrightarrow{k_3} \frac{1}{2}O_{2(g)} + V^{\bullet\bullet}_{O} + 2e'_{AuNP}$$

$$AuNP^{\bullet\bullet} + 2e'_{AuNP} \xleftrightarrow{k_4} AuNP$$

Core



Hydrogen Reactions

$$H_{2(g)} + O'_{(s)} \xleftrightarrow{k_6} H_2O_{(g)} + V^{\times}_{(s)} + e'_{AuNP}$$

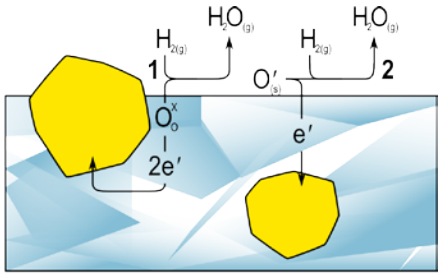
$$AuNP^{\bullet} + e'_{AuNP} \xleftrightarrow{k_6} AuNP$$

Surface

$$H_{2(g)} + O^{\times}_{O} \xleftrightarrow{k_7} H_2O_{(g)} + V^{\bullet\bullet}_{O} + 2e'_{AuNP}$$

$$AuNP^{\bullet\bullet} + 2e'_{AuNP} \xleftrightarrow{k_8} AuNP$$

Core



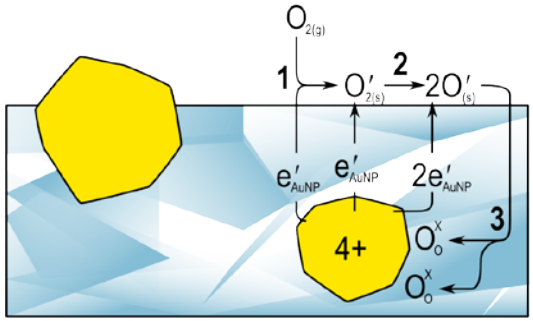
Net Reactions

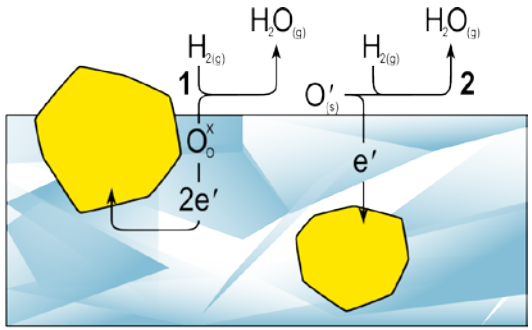
$$H_{2(g)} + 2O'_{(s)} \xleftrightarrow{K_a} H_2O_{(g)} + \frac{1}{2}O_{2(g)} + 2V^{\times}_{(s)} + 2e'_{AuNP}$$

$$2AuNP^{\bullet} + 2e'_{AuNP} \xleftrightarrow{K_b} 2AuNP$$

$$H_{2(g)} + 2O^{\times}_{O} \xleftrightarrow{K_c} H_2O_{(g)} + \frac{1}{2}O_{2(g)} + 2V^{\bullet\bullet}_{O} + 4e'_{AuNP}$$

$$2AuNP^{\bullet\bullet} + 4e'_{AuNP} \xleftrightarrow{K_d} 2AuNP$$





$$K_a = \frac{P_{H_2O}\left[V^{\times}_{(s)}\right]^2\left[e'_{AuNP}\right]^2}{\left[O'_{(s)}\right]^2}\frac{P^{1/2}_{O_2}}{P_{H_2}}$$

$$K_b = \frac{[AuNP]}{\left[AuNP^{\bullet}\right]\left[e'_{AuNP}\right]}$$

$$K_c = \frac{P_{H_2O}\left[V^{\bullet\bullet}_{O}\right]^2\left[e'_{AuNP}\right]^4}{\left[O^{\times}_{O}\right]^2}\frac{P^{1/2}_{O_2}}{P_{H_2}}$$

