This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R829619

Nanostructured Porous Silicon and Luminescent Polysiloles as Chemical Sensors for TNT and Carcinogenic Chromium(VI) and Arsenic(V)

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August 19, 2004

Safe Drinking Water Act

The US Congress passed the Safe Drinking Water Act in 1974 to establish regulations that ensure the safety of drinking water in all states

The EPA sets the Maximum Contaminant Level (MCL) for various impurities in water at a concentration deemed safe for public health

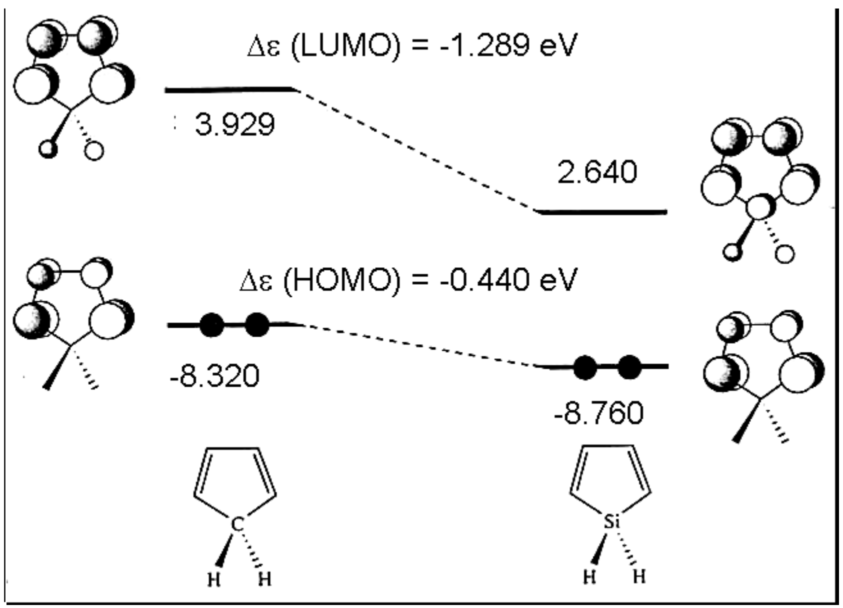
	MCL
Chromium	100 ppb
Arsenic	10 ppb*
TNT	2 ppb**

* Current MCL for Arsenic is 50 ppb; new 10 ppb standard due in effect Jan 2006

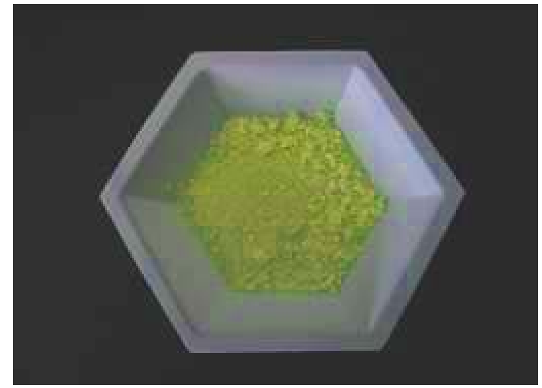
** For TNT, the standard is EPA Health Advisory standard, a non-binding technical guide to authorities

Fluorescent Siloles

The small band gap makes siloles luminescent materials



The σ*-π* conjugation reduces the band gap as compared to cyclopentadiene

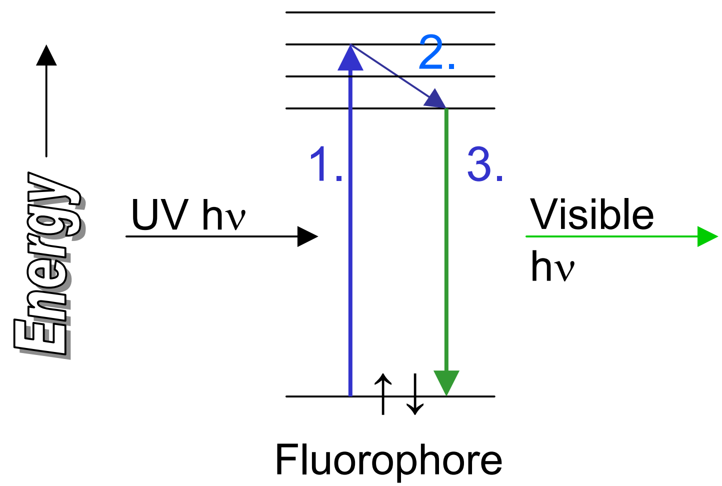


UV light

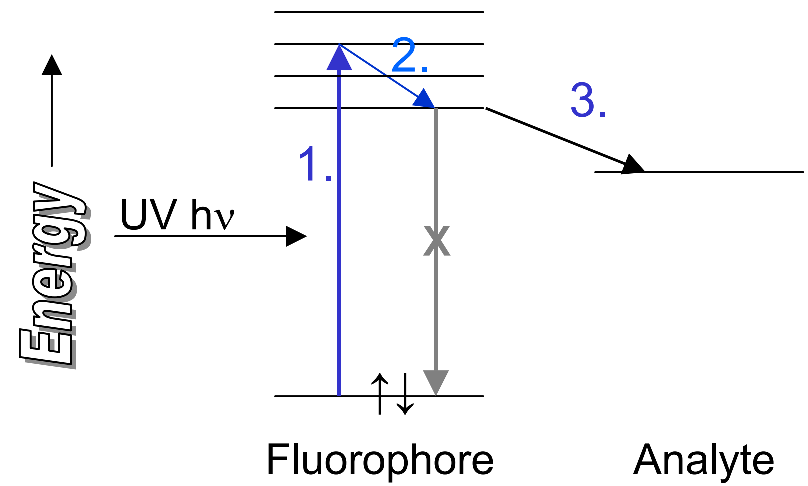
Solid state: Yellow powder fluoresces green under UV light

The Chemistry of Organic Silicon Compounds, Vol. 3, Rapport & Apeloig, 2001.

Fluorescence Quenching



No quencher present



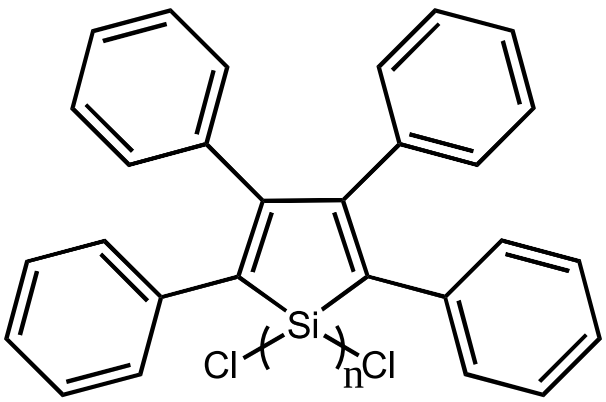
Quencher present

1. UV light excites an electron
2. Non-radiative decay
3. Electron relaxes to original energy, emitting excess energy as visible light (Fluorescence)

1. UV light excites an electron
2. Non-radiative decay
3. Excited electron transfers to electron-deficient analyte (Quenching)

Siloles as Detectors

Siloles are sensitive, selective sensors for nitroaromatic species*



Polysilole:
A 2 μm toluene solution detects 50 ppb TNT*

Cr(VI) and As(V), like nitroaromatics, are oxidizers, so perhaps siloles may be used for their detection as well

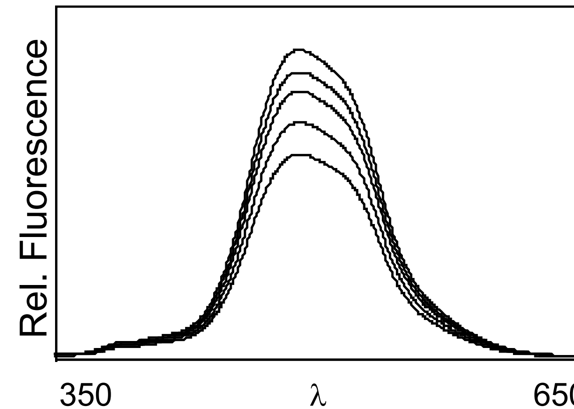
***Sohn, H.; Sailor, M.J.; Magde, D; Trogler, W.C., *JACS*,** 2003**, *125*, 3821**

Polysilole as TNT Detector

Polysilole detects TNT through luminescence quenching

The left hand was contaminated w/ TNT, and touched to filter paper. The paper was then coated with polysilole.

A polysilole coated ticket shows quenching from TNT on a thumb that had handled TNT.

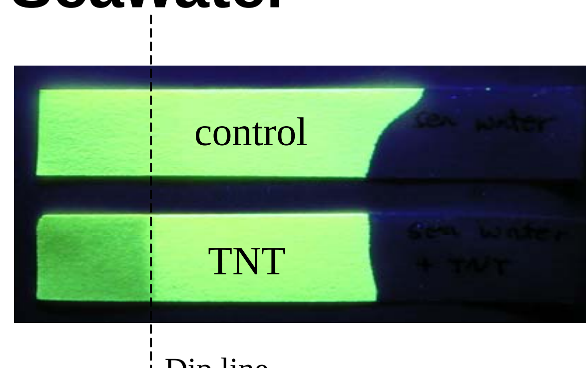


Fluorescence spectra of a toluene solution of polysilole shows quenching upon successive addition of TNT.

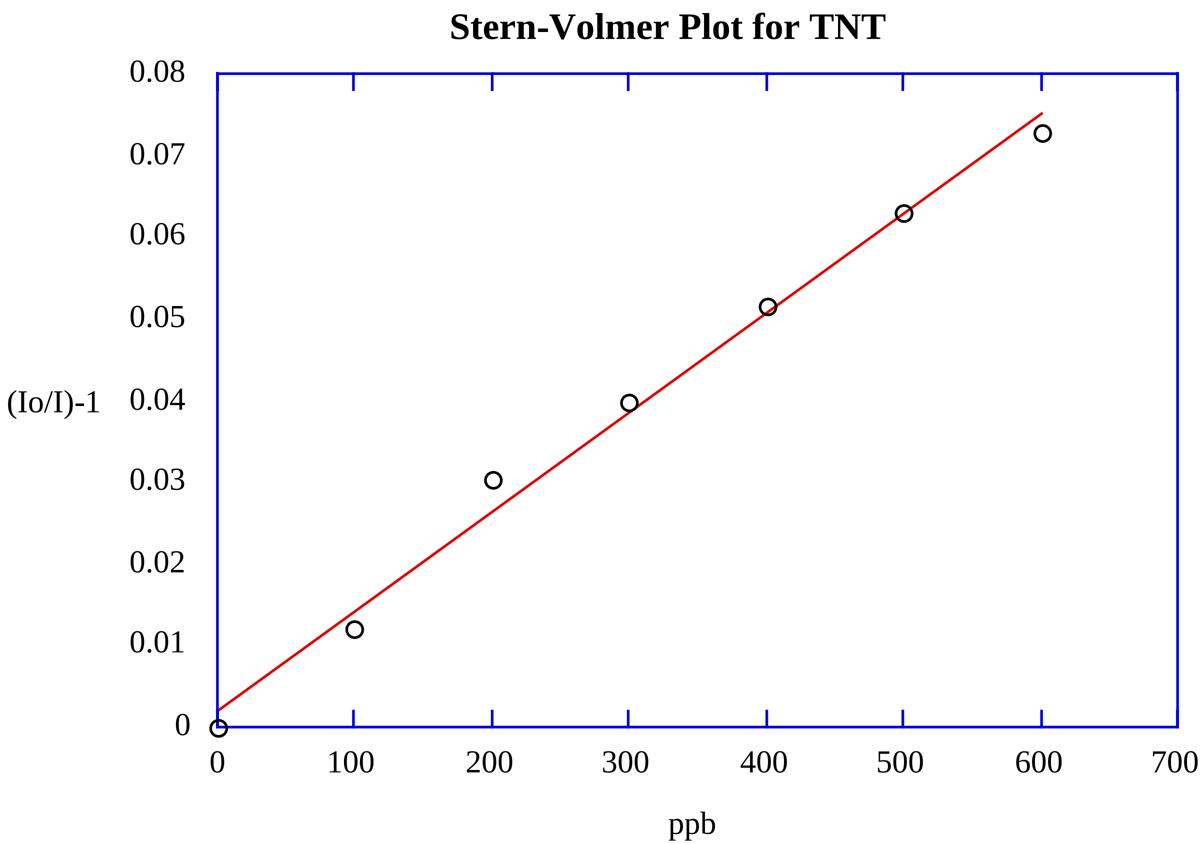
Detection of Explosives in Seawater

Polysilole coated filter paper dipped in seawater.

