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Nano-Enabled Smart Chemiresistor for Improved Chemical Sensing

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Miniaturization of Analytical Capabilities

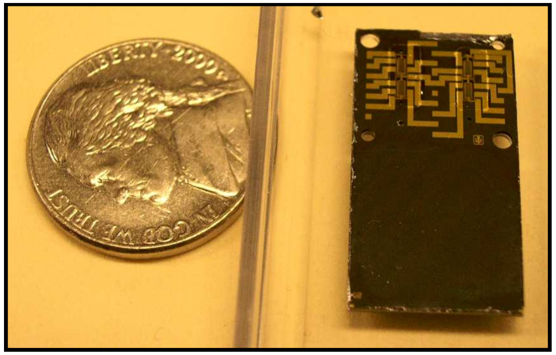
Goal:
- High Sensitivity
- Portable
- Reliable
- Low Power

Desktop

Handheld

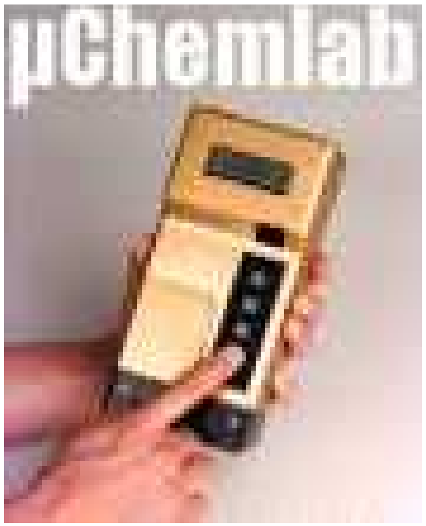
Micro Chem Lab™
Courtesy of Pat Lewis

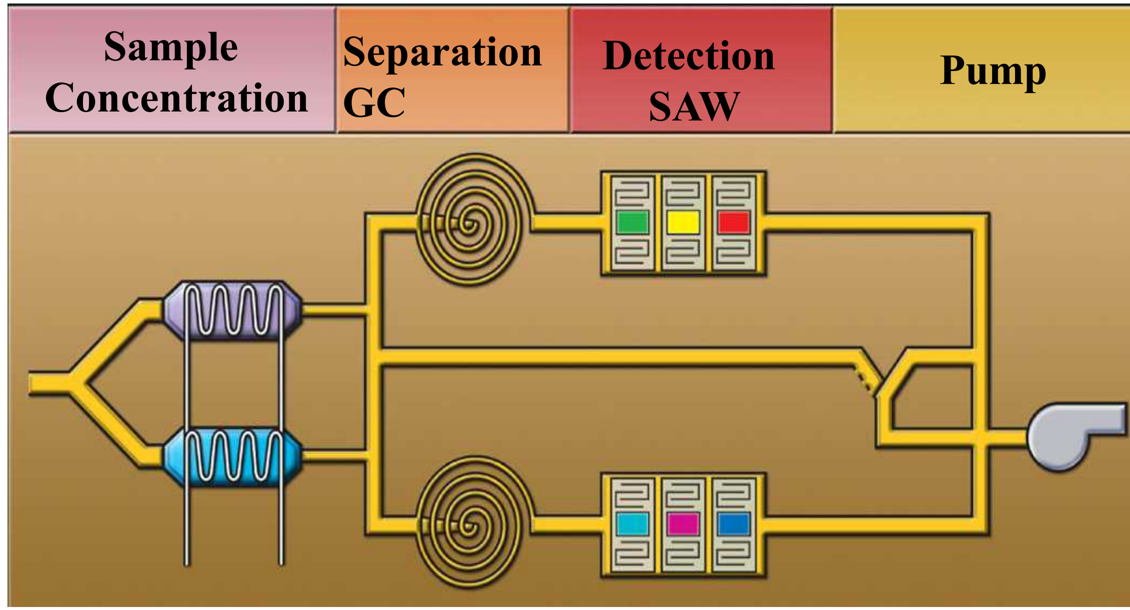
Embedded



Courtesy of Ron Manginell and Matt Moorman

Our Approach to Chemical Sensing (µChemlab™)



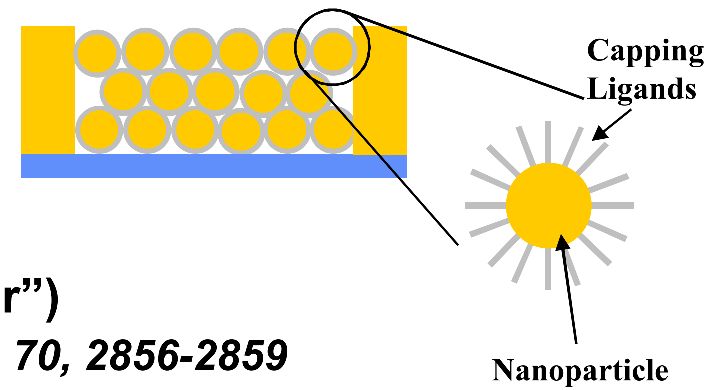


•Vast majority of sensors have limited selectivity (reacting to classes of analytes)

•To improve identification of chemical species and sensitivity, we use:
- •Selective preconcentration
- •Temporal separation (commercial GC or MEMS columns)

Moving Beyond The SAW

Nanoparticle Sensor Background

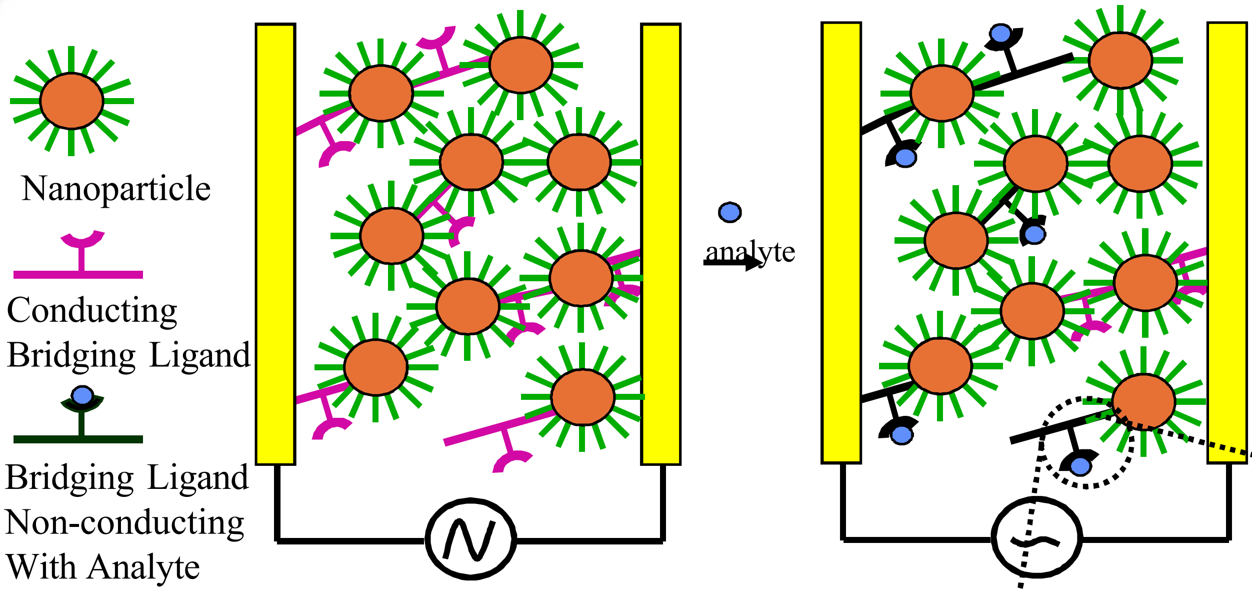


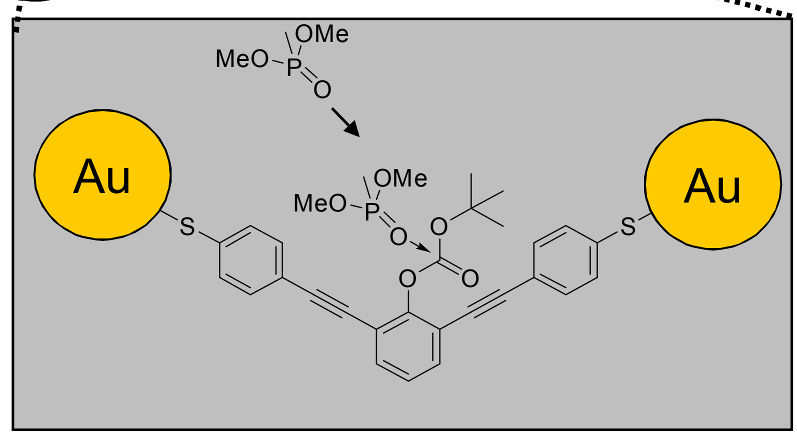
- Mechanisms of transduction
  - Adsorptive swelling ("Chemiresistor")
    - *Snow & Wohltjen Anal. Chem. 1998, 70, 2856-2859*
  - Dielectric modification to the nanoparticle capping layer
    - *Joseph et al., Sensors and Actuators B 98 (2004) 188-195*
  - Molecular electronic
    - Sandia

Why use nanoparticle based sensors?

- Much easier to measure a change in resistance
- Consume less energy

Molecular Electronic Approach: Smart Chemiresistor (SCR)





- Nanoparticles serve as mini-electrodes scaffolding
- HOMO LUMO gap altered changing conductivity
- Characterize analyte by measuring change in resistance (low power)
- More specific response

This is an extension to the Chemiresistor developed by *Snow & Wohltjen Anal. Chem. 1998, 70, 2856-2859*

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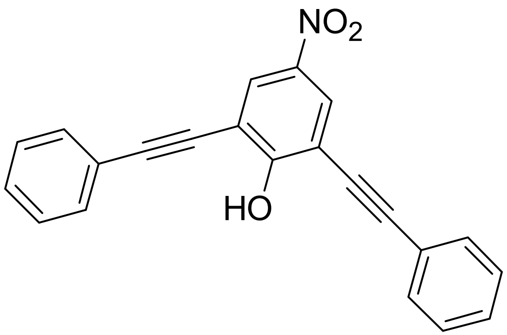
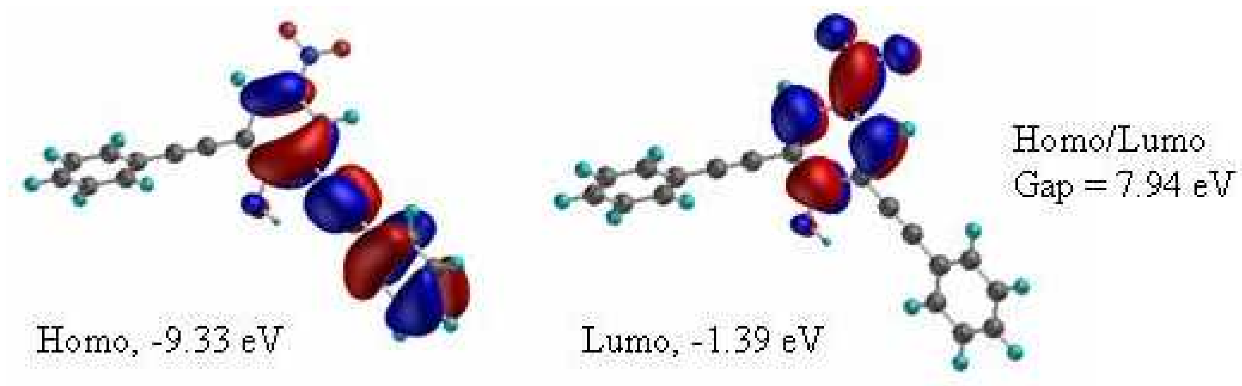
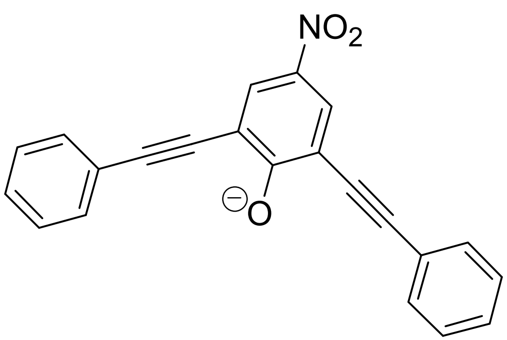
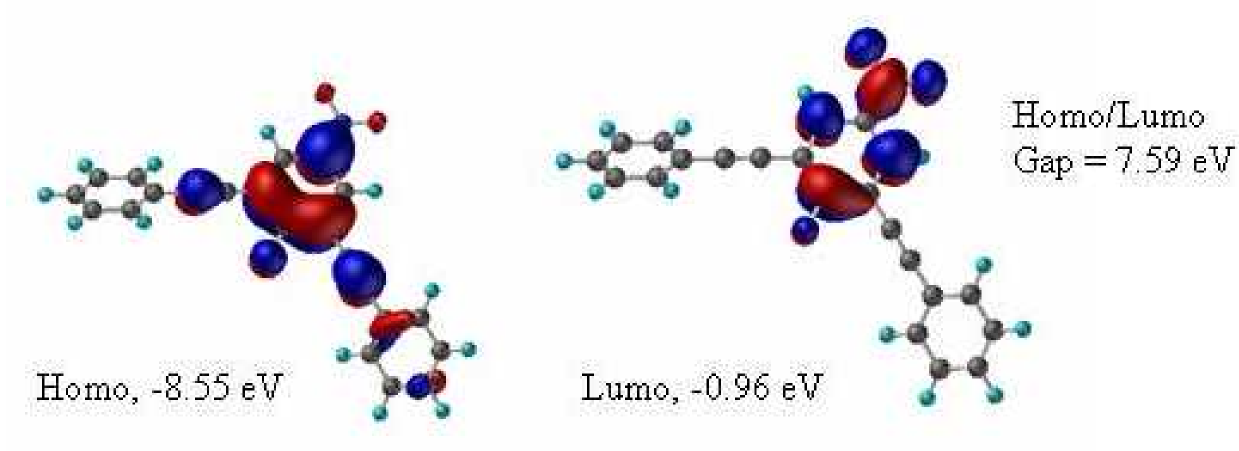
HOMO-LUMO Modifications



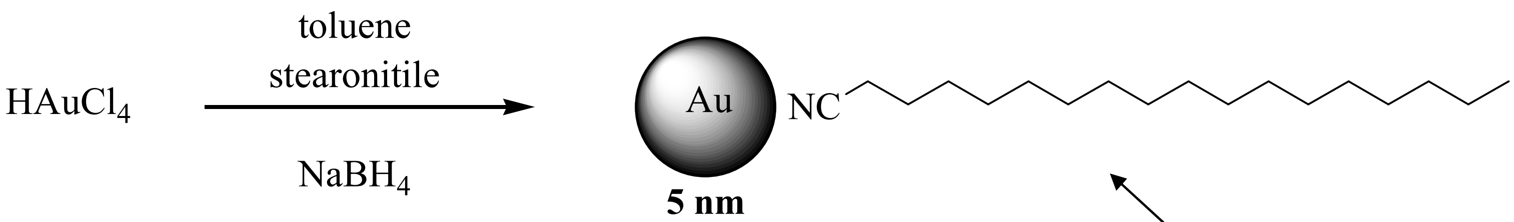




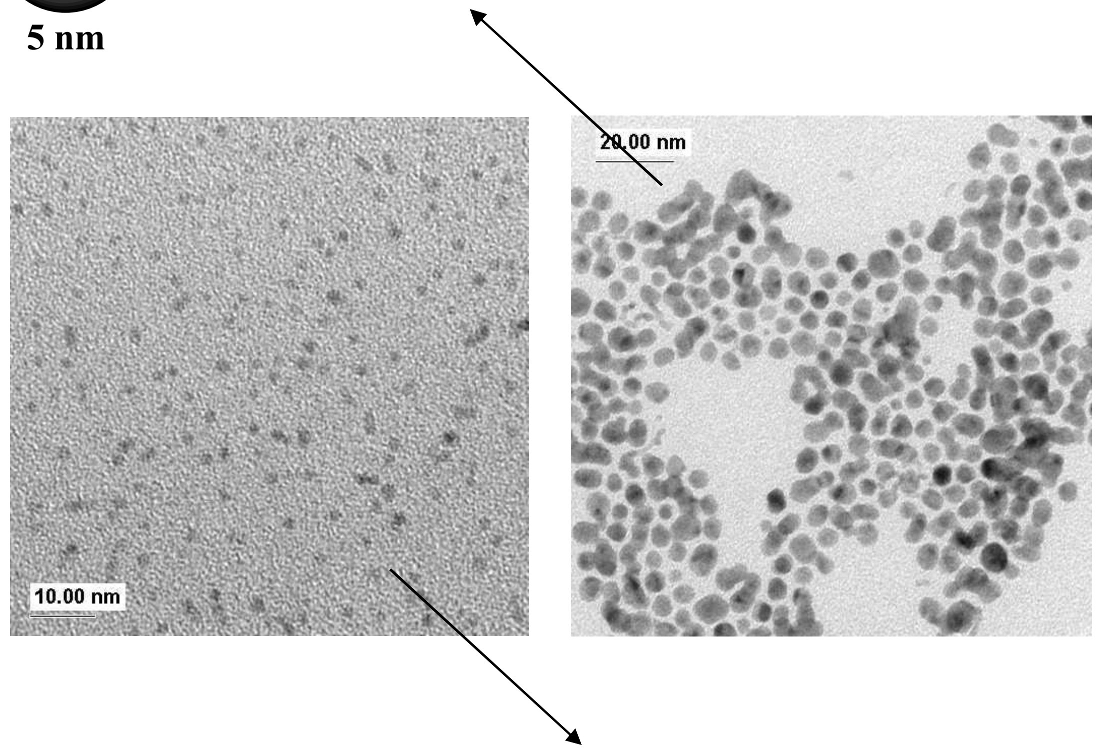


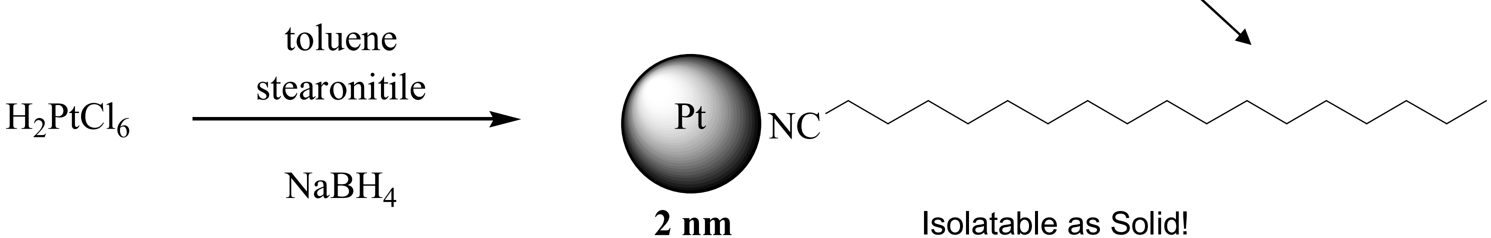
Difference in HOMO/LUMO Gaps = 0.35 eV (14 x kT at RT)

Novel Nanoparticles



We have accomplished the first synthesis of stable nitrile capped nanoparticles by modification of the Brust method. The nitrile capping agent serves as a sacrificial layer which may easily be replaced by stronger binding ligands (e.g. thiol, isonitrile or diazonium groups).





Isolatable as Solid!

