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SMR.1825 - 2

## Advanced Workshop on

## Recent Developments in Nanomaterials

15 - 19 January, 2007, ICTP, Trieste, Italy

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# Sol-Gel Methods for Assembly of Nanoparticles: NOT just for Oxides

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# Sol-Gel Methods for Assembly of Nanoparticles: *NOT Just for Oxides*

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*ICMR-ICTP Advanced Workshop on Recent Developments in Nanomaterials*

# Grand Challenges for Nanotechnology

*Nanoparticle components*

I: New chemistry to expand the range of properties available to components

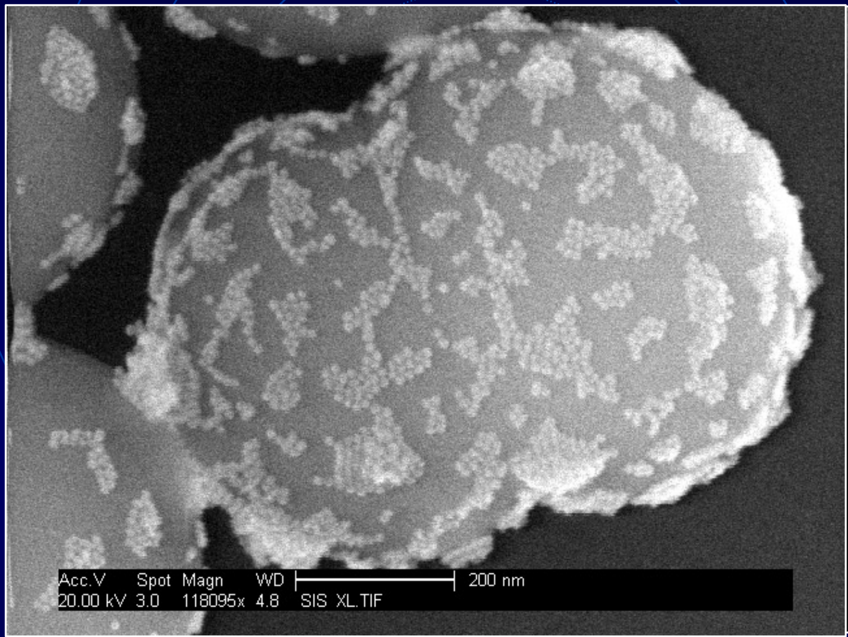
- ternary, quaternary compositions
- unique architectures (core:shell)
- size and shape modulation

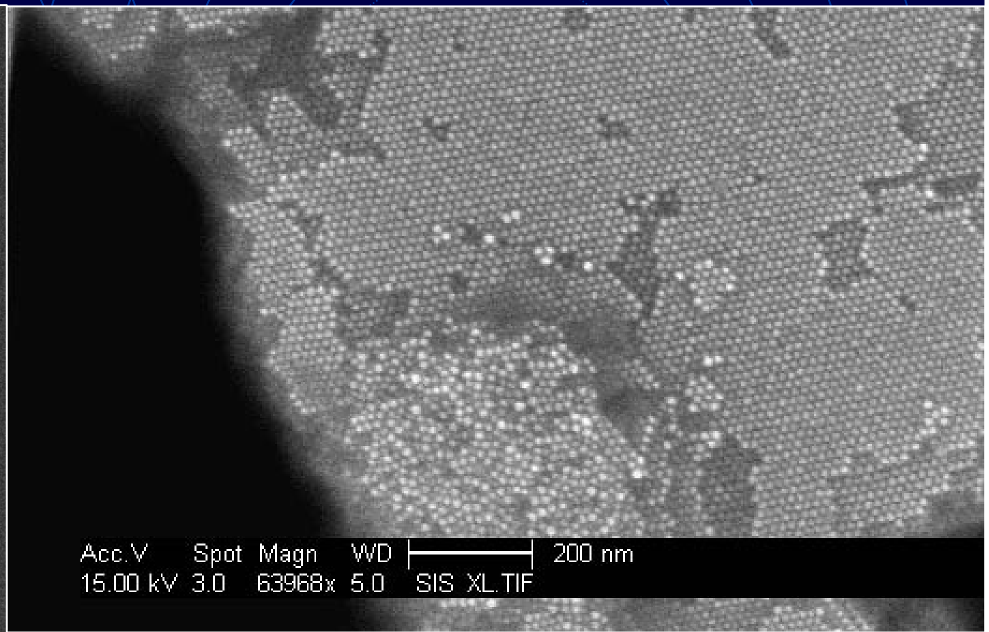
II: Development of versatile nanoparticle assembly techniques

- integration into devices
- interfacing different properties together for synergy
- maintaining nanoparticle properties in a connected network

# Integrating Nanoparticles Together for Functional Materials

## Common Approaches




Silica-gold composite held together by covalent bonding of the capping ligands

Colloidal crystal of ligand-capped gold nanoparticles held together by Van der Waals forces

*Photos from Frank Osterloh, UC Davis*

# Disadvantages of the Use of Ligands or Polyelectrolyte Layers for Assembly

Organic linkers/polyelectrolyte layers decrease the efficiency of:

(1) Interparticle dipole-dipole interactions

(2) Electron transport

## Sol-Gel Method

A method of directed self-assembly to form a self-supported array of nanoparticles

Particles are physically attached to each other without any intervening ligands

The resulting structures are porous, permitting access to the individual nanoparticle components