Luminescence quenched by TNT spiked (50 ppb) seawater.

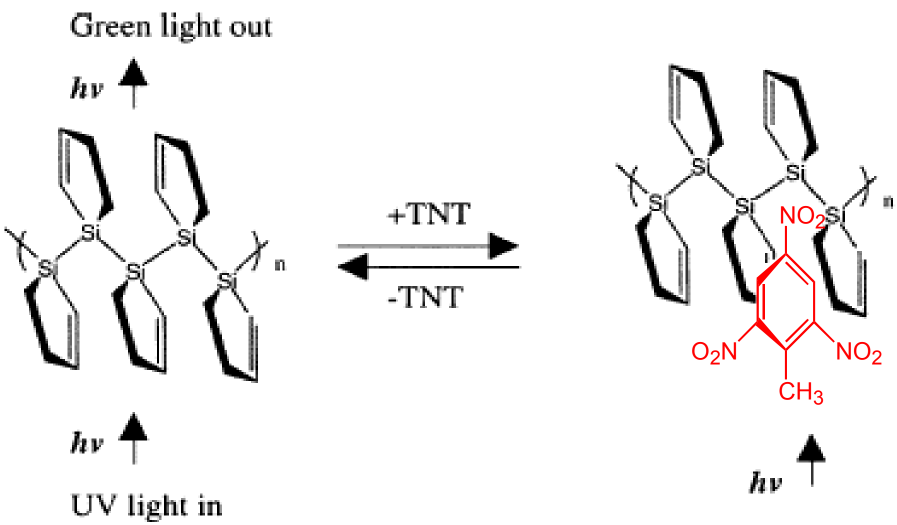


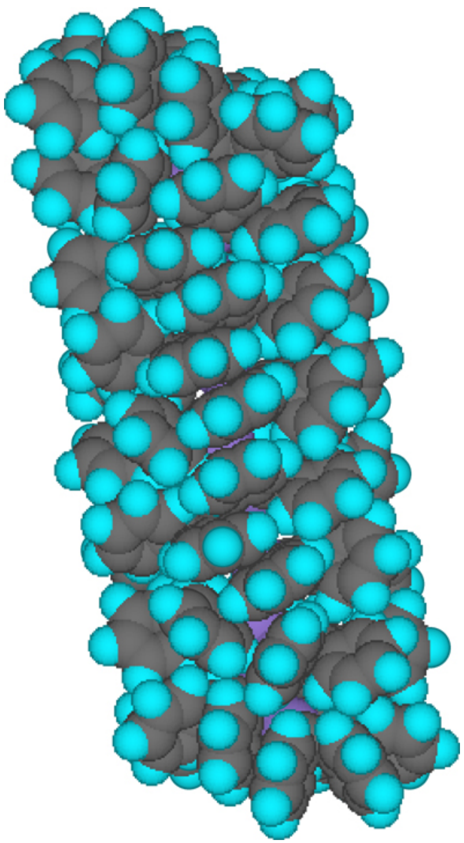
Luminescence Quenching by TNT



TNT Intercalation

Static quenching mechanism is presumably due to TNT intercalation into receptor sites

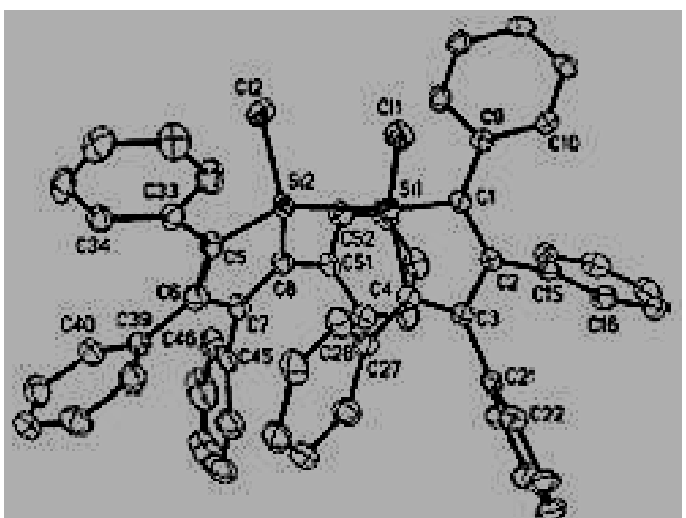




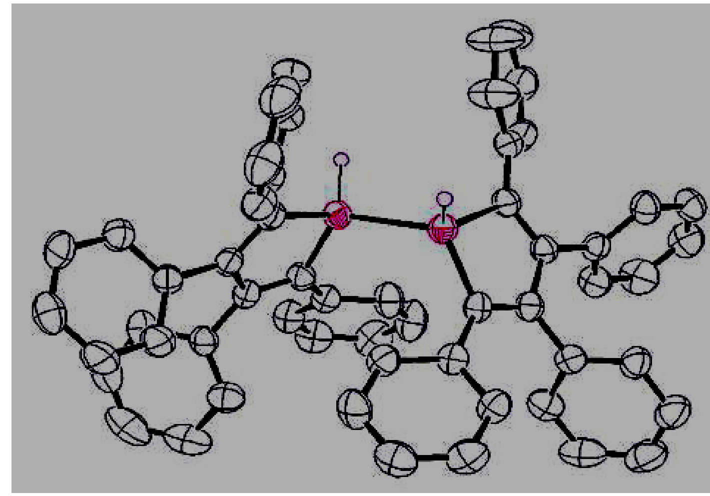
Polysilole space filling model shows helical structure

Tetraphenylsilole Dimers

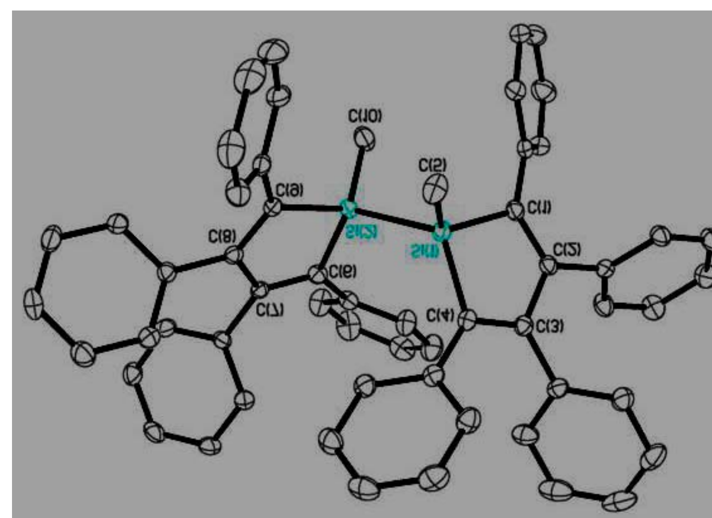
- H-terminated and Me-terminated dimers, compared to Cl-terminated dimer*, all show torsion angle of rings between 50-90°, which leads to a helical polymeric structure.



Cl: ∠Cl1-Si1-Si2-Cl2 = **51.2**°; Si1-Si2 = 2.369(2) Å



H: ∠H1-Si1-Si2-H2 = **90.2**°; Si1-Si2 = 2.363(2) Å



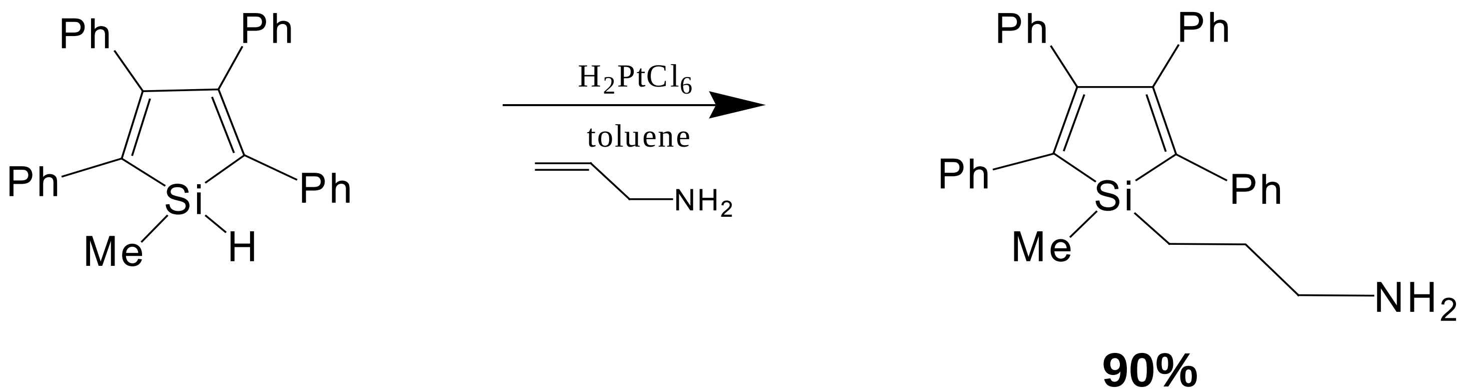
Me: ∠C5-Si1-Si2-C10 = **92.3**°; Si1-Si2 = 2.3745(6) Å

Siloles as Cr(VI) and As(V) Sensors

- Chromium and Arsenic, like TNT, are oxidants
  - Possible luminescence quenching, like TNT
- Polysilole is selective to TNT
  - Due to organic bulk and intercalation sites for the planar aromatic

- By surface modification of the silole, perhaps siloles can become selective sensors for inorganic oxoanions

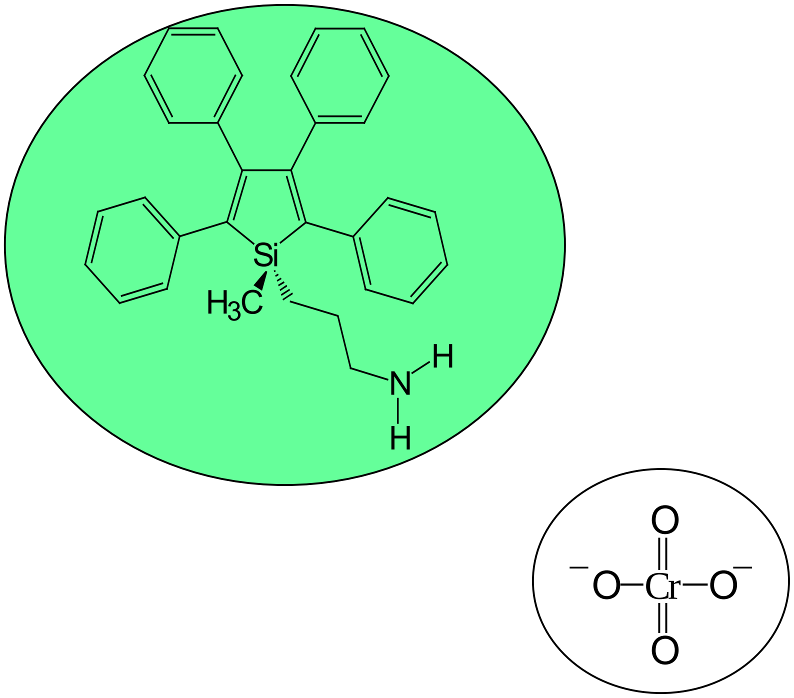
Hydrosilation Imparts Hydrogen-Bonding Amino Group