Iterative Nanoparticle Ligand Assembly

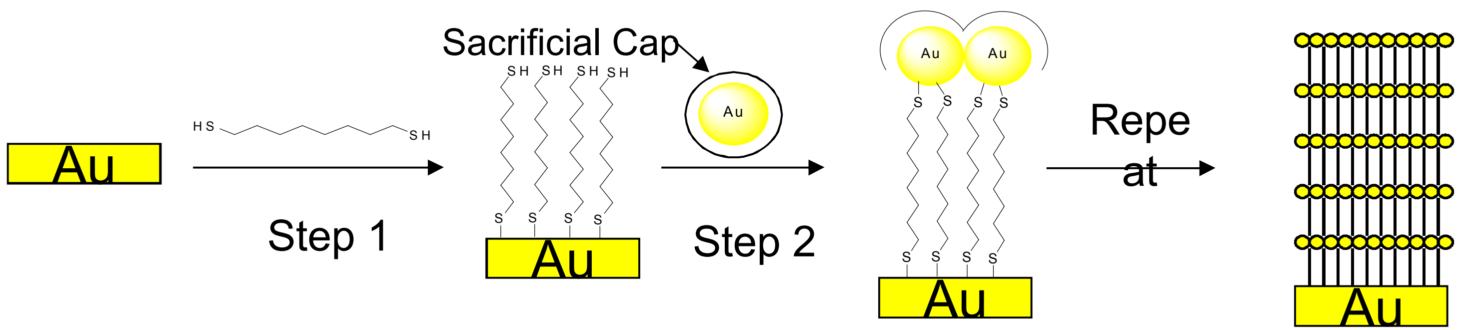
Substrates
- **Glass, Gold, Silicon**

Nanoparticles
- **Gold (5nm)**
- **Platinum (2nm)**

Molecules
- **phenylene ethynylene (PE)**
- **octanedithiol (ODT)**

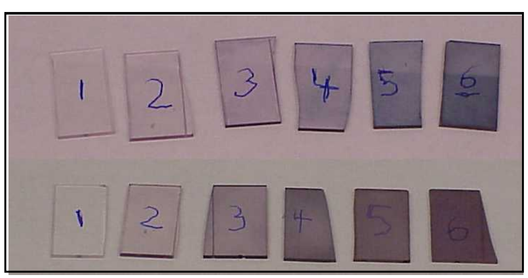
Process
- **Synthesis of stable nitrile capped nanoparticles by modification of the Brust method**
- **Piranha cleans and hydrates the surface**
- **Treat with tetrakisdimethylamino silane and react with a dithiol**
- **Ready for nanoparticle attachment**
- **Tune resistance with each applied layer**

•Automation was required for reproducibility



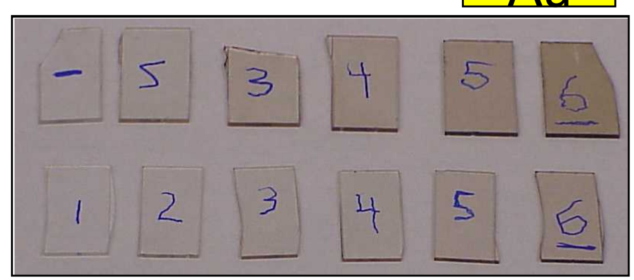
Au/DIH

Au/PE



Pt/PE

Pt/DIH



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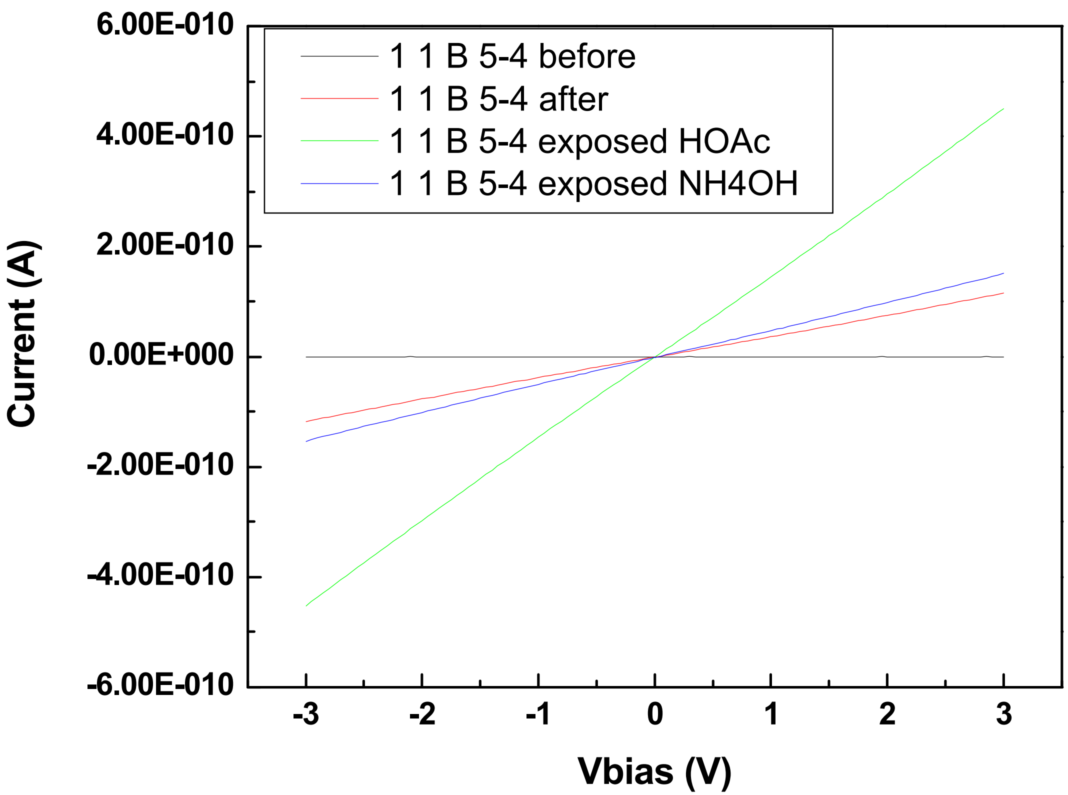
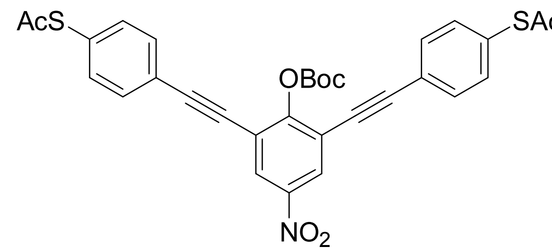
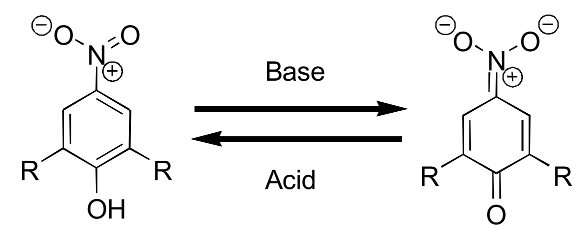
Initial Liquid Phase Sensing Experiment

- Au nanoparticle film crosslinked with nitrophenol phenylene ethynylene



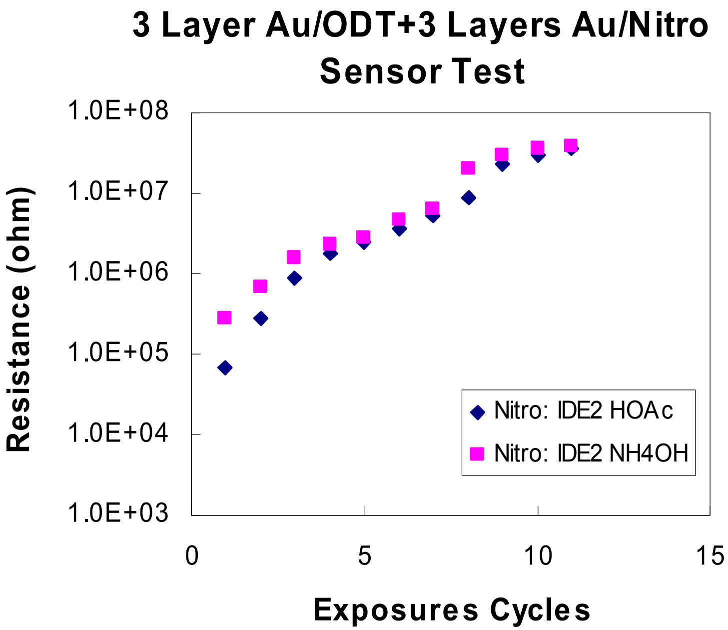


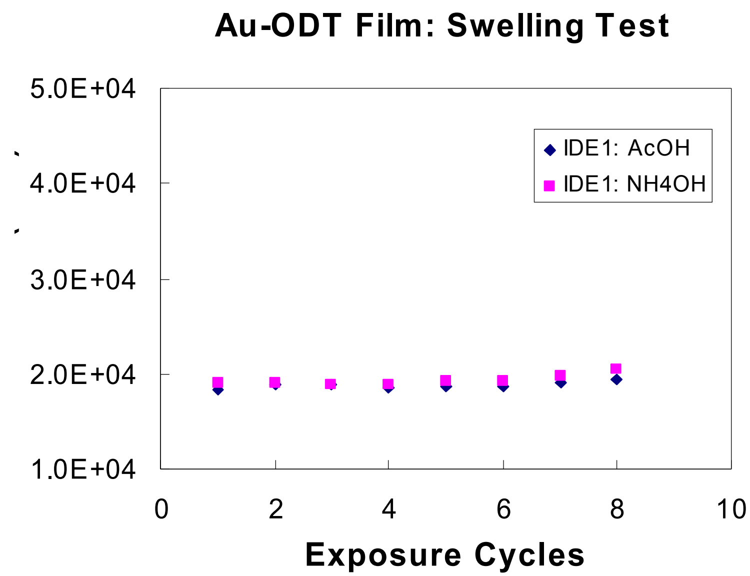


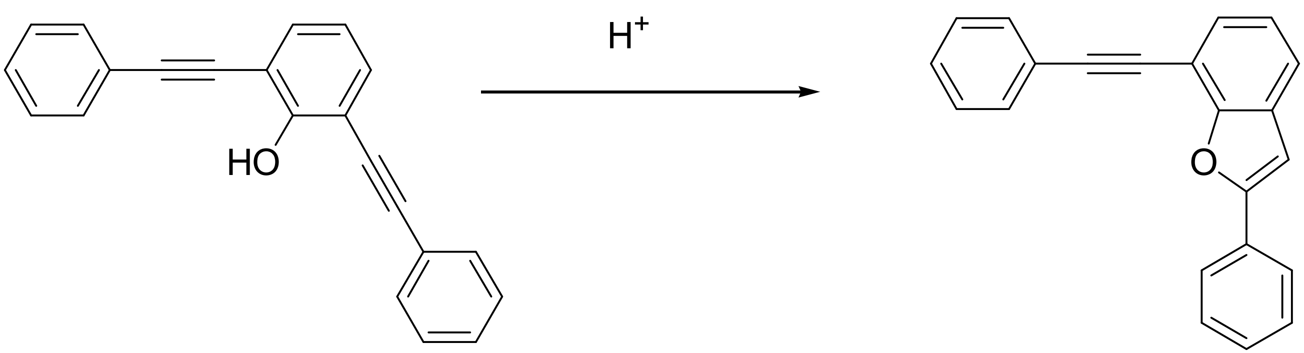
Conjugated

Cross Conjugated

Multiple Liquid Phase Exposures

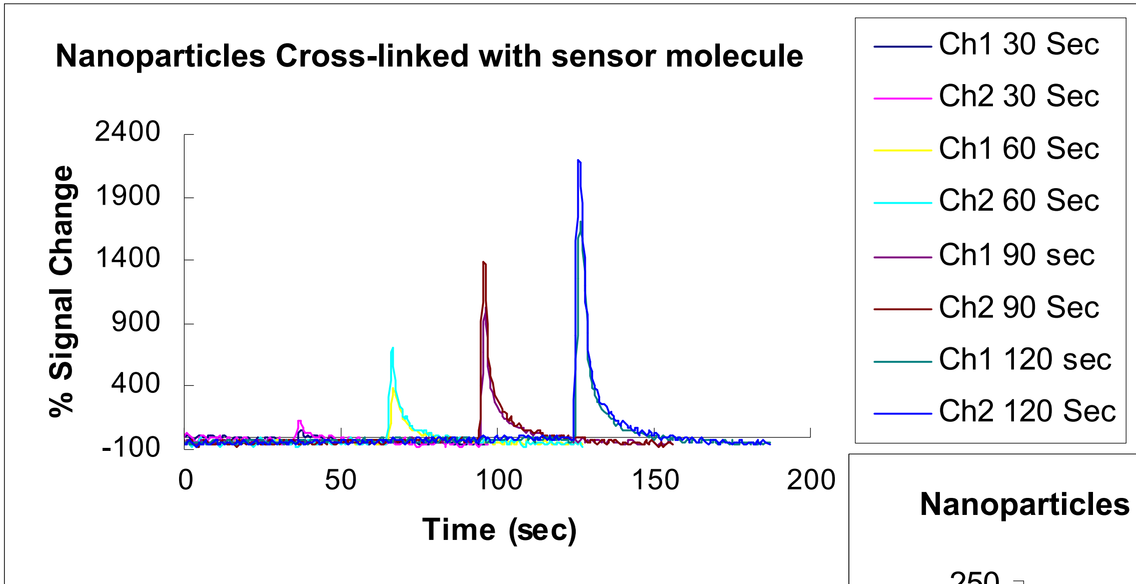




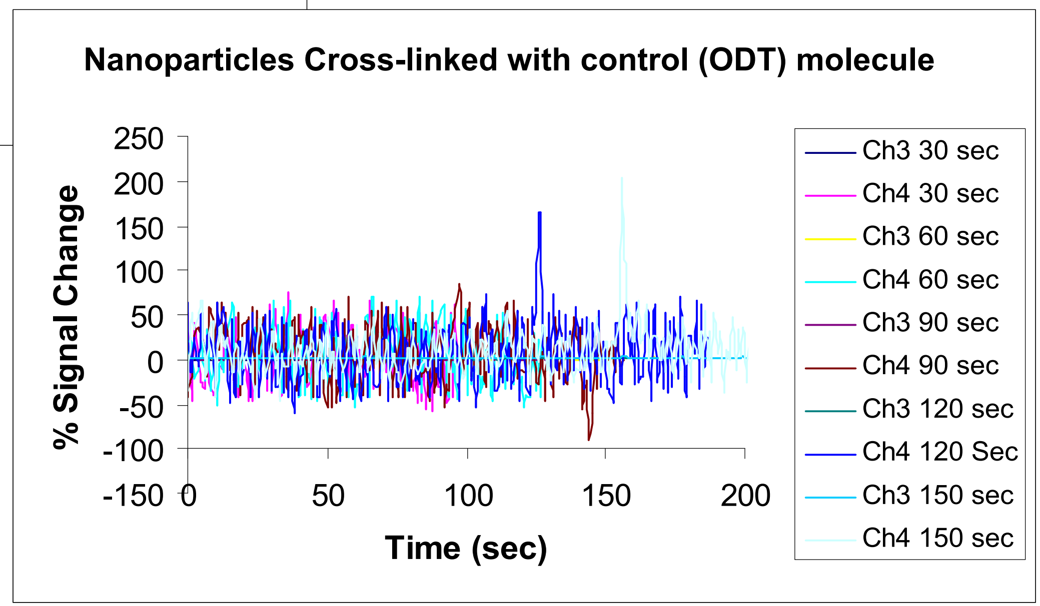


Acid Catalyzed Benzofuran Formation

Initial Vapor Sensing of Dimethyl Methyl Phosphonate (DMMP)



- Deposited Au nanoparticle films cross-linked with sensing and control molecules
- Films exposed to DMMP preconcentrated for increasing times (source emission ~ 7 ppm)



- Films cross-linked sensing molecule have greater response to DMMP than ODT control films

- **We see a specific response**

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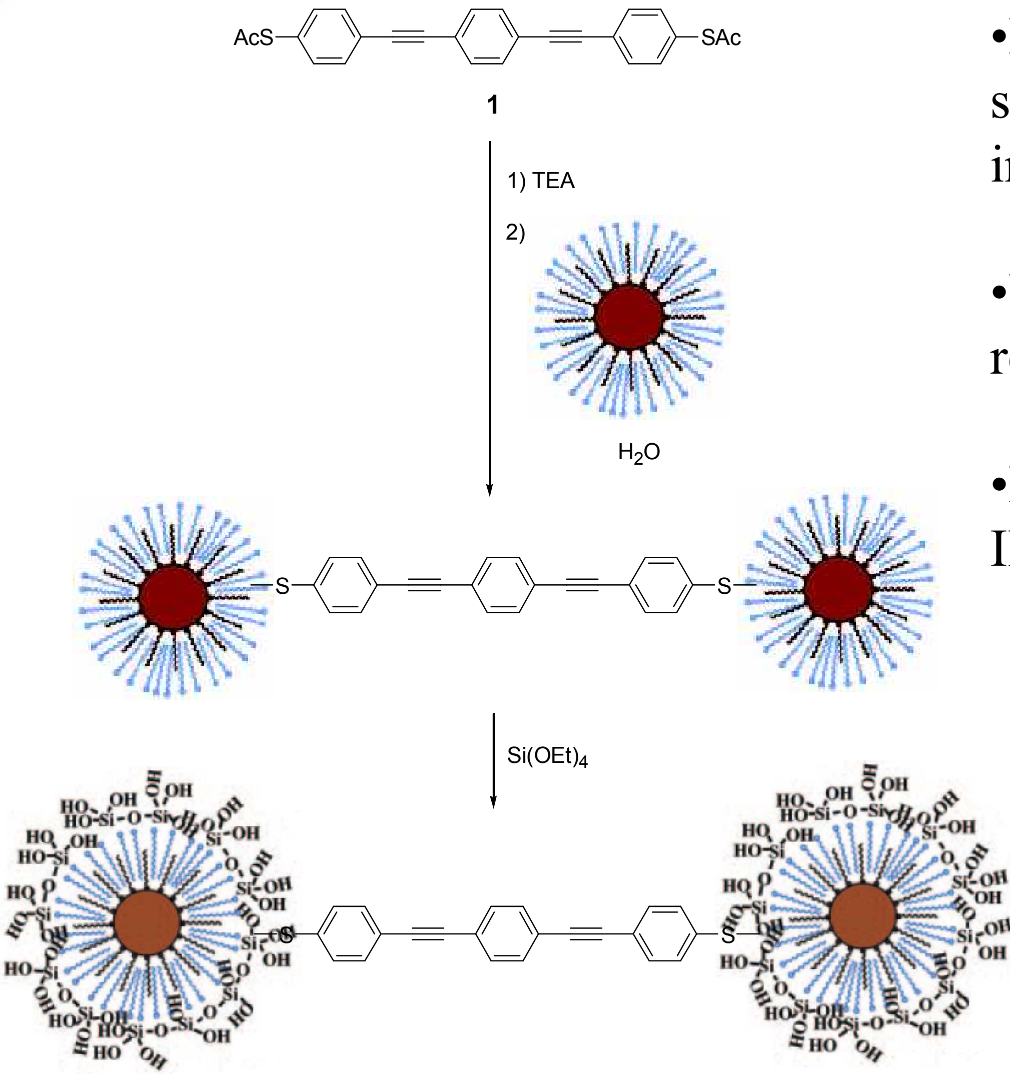
An Improved Approach



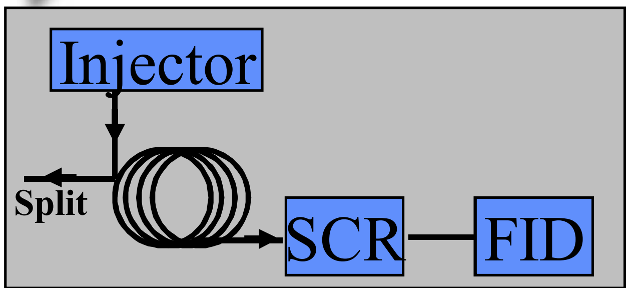
- Do to problems with stability, we started assembling cross-linked films in silica matrix

- We see both improved stability, reproducibility and sensitivity

- Films as simple drop coated on to IDE's

Silica Matrix

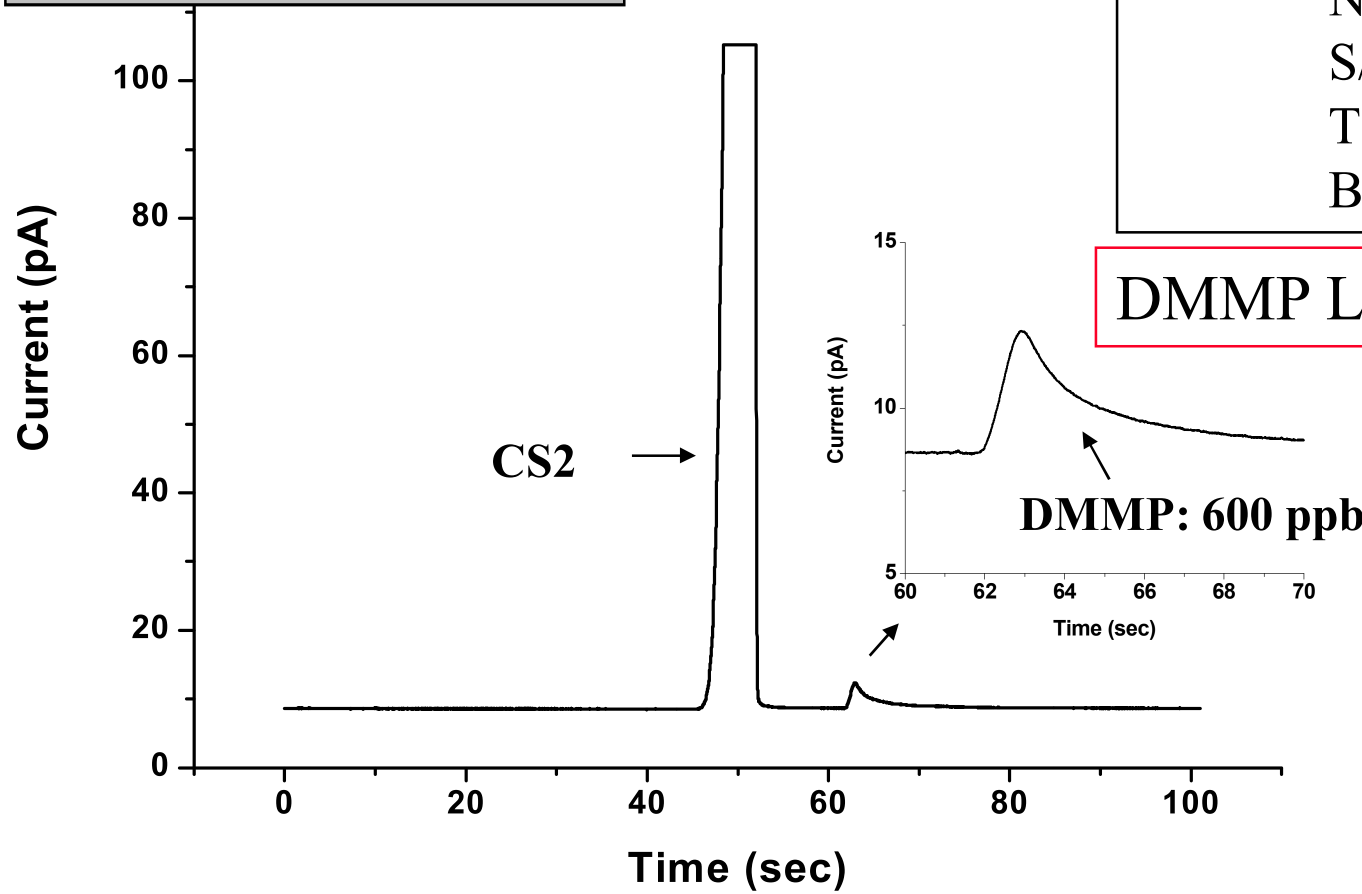
Typical SCR Response to DMMP (0.1 µl DMMP in 1.0 mL CS2)



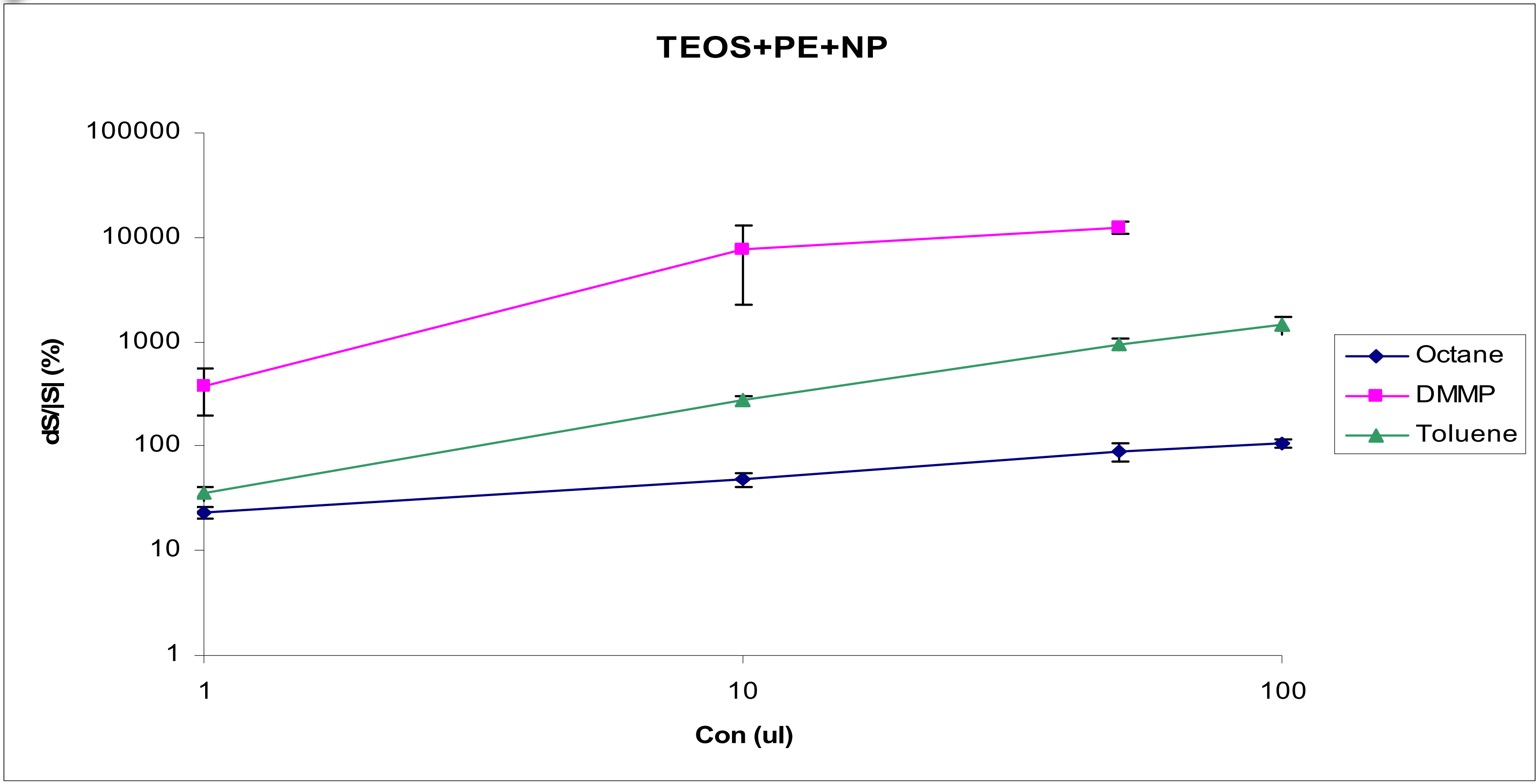
- GC operated using a split

- For 600 ppb of DMMP:
  - Response: 5 pA
  - Noise: 50 fA
  - S/N: ~ 100
  - TC: 100 ms
  - Bias: +10 V

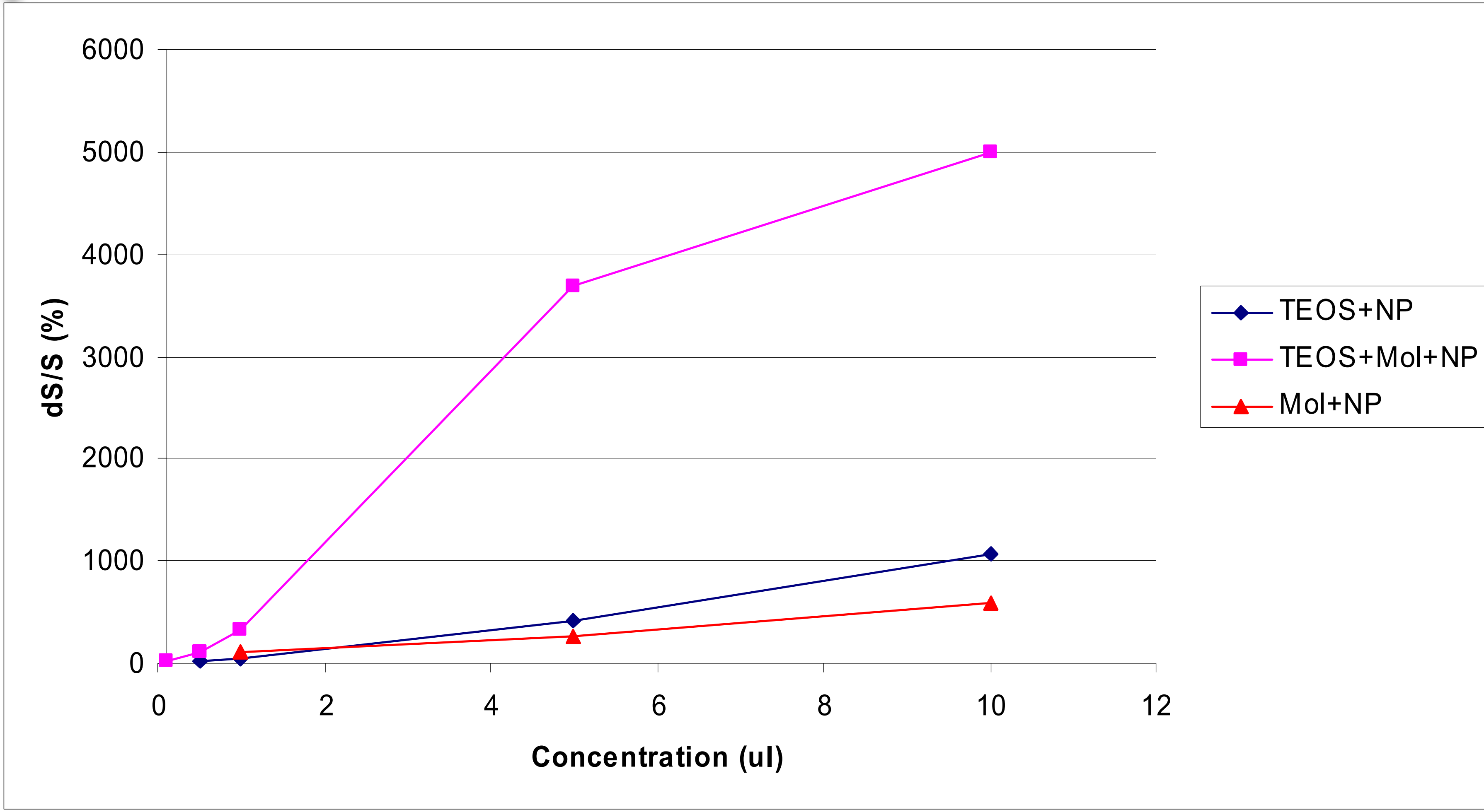
DMMP LOD: XXX



SCR Response to Different Analytes



Comparing DMMP Sensitivity for Different SCR Types



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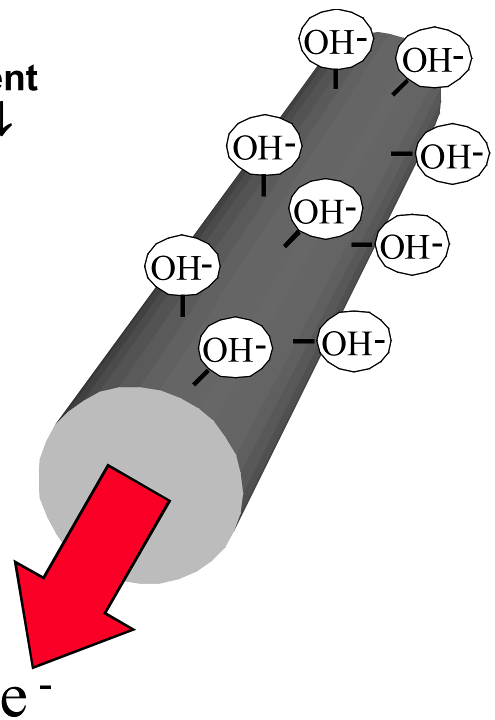
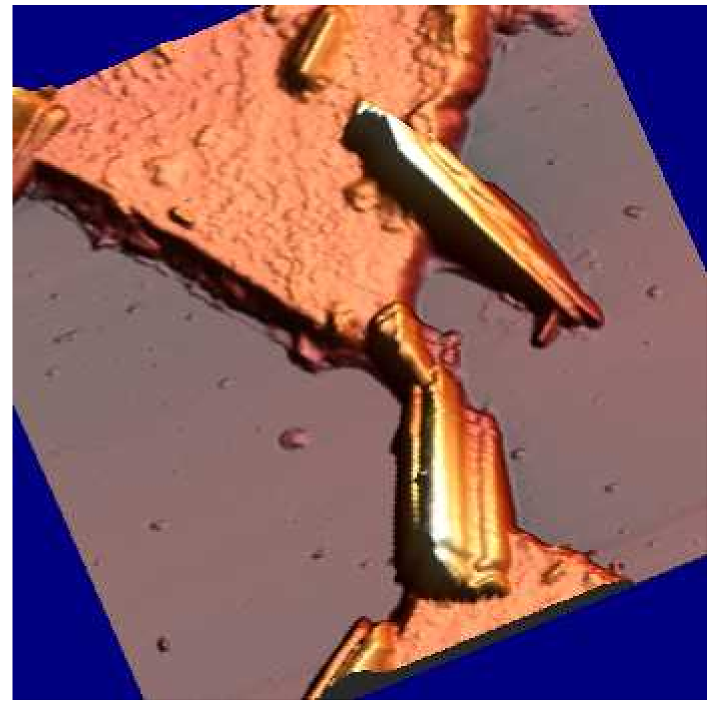
ZnO Nanowires

Reducing agent
Resistance ↓



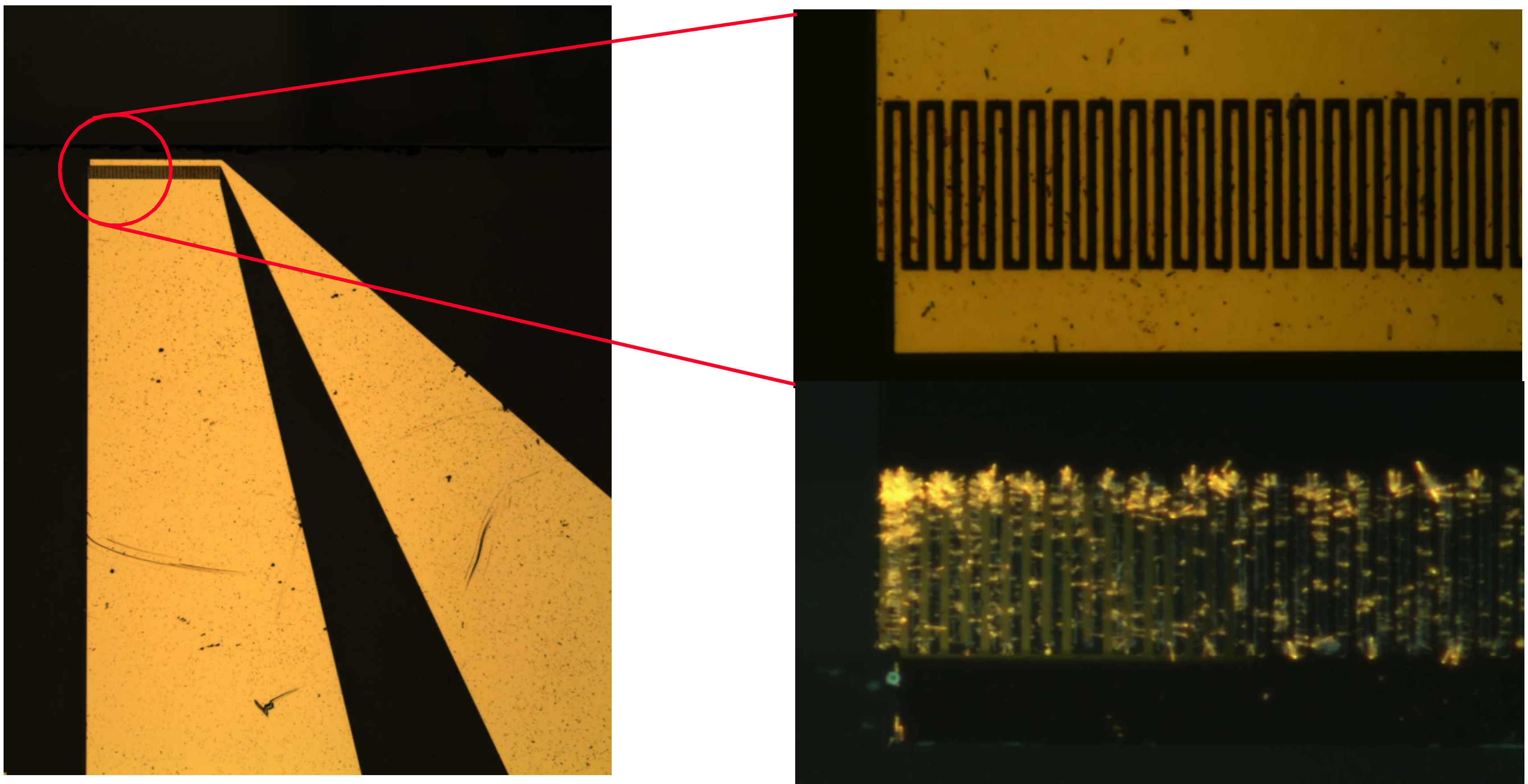


Mechanisms of Resistive Oxide Sensors

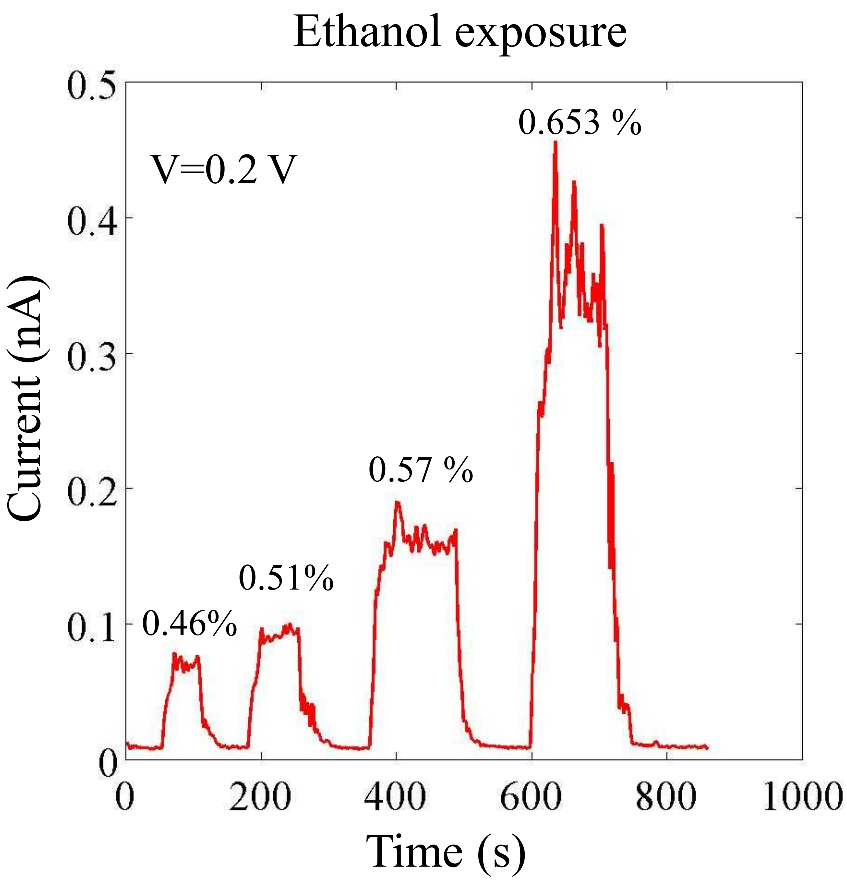
- Chemisorbed oxygen species on surface bind conduction electrons
- Reducing species react with oxygen and releases electrons

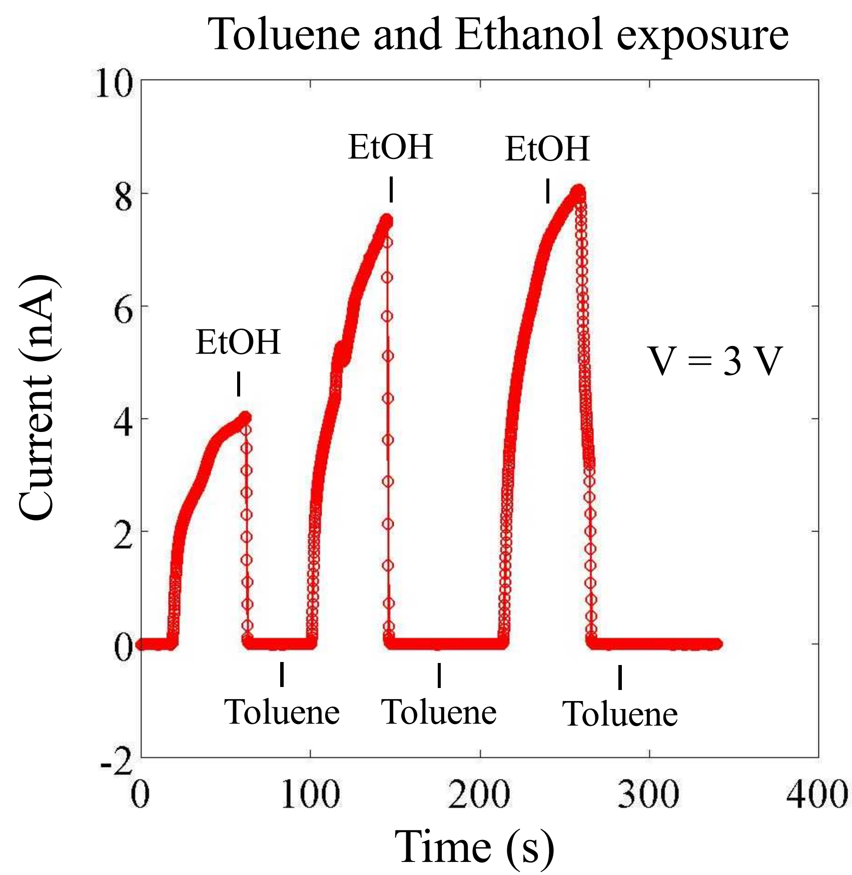
Structured Sensors

- Assembled on interdigitated electrodes with 2 μm gaps
- Deposition parameters   10 kHz, 10 Vac, 10 minutes
- Densities ~ 1.5 rods / 10 μm



Sensitivity of Random ZnO NW Network Deposited on 8 μm Gap





Sensitivities $\left|\frac{\Delta R}{R_c}\right| \sim 35$ @ 0.65%

Selective Response to EtOH

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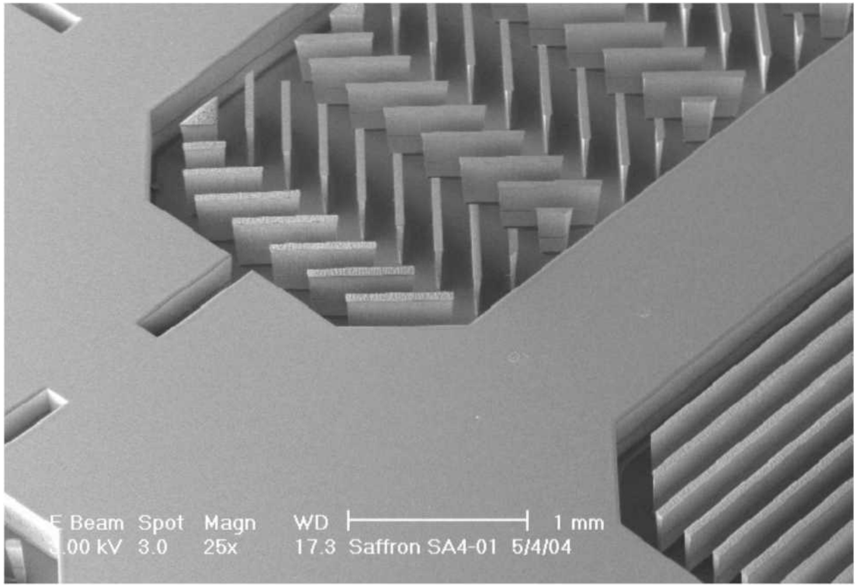
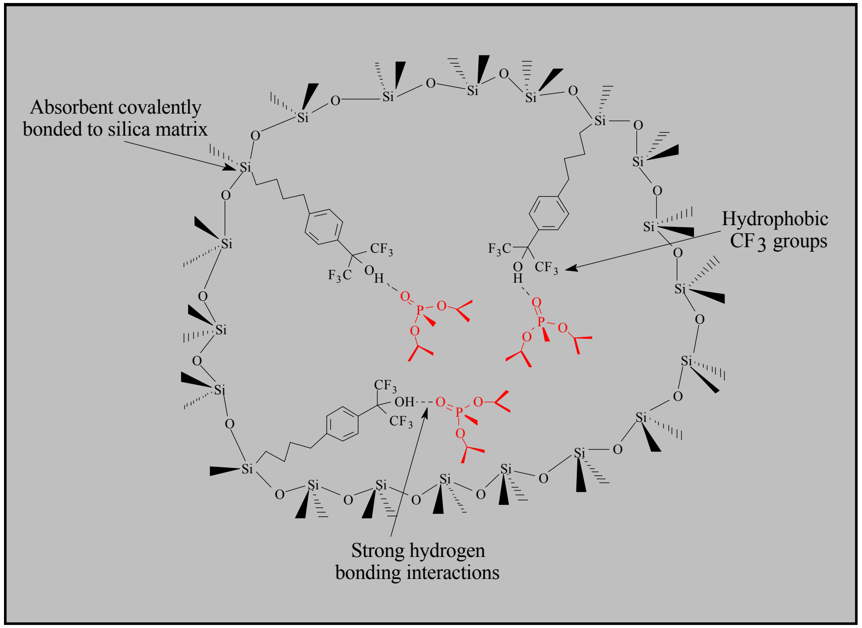
System Integration of SCR: Micro-Preconcentrator (3D PC)





- Micro PC consist of conductive heater supported by thin membrane
- Coated with base-catalyzed Sol-Gel
- Low thermal mass enables rapid heating producing sharp analyte pulse

- By using a PC and appropriate coating, the PC can share the burden of selectivity with the sensor

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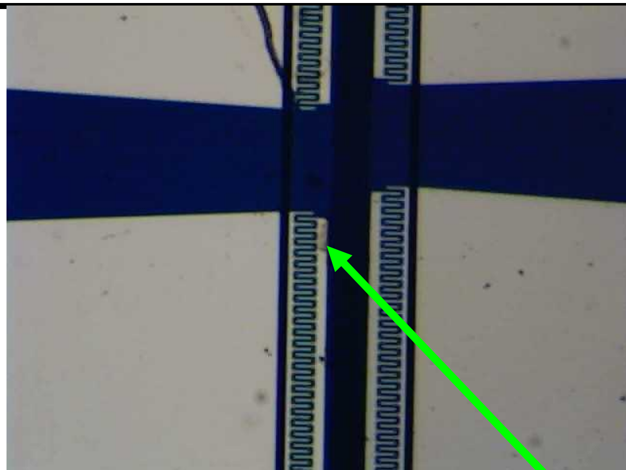
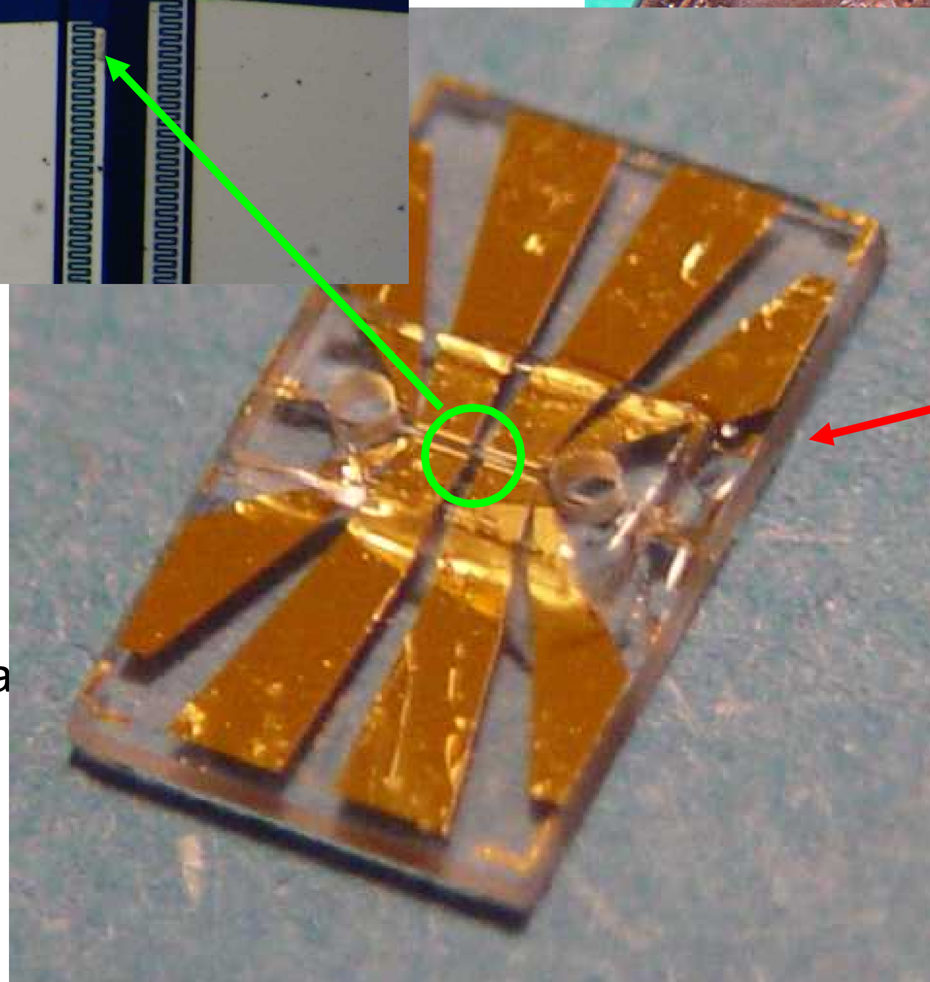
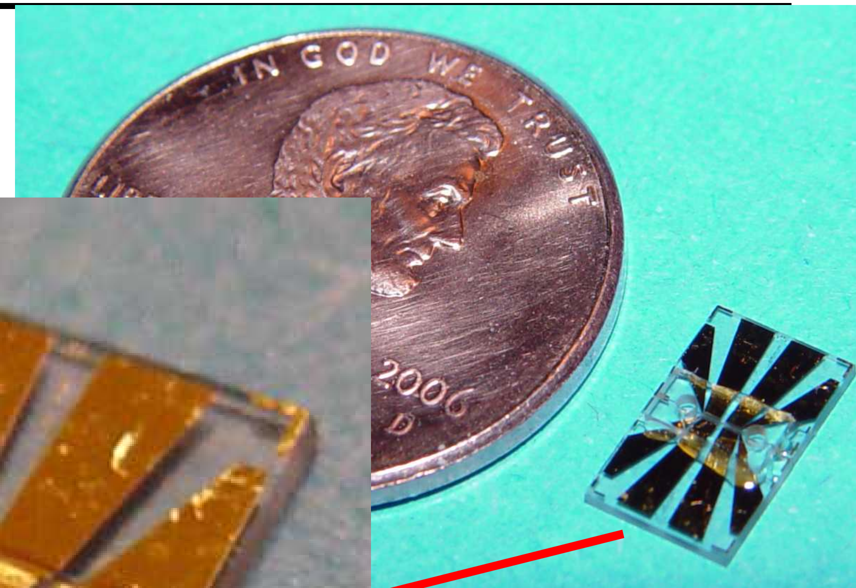
SCR Packaging (Minimum Dead Volume)



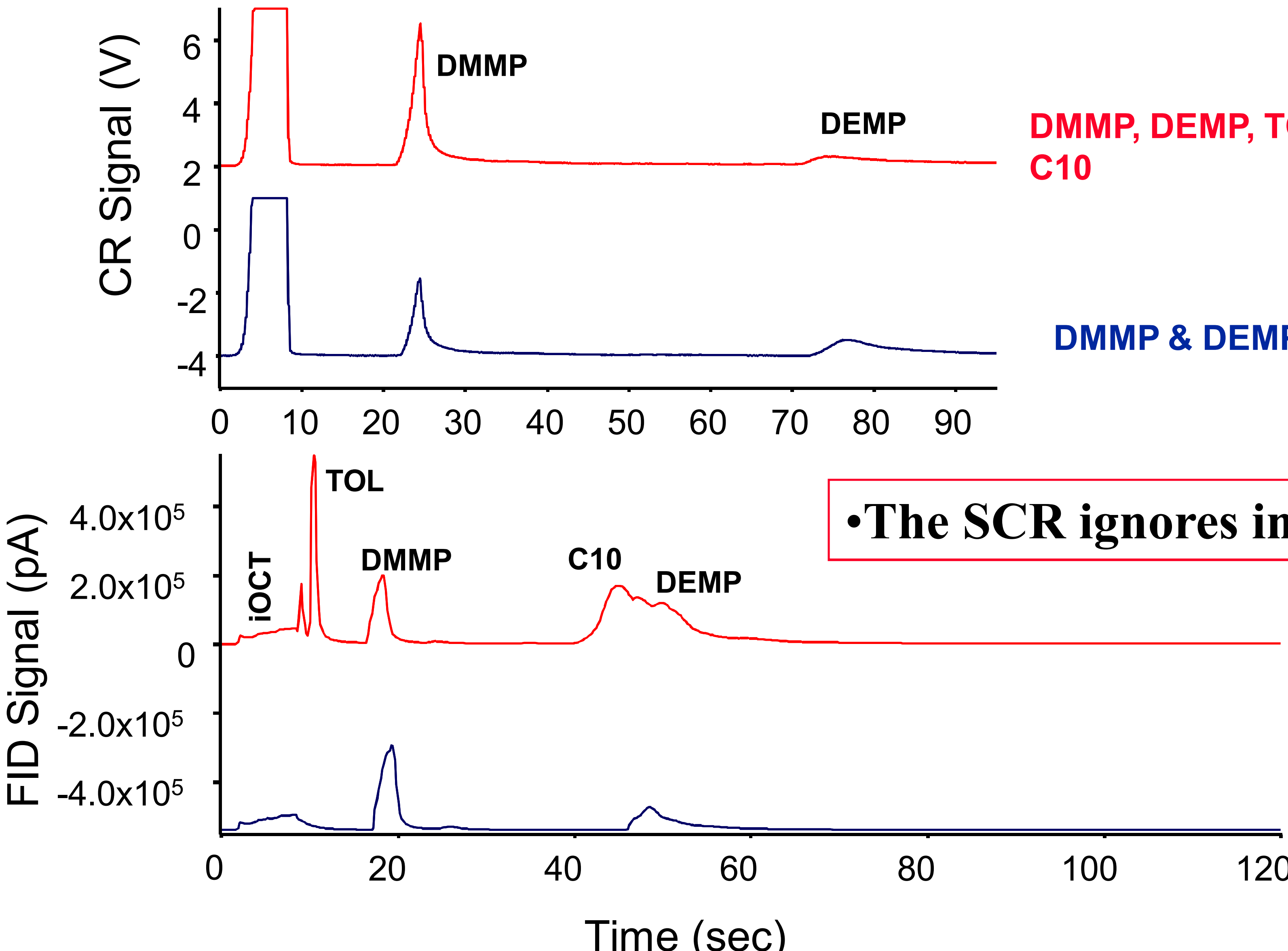




Two quartz nanoparticle IDT chips covered by a flow lid

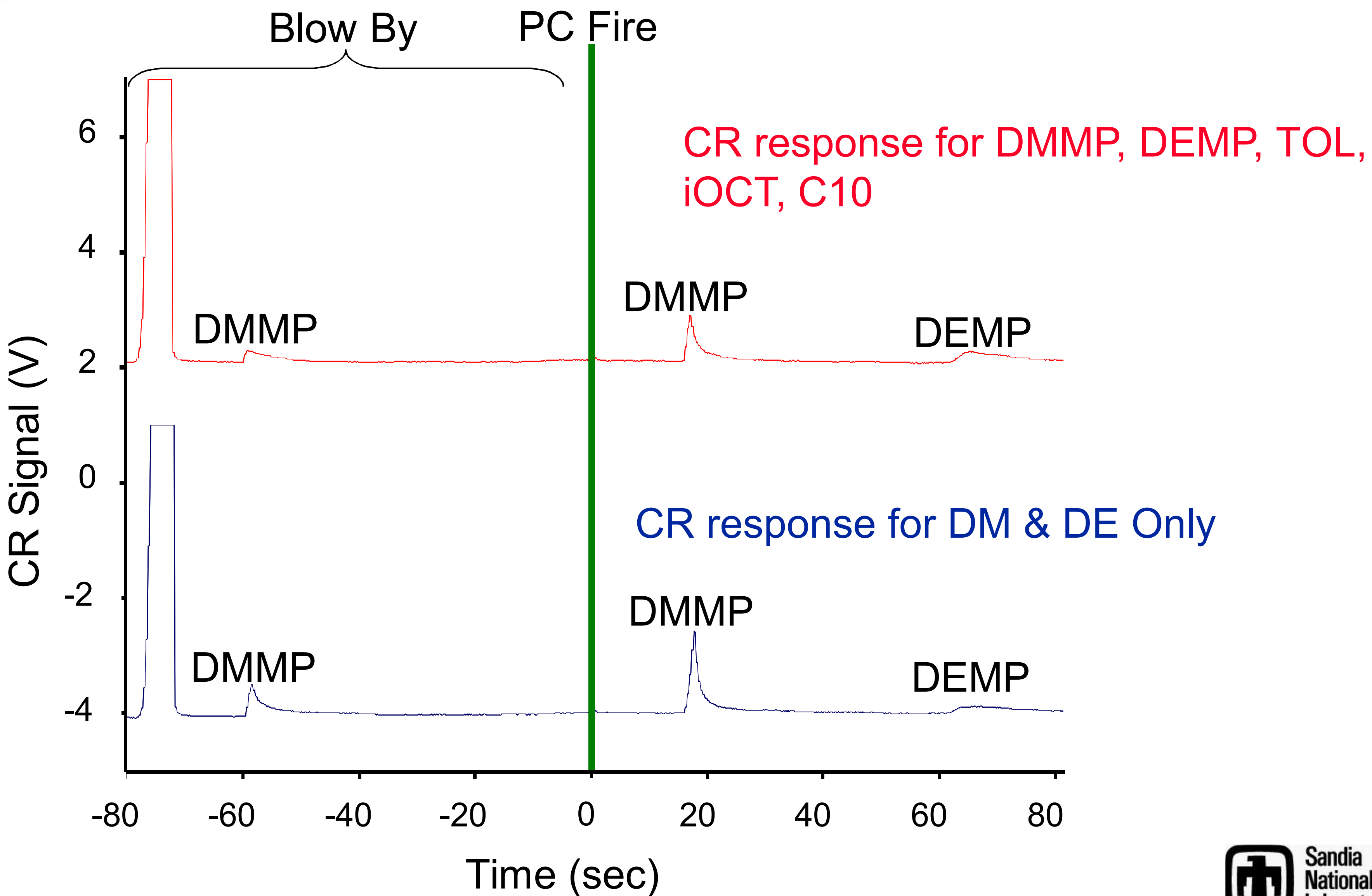
0.5 mm thick glass with 685 micron capillary holes

SCR and FID Comparison Using Commercial CG column



•The SCR ignores interferant

SCR and FID Comparison Using Commercial CG column and PC



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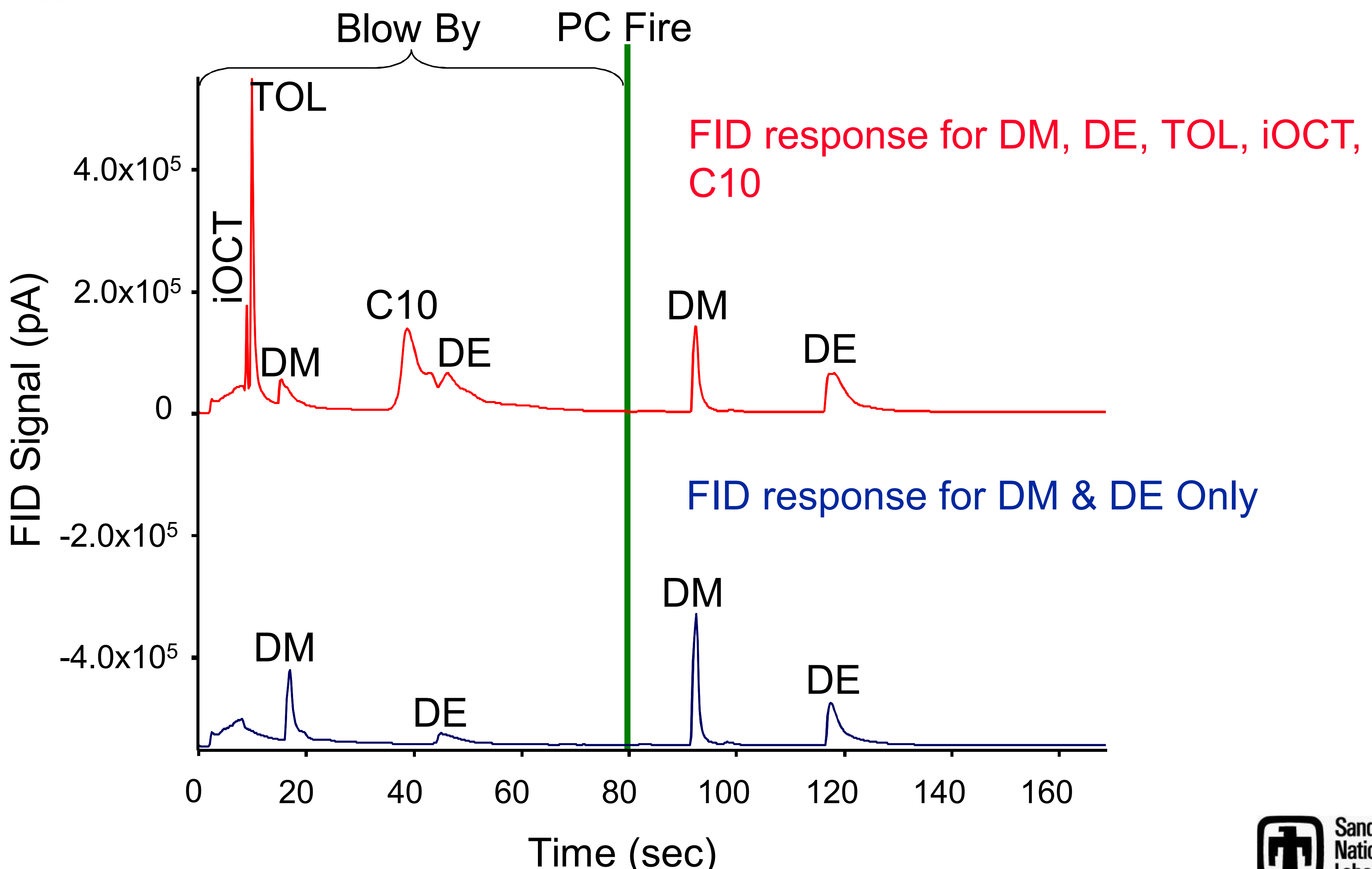
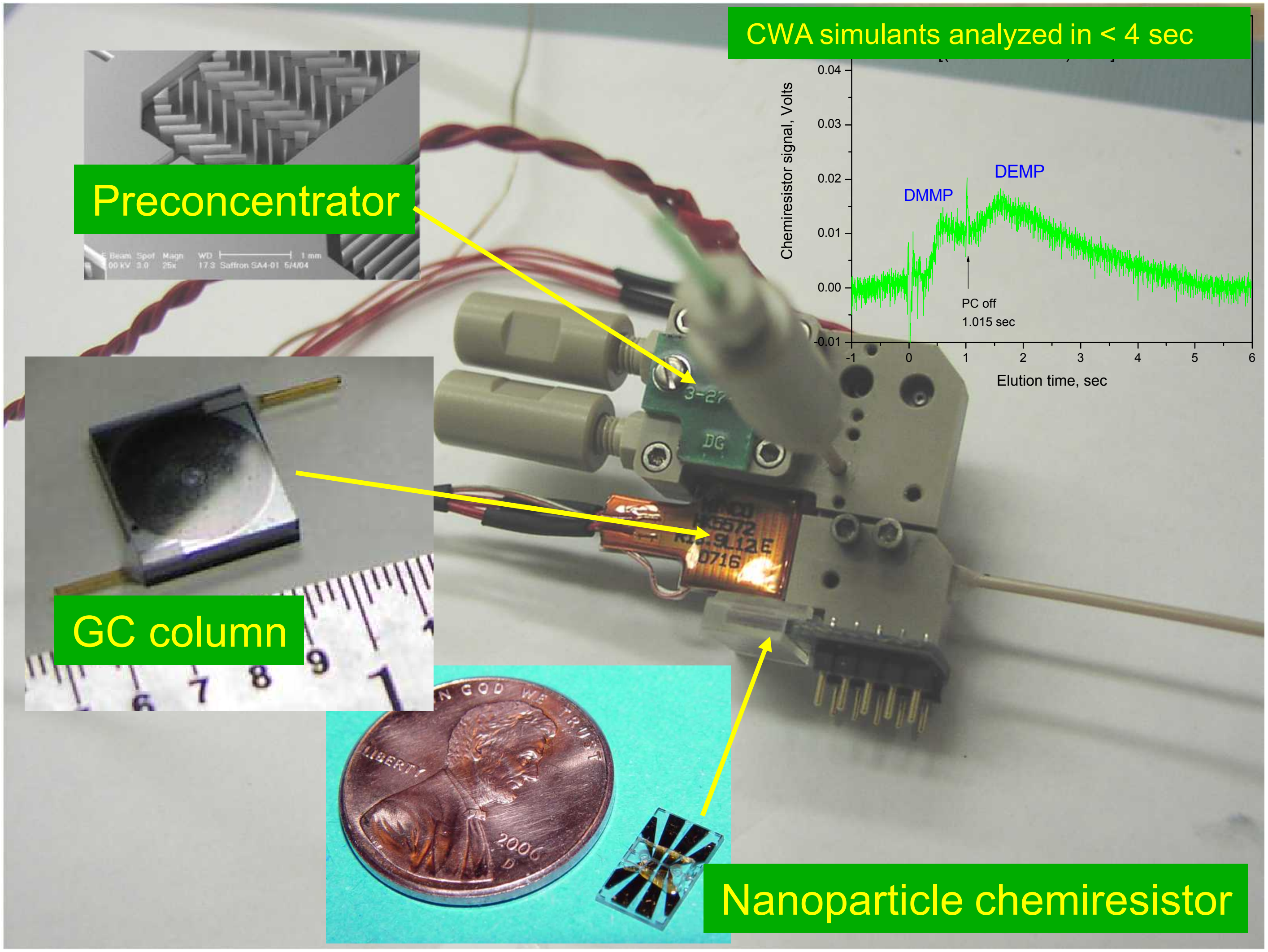
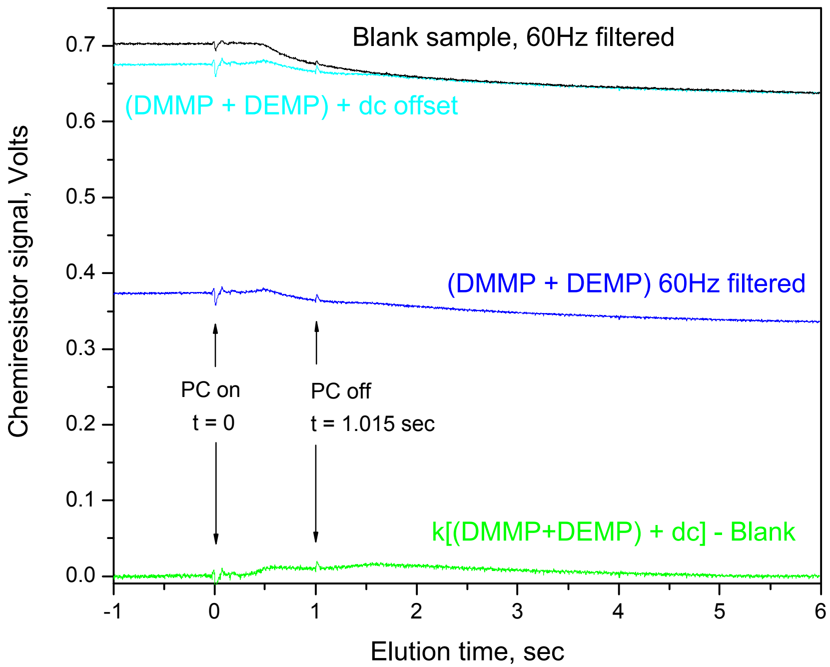
Selective Preconcentration



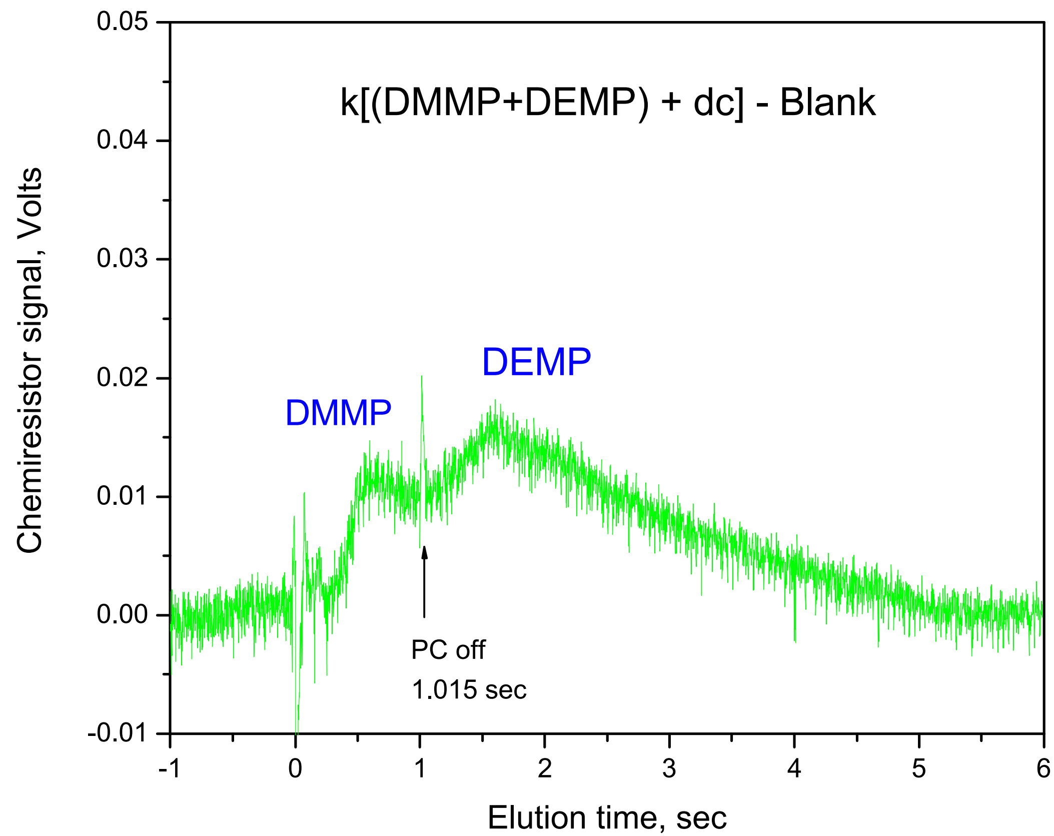
Sandia Micro Gas Analyzer – DARPA Phase II



FAR “Jitter test” and Interferant Tests at MIT-LL



Acquired >11,300 chromatograms using complete system (micro PC, micro GC, micro detector)



- **DMMP + DEMP delivered by MIT-LL sample manifold.**
- **Also completed 2 full interferent matrices**
- **Still working on data reduction**

•The bad news: 80 sec PC load at 1500 ppb

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Conclusions

- Enhanced selectivity of SCR using electronically active cross-linking ligands
- When packaged in low dead-volume cells, typical film's LOD detection was measured the single ppb range
- Developed films that are stable under constant bias conditions for weeks
- Integrated films with micro-PC and MEMS GC columns

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Acknowledgements

- Funding
  - This work was funded through DARPA's micro gas analyzer program
  - Internal funding through Sandia's laboratory directed research and development program (LDRD)

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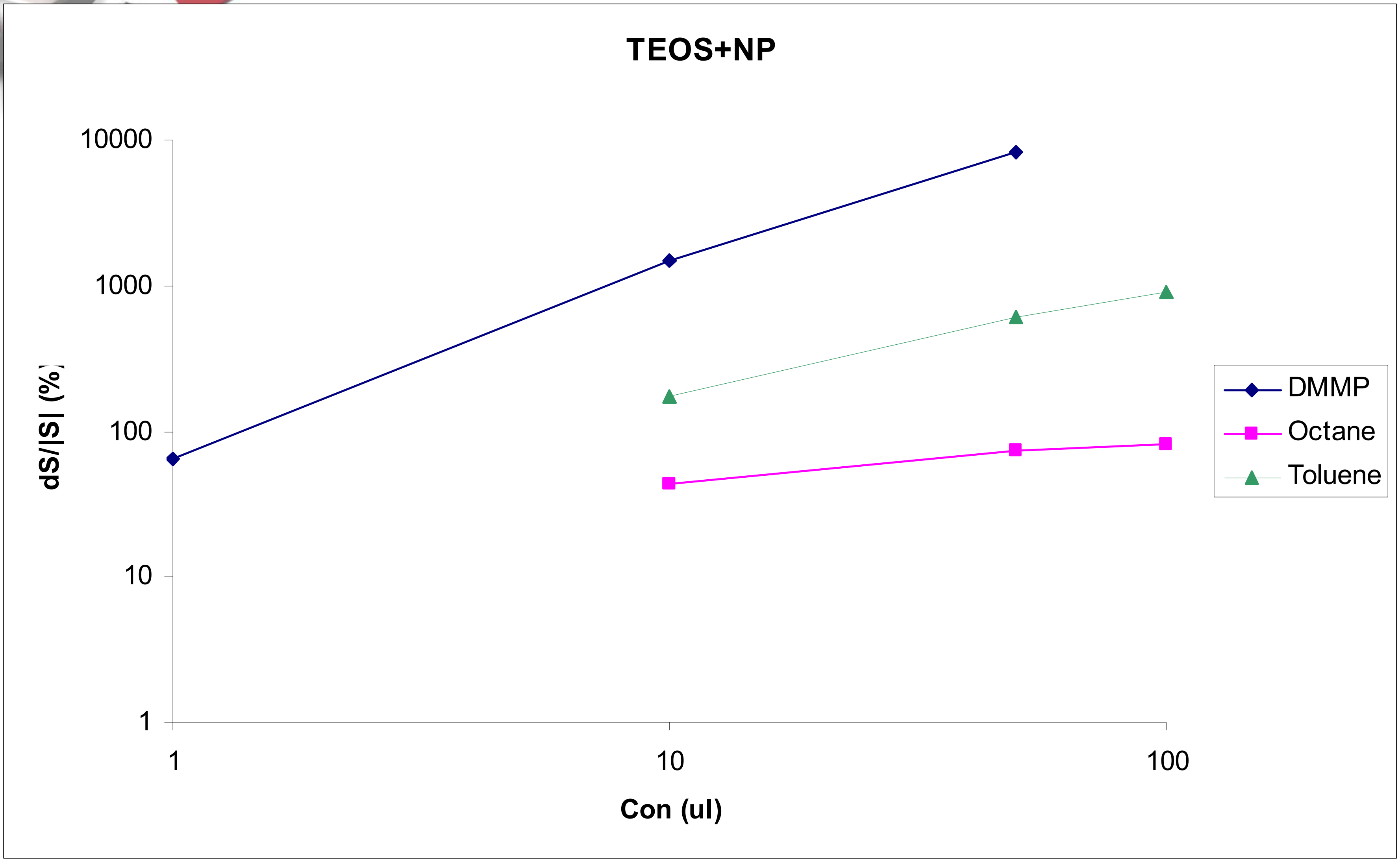

Figure A2. Comparison of TEOS TEA +NP with different analytes (octane, toluene and DMMP) (log/log plot)

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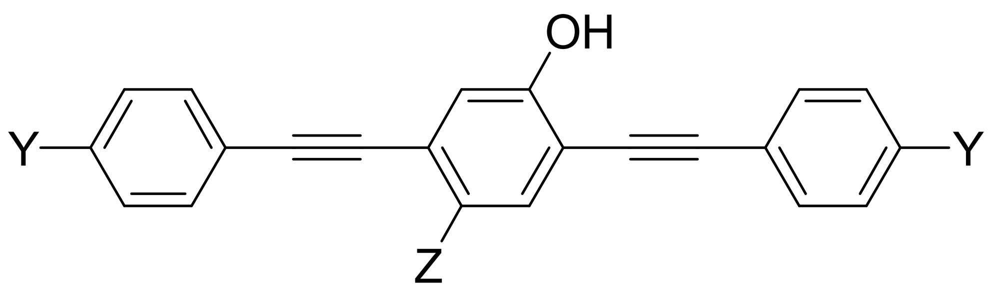
Conclusions

- Developed a novel nanoparticle synthesis
- Developed an array of unique chemistries for both functionalization and sensing
- Designed and fabricated a robotic preparation system
- Observed a linear drop in resistance for layer-by-layer assemblies for different combinations of nanoparticles and crosslinker ligands
- Observed a change in film resistance due to modification in conductance of the crosslinking molecules
- Observed vapor detection of preconcentrated DMMP
- Developed several nanogap fabrication methods

Components Required for Detector

- **Organic Sensing Molecules**
  - **Conjugated phenylene ethynylene**

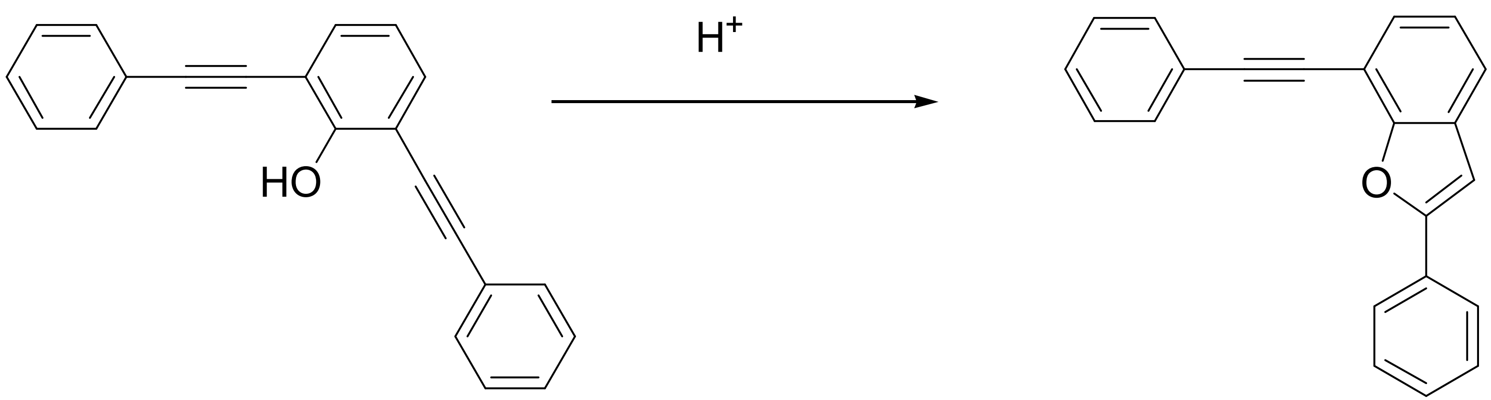


- **Metal Nanoparticles**
  - **Sacrificial ligands to stabilize in solution**
- **Nano/Micro Gaps**

Sensing Degradation

One Possible Explanation for Cessation of Switching

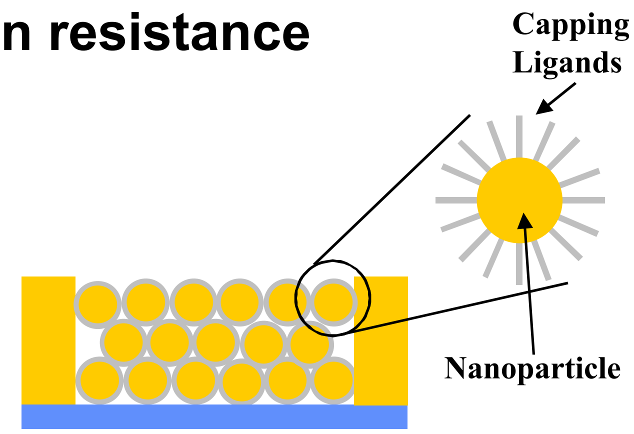
Acid catalyzed benzofuran formation



Moving Beyond The SAW

Why use nanoparticle based sensors?

- Much easier to measure a change in resistance
- Consume less energy



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    - *Snow & Wohltjen Anal. Chem. 1998, 70, 2856-2859*
  - Dielectric modification to the nanoparticle capping layer
    - *Joseph et al., Sensors and Actuators B 98 (2004) 188-195*

Molecular Lengths

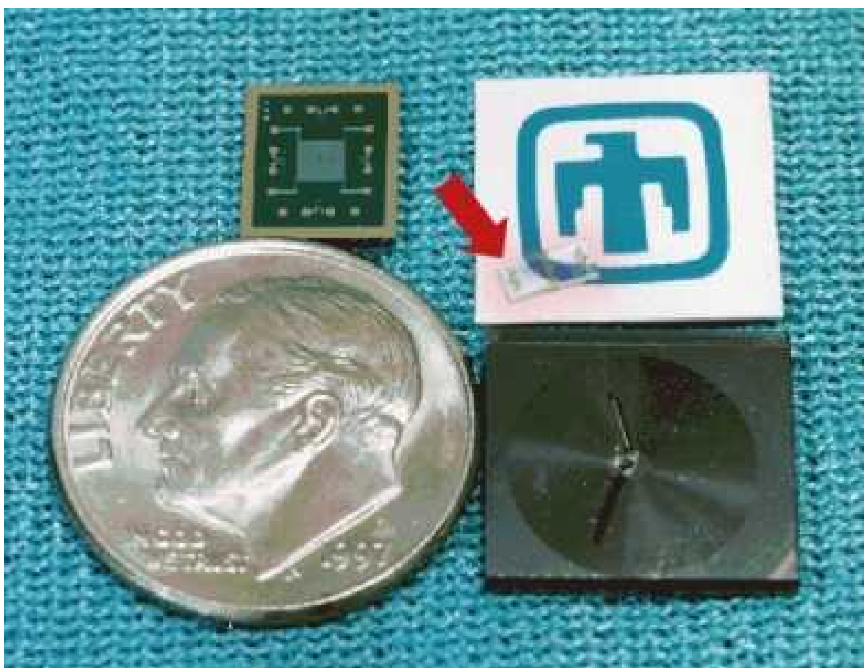
Structure	Length/nm
meta-phenylene ethynylene diisocyanide	1.88
Boc protected nitrophenol *meta*-phenylene ethynylene diithiol	1.72
1,8-octanedithiol	1.17
Au-S bond	0.23
Pt-S bond	0.23
RNC-Au*	0.2
RNC-Pt**	0.11

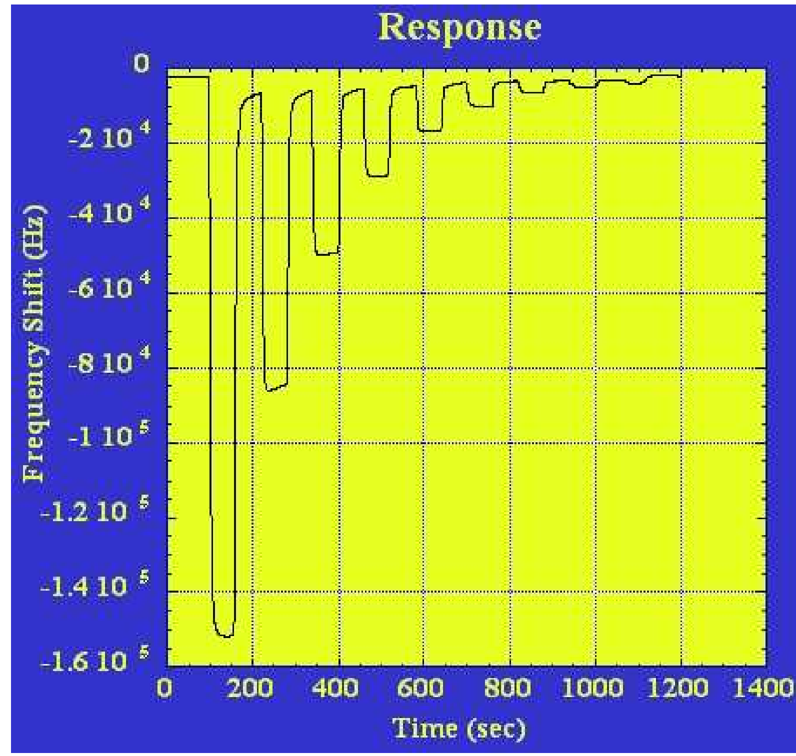
*Journal of the Chemical Society, Dalton Transactions (2001), (8), 1196-1200.

**Organometallics (2003), 22(16), 3316-3319.

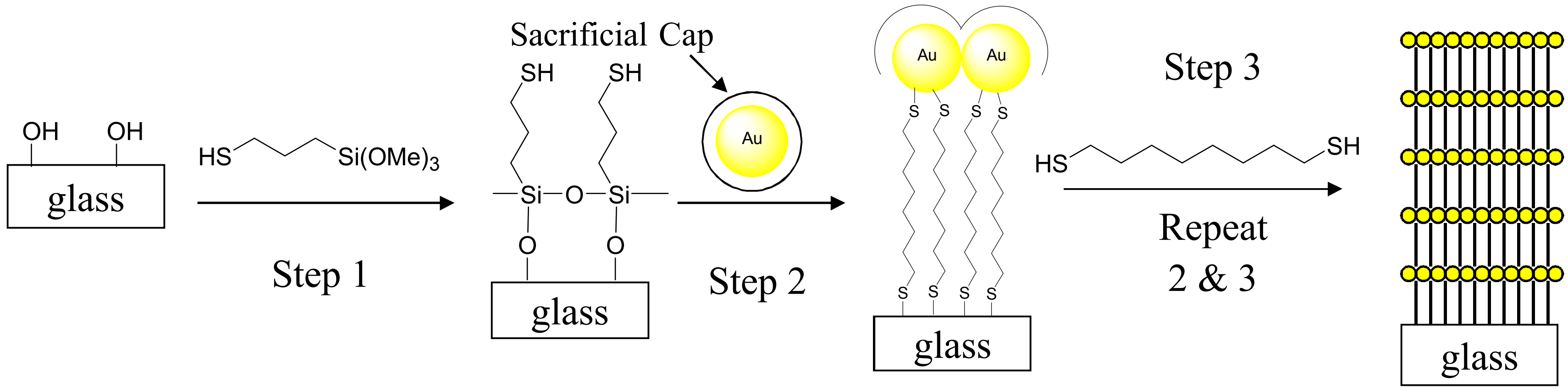
µChemlab™ - Detection

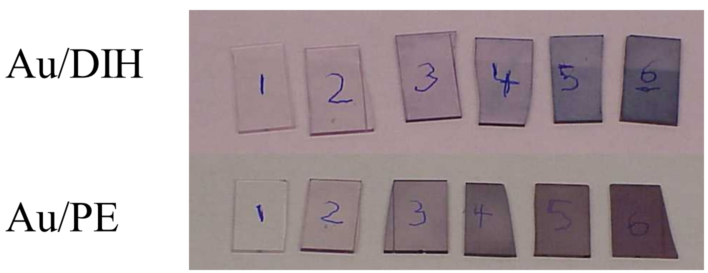
Each SAW device consists of an input and output interdigital transducer patterned on a piezoelectric substrate.

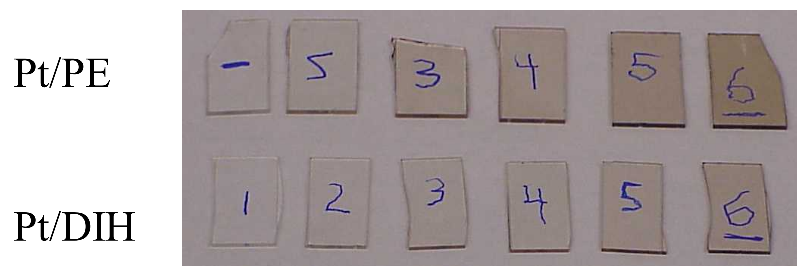




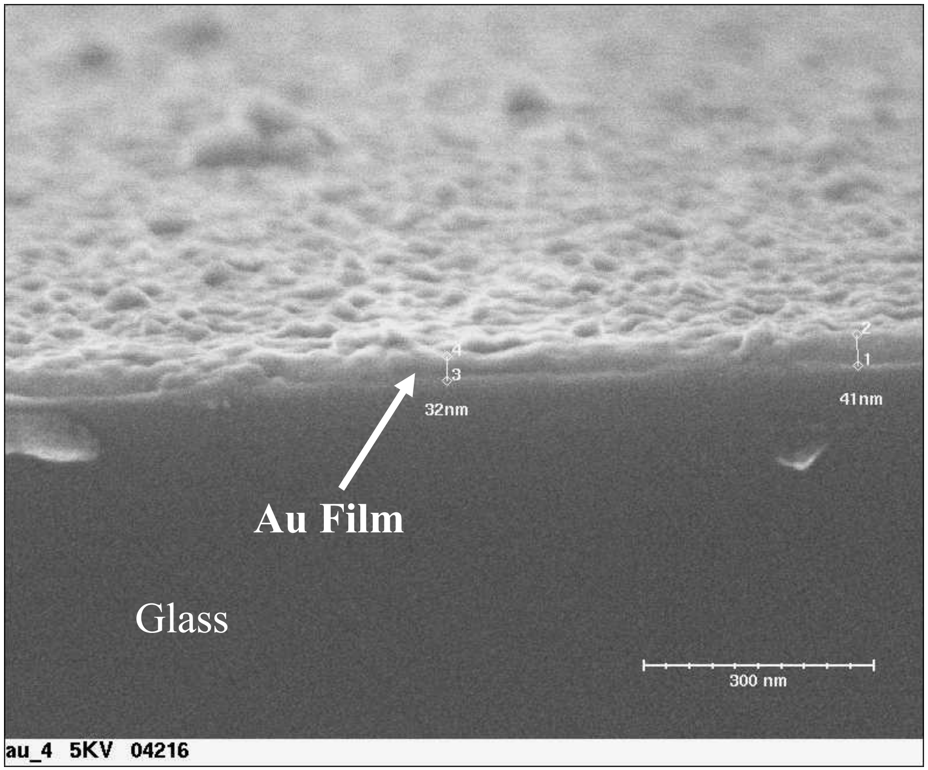
Ligands and Nanoparticles

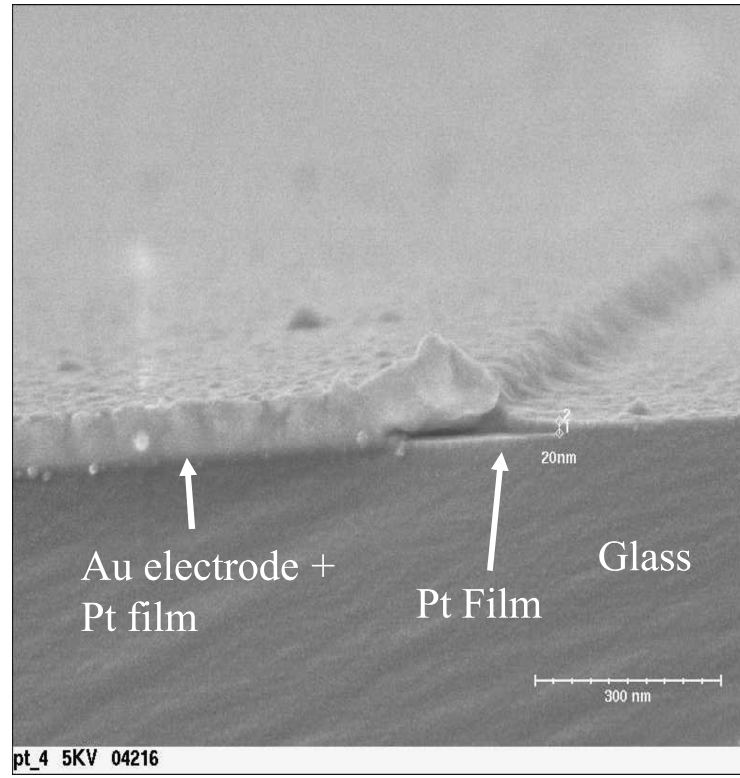




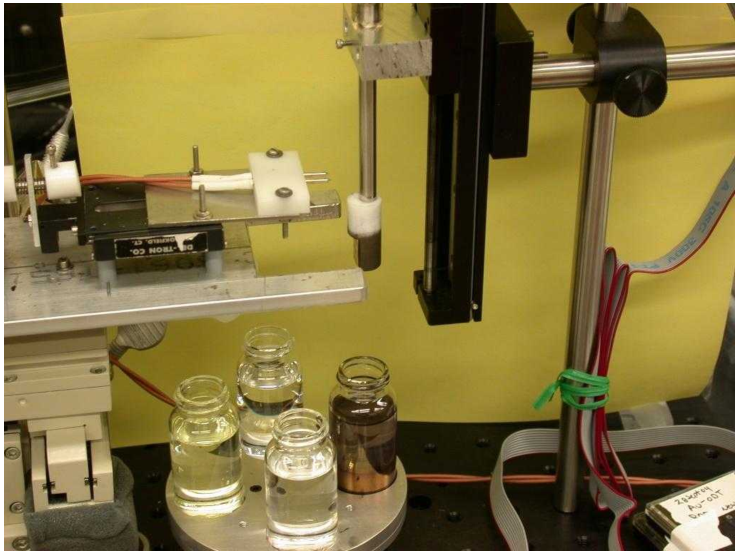


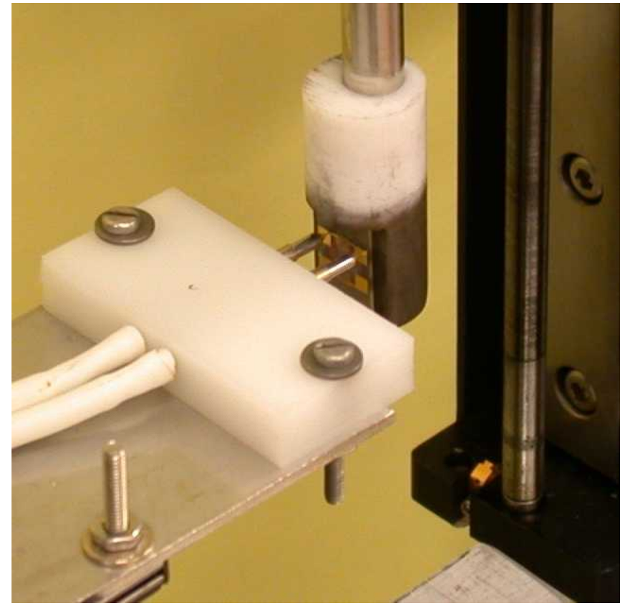
Cross-Sectional SEM

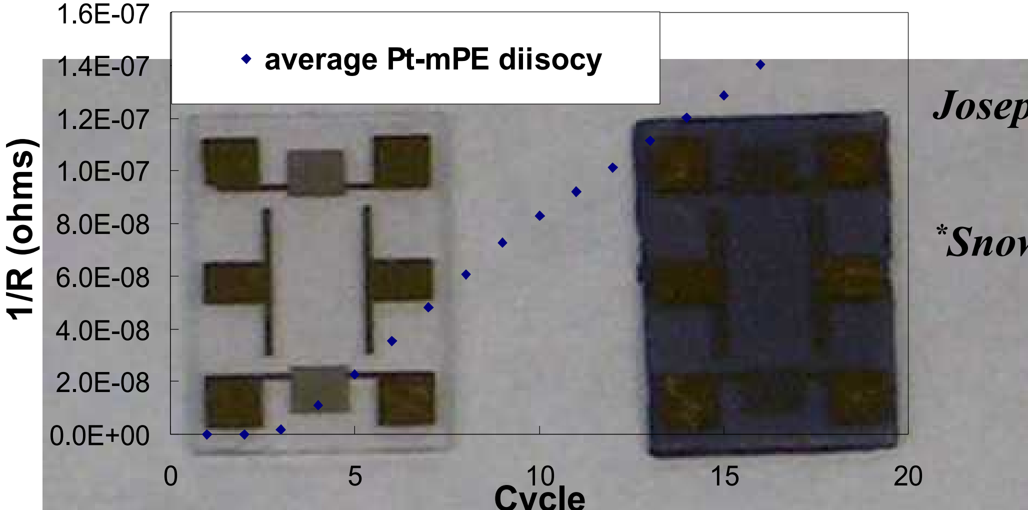




Robotic Preparation







Joseph et al., J. Phys. Chem. B 2003, 107, 7406-7413

- Observed a linear increase in $1/R_{film}$

[*] *Snow et al., J. Mater. Chem., 2002, 12, 1222-1230*

- Observed a alternating current with each additional layer

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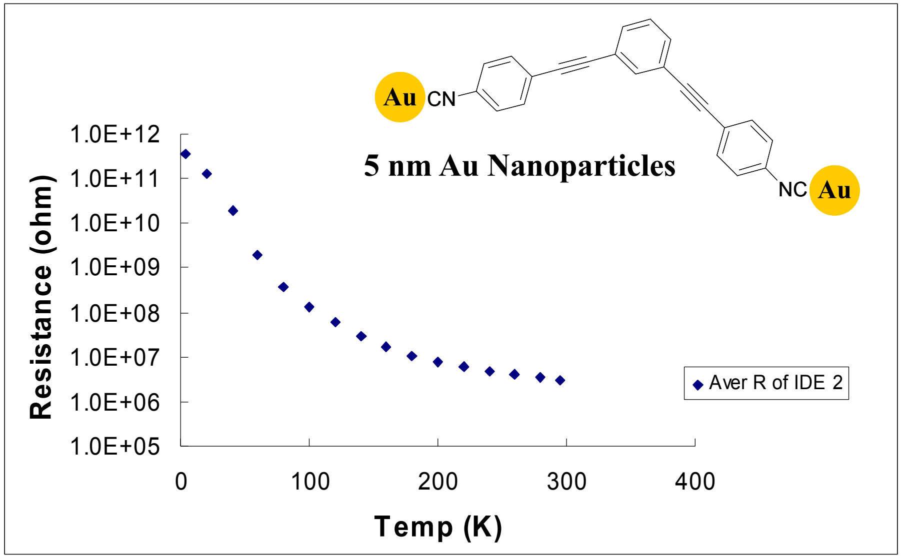
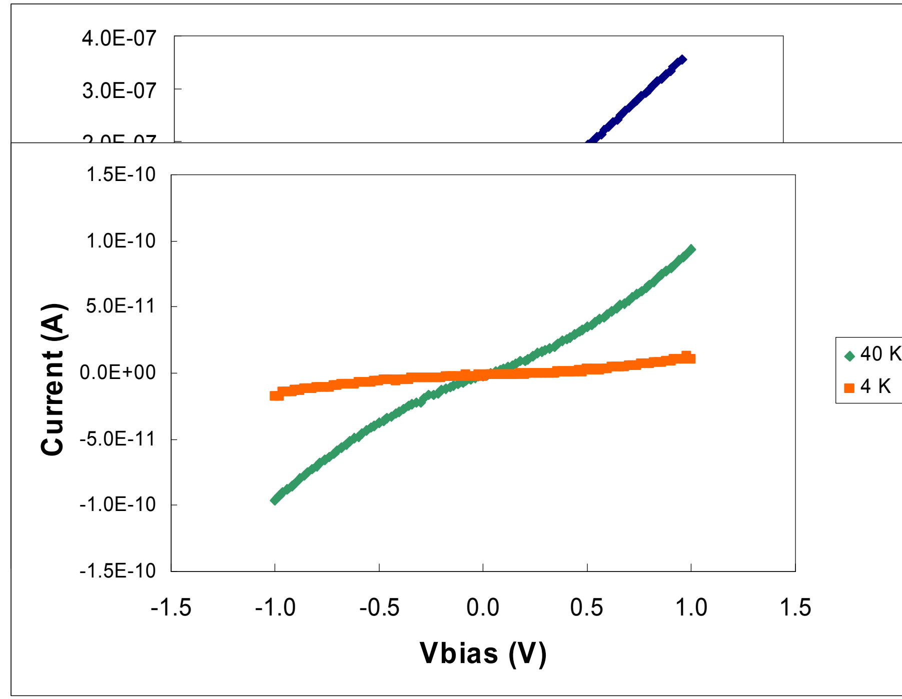
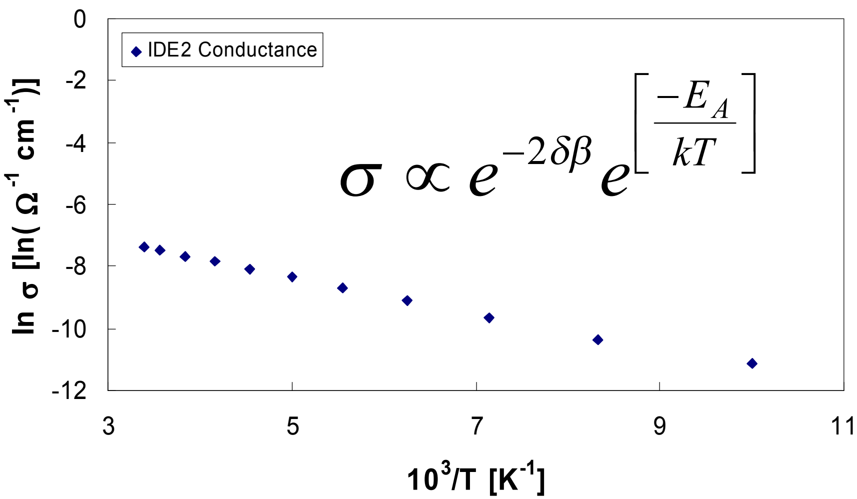
Initial Low Temperature Studies







Evans et al., J. Mater. Chem., 2000, 10, 183
Joseph et al., J. Phys. Chem. B 2003, 107, 7406-7413
Wuelfing et al., J. Am. Chem. Soc. 2000, 122, 11465-72

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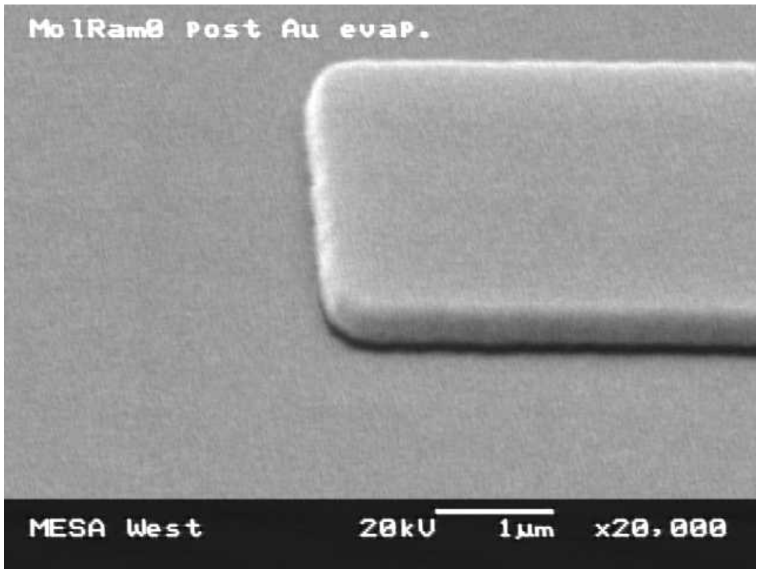
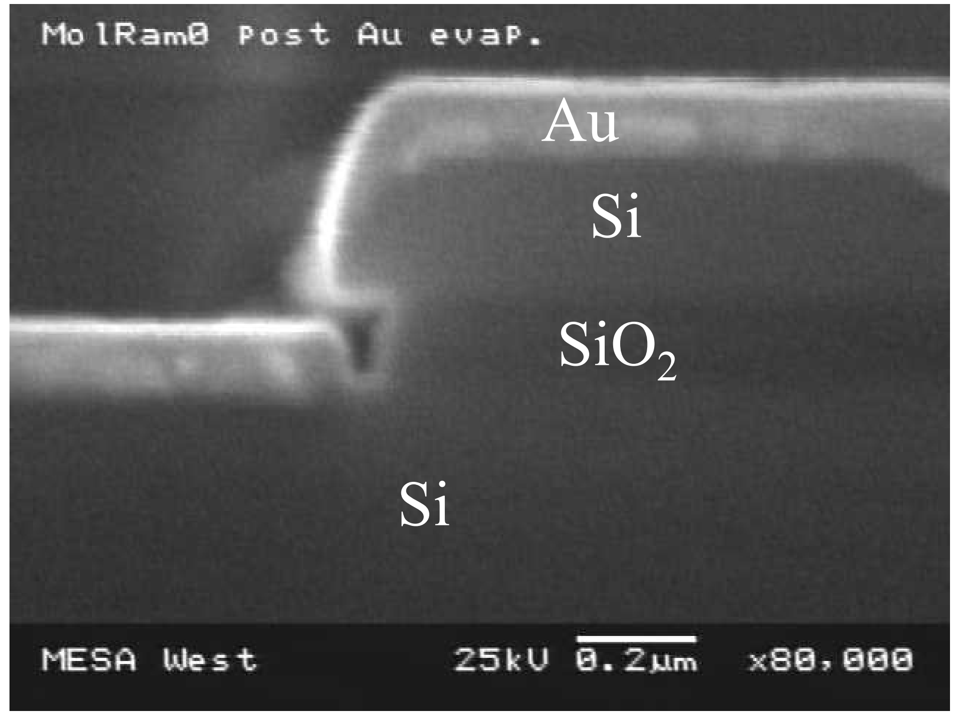
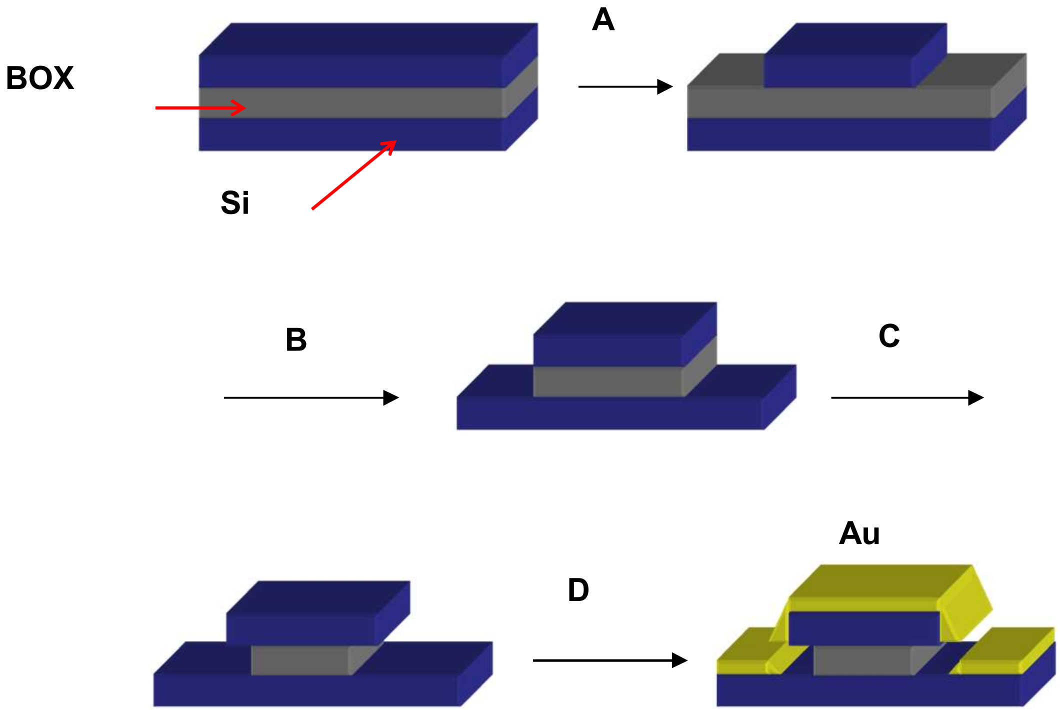
Gold Nanogaps



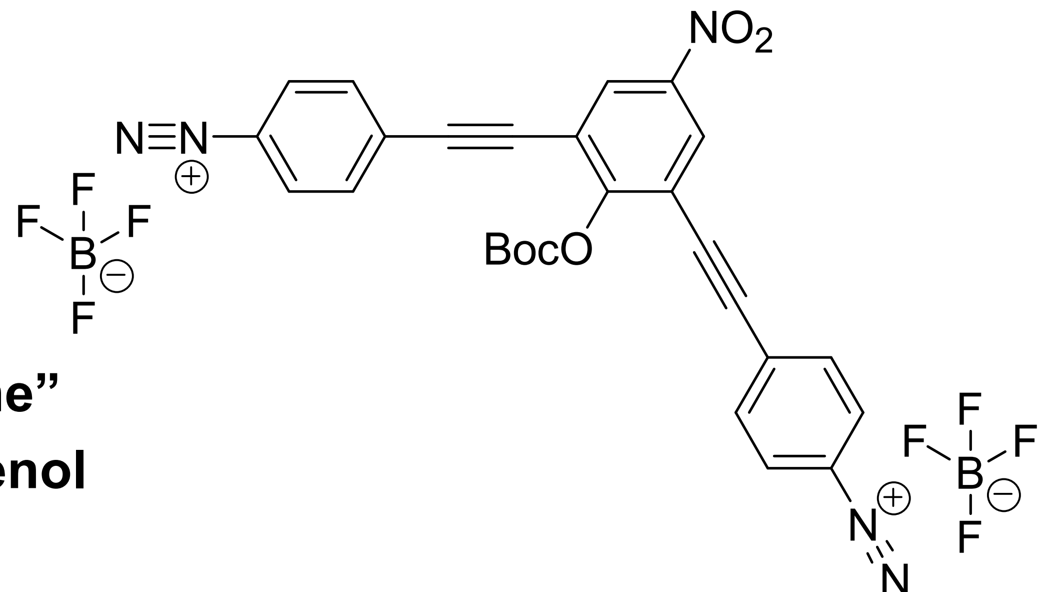


Gold Nanogap Fabrication



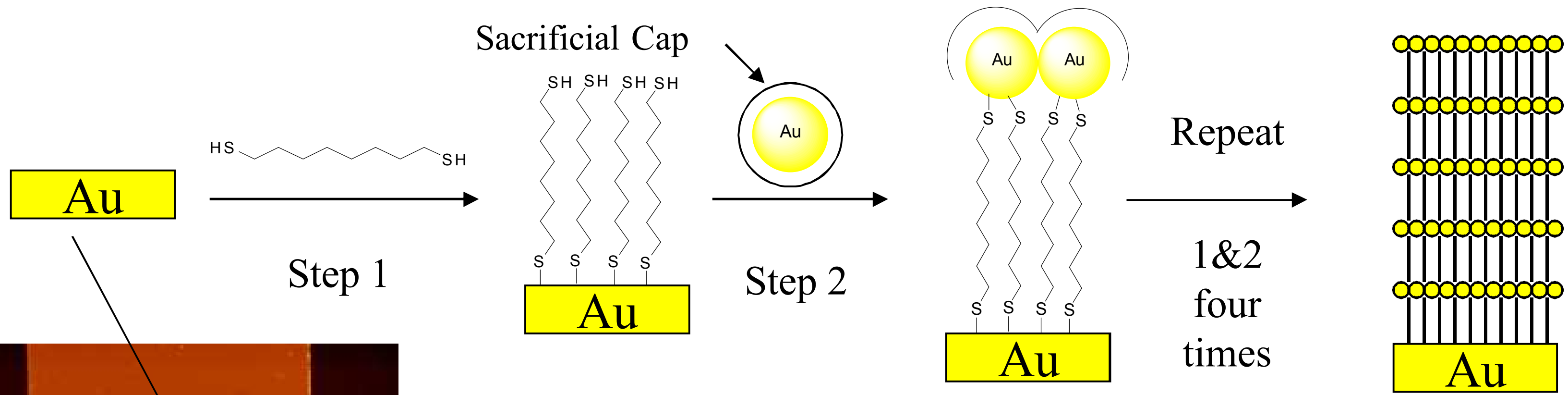
Organic Molecules

- Number of different functionalization chemistries available to use including:
  - Diazonium salt
  - Thiol
  - Nitrile
  - Amine
  - Isonitrile
- Conjugated “backbone”
- Electron deficient phenol

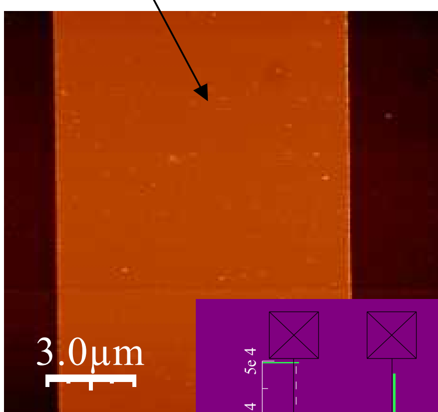


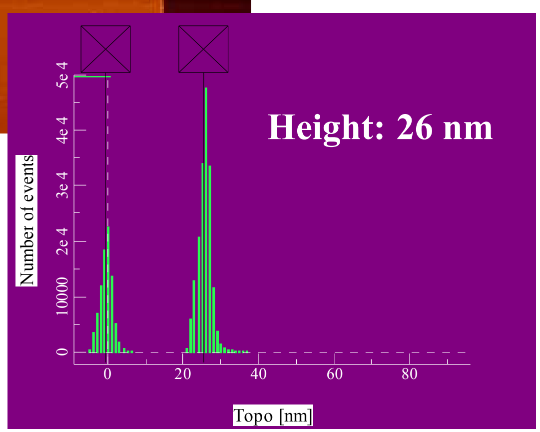
*Synthesized by Dirk and Wheeler

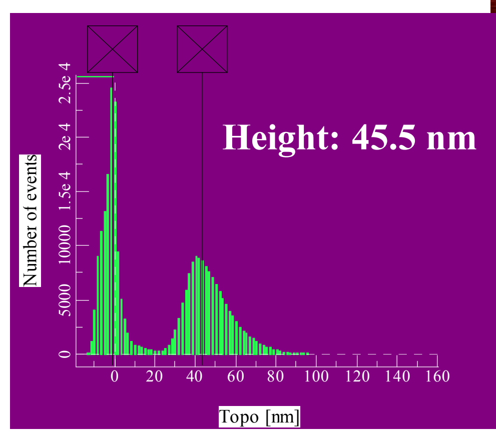
Ligands and Nanoparticles

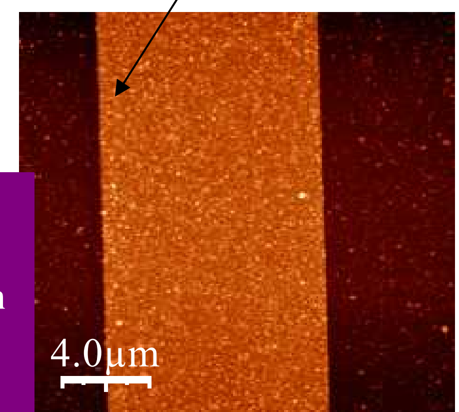


Stearonitile capped Au nanoparticles were assembled in a stepwise fashion onto a Au electrode.









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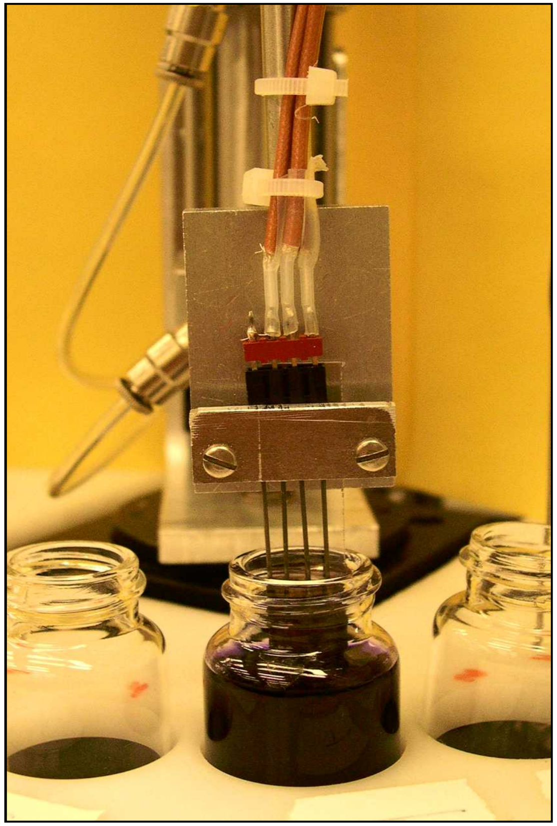
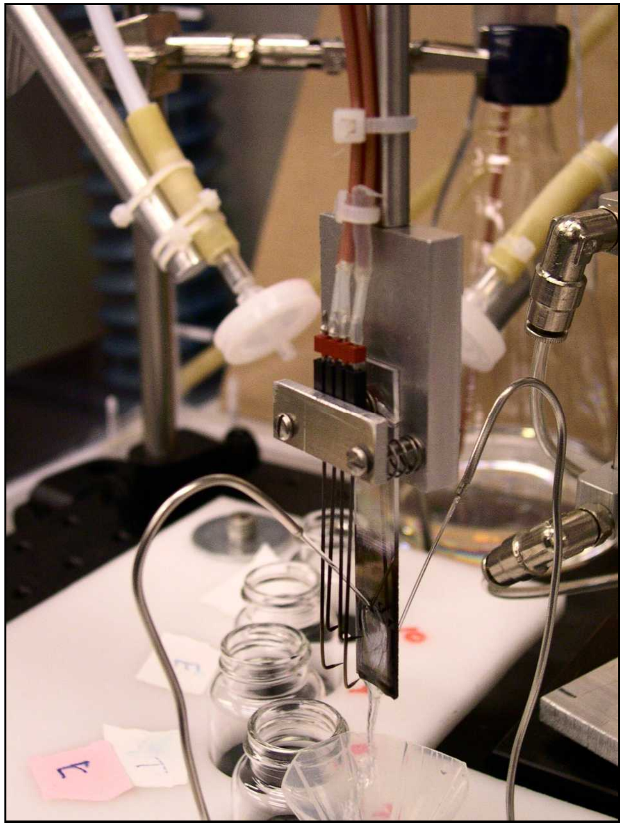
Robotic Assembly



•The substrate is dipped into the nanoparticle solution.



•A rinse stage removes excess nanoparticles and ligands.

•The sample holder has the capability to interface with electrodes on substrate.

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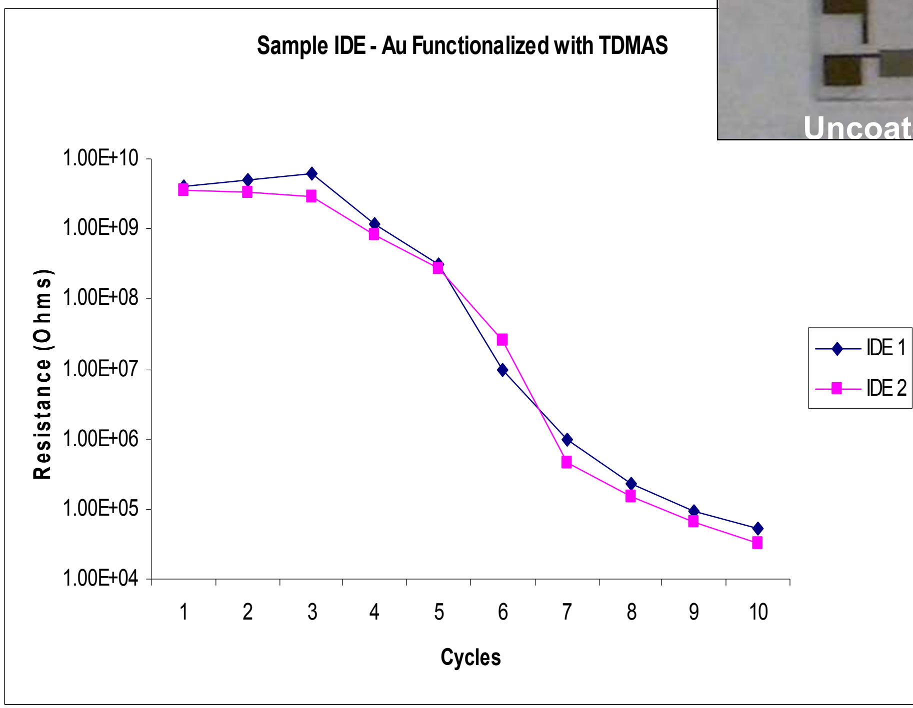
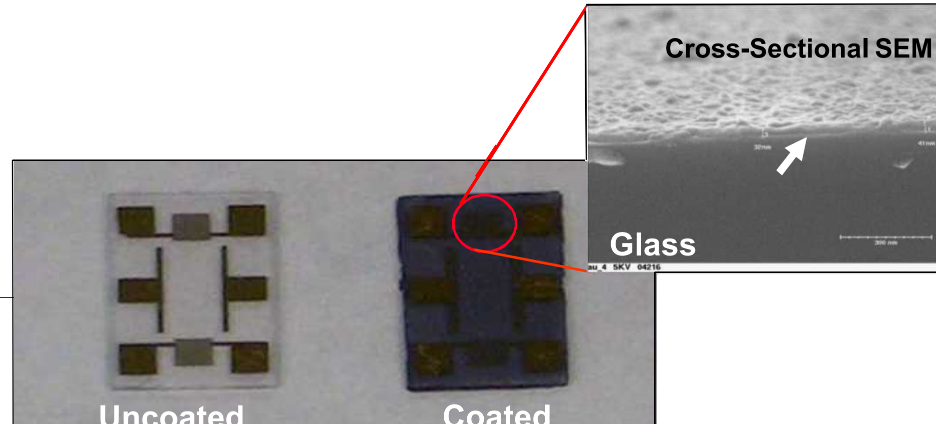
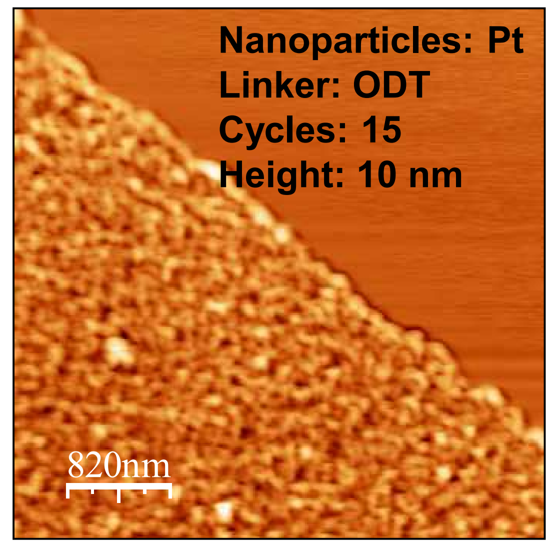
Characterization of Assembled Films

Nanoparticles: Au
Linker: ODT
Cycles: 10

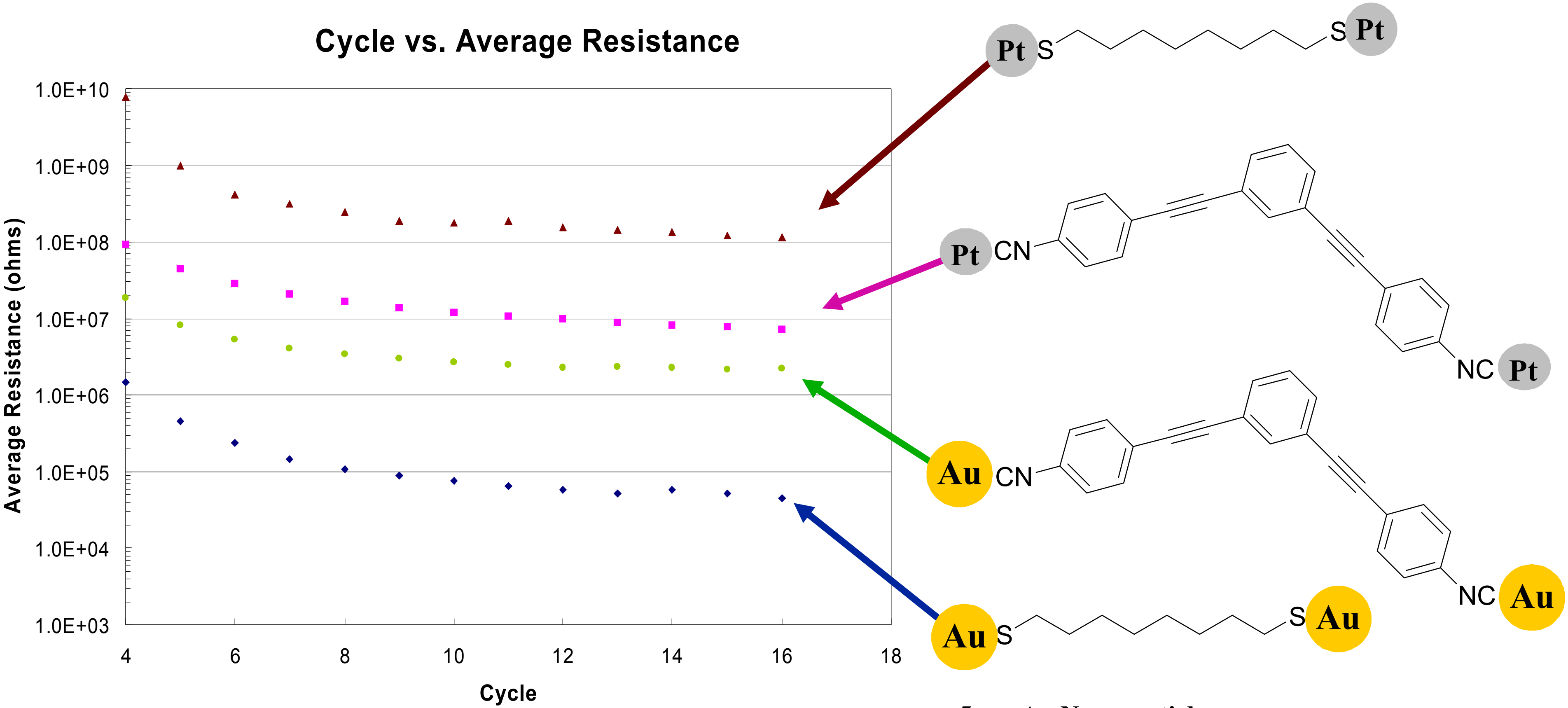






Ligand-Nanoparticle Combinations

2 nm Pt Nanoparticles



5 nm Au Nanoparticles

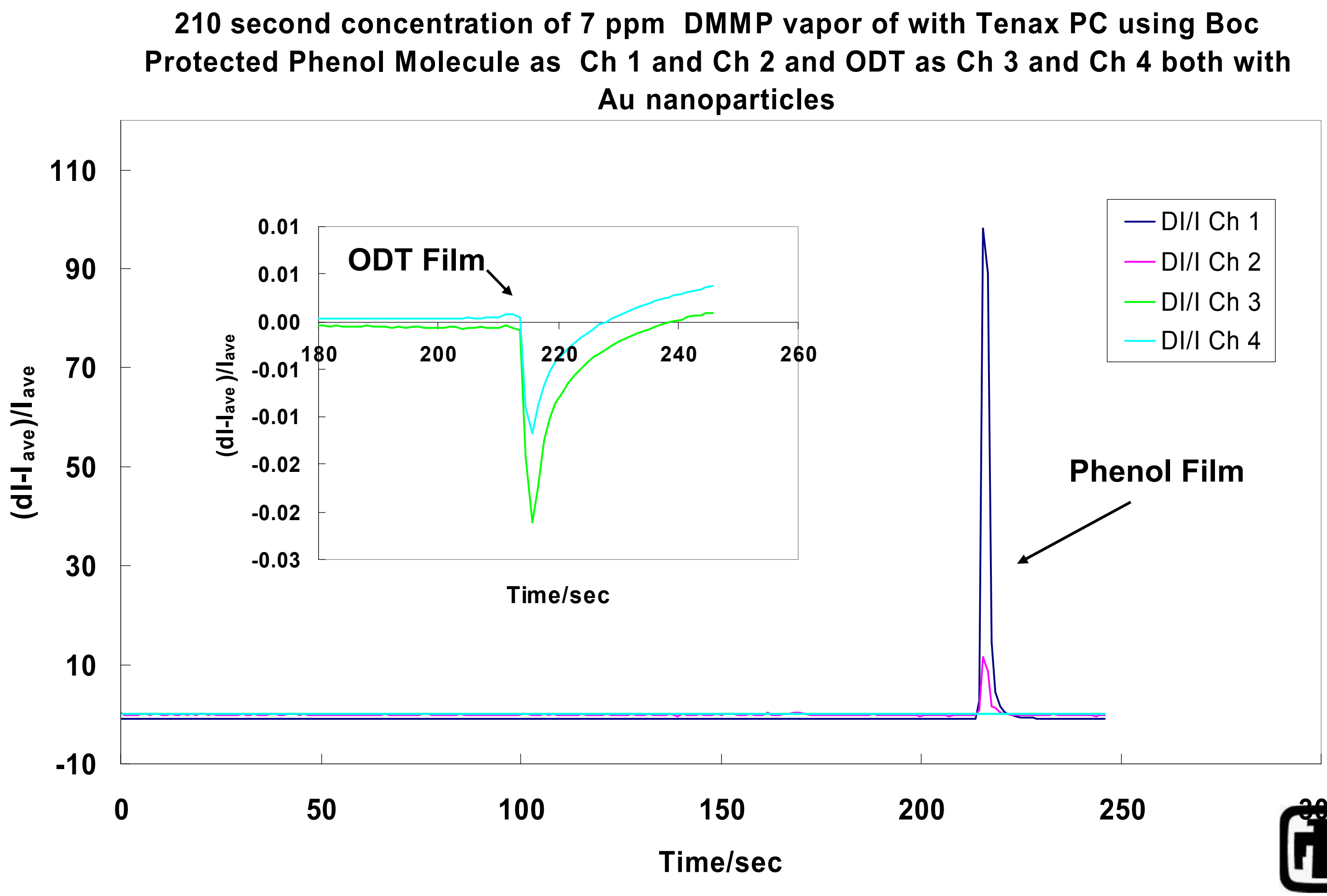
$$\sigma \propto e^{-2\delta\beta} e^{\left[\frac{-E_A}{kT}\right]} \qquad E_A \approx \frac{e^2}{4\pi\varepsilon_r\varepsilon_o r}$$

Zhang et al., Nanotechnology 2002, 13, 439
Neugebauer & Webb, J. Appl. Phys., 1962, 33, 74

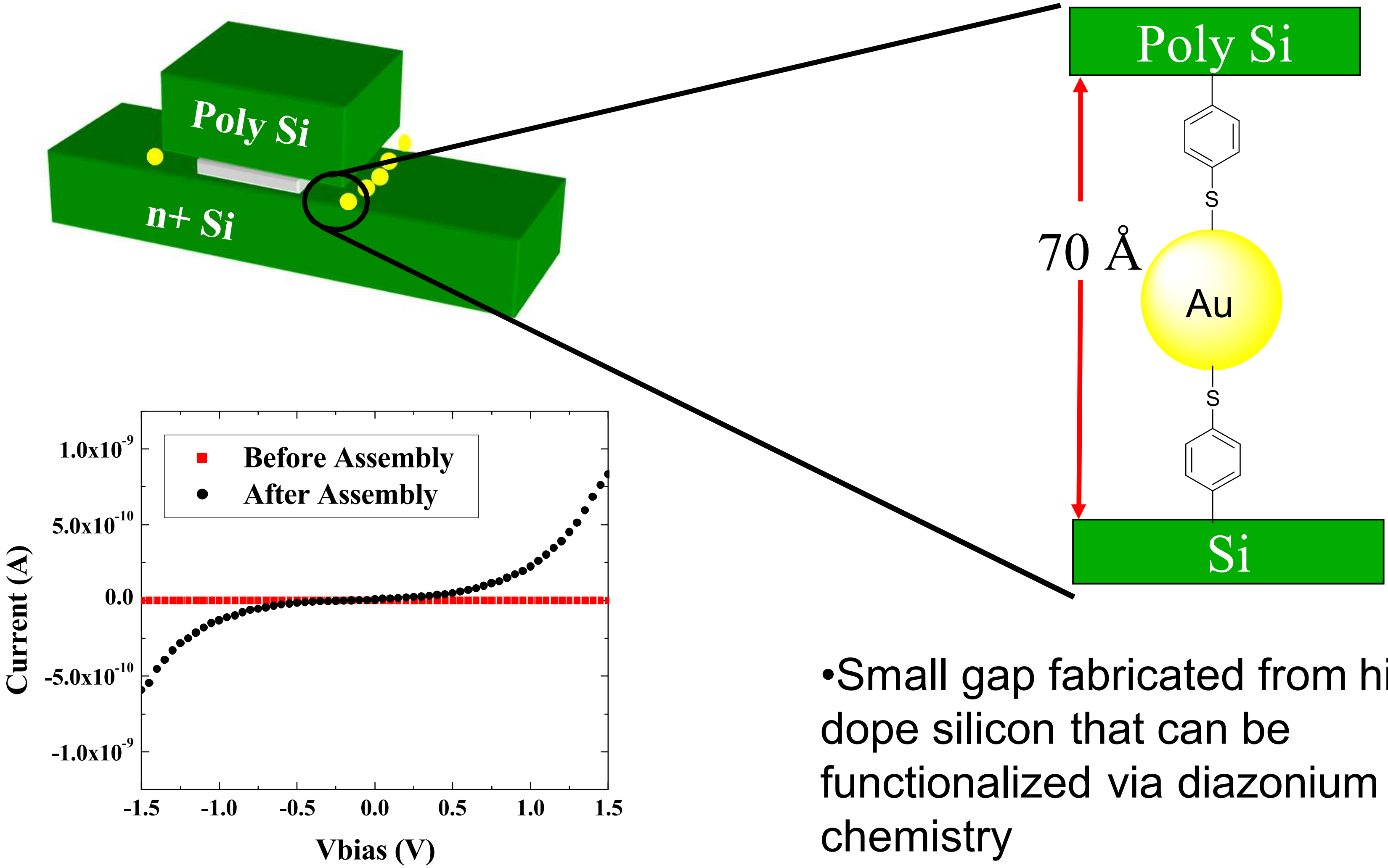
Initial Vapor sensing of DMMP using a protected phenol

Our initial observation during exposure to DMMP show:

- Protected phenol-Au films have dramatically increased conduction (molecular electronic effect)
- Control ODT-Au films have a slight decrease in conduction (swelling)
- Films response is rapid



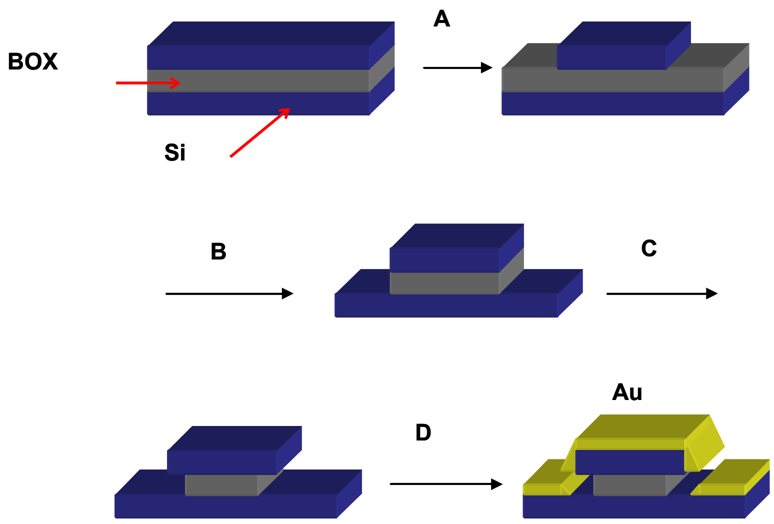
2-D Nanogap Concept

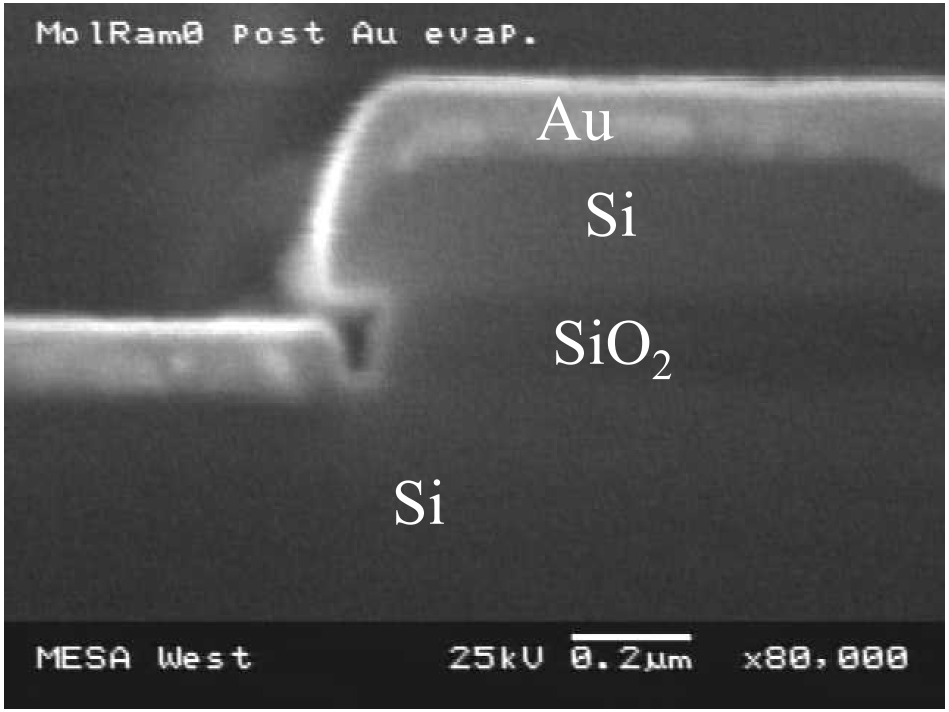


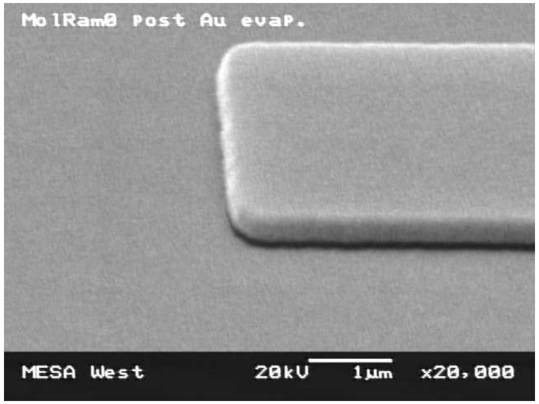
- Small gap fabricated from highly dope silicon that can be functionalized via diazonium chemistry

S. W. Howell *et al.*., *Nanotechnology*, **16(6)**, 754-758, 2005.

Gold Nanogaps







S. M. Dirk *et al.*, *Nanotechnology*, **16(10)**, 1983-1985, 2005.

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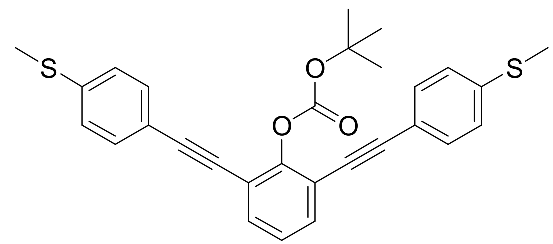
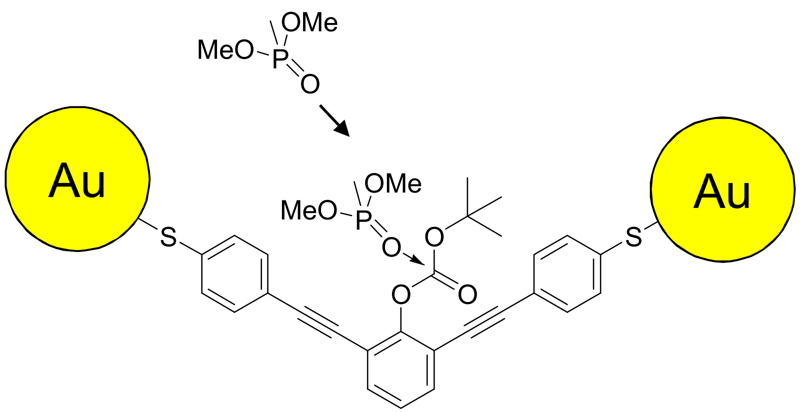
HOMO/LUMO Modification

Sensing Protected Phenol Molecules

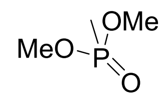


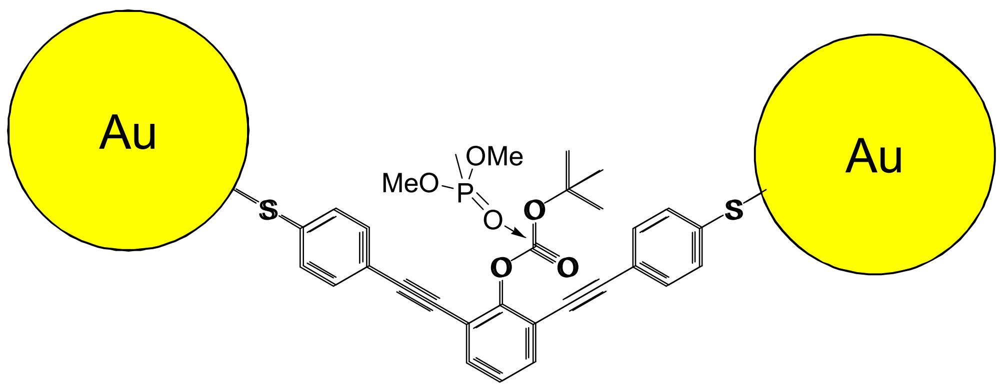


Additional electron density is added to the phenol via the phosphonate thus modifying the HOMO/LUMO gap in the protected phenol compound

HOMO/LUMO Modification

Sensing Protected Phenol Molecules





Additional electron density is added to the phenol via the phosphonate thus modifying the HOMO/LUMO gap in the protected phenol compound