# The Sol-Gel Process

## Formation of silica gels

**Hydrolysis:**

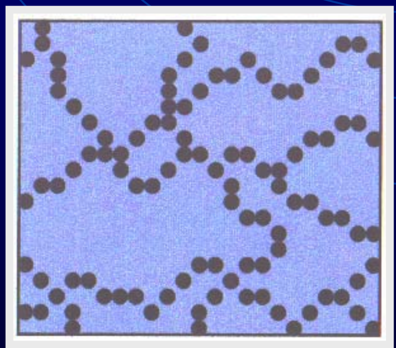
$$Si(OMe)_4 + H_2O \longrightarrow (HO)Si(OMe)_3 + MeOH$$

**Condensation:**

$$(HO)Si(OMe)_3 + Si(OMe)_4 \longrightarrow (OMe)_3Si\text{-}O\text{-}Si(OMe)_3 + MeOH$$

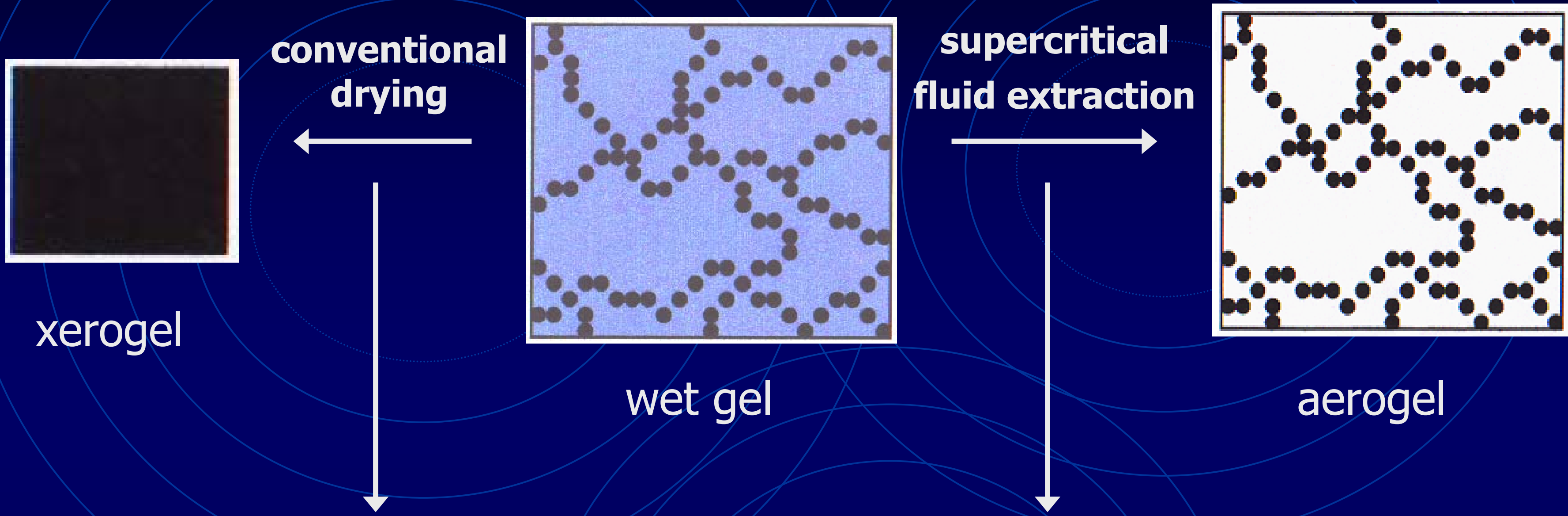
further condensation

$SiO_x$ gel in methanol



*Kinetics and thermodynamics favor formation of a swollen polymer over precipitation for silica. Morphology is controlled by the relative rates of hydrolysis and condensation*

# Preserving the Structure of Wet Gels During Drying

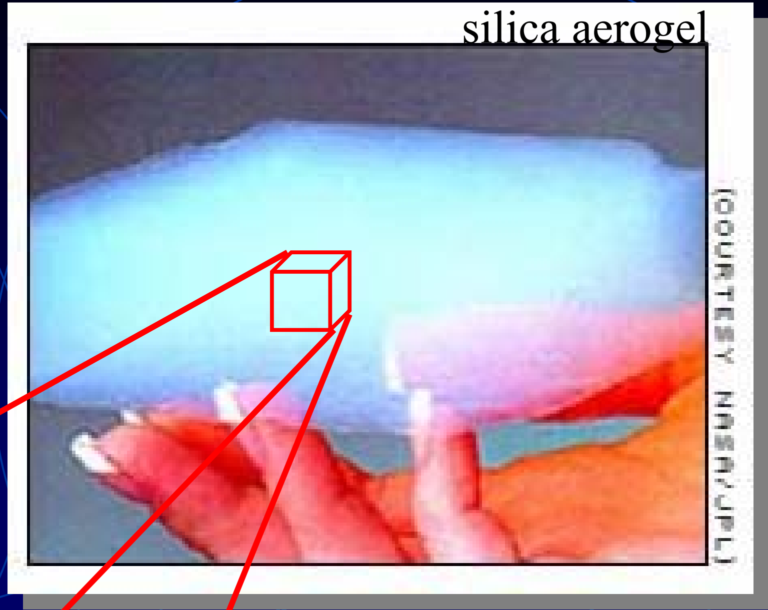



*Pore-collapse due to the action of capillary forces on the walls as the solvent evaporates leads to densification*