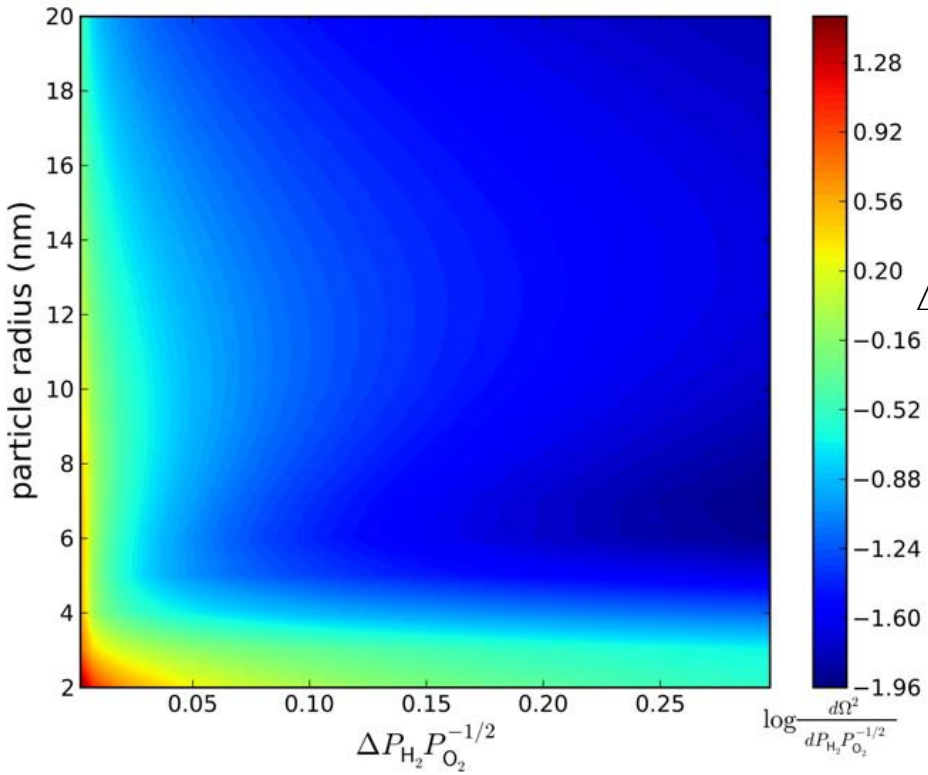
$$K_d = \frac{[AuNP]}{\left[AuNP^{\bullet\bullet}\right]\left[e'_{AuNP}\right]^2}$$

Must numerically solve :

$$\Delta\Omega^2 \propto \Delta\left[e'_{AuNP}\right] = f\left(\Delta\frac{P_{H_2}}{P^{1/2}_{O_2}}, K_a, K_c, \left[V^{\bullet\bullet}_{O}\right]_0, \left[V^{\times}_{(s)}\right]_0, \left[e'_{AuNP}\right]_0\right)$$

Analysis Results - Sensitivity Predictions

Sensitivity Plot



From Drude model with interband contributions:

$$\Omega^2 = \frac{N_{AuNP} e^2}{\left(1 + 2\varepsilon_m + \mathrm{Re}\,\chi^{ib}(\Omega) + i\,\mathrm{Im}\,\chi^{ib}(\Omega)\right)\varepsilon_0 m_e}$$

$$\Delta\Omega^2 \propto \Delta[e'_{AuNP}] = f\left(\Delta \frac{P_{H_2}}{P_{O_2}^{1/2}}, K_a, K_c, [V_O^{\bullet\bullet}]_0, [V_{(s)}^{\times}]_0, [e'_{AuNP}]_0\right)$$

<u>Parameters used to generated this plot:</u>

- 5 wt % Y_2O_3 in ZrO_2
- 8 at % Au
- Constant gold content
- Constant total vacancies

Experimental Results: Model fits

Small Particle

Given:

$R = 4\,\text{nm}$

$P_{H_2O} = 1\times10^{-6}$

$[V_O^{\bullet\bullet}]_0 = 1720$

$\varepsilon_m = 4.41$

From Fit:

$K_a = 5.55\times10^{5}$

$K_c = 7.50\times10^{7}$

$[V_{O(s)}^{\times}]_0 = 425$

$\chi^2 = 0.00175$ (last 8 data pts ignored for fit)

Large Particle

Given:

$R = 9\,\text{nm}$

$P_{H_2O} = 1\times10^{-6}$

$[V_O^{\bullet\bullet}]_0 = 19596$

$\varepsilon_m = 4.41$

From Fit:

$K_a = 6.24\times10^{6}$

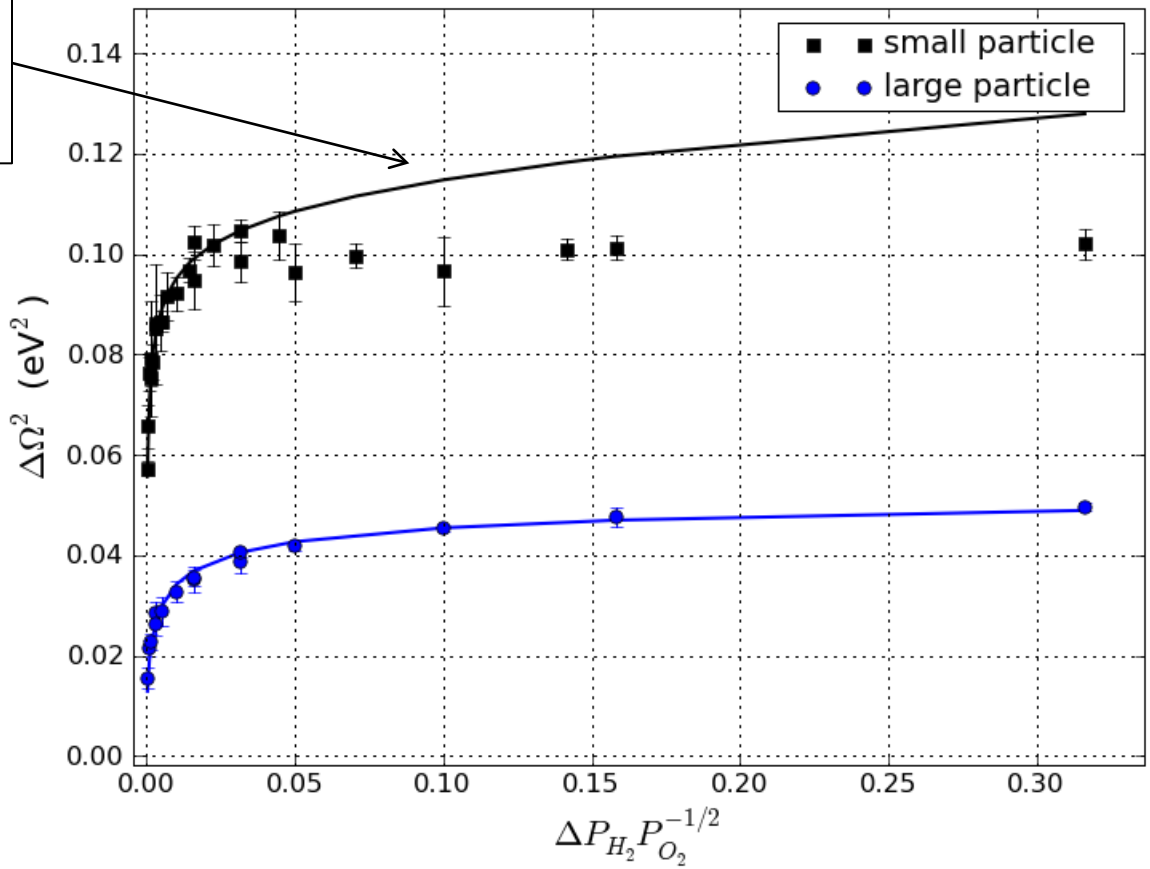
$K_c = 8.68\times10^{8}$

$[V_{O(s)}^{\times}]_0 = 2496$

$\chi^2 = 0.00122$

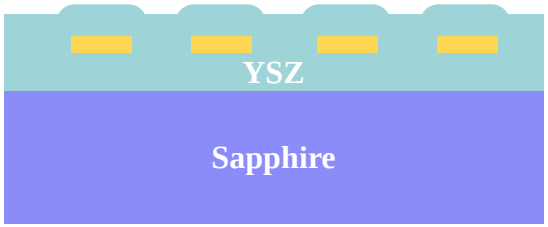
model predicts greater sensitivity due to ongoing removal of electrons