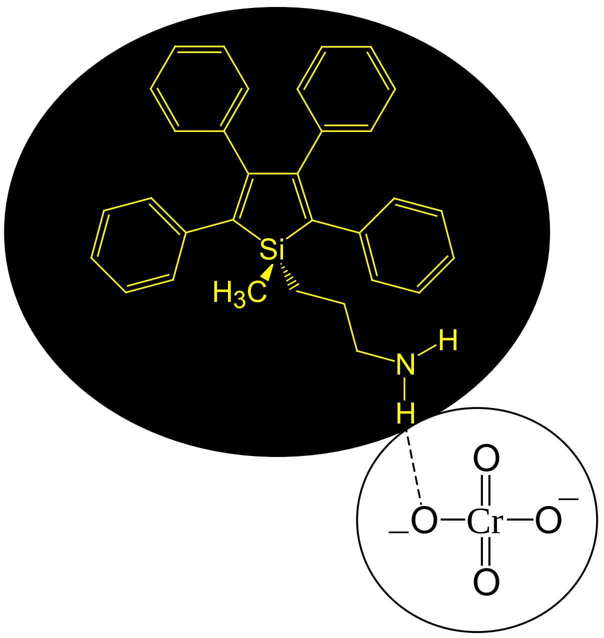


Mass Spec [ES] (M+1) = 458.8

- This is the first hydrosilation known of a silole Si-H bond
- Methylhydrosilole is completely consumed (by NMR)

Hydrogen-bonding Functionality

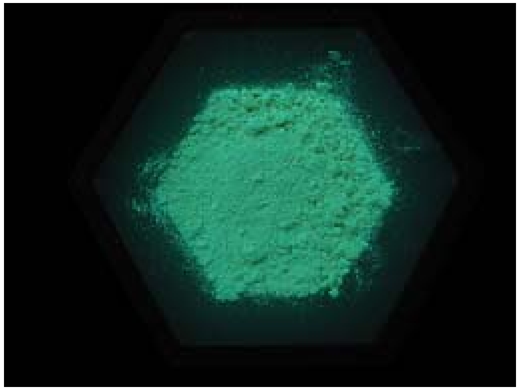




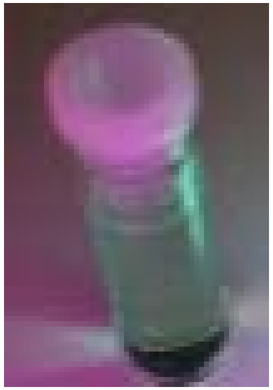
Silole fluoresces green under UV light

Chromate binds to amino silole through hydrogen bonds, and fluorescence is quenched

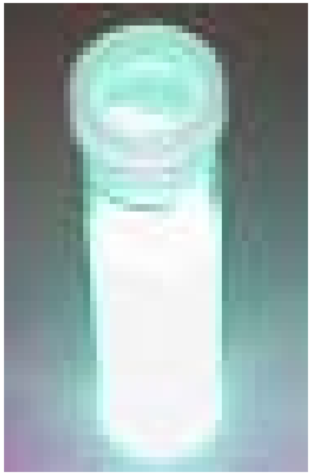
Preparation of Nanoparticles



Solid state is highly luminescent



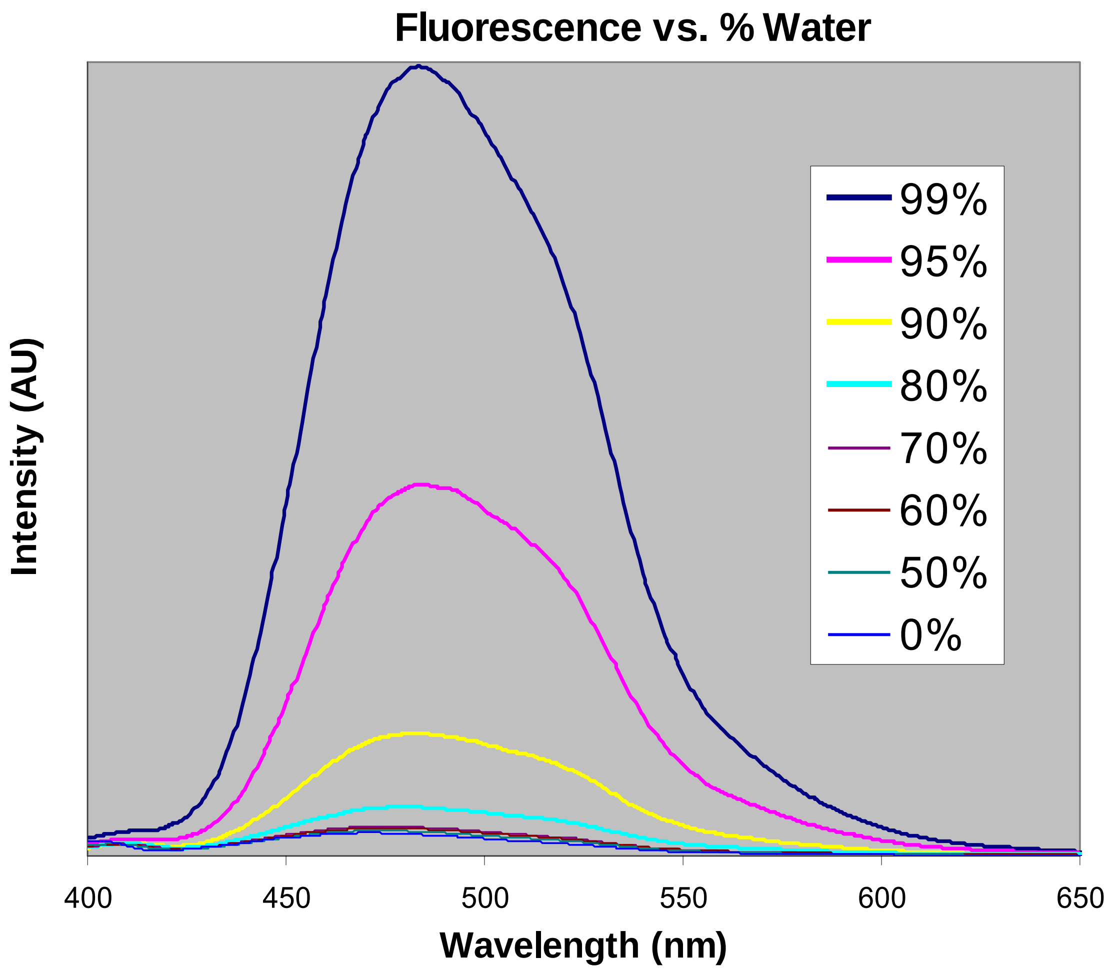
Organic solution is weakly luminescent



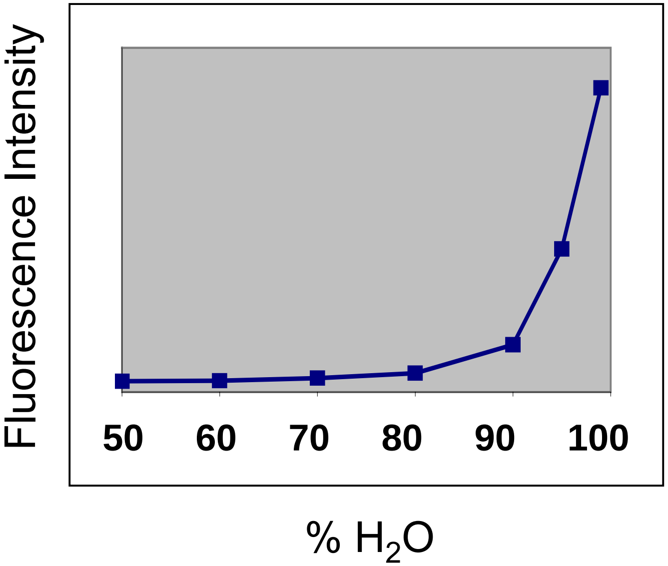
Aqueous/Organic colloid is more highly luminescent*

10 μM silole amine solution

Solvent Effects on Colloid Formation

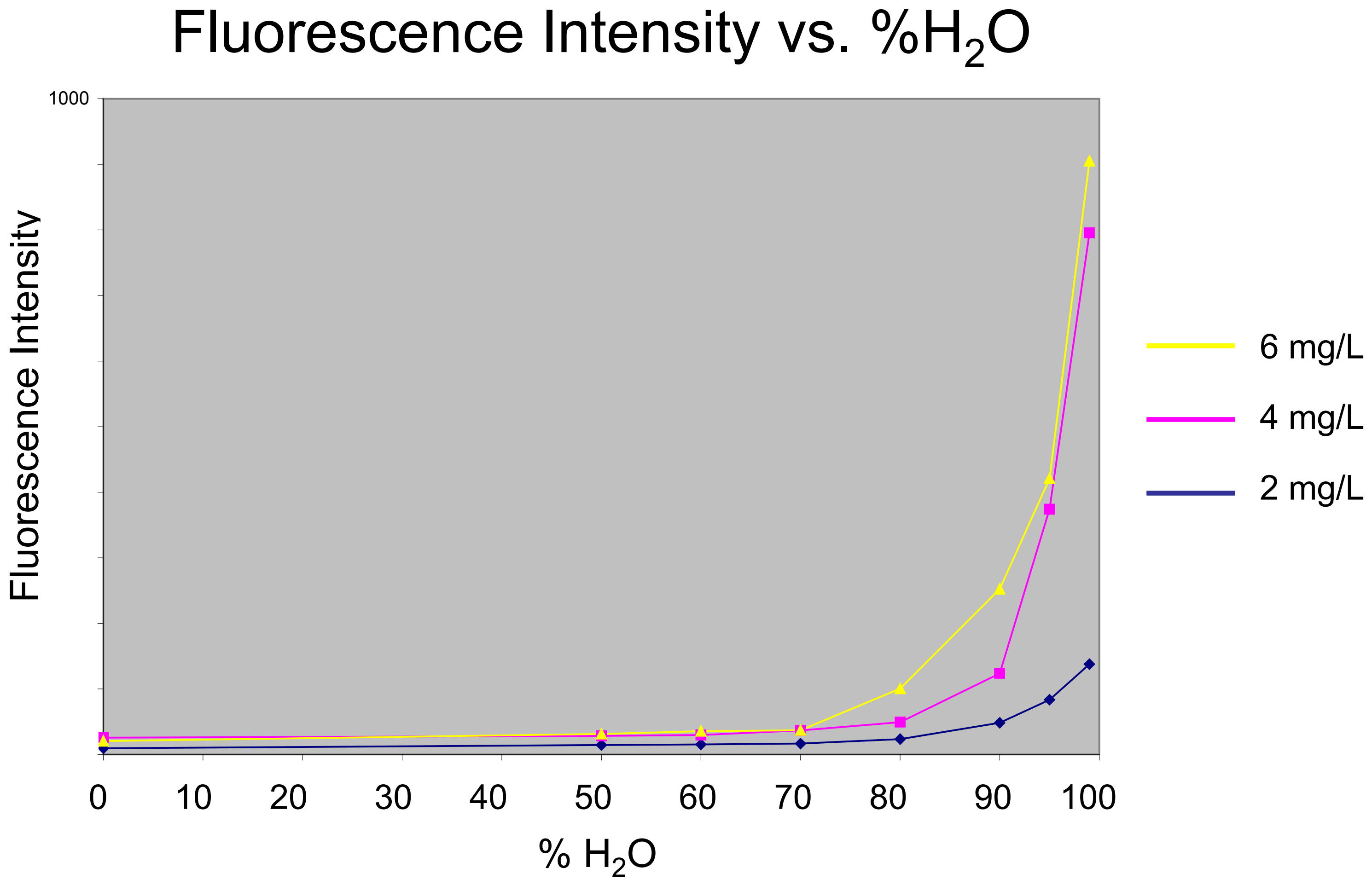


Aggregation begins at ~70% H_2O



For a 4 mg/L solution of siloleamine

Concentration Effects



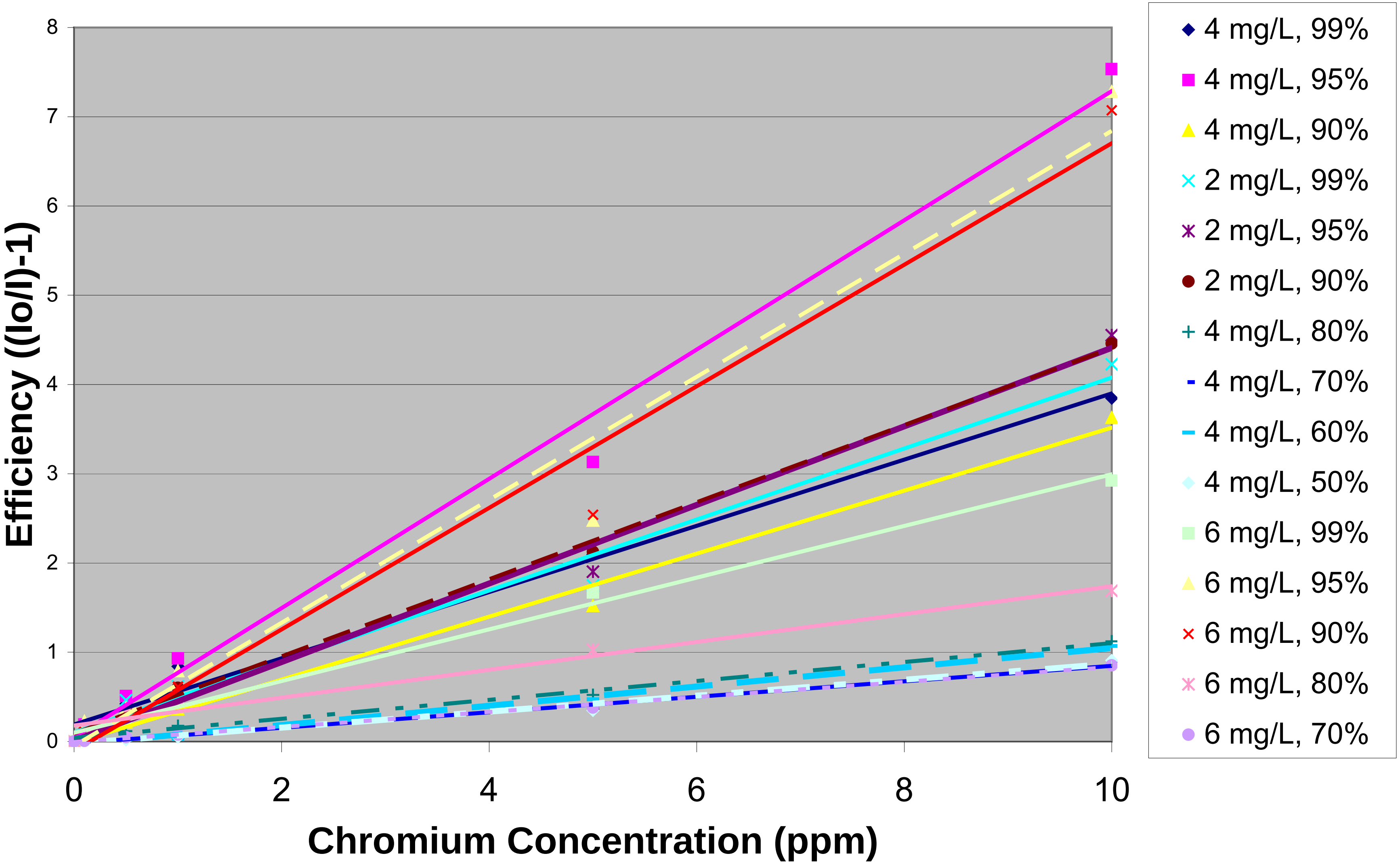
Aggregation begins at >70% H_2O, regardless of concentration

Detection through Quenching

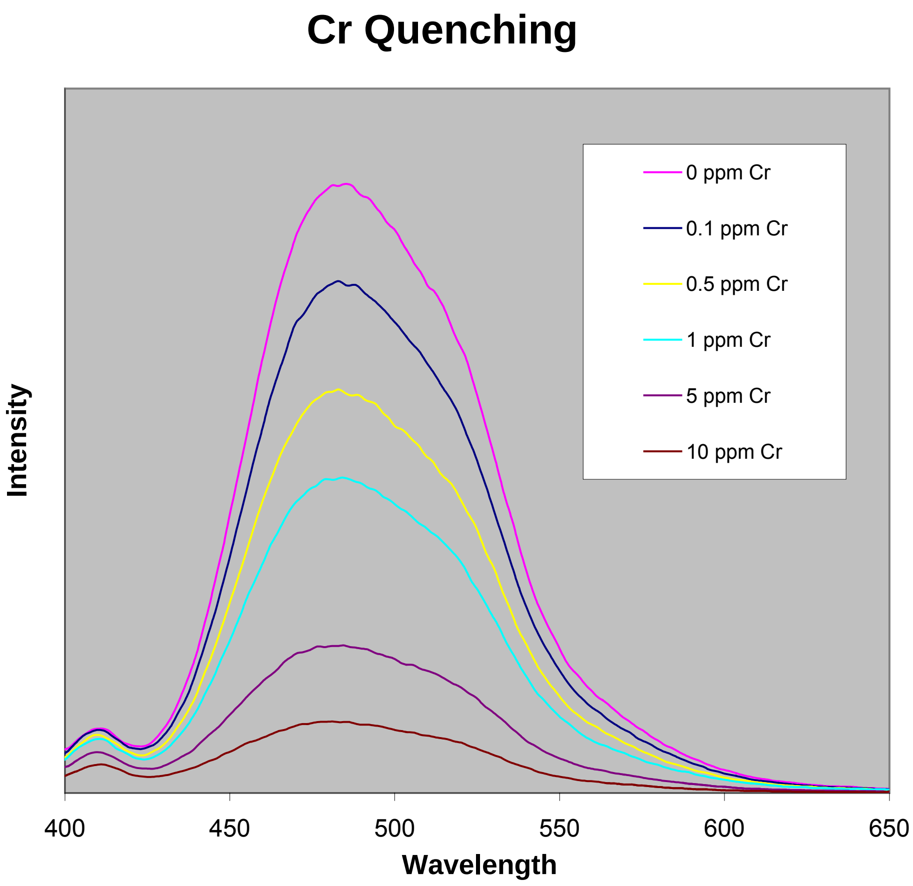
Nanoparticles   0.5 ppm Cr^{VI} 1 ppm Cr^{VI}

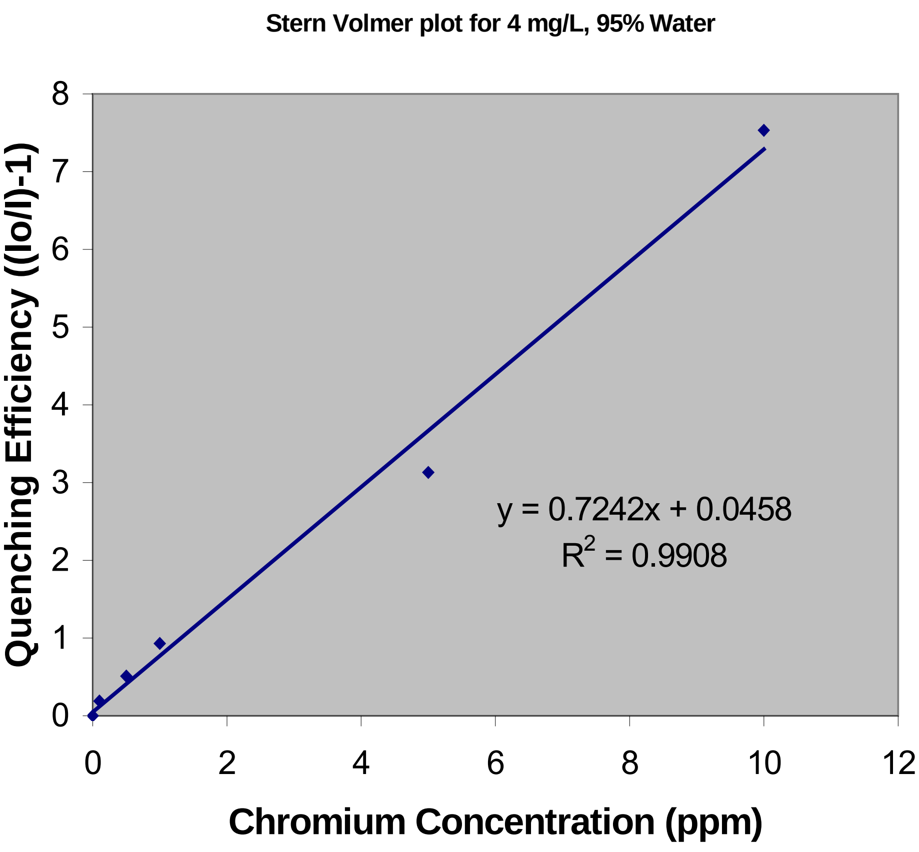
Visible quenching of luminescence
is observed with only 0.50 ppm Cr(VI)

Stern Volmer Plots of Various Colloids

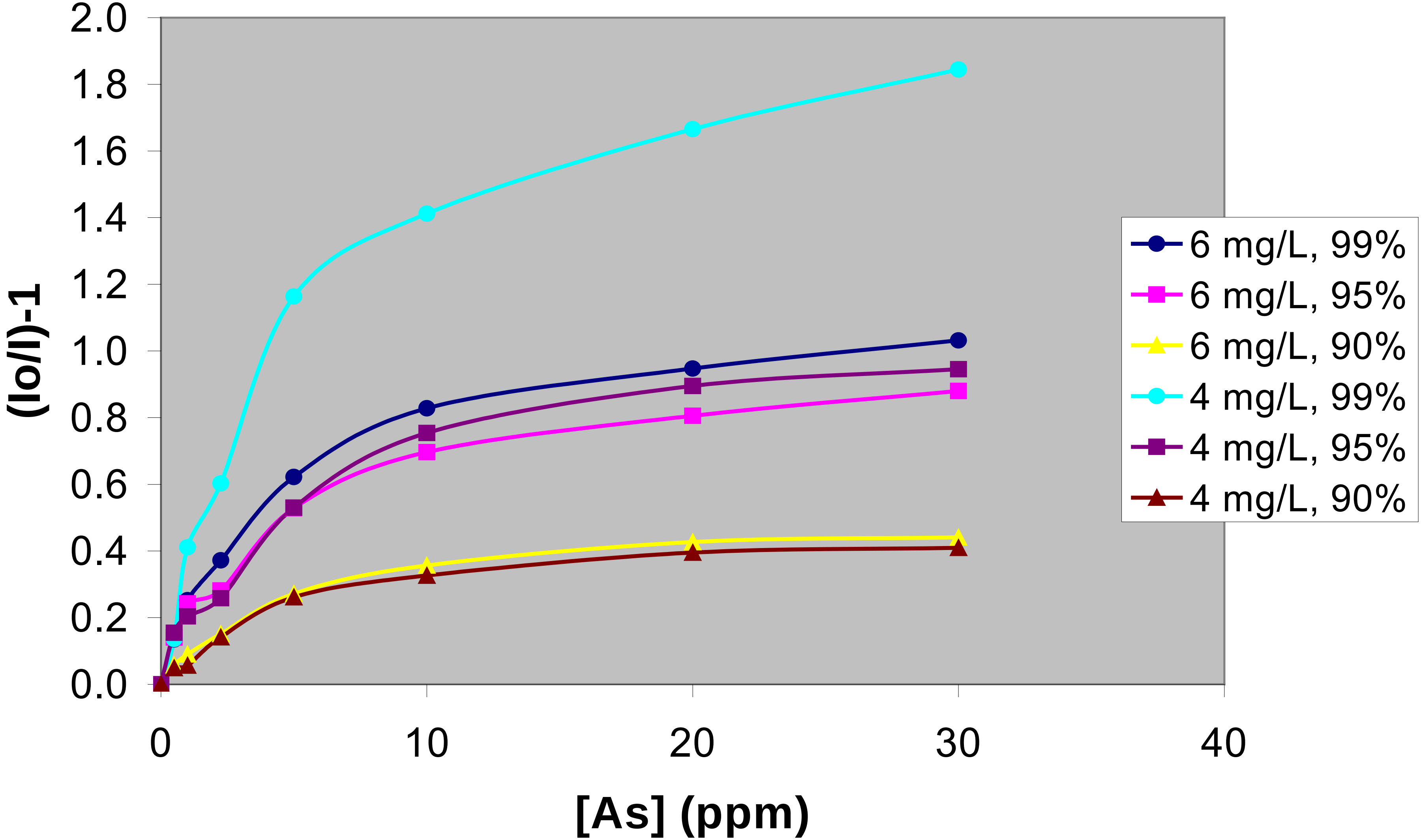


Luminescence Quenching by Cr(VI)

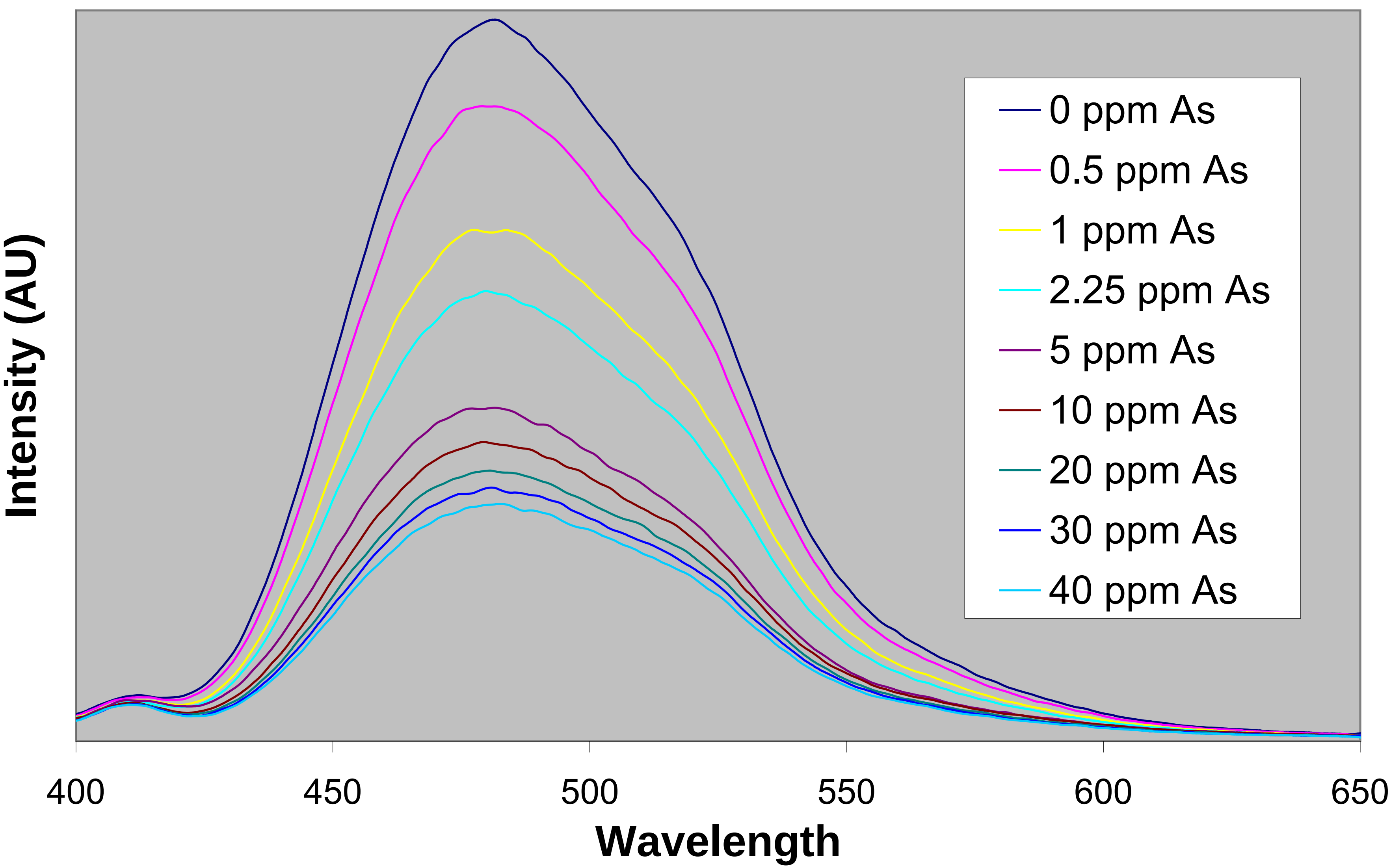




Stern Volmer Plots (As) of Various Colloids



Quenching with Arsenic (V)

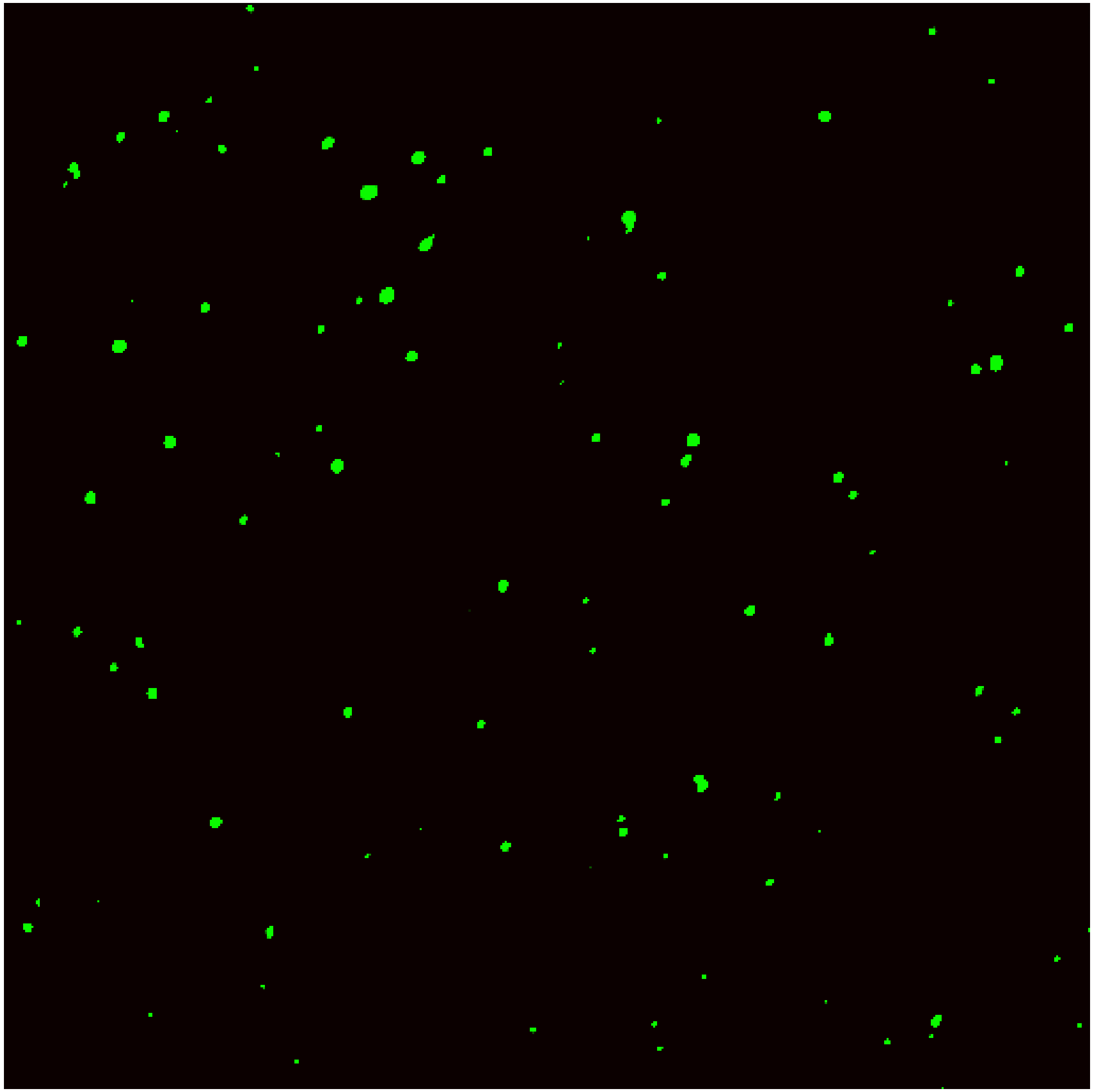


Selectivity to Interferents

- Silole-amine less sensitive to some common aqueous oxoanions
  - $NaNO_3$ (2 ppth), $NaNO_2$ (200 ppm)
- However, an *increase* in luminescence was observed with other analytes
  - Na_3PO_4 (10ppm), Na_2SO_4 (25 ppm)
  - $NaClO_4$ (150 ppm), $NaClO_3$ (500 ppm)

  - Oxidative power versus kinetic/binding factors?

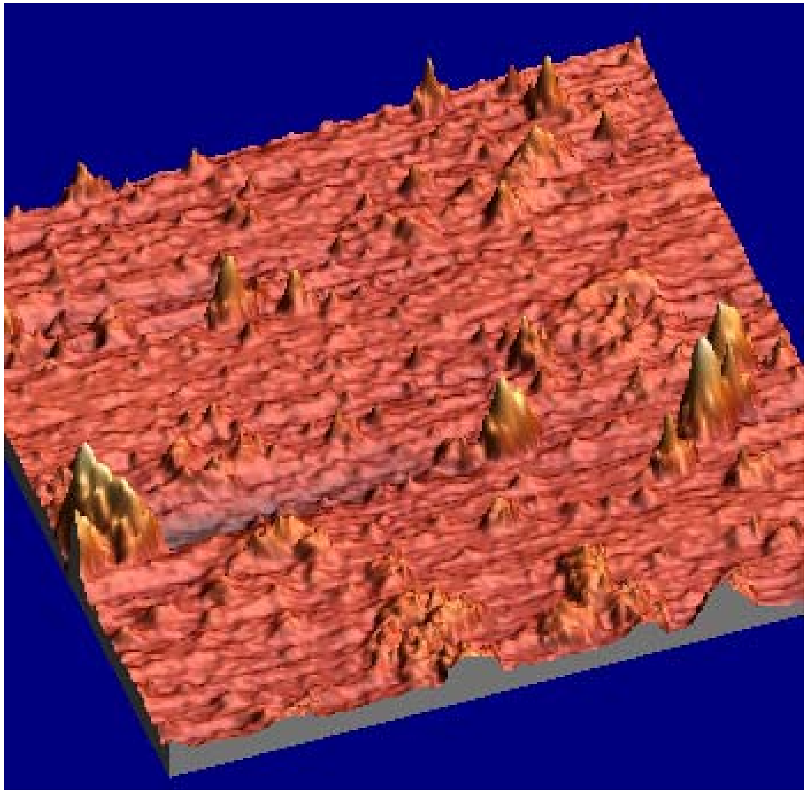
Fluorescence Microscopy of Polysilole Nanoparticulates



Resolution Limit:
1 micron

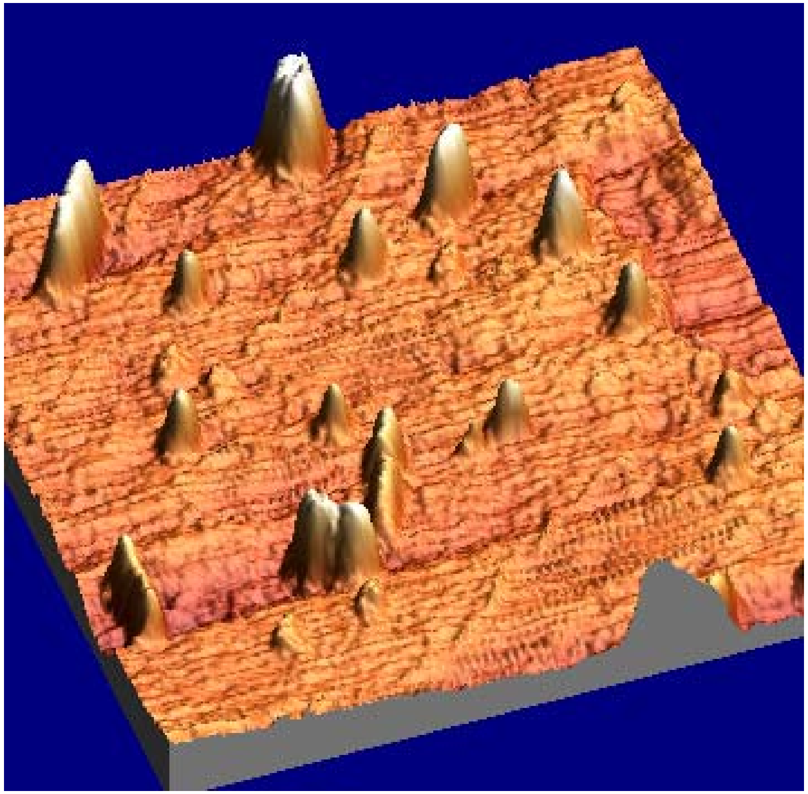
Field of view:
164 x 164 microns

AFM Imaging of Aminosilole Nanoparticulates



1 μm x 1μm

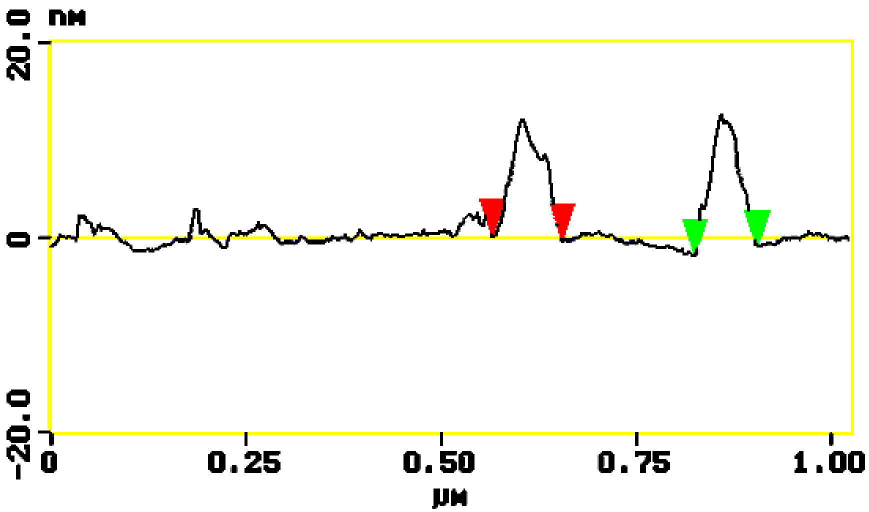
Aminosilole

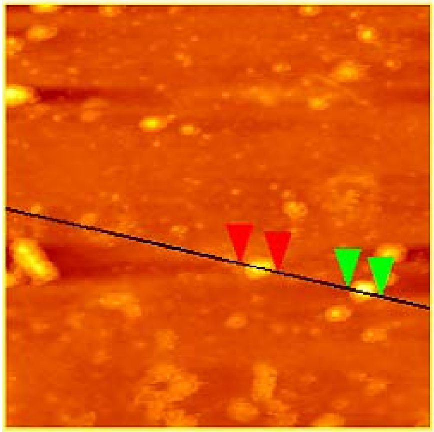


1 μm x 1μm

Aminosilole coated with SiO_2

AFM Nanoparticle Characterization





- Atomic Force Microscopy (AFM) was used to characterize size and distribution of silole nanoparticles
- Average Particle Size:
  70 - 90 nm

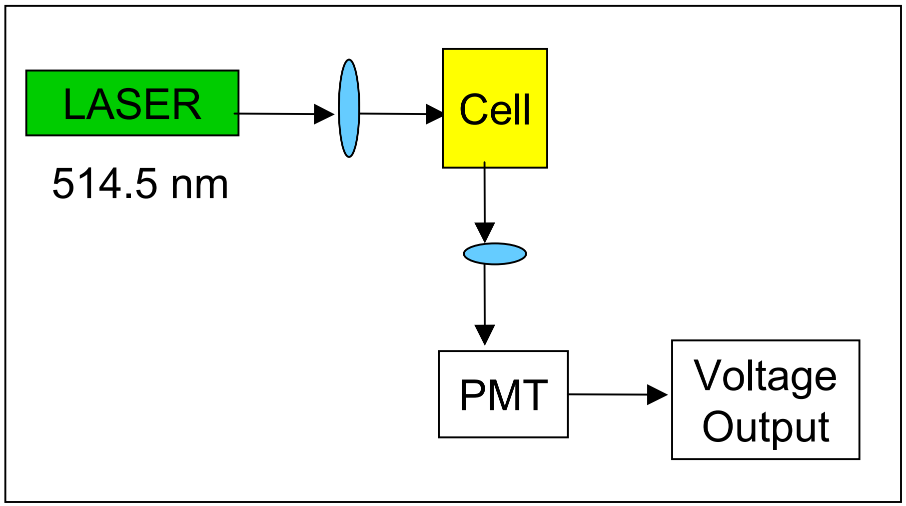
However, it would be instructive to study nanoparticles in the colloid itself.

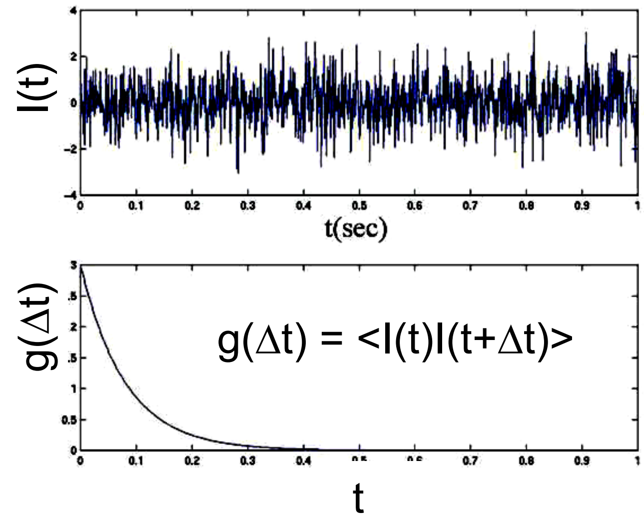
Nanoparticle Stability

- Fluorescence intensity of nanoparticles decreases over time
  - Dissolved O_2 affecting stability?
  - Change in particle size?
  - Aggregation of particles?
    - Sonication does not cause return of fluorescence
  - Instability of silole in aqueous media?
    - pH dependent?

- Nanoparticles are being characterized by both fluorescence and light scattering methods

Dynamic Light Scattering & Particle Size





PMT
V output

AC
FXN

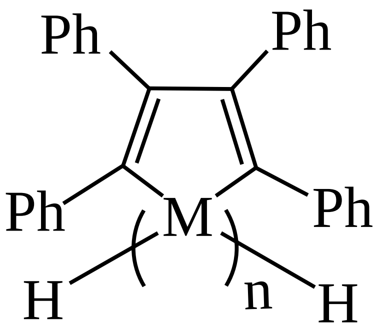
Diffusion Coefficient: $D \sim 1/\tau_c$
Radius: $r = k_b T / 6\pi\eta D$

Use DLS to study:

- Silole concentration and H_2O/THF ratio on particle size
- Compare this data to fluorescence data
- Correlation with particle size and fluorescence?

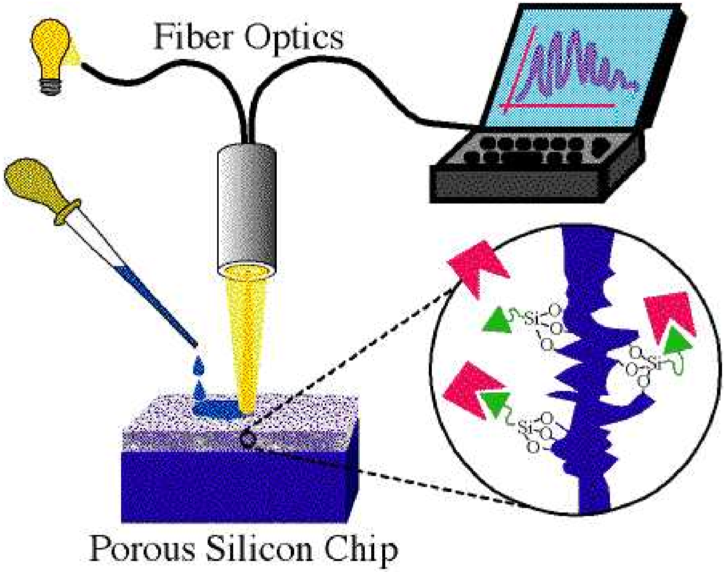
www.phys.ufl.edu/REU/2000/talks/dunn.ppt

DLS of Polysilole

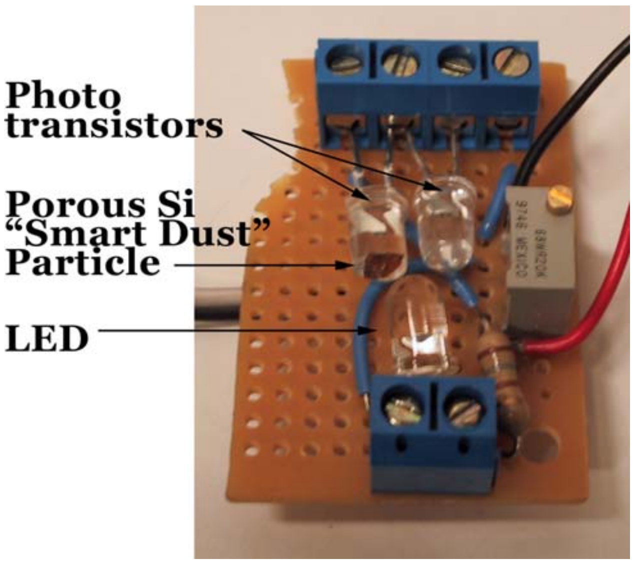


- Preliminary DLS experiments on polysilole have shown:
  - Particle size is less dependent on concentration than on solvent composition
  - Particles seem to decrease in size with added water
  - Particle diameter ranges: 60-200 nm

Optical Sensors Methodology



- Recognition Element
  -What is there?
  -Provides specificity



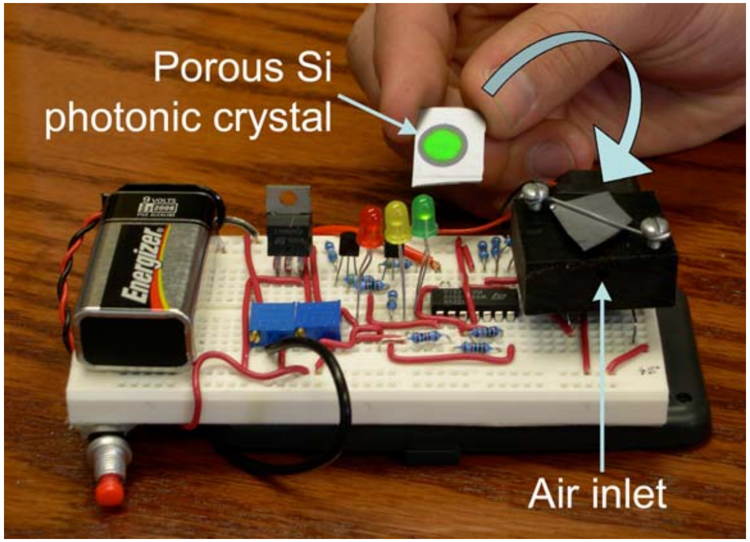
- Transduction
  -Communicate with the outside world
  -Provides sensitivity

Pollution sensors based on nanostructured Si

Objective

1. Construct and study porous Si sensors for pollutants
2. Develop minature, low power devices for integration into systems

Integrated Sensor Circuit



Results

1. Constructed and tested a low-power, battery powered sensor for VOCs.
2. Constructed a prototype for luminescence-based (polysilole) sensors
3. Demonstrated surface chemistry that allows sensor to detect VOCs in the presence of background humidity.
4. Discovered a method to construct active SERS substrates on porous Si supports

Amplified Vapor Sensing in Microporous Media

Capillary condensation: Liquids spontaneously condense from vapor into cracks and pores as bulk liquid.

Schematic of a PS sample

Kelvin Equation:

Surface energy

$$k_B T \ln(\frac{P}{P_s}) = \gamma V_m (\frac{1}{R_K})$$

Effective pore radius

Molar volume of the liquid

Gao, J.; Gao, T.; Sailor, M. J., *Appl. Phys. Lett.*, **77**, 901-3 (2000).

Limits of Detection

for vapors in N_2 carrier, 23 ℃

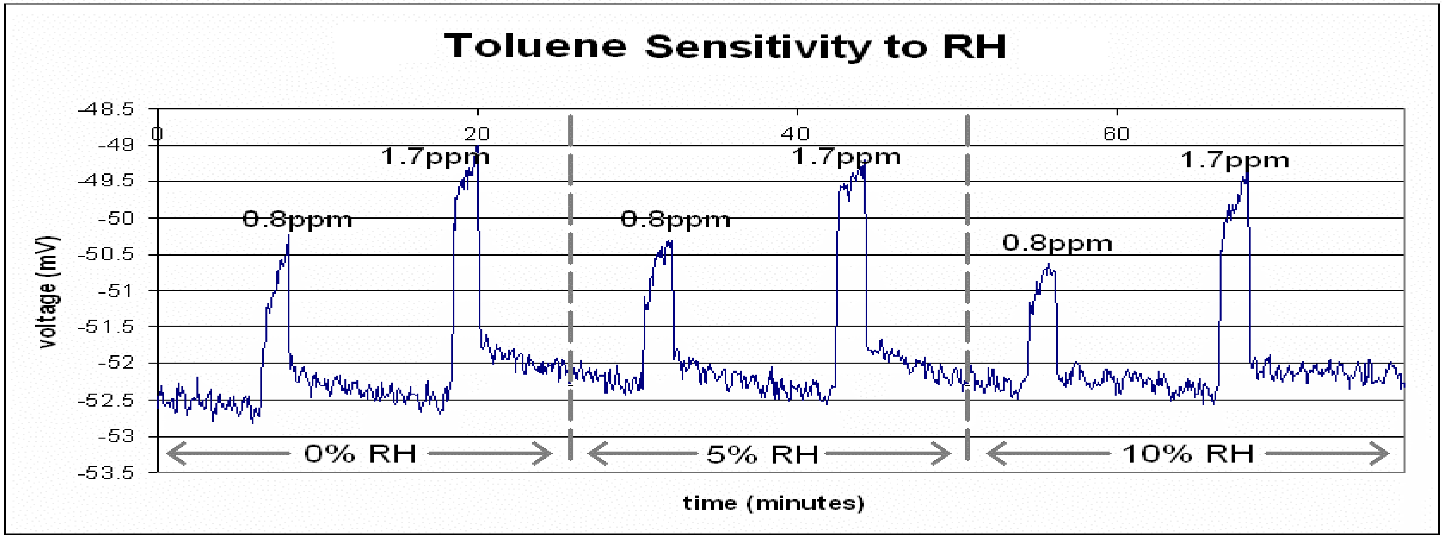
Gas	Vapor Pressure (Torr)*	Detection Limit
Ethanol	52	**172 ppb**
Toluene	26	**19 ppb**
DMMP	3	**2.7 ppb**

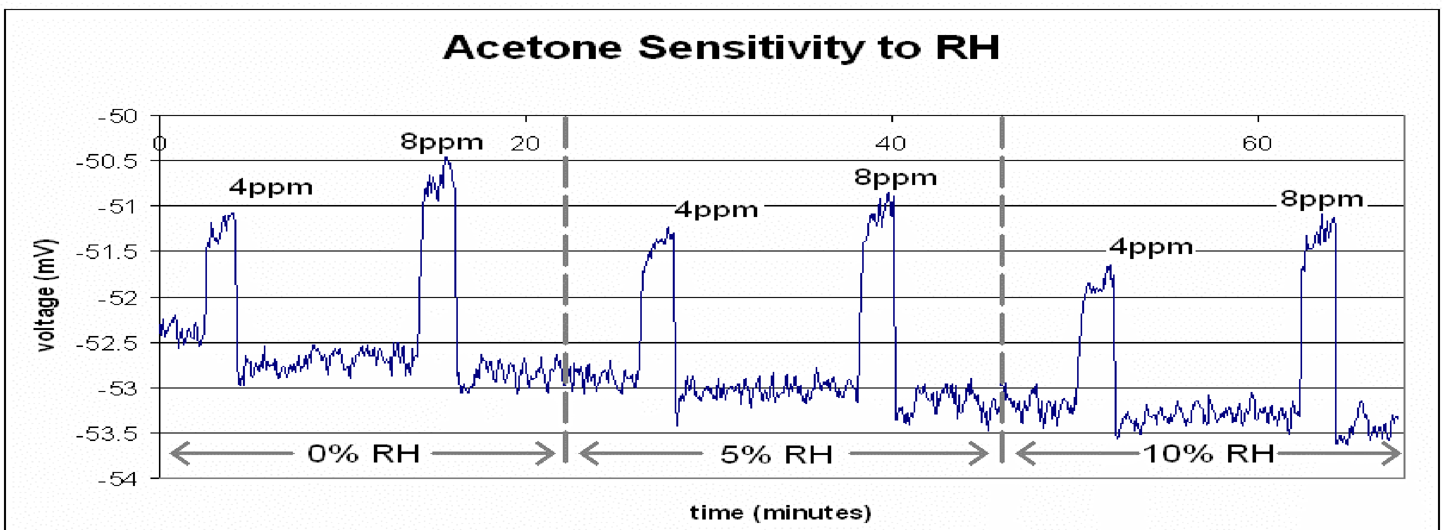
*25 °C

Etch conditions: 13 mA/cm^2, 10 min

Lower vapor pressure = lower detection limit

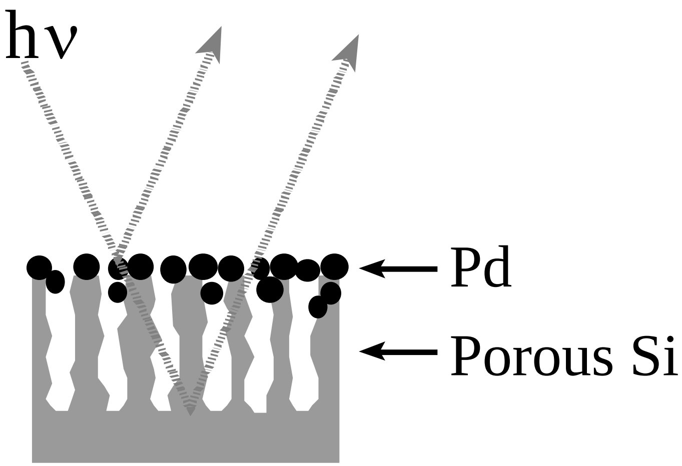
Photonic Crystal Sensor - Hydrophobic





simple response is not sensitive to changes in humidity

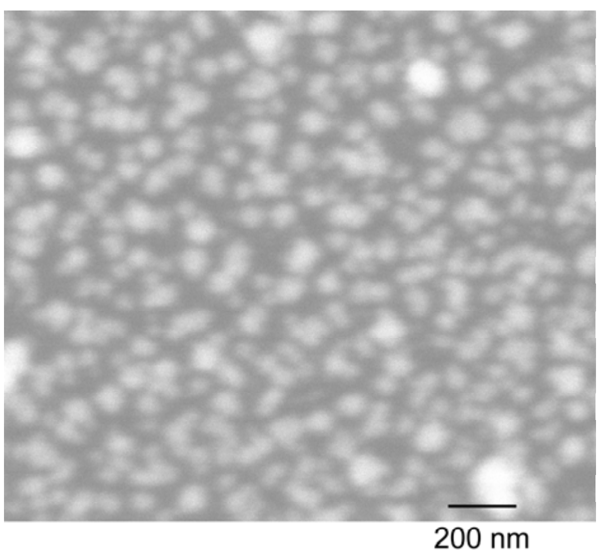
Palladium Coated Porous Silicon – Hydrogen Sensing



$$2Si_{(surface)} + H_2O \longrightarrow Si\text{-}O\text{-}Si_{(surface)} + 2H^+_{(aq)} + 2e^-$$

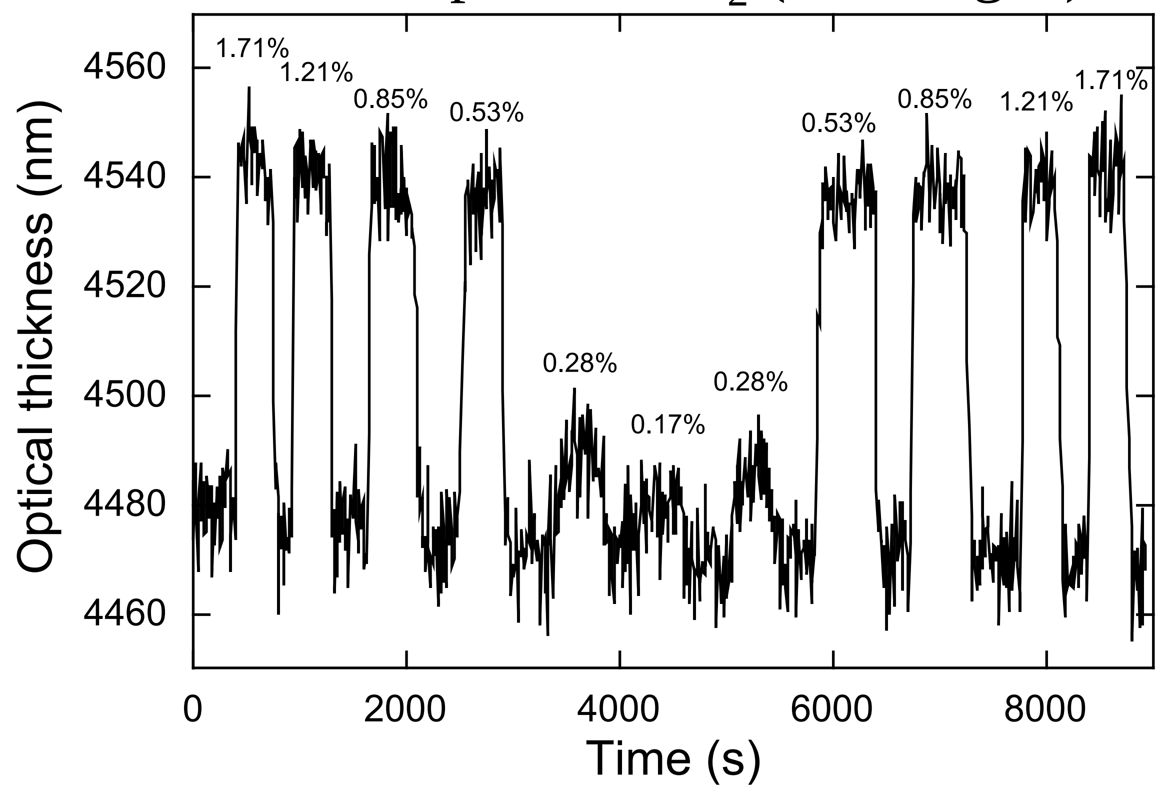
$$2Si\text{-}H_{(surface)} + H_2O \longrightarrow Si\text{-}O\text{-}Si_{(surface)} + 4H^+_{(aq)} + 4e^-$$

$$Pd^{2+}_{(aq)} + 2e^- \longrightarrow Pd_{(s)}$$



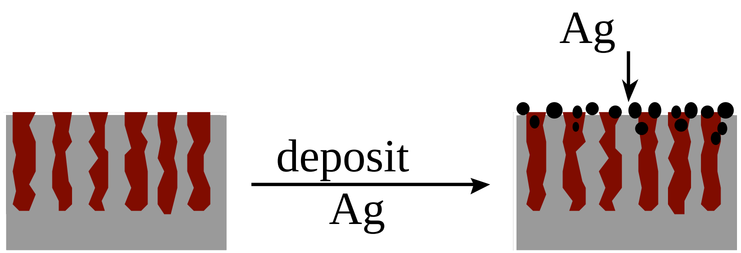
Pd nanoparticles on porous Si

Response to H_2 (in nitrogen)



Langmuir **2004**, *20*, 5104-5108.

SERS spectrum of Adenine on Ag:pSi

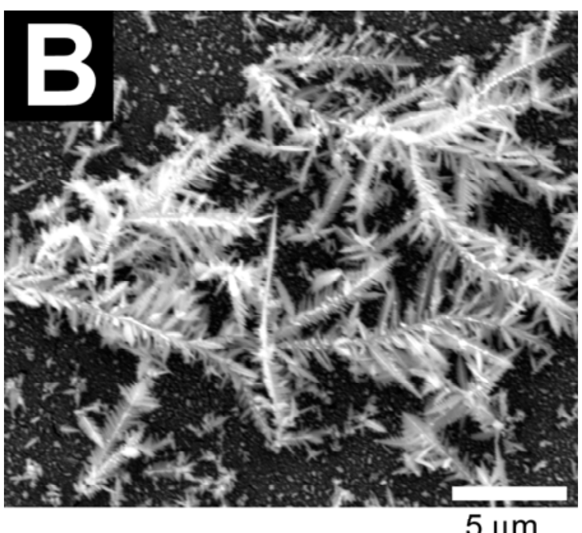


Porous Si

$$2Si_{(surface)} + H_2O \rightarrow Si\text{-}O\text{-}Si_{(surface)} + 2H^+_{(aq)} + 2e^-$$

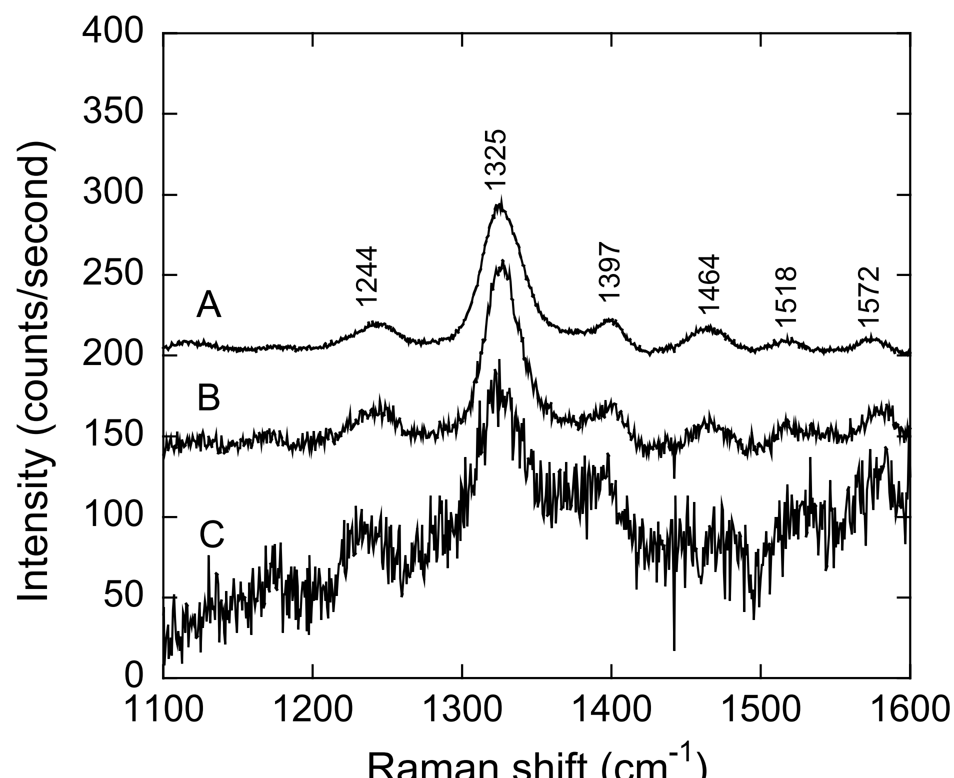
$$2Si\text{-}H_{(surface)} + H_2O \rightarrow Si\text{-}O\text{-}Si_{(surface)} + 4H^+_{(aq)} + 4e^-$$

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$$



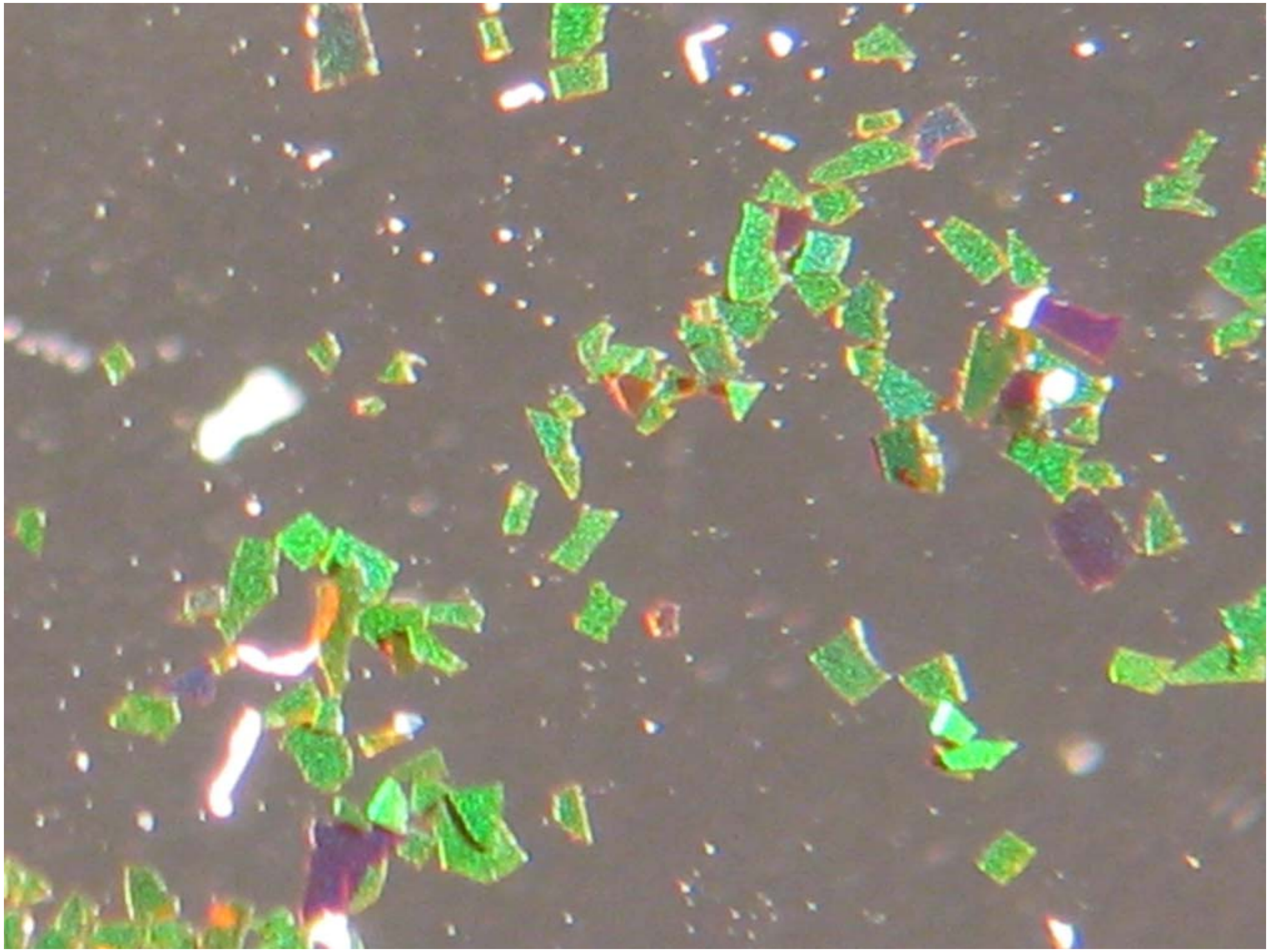
Ag crystallites on porous Si

J. Phys. Chem. B **2004**, *108*.



Sensor arrays

Video imaging of "smart dust" photonic crystal sensors



With AVAAK, inc.

Acknowledgments

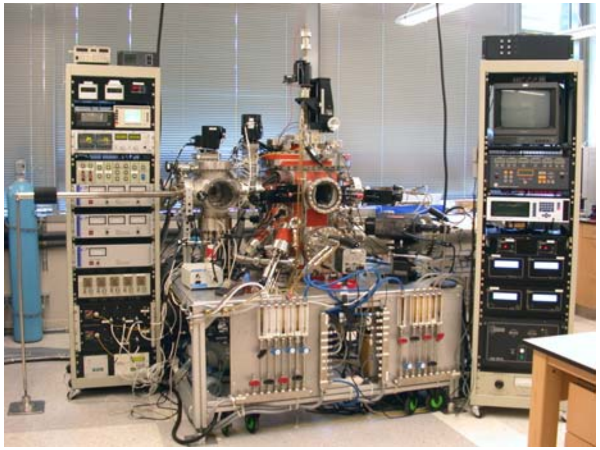
Kelsey Jones – high school student
Sarah Toal – graduate student
Sarah Urbas – graduate student
Professor Douglas Magde
Professor Michael J. Sailor
Jason Dorvee – undergraduate student
Kenneth MacGillivray – graduate student
Jamie Link – graduate student
Haohao Lin – graduate student
Professor Arnold L. Rheingold
Lev N. Zakarov, Scott Kassell, James A. Golan

Environmental Protection Agency
ARCS Foundation
San Diego Fellowship
CALIT Fellowship

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R829619

UCSD Nanosensors Lab

- DC Magnetron Sputtering
- Laser Interferometric Height Gauge
- Quartz Tube Annealing Furnace
- Microscopes
- Probe Station
- Plasma Cleaner
- Wire Bonder

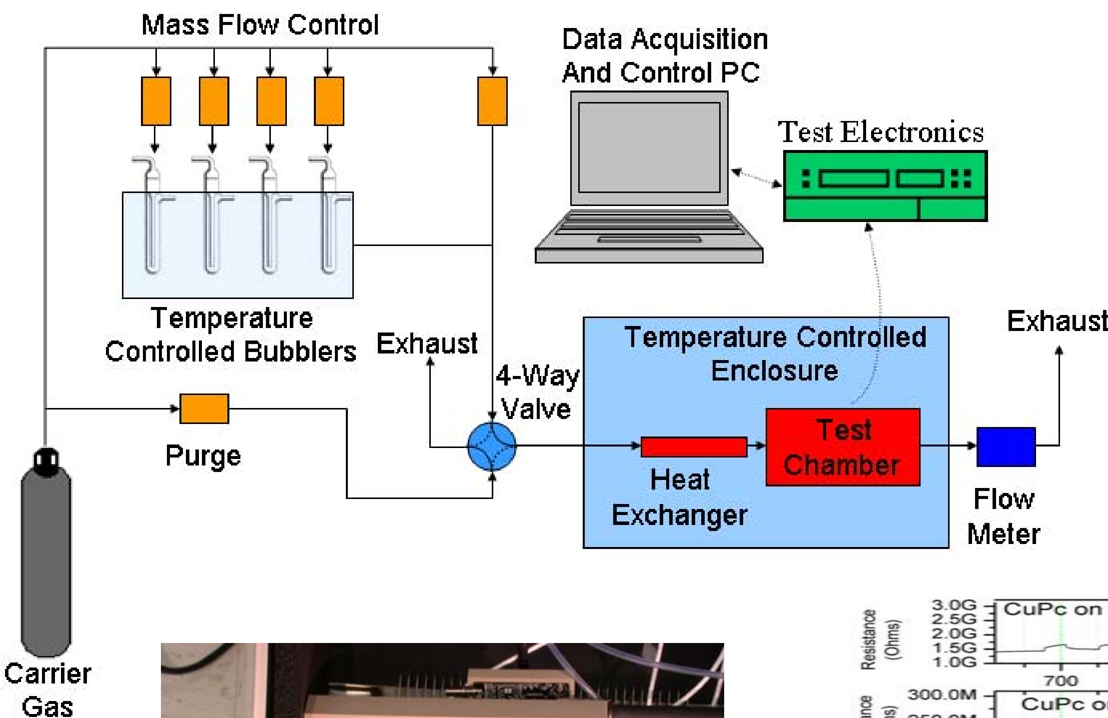


Organic MBE

In-Situ

Device Preparation

Sensor Test System



- **Automated**
- **Small volume (<15cm^3)**
- **Flexible**
- **Analyte delivery**
- **Simultaneously 10 sensor**

Examples: Concentrations

- **Acetone: ~20 ppm**
- **DIMP: ~25 ppb**