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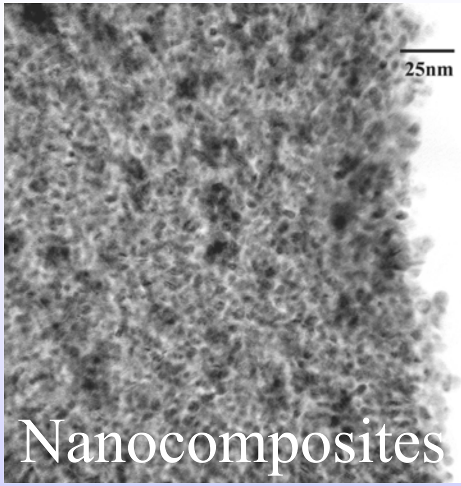

Feasibility of a Stack Integrated SOFC Optical Chemical Sensor

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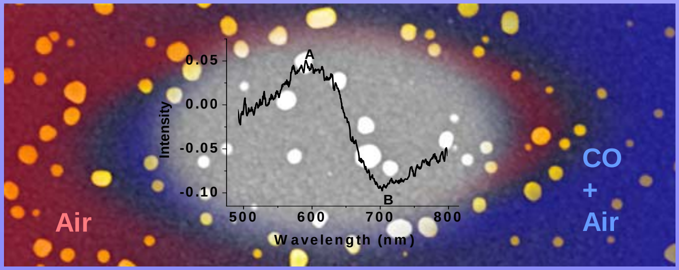
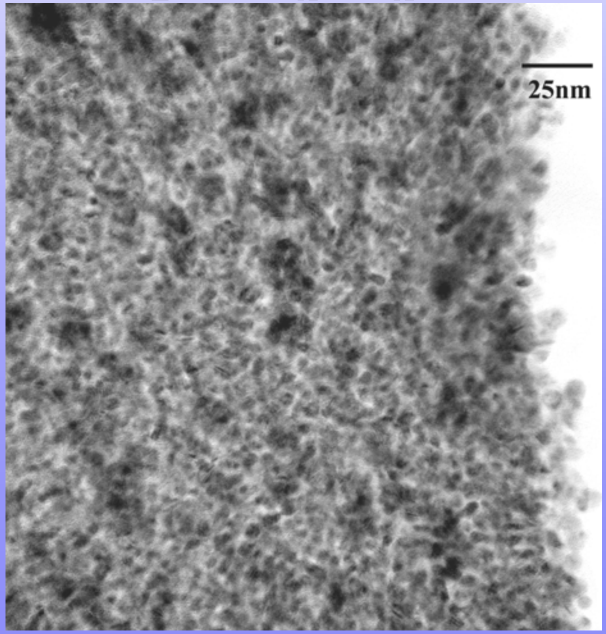


Harsh Environment Chemical Sensors

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

Nanocomposite Materials

- Optical analysis of Au SPR bands
- 500-800°C operating environment
- SOFC, Jet engines, turbines
- CO, H_2, NO_x, R_xS



TEM image, Au-YSZ nanocomposite

Goals of Research are Two-Fold

1. Develop prototype materials for use in next generation sensing devices
   - Sensitivity, reliability, selectivity
   - Integration - Need industrial partner
   - Prototypes
2. Determine fundamental material properties/dynamics/kinetics which govern the sensing mechanism

Materials Choice: why Au?

Catalytic Activity of Au Nanoparticles

- **Au in nanoparticle form exhibits surprisingly high catalytic activity**
  - 30nm Au nanoparticles were found to be active for the oxidation of CO

- **Supporting Au nanoparticles on metal oxides such as TiO_2 and ZrO_2 enhances their catalytic activity**
  - At temperatures below 200 °C TiO_2-supported exhibit higher catalytic activity than ZrO_2-supported Au nanoparticles
  - Above 200 °C both TiO_2 and ZrO_2-supported Au nanoparticle exhibit similar catalytic activity

- **Au nanoparticles exhibit significant potential as a sensing element for all-optical CO sensors**
  - catalytic reactions that are taking place during the CO oxidation on the perimeter of the nanoparticles are expected to have a discernable influence on the SPR band.

M. Haruta, M. Daté, Appl. Catal. A: Gen. 222, 427 (2001)
S. Arrii et al, J. Am. Chem. Soc. 126, 1199 (2004)

Metal Nanoparticles: Optical Properties

- **According to Mie theory the extinction cross section σ_{ext} of a *spherical Au* particle which is much smaller than the wavelength of incident light :**

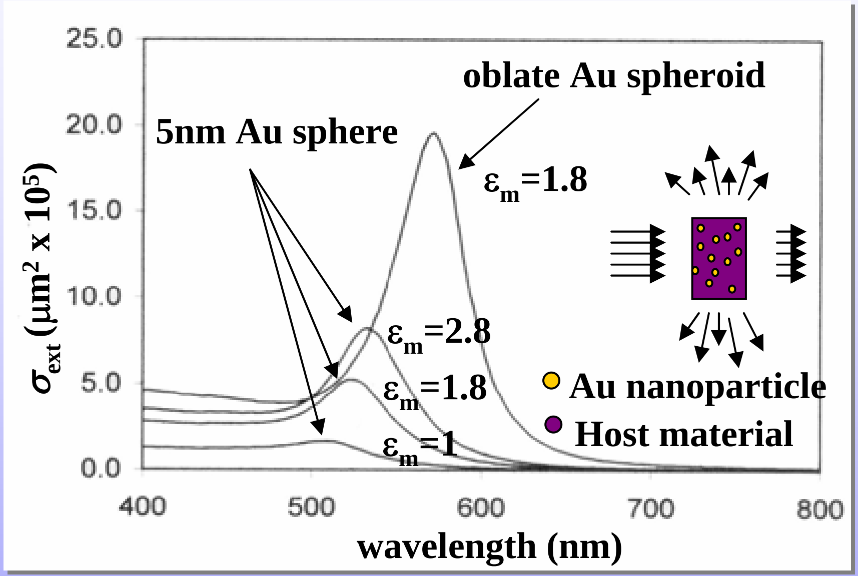
$$\sigma_{ext} = 9\frac{\omega}{c}\varepsilon_m^{3/2}V\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2(\omega)^2}$$

$\varepsilon=\varepsilon_1+i\varepsilon_2$: dielectric function of particle

ε_m: dielectric function of host material

V: particle volume, c: speed of light

ω: frequency of incident light



- **Plasmon resonance condition:**

$$\varepsilon_1(\omega) = -2\varepsilon_m$$

The surface plasmon resonance (SPR) extinction maximum can be shifted by changing the shape and/or the environment of the metal nanoparticle

D. L. Feldheim et al, Metal Nanoparticles: Synthesis, Characterization, and Applications, (Marcel Dekker, 2001)

Metal Nanoparticles: Optical Properties (cont.)