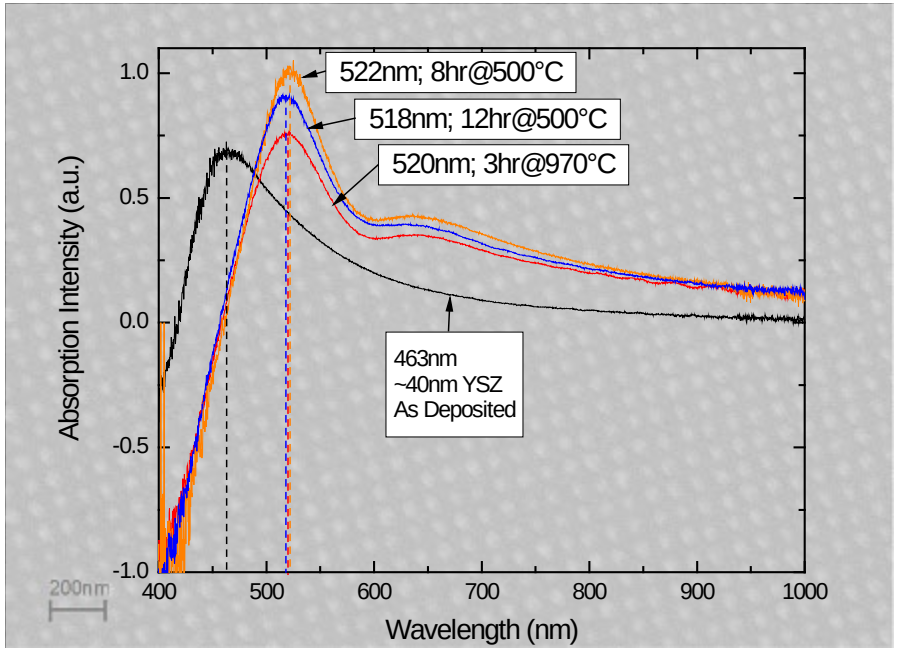
Calibration curves for small and large particle samples with model fits



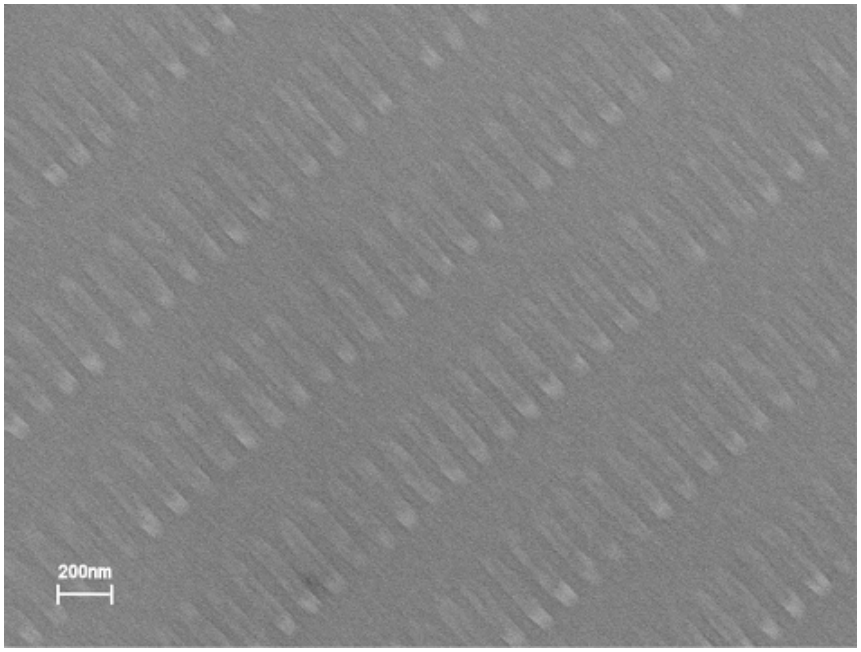
e-beam Patterned Gold

- **Excellent size control**
- **Encapsulation in YSZ for high-temperature stability**
- **Geometry control for multiple SPR modes**