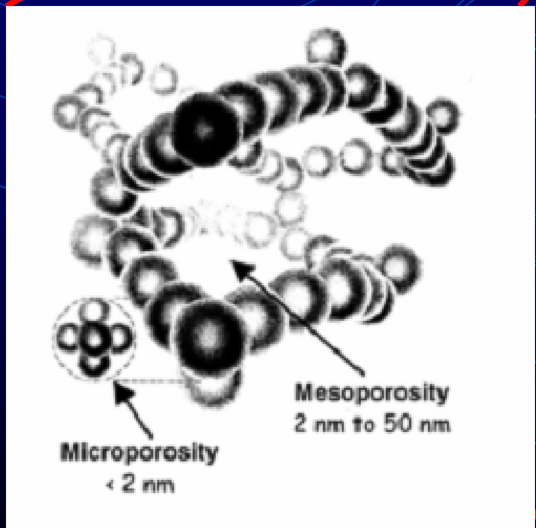
*The absence of a liquid-gas interface in supercritical fluids enables the wet-gel structure to be maintained during drying*

# Aerogels

- inorganic polymers composed of nanoscale building blocks
- high surface area
- low density

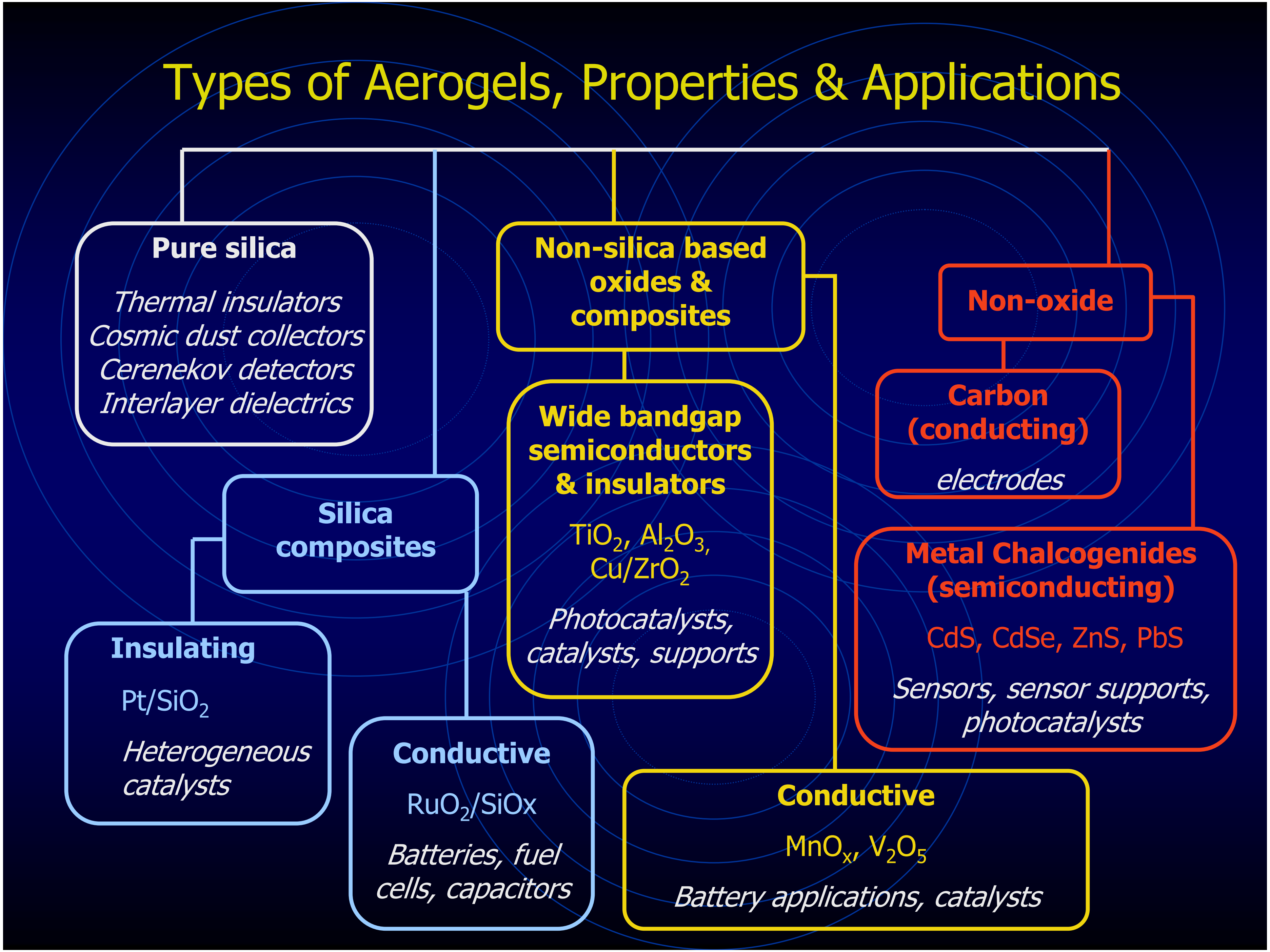



CNN.com/space August 9, 2002




- high porosity (micropores and mesopores)
- 3-D interconnected porous network
- Largely oxide based

Rolison, D. R.; Dunn, B. *J. Mater. Chem.* **2001**, 11, 963.


Types of Aerogels, Properties & Applications
Pure silica
Thermal insulators
Cosmic dust collectors
Cerenekov detectors
Interlayer dielectrics
Silica composites
Insulating
$Pt/SiO_2$
Heterogeneous catalysts
Conductive
$RuO_2/SiOx$
Batteries, fuel cells, capacitors
Non-silica based oxides & composites
Wide bandgap semiconductors & insulators
$TiO_2$, $Al_2O_3$, $Cu/ZrO_2$
Photocatalysts, catalysts, supports
Conductive
$MnO_x$, $V_2O_5$
Battery applications, catalysts
Non-oxide
Carbon (conducting)
electrodes
Metal Chalcogenides (semiconducting)
CdS, CdSe, ZnS, PbS
Sensors, sensor supports, photocatalysts

# Metal Chalcogenides for Photovoltaics and Sensing

Main group metal chalcogenides are semiconductors with direct band gaps that range from the IR to the UV, depending on composition

Photovoltaics: achieve solar energy absorption without the need for dye sensitization

Nanoparticle composites--CdSe with hole conducting polymer--Inexpensive, but inefficient (Alivisatos & co.)

*Efficiencies are limited by electron conduction, which occurs by hopping between quantum dots. Improved by the use of tetrapod-shaped nanoparticles in a high weight percentage (70-90%) composite (up to 1.8% efficiency)*

# Metal Chalcogenides for Photovoltaics and Sensing

Chemical sensors: Conductivity, photoconductivity, or photoluminescence response depending on the Lewis Acid/Base character of the molecular adsorbant

- Single crystals of CdSe exhibit reversible photoluminescence quenching or augmentation depending on analyte (Ellis & co.)
- CdSe nanoparticles in polymeric thin films have demonstrated a photoluminescence response to amines (Peng & co.)

*Photostimulation needed to activate polymer and facilitate molecular diffusion—hundreds of seconds needed to obtain a steady response.*

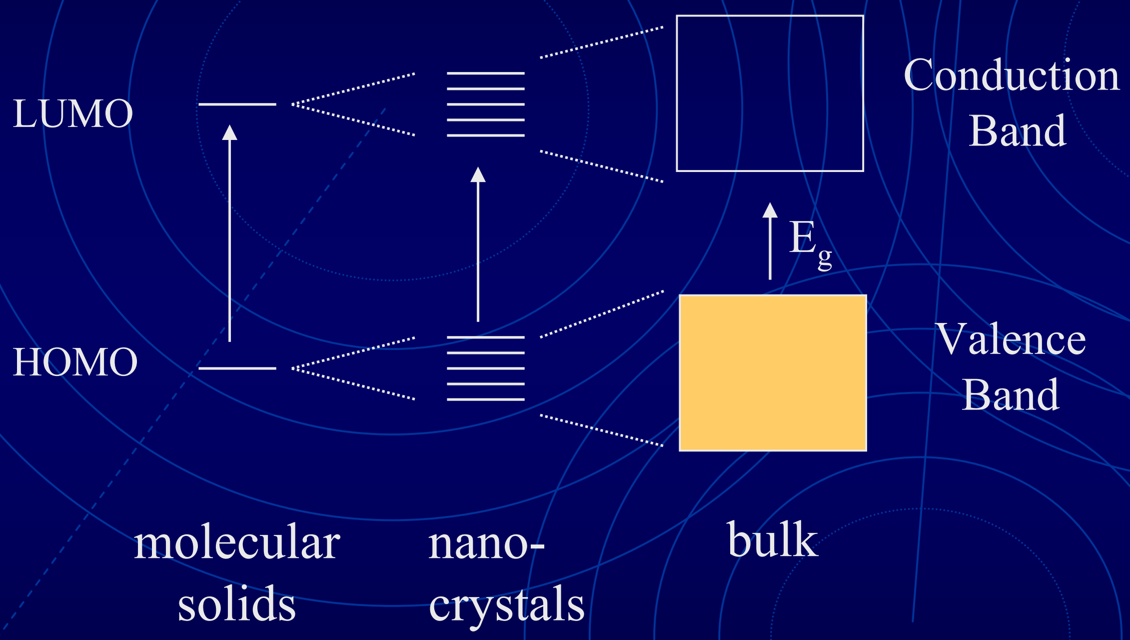
# Sol-gel Chemistry of Metal Chalcogenides-Aerogels and Xerogels

- Sol-gel routes permit engineering of connectivity of matter on the nanoscale for transport of electrons, and connectivity of pores for transport of molecules—chemical sensors
  - High internal surface area for transport of charge across the interface—composite photovoltaics
- Powerful strategy for assembling nanoparticles together into functional architectures
- Provide a system for evaluating the effect of dimensionality on quantum confinement effects in a nanoparticle network—the dimensionality of the system can be tuned by controlling the porosity

# Quantum Confinement Effects

*observed in nanometer sized semiconductor particles*

## Molecular Orbital Diagram




*blue shift in absorbance band of nanoparticles relative to bulk. Sharp band-edge luminescence*

**# atoms:** $A_2$ $A_{10\text{-}10{,}000}$ $A_{\infty}$

Increasing particle size

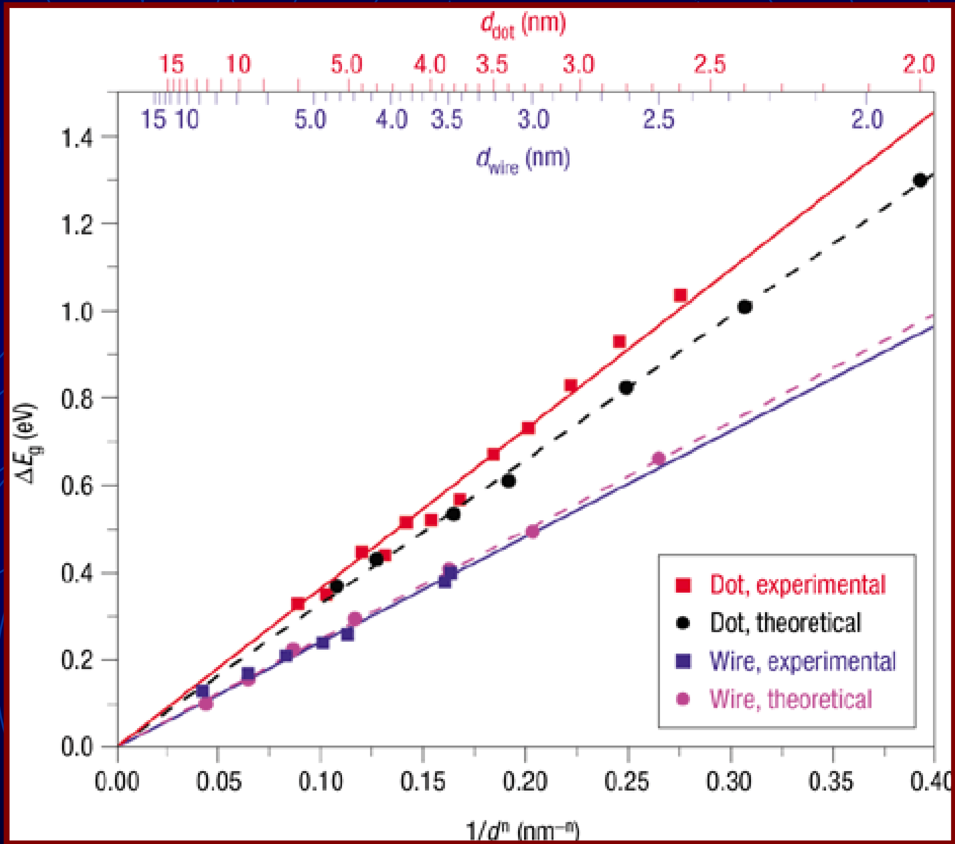
2 nm 6 nm

Steigerwald and Brus, *Acc. Chem. Res.* **1990**, *23*, 183

# Influence of Dimensionality on Quantum Confinement Effects : Dots Vs. Wires

- 0-D Quantum dots
- 1-D Nanowires

Introducing anisotropy into semiconductor nanoparticles weakens the quantum confinement




Yu, H.; Li, J.; Loomis, R. A.; Wang, L.-W.; Buhro, W. E. *Nature Mater.* **2003**, *2*, 517-520

# Chalcogenide Gels

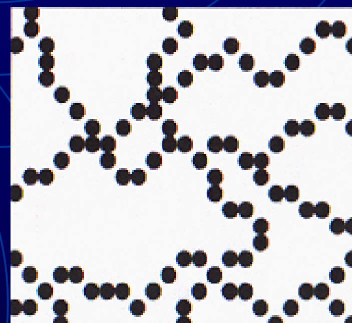
Reports of chalcogenide gels are rare; aerogels non-existent

Gacoin et. al. reported that thiol capped nanoparticles of CdS gelled upon slow oxidative removal of capping groups using air or $H_2O_2$

CdS gels were reported to demonstrate quantum confinement effects due to the nanoparticle building blocks

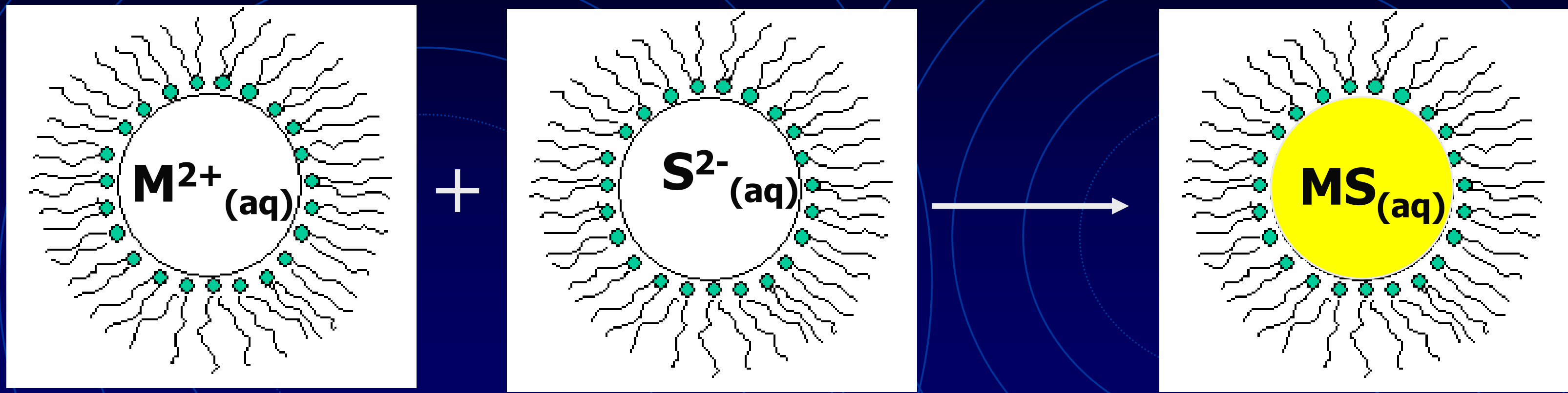
This route should mimic base catalyzed silica

"Pearl necklace" architecture



*Can we transform these to monolithic aerogels? Will they retain their optical properties? Can we apply this methodology to other metal chalcogenides?*

# Sol-Gel : MS Nanoparticles & Capping



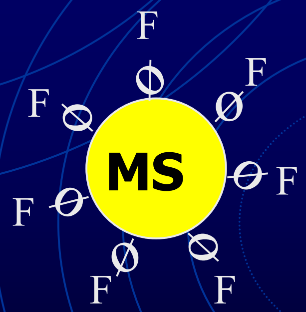

Reverse micelles : AOT / $H_2O$ / heptane
Varying ratio → variable particle size

surface capping
& precipitation
(4FPhSH, TEA)

Initial target: CdS

Optical properties well explored

Can adopt cubic or hexagonal diamond-like structures

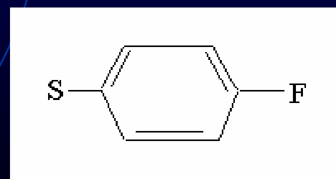



heptane wash, 3X

dispersed in acetone

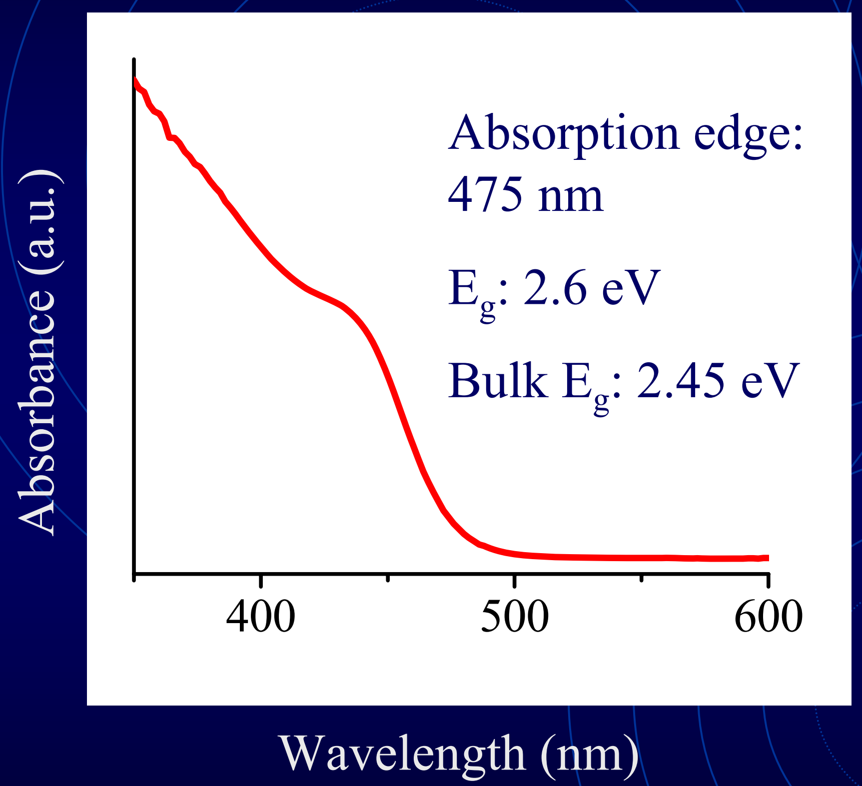
**M = Cd, Pb, Zn**

ØF =

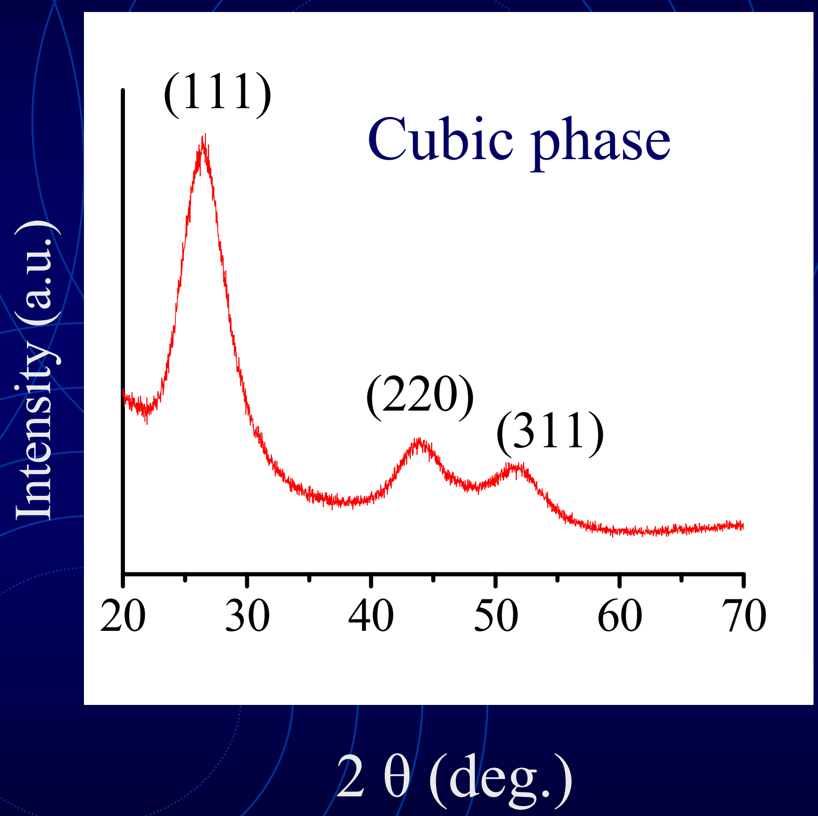


# Characterization of CdS Nanoparticles

UV-Visible

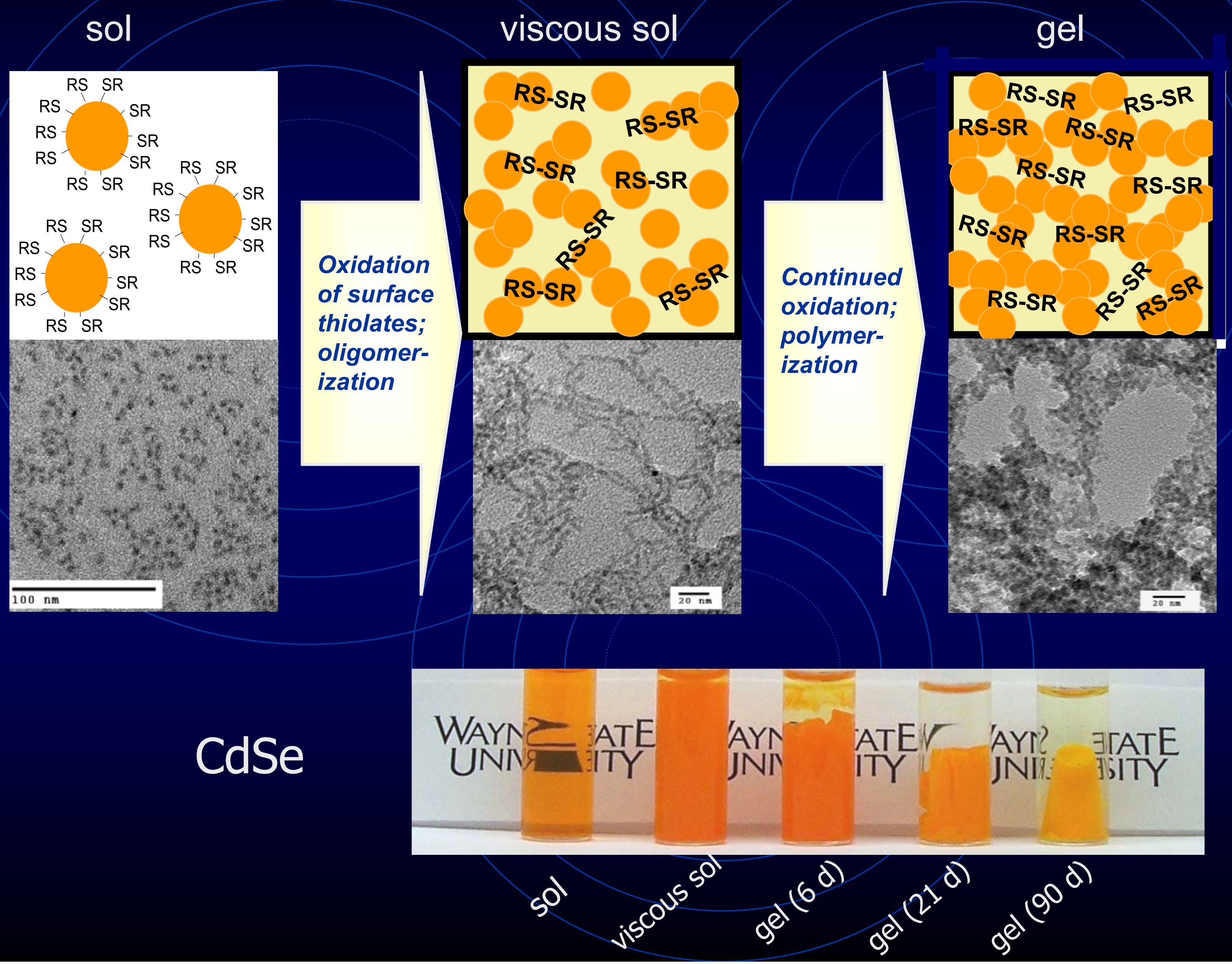



X-ray powder diffraction



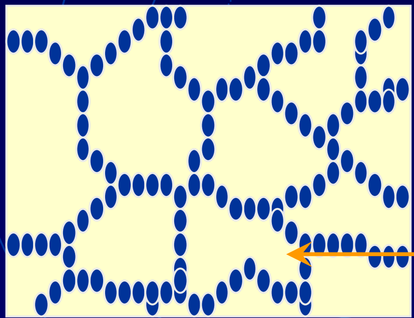

Cd/F ratio 4/1 → **1.6 nm**

# Chalcogenide Gelation Process



# Preparation of Metal Chalcogenide Aerogels

wet gel
Aged 4-7 days
acetone washed 2-3 times

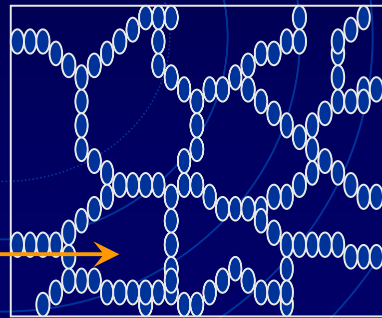


Acetone

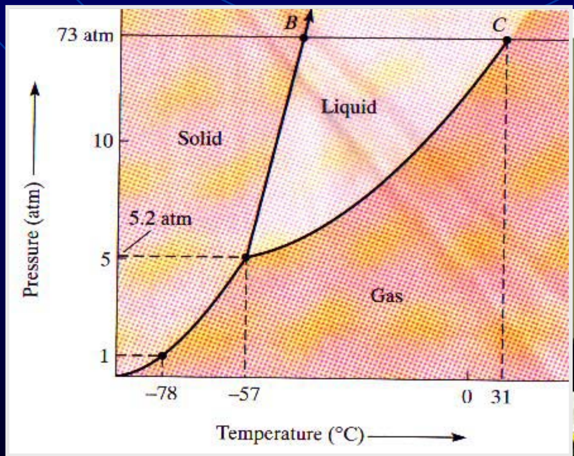
Supercritical fluid extraction

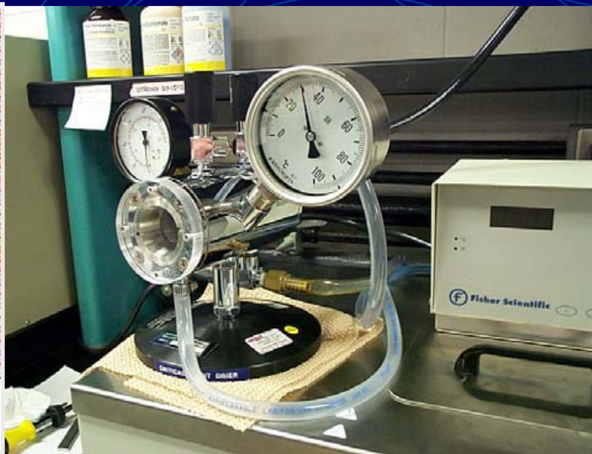
*$CO_2$ Critical point drying*

Aerogel



Air



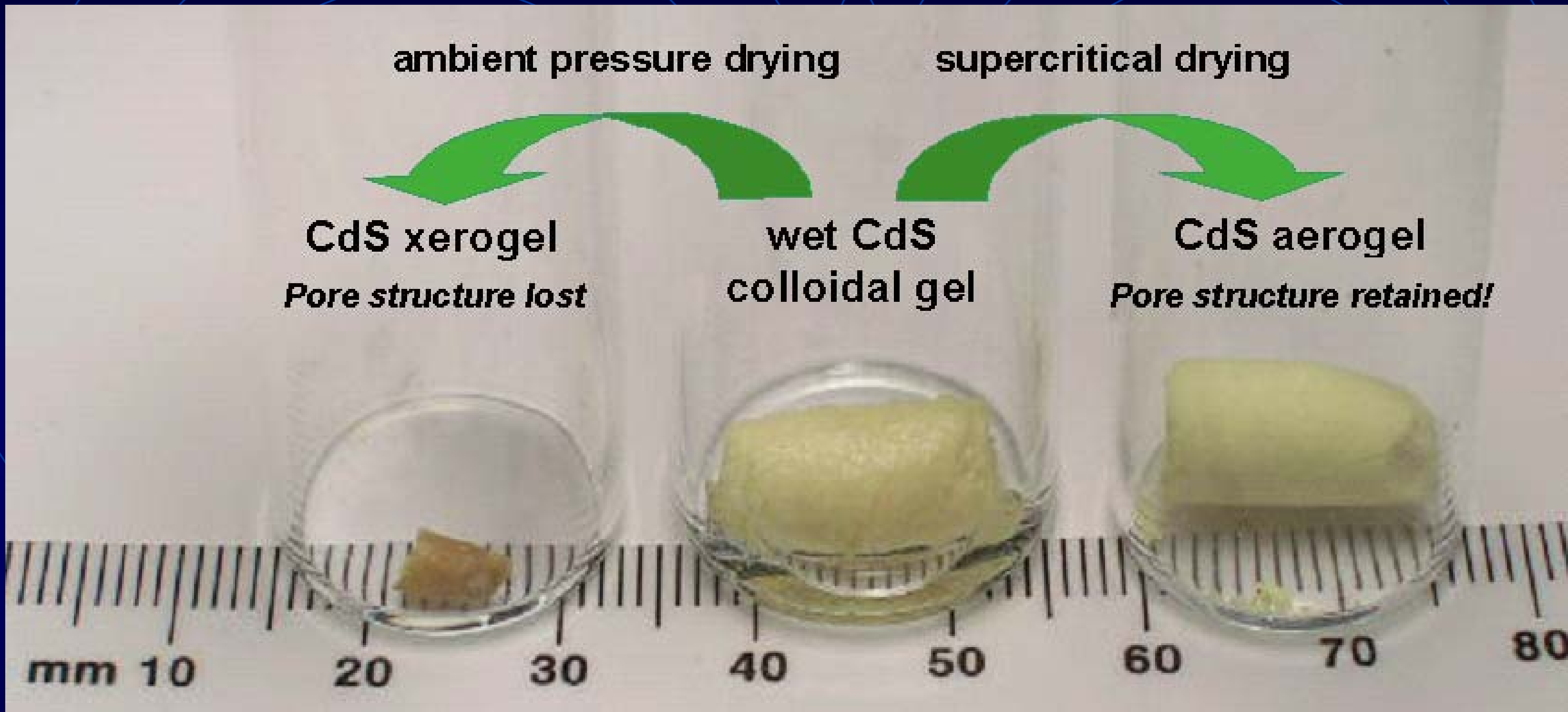