- **For free-electron metals:**

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \approx \underbrace{\left(1 - \frac{\omega_p^2}{\omega^2}\right)}_{\varepsilon_1} + i\underbrace{\left(1 - \frac{\omega_p^2}{\omega^3}\gamma\right)}_{\varepsilon_2}$$

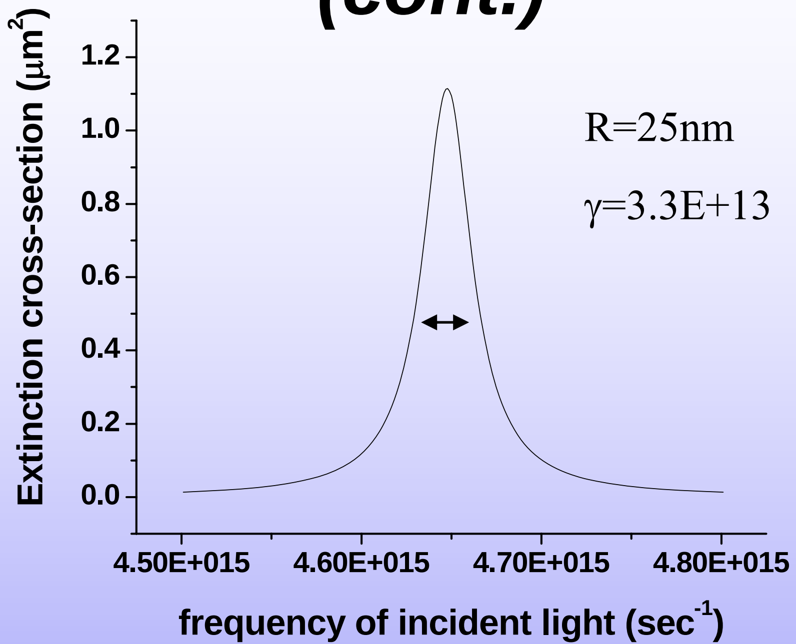
ω_p: plasma frequency

γ_b: damping constant for bulk conduction electrons

υ_F: fermi velocity

A: slope parameter

R: particle radius



- **For particles with sizes smaller than or comparable to the bulk mean free path:**

$$\gamma(R) = \gamma_b + A\frac{\upsilon_F}{R}$$

Modified Drude damping constant; additional term due to surface scattering

- **The A parameter depends on the nature of the interface between the nanoparticle and the surrounding medium**

Physisorption, chemisorption or chemical interface reactions are expected to affect the width of the SPR band

U. Kreibig et al, Optical properties of metal clusters, Springer, New York, 1995, vol. 25.

High Temperature Compatible Chemical Sensors: Materials Deposition

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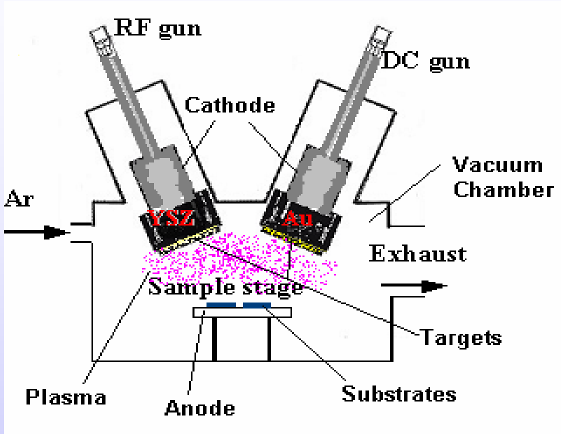
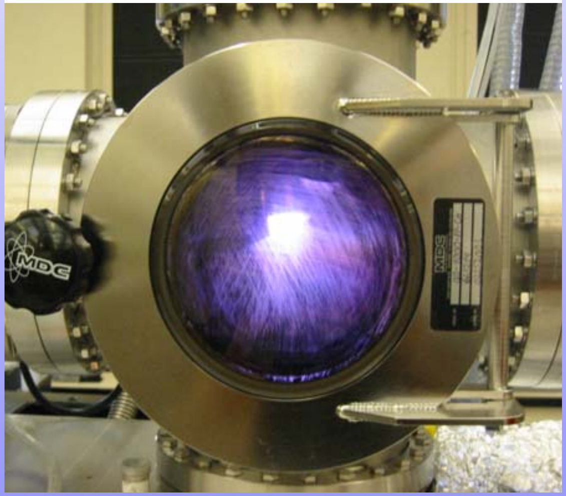
- YSZ matrix with embedded Au or Pd nanoparticles
- Material set is compatible with DOE Vision 21 initiatives



- Films deposited using multi-target sputtering chamber for tailored composition
- Annealed and processed to tailor material properties



Sputtering Parameters	Annealing Parameters
Process pressure: 5 mTorr	Atmosphere: Ar at 760 Torr
R.F. power (YSZ): 200 W	Temperature: 600, 700, 800, 900, 1000°C
R.F. power (Au): 20 W	
YSZ target-substrate distance: 50 mm	Time: 2 h
Au target-substrate distance: 85 mm	

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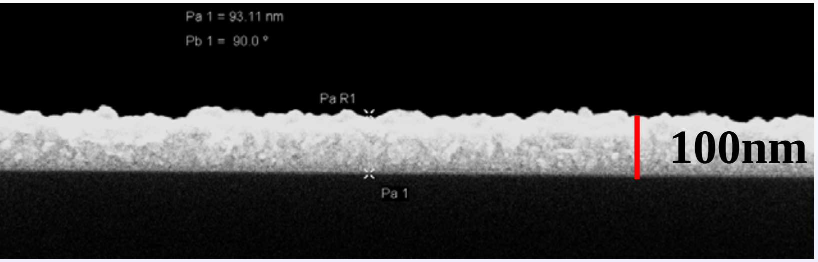
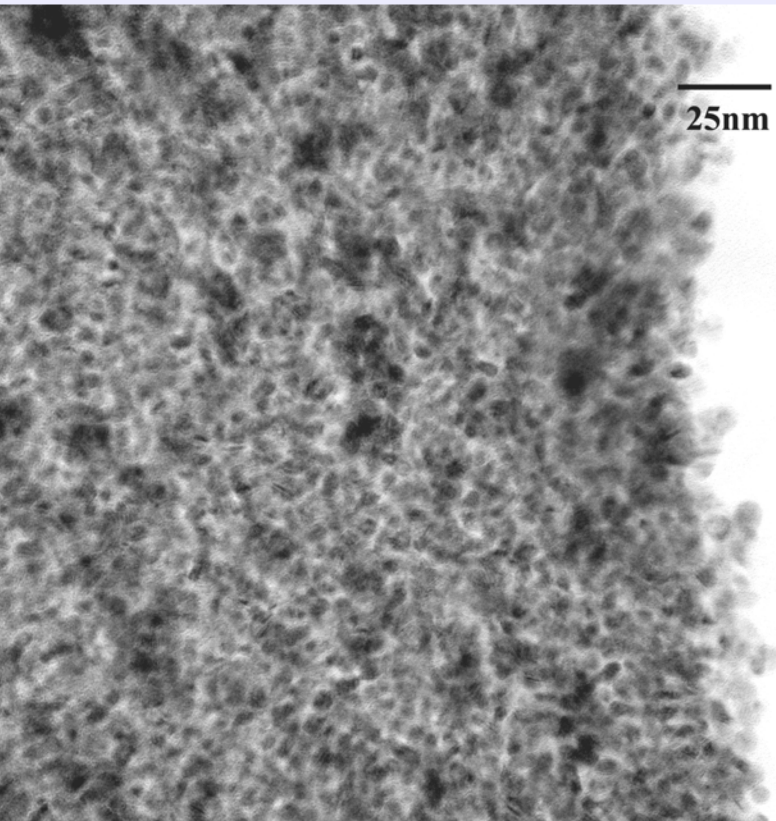
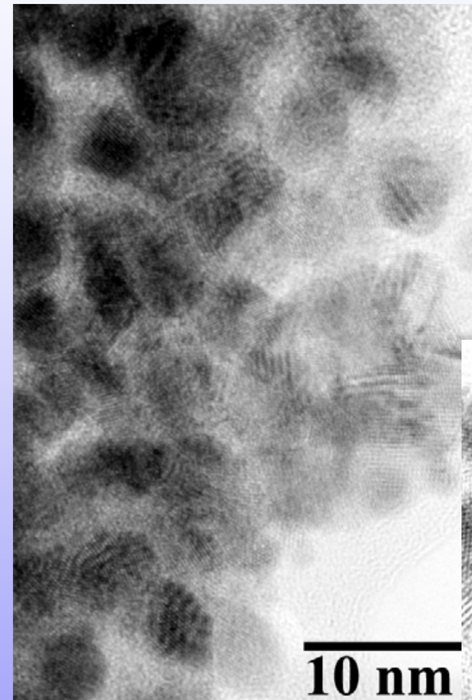
SEM/TEM Analysis of Films