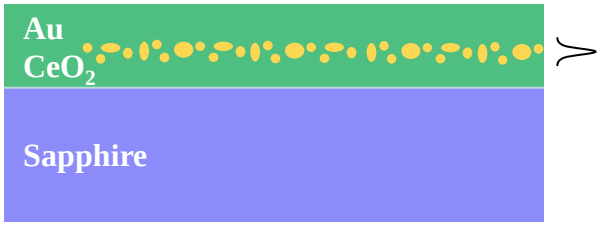
30nm platelets

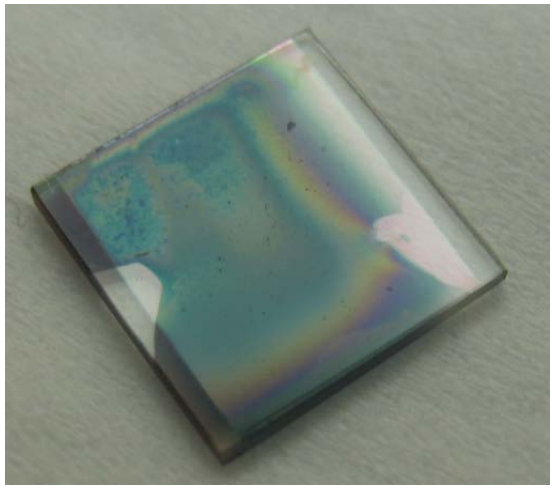


40 x 300nm rods

MBE Grown Cerium Dioxide

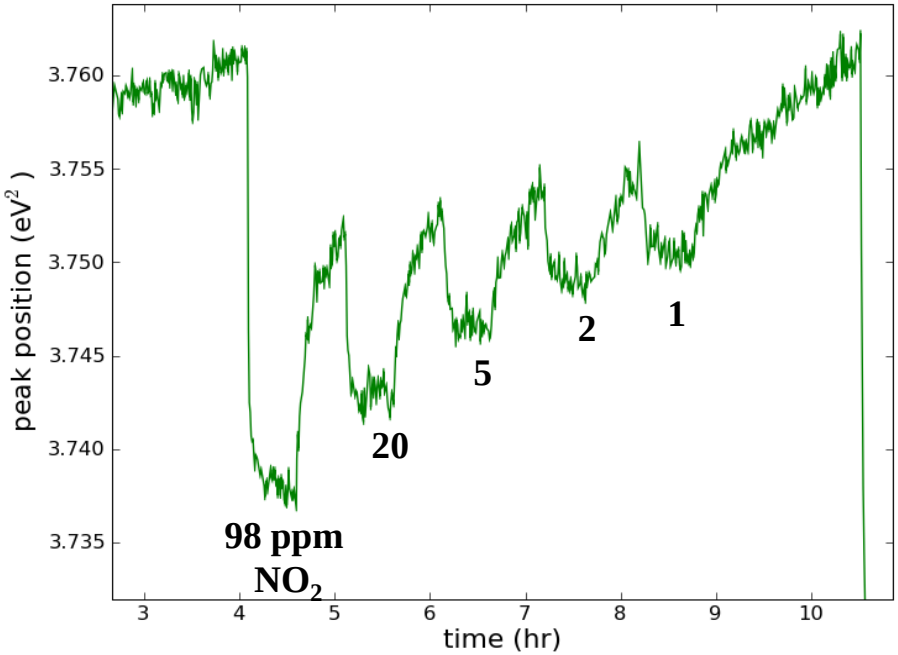
- **Different metal oxide affects:**
  - Catalytic properties
  - Oxygen ion conductivity
- **Improved crystalline quality**
- **Implanted Au - depth control**





Prepared by Pacific Northwest National Lab

Initial NO_2 exposure test
500 C, 0.1% O_2 background



Summary

- Plasmonic-based sensors are a promising candidate for harsh-environment sensing of emissions gases
  - *Robust / reliable*
  - *Optical method with no lasers required*
  - *SPR peak shift relates to analyte partial pressures*
- The SPR peak can also be used to monitor reaction kinetics
  - *e.g. Hydrogen dissociative adsorption*
- Gold Particle size investigated for selectivity
- Equilibrium model expanded to account for:
  - *Gold particle size*
  - *Surface reactions*
- e-beam patterned gold for size and shape control has begun
- Cerium dioxide grown by molecular beam epitaxy is being investigated for sensitivity and selectivity

Future Efforts

- Material Control for Sensitivity and Selectivity
  - Gold particle size:
    - e-beam lithography
    - Aerosol Assisted Deposition
    - Colloidal, wet-chemistry
  - Metal oxide matrix:
    - Molecular Beam Epitaxy
    - Alternative materials (cerium dioxide, titanium dioxide…)
- Experimental Methods
  - Multi-variable sensor array development
- Analysis
  - Multivariate analysis of arrays
  - Development of equilibrium and kinetic models

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- Prof. Michael Carpenter
- Dr. Phil Rogers*
- Pacific Northwest National Laboratory
- Prof. John Hartley & Ananthan Raghunathan

*Former Member

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- DOE – NETL
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