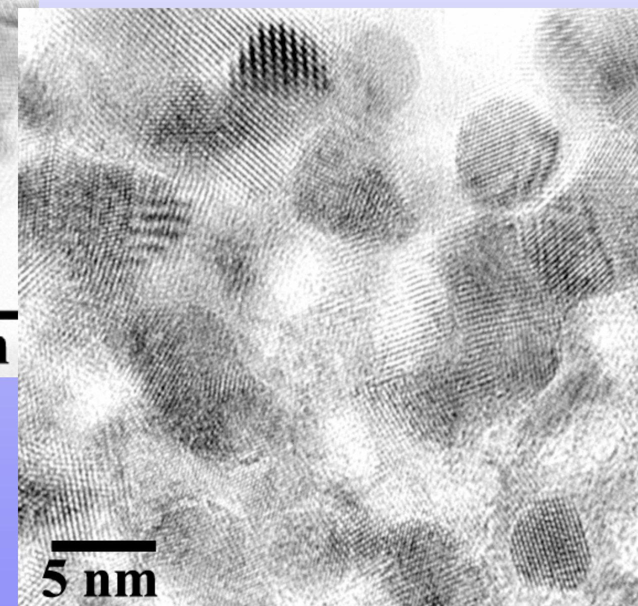
- SEM cross section of 100nm film on glass



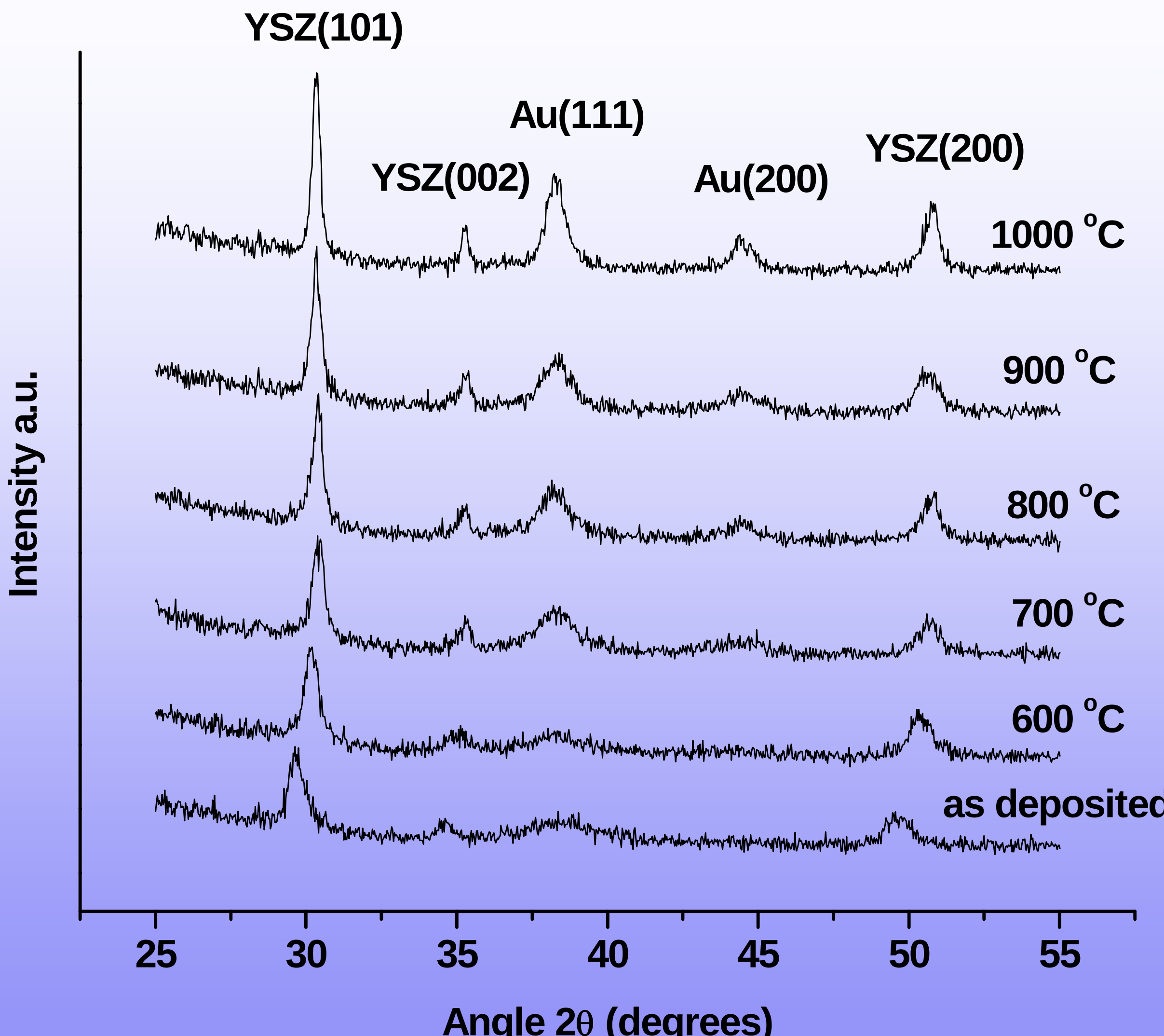


- TEM analysis of an as deposited 30nm film
- Sized 50 particles: 4.7nm±0.9nm

- Annealed sample to 500°C for 2 hrs
- Sized 50 particles: 5.2nm ±0.7nm



XRD Analysis



- With increase in annealing temperature both YSZ and Au peaks increase and become narrower, indicative of grain growth
- Average grain size, D, determined by Scherrer formula

$$D = 0.9\lambda / B \cos\theta$$

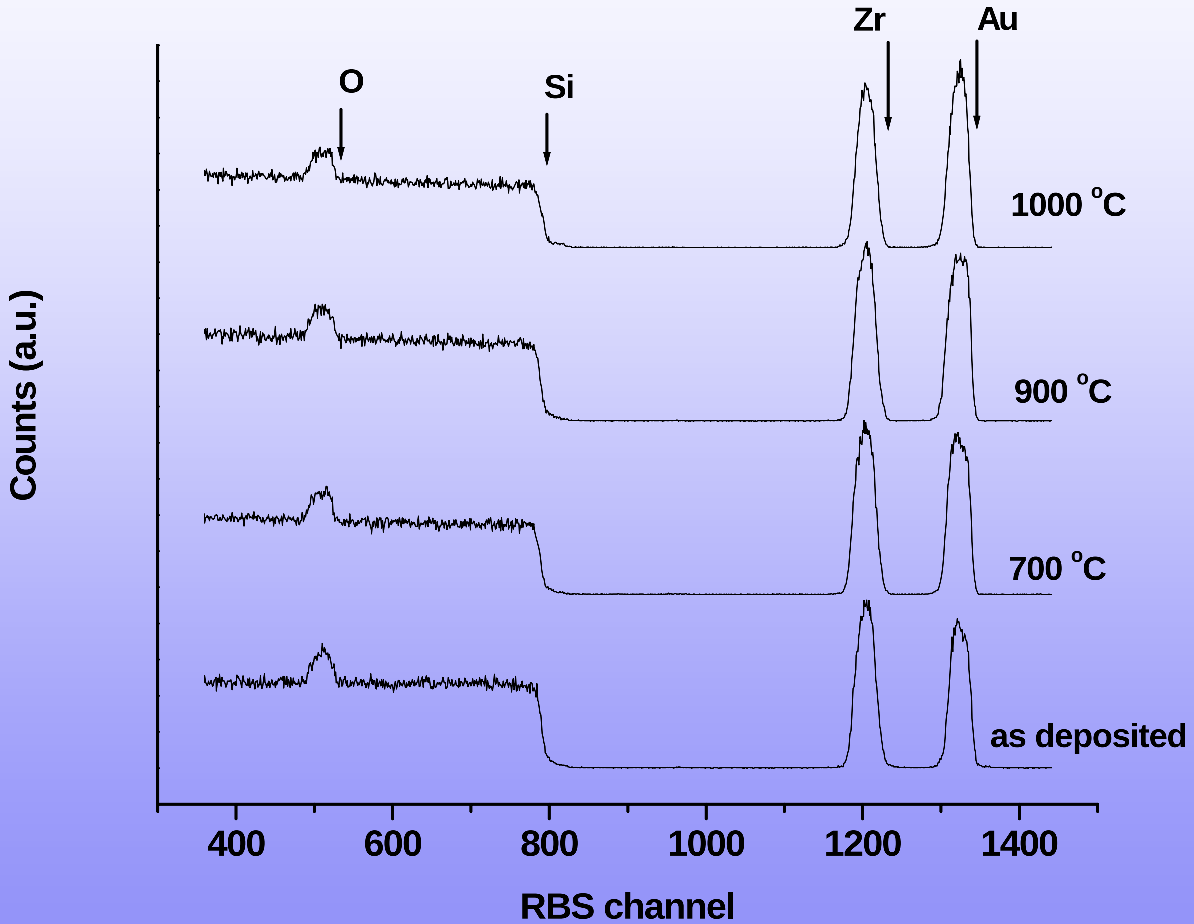
λ= wavelength

B=FWHM

θ=diffraction angle

RBS analysis

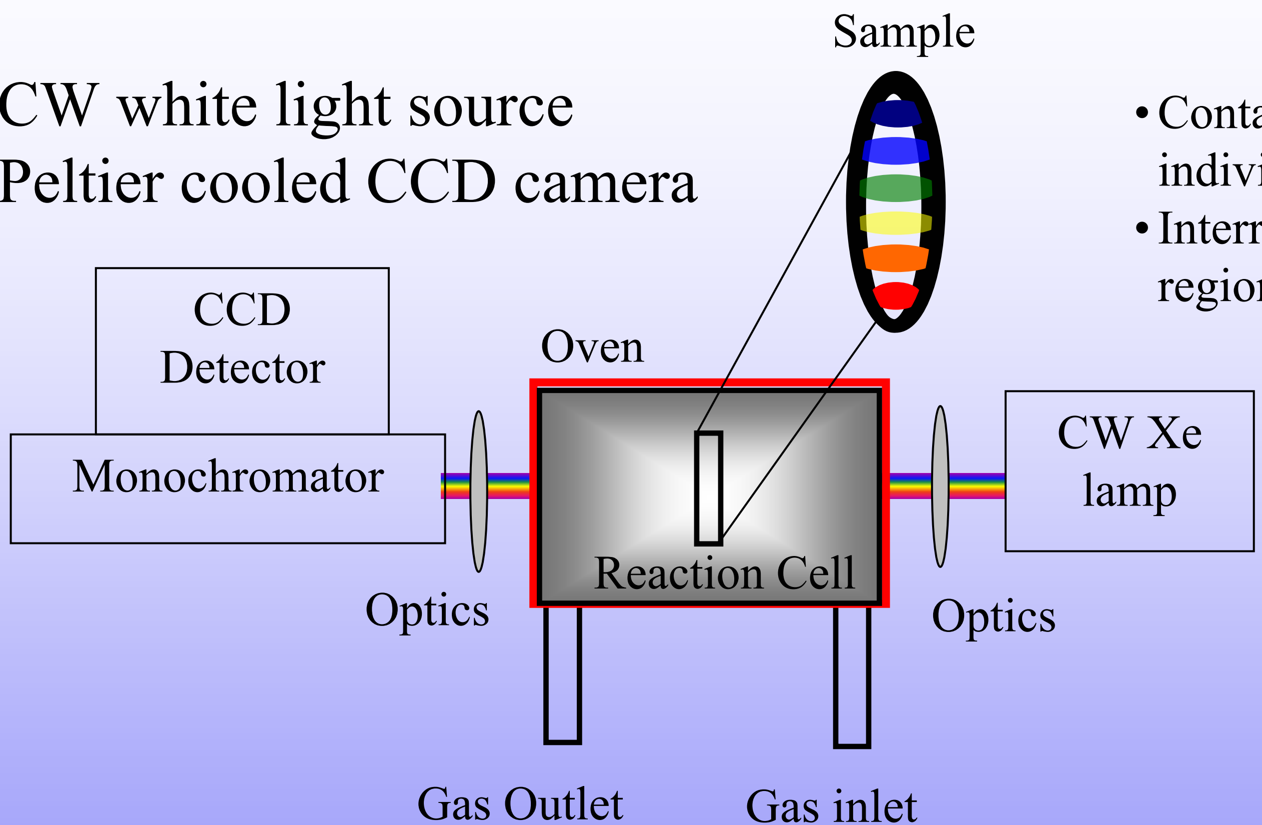
RBS spectra of Au-YSZ nanocomposite films as a function of annealing temperature.



- The as-deposited and the annealed films have uniform composition as a function of depth
- No surface migration of gold after the anneals

Sensor testing station

- CW white light source
- Peltier cooled CCD camera

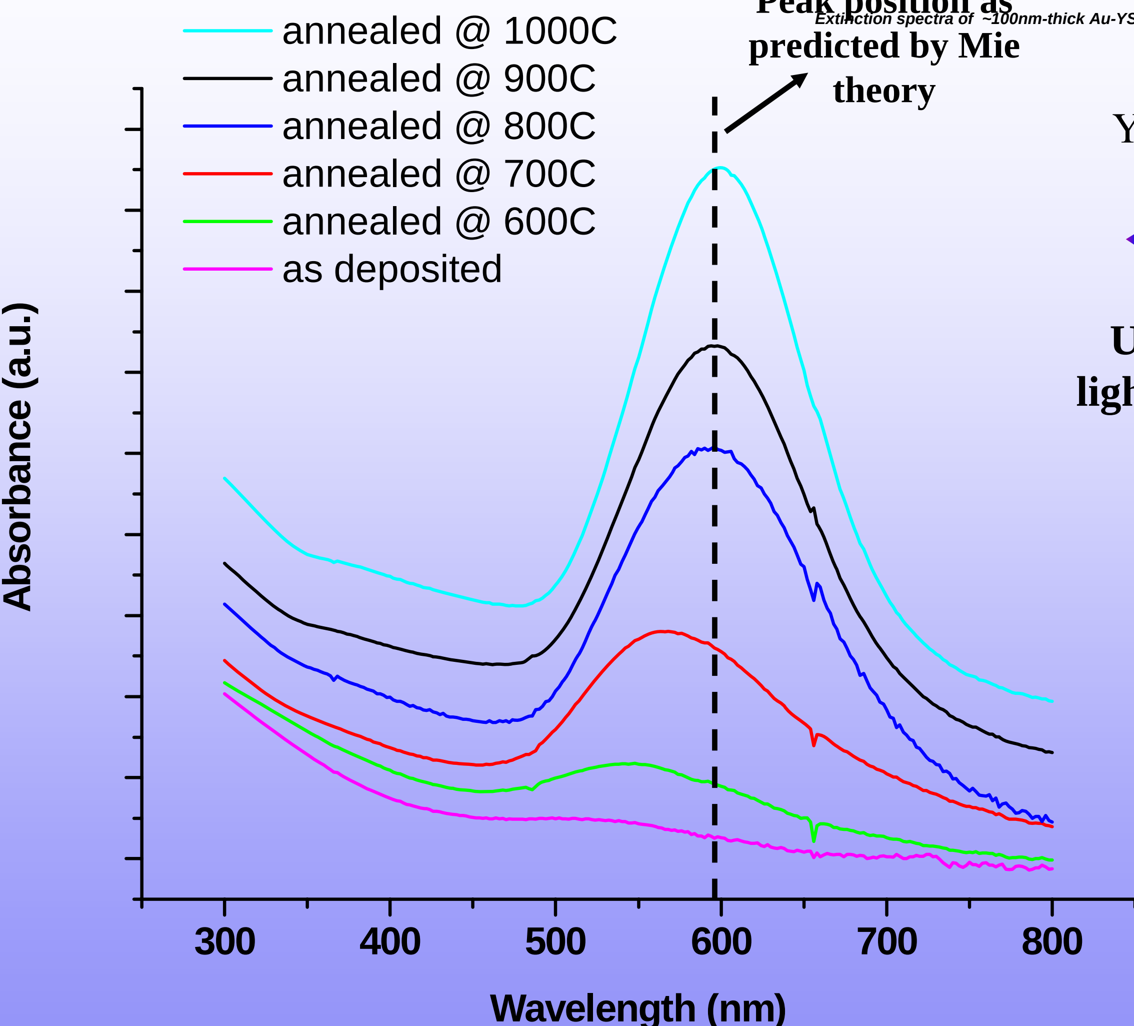


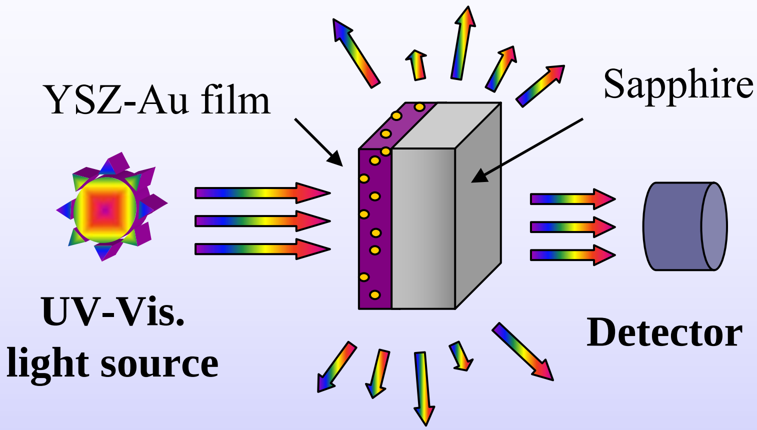
- Contain regions with individual film recipes
- Interrogate/image each region simultaneously

- In a single experiment can monitor SPR bands as function of particle diameter, temperature and reaction gas composition
- Fast acquisition times of CCD will allow for a kinetics study to be performed
- Parallel materials deposition and analysis

Nanocomposite Optical Properties

Ex-situ



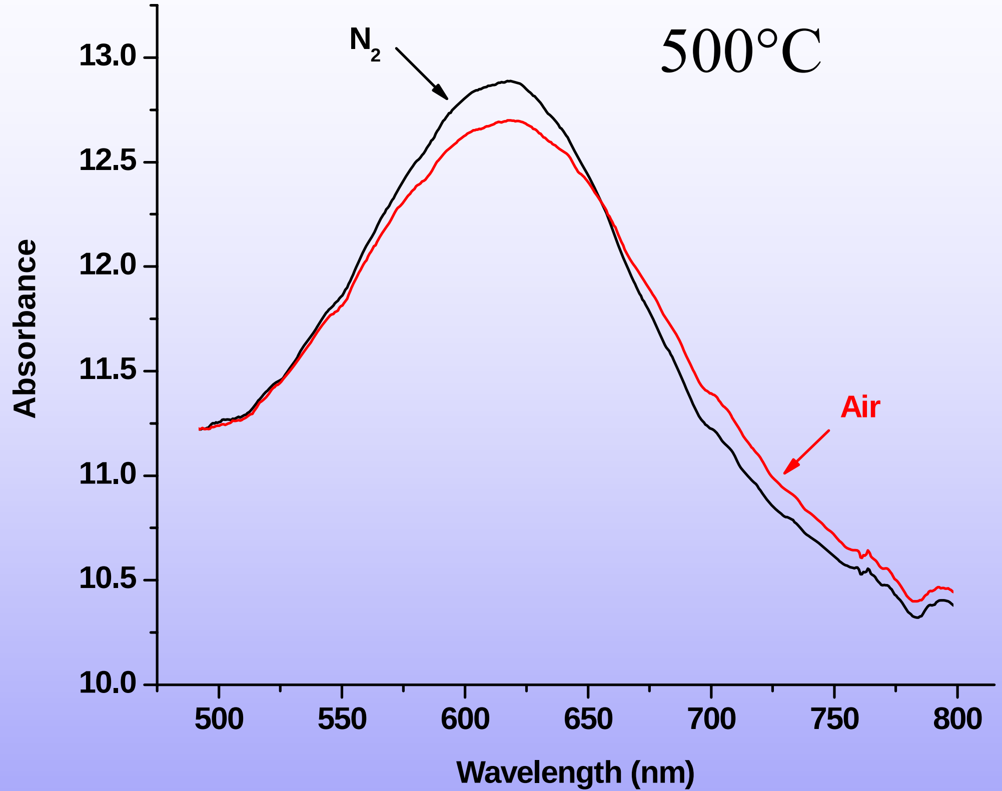


- SPR band redshifts by ~55nm with increase in particle diameter
- SPR band narrows by ~50nm

- Red shift in SPR band coincides with particle growth, expected behavior according to Mie theory

Results: Air exposures

In-situ



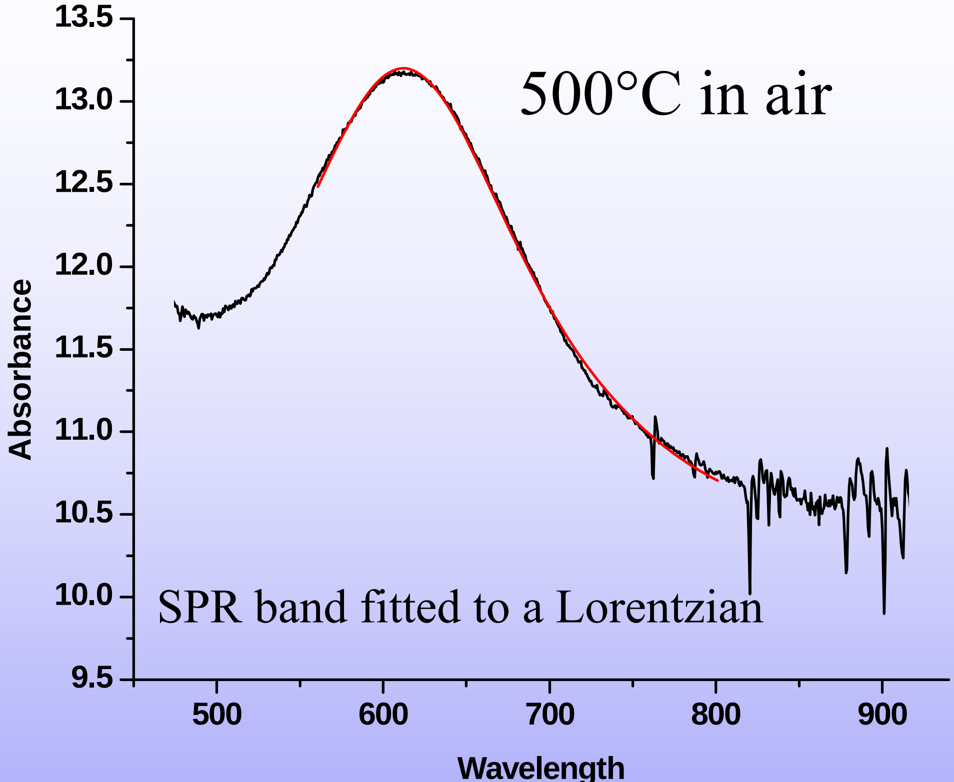
Baseline Conditions

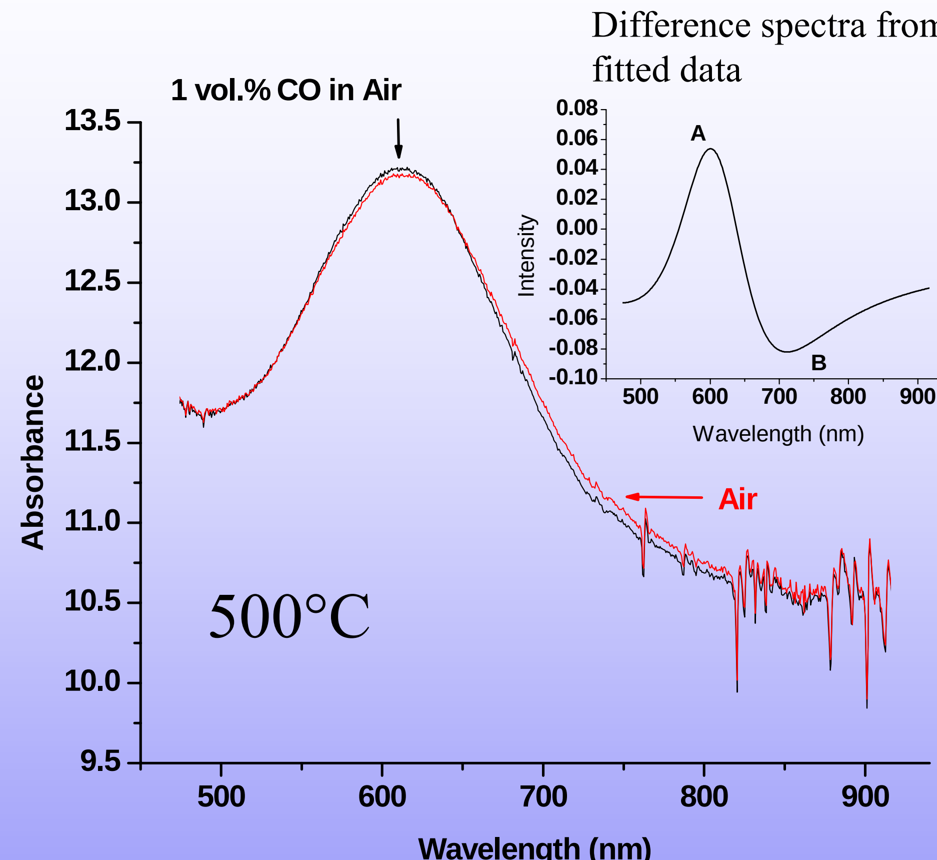
- Upon the change from nitrogen to air, oxygen reacts at the 3-phase boundary producing O^{2-} species within the matrix
- As a result the Au NPs become charged, causing a redshift and broadening of the SPR band

$$\text{Air} + \text{Au/YSZ} \rightarrow O^{2-}(\text{matrix bound}) + Au^{2+}/\text{YSZ} + \text{Air}$$

Experiments in progress on the oxygen titration as a function of temperature

CO exposure experiments

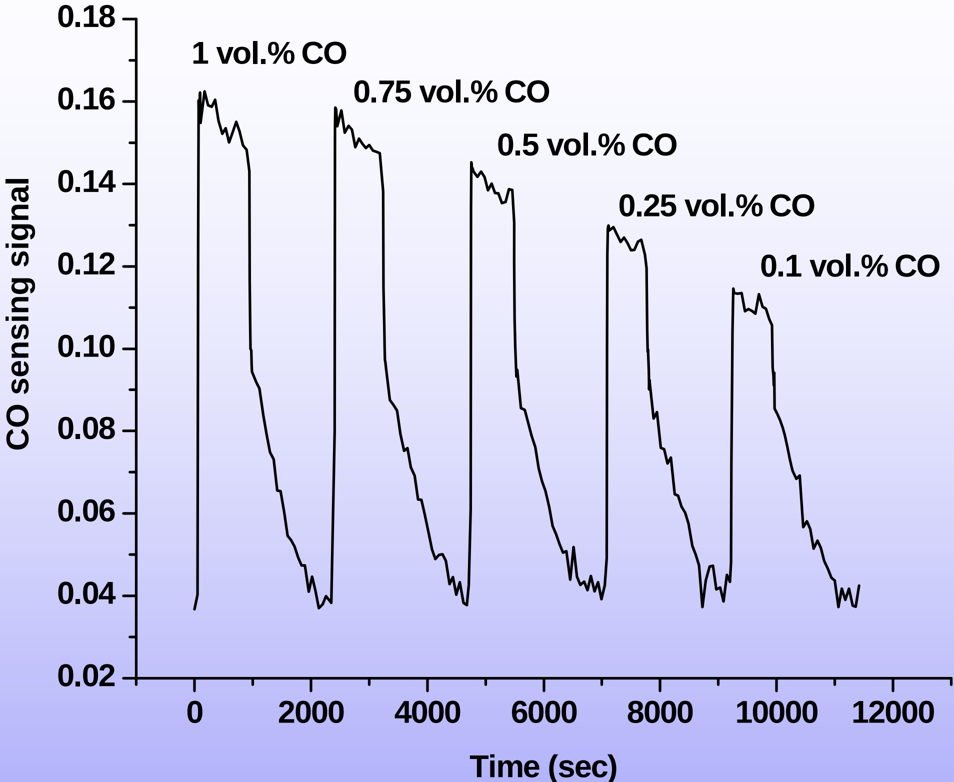


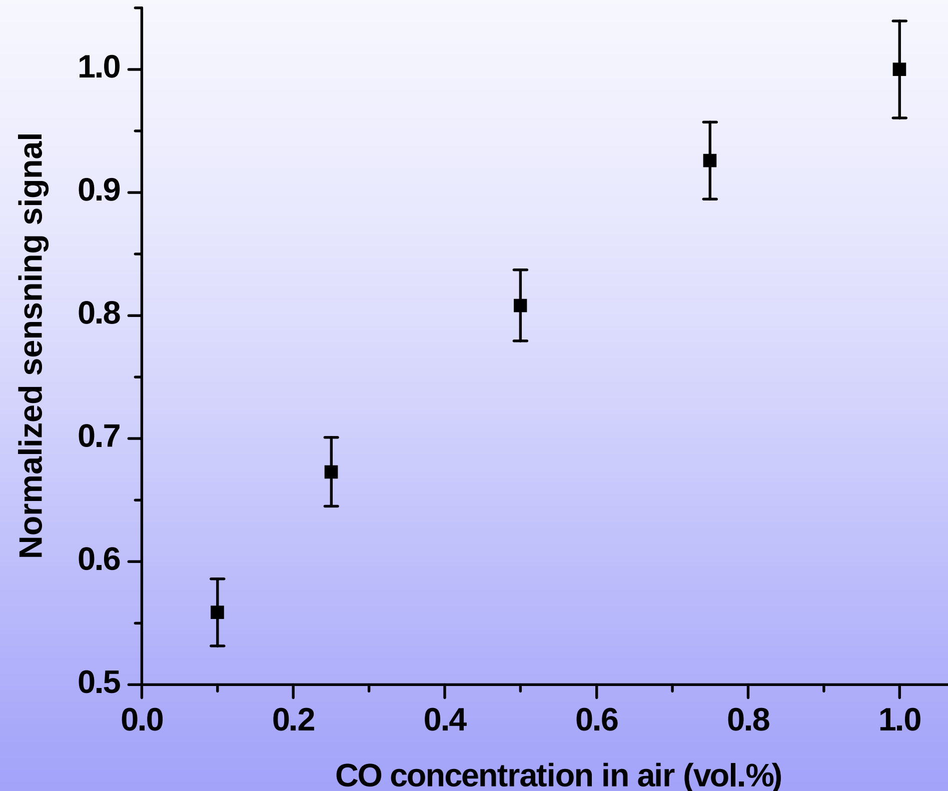


$$O^{2-}/Au^{2+}/YSZ + CO + air \rightarrow CO_2 + Au/YSZ + air$$

- Upon exposure the SPR band blue shifts due to charge transfer to the Au NP
- CO sensing signal defined as signal between A &B on the difference spectrum

Sensing Details

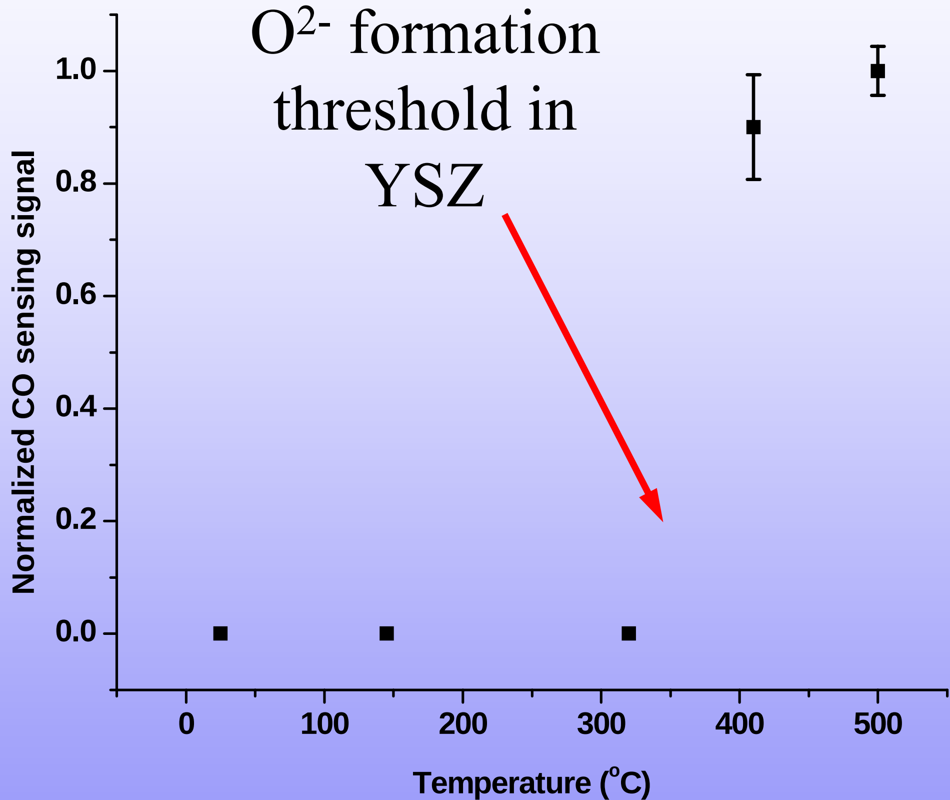




- Signal change is reversible
- Response time ~40 s
- Recovery has 2 stages,
  - Fast ~60s
  - Slow ~1000s

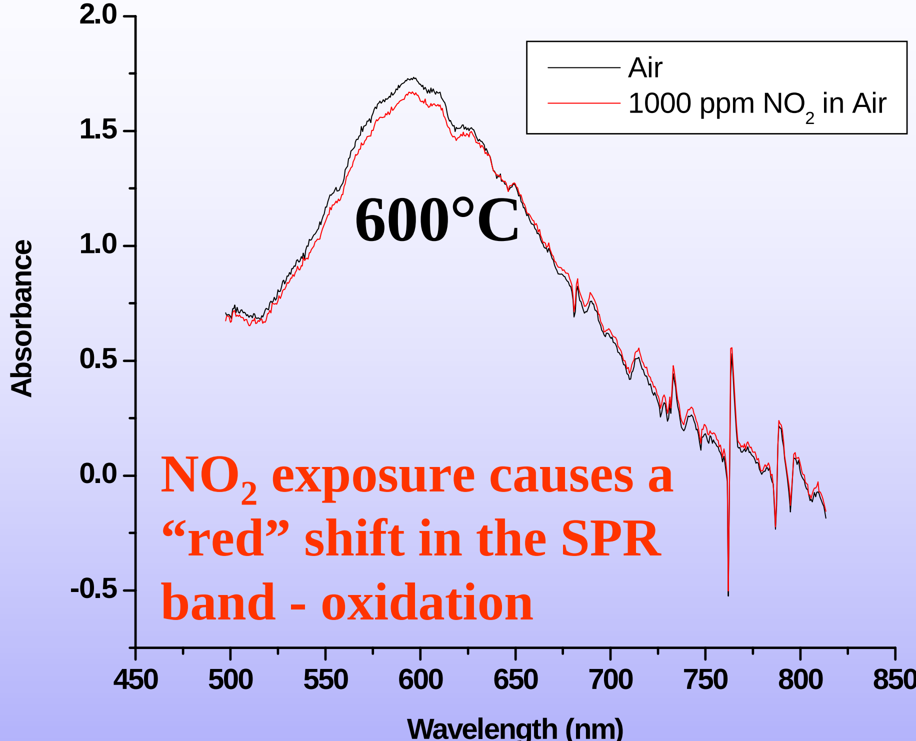
- Data ave. over 3 runs
- Nearly linear response

CO Sensing vs. Temperature

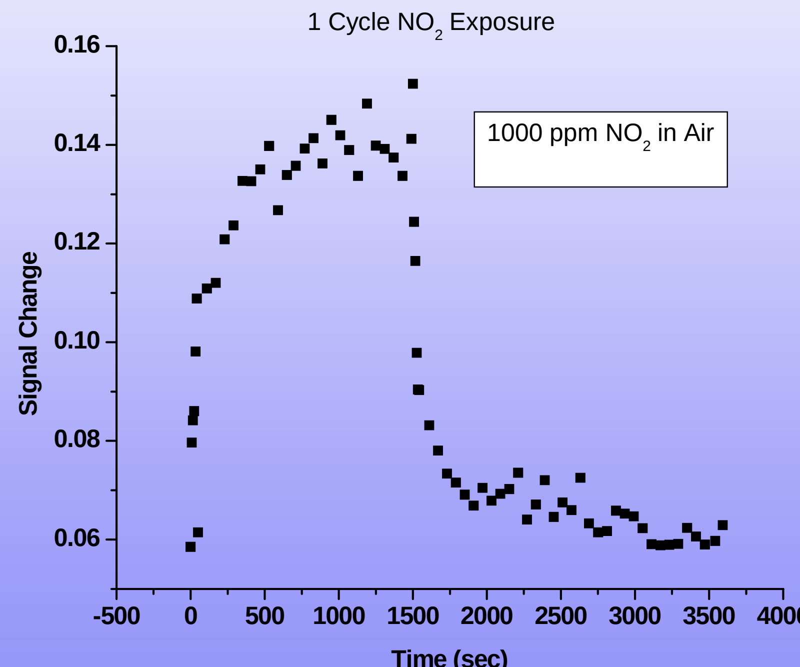


- No signal observed until above threshold for formation of O^{2-} within the YSZ matrix
- Consistent with Au NP charging/discharging concept

NO_2 Testing Details



- NO_2 reacts catalytically with hot gold to form NO – *oxidation of the nanocomposite matrix*
- ***Increases charge in the YSZ matrix through donation of O species***



- Red shift of the SPR band is an indication of the oxidation reaction
- Opposite of the change caused by CO reaction
- Response time = ~60s, sensitivity to 10ppm

Detection of H_2

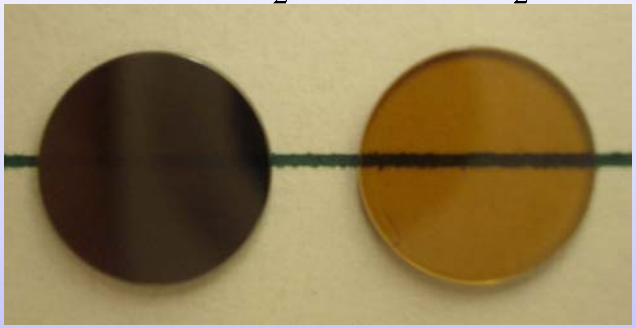
- The presence of reducing gases such as H_2, CO, CH_4, or changes in the partial pressure of oxygen or temperature can significantly affect the phase equilibrium of the Pd/PdO system

Oxidation of Palladium:

$$2Pd + O_2 \leftrightarrow 2\,PdO$$

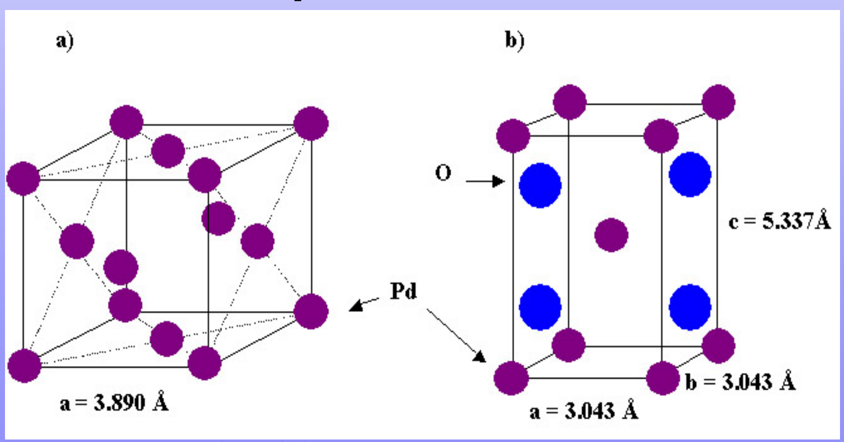
Interaction with Hydrogen:

$$PdO + H_2 \longrightarrow Pd + H_2O$$



As Deposited **Oxidized**

- **Significant reconstruction occurs during the phase transformation**
  - change in the particle size and morphology of the catalyst
  - change in the optical properties

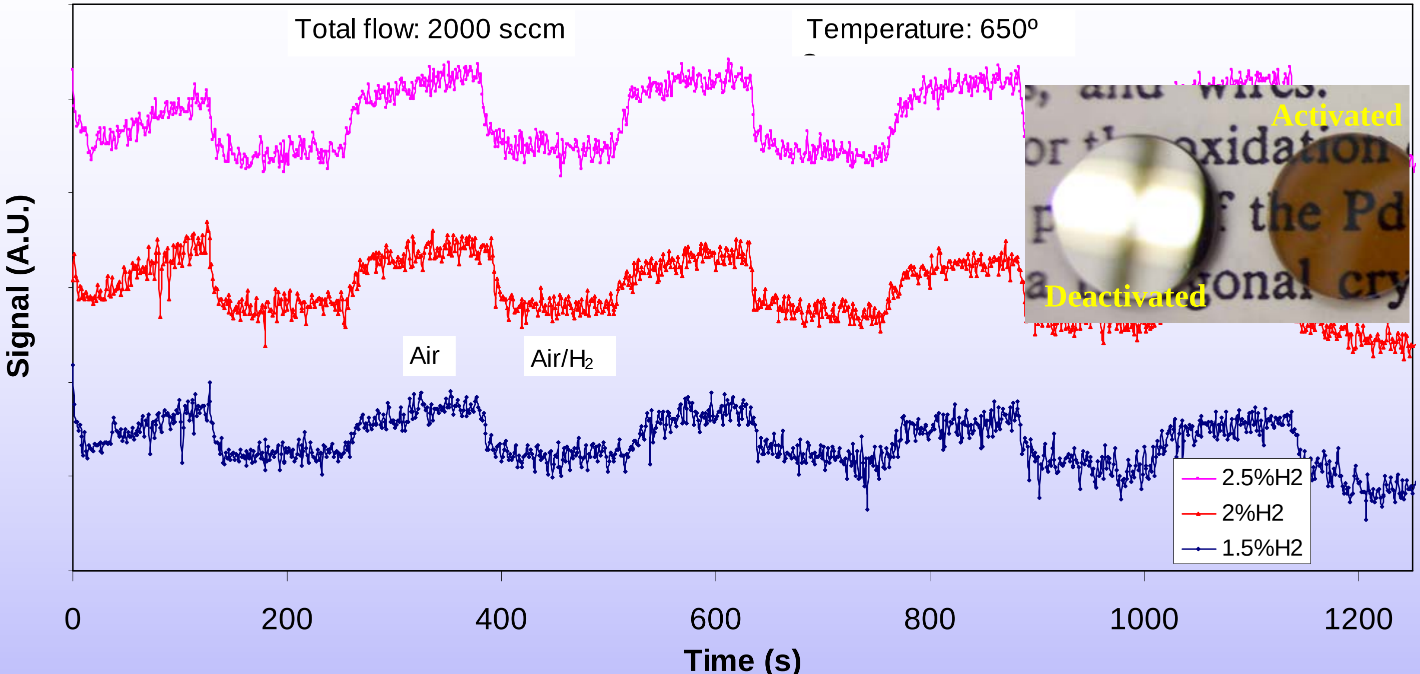


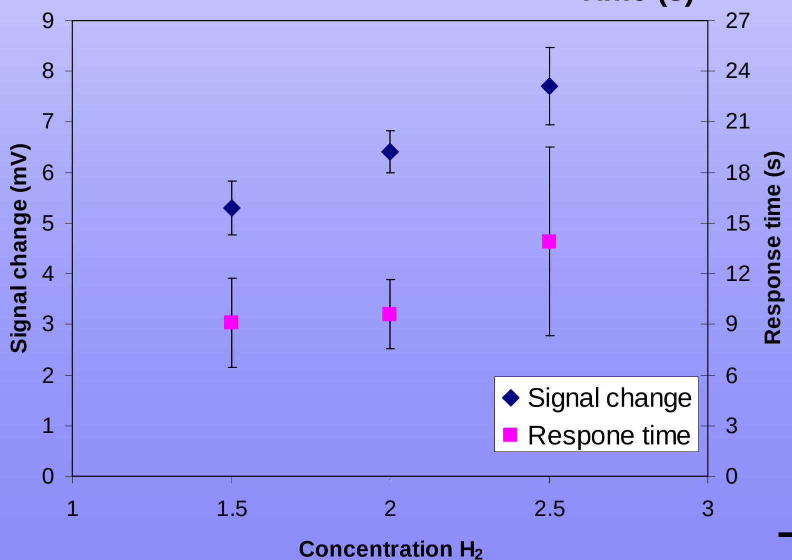
Face-centered cubic structure

Tetragonal

D. Ciuparu et al, Catal. Rev. 44, 593 (2002)

Hydrogen Results

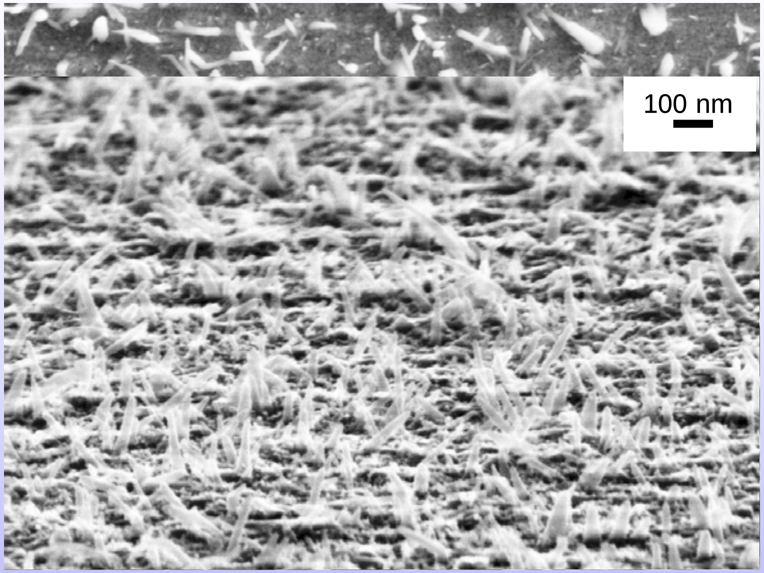




Hydrogen or Hydrocarbons *react* catalytically with the Pd/PdO – YSZ matrix and cause *change in reflectivity of matrix*

- **Response times 10s**
- **Tested as low as 1.5% hydrogen in air**

Conclusions/Future Work



Tailored Nanostructures

- Demonstrated optical sensing technique for CO, NO_2 and H_2 detection at elevated temperatures
- Experiments underway to further characterize their sensing mechanisms
- Develop a detailed understanding of the sensor dynamics, lifetime and response characteristics as a function of the material properties

- Optimization of response
    - Tailored matrix materials(YSZ, TiO_2)

- Cross Sensitivity measurements
- Test material systems for sulfur gas sensitivity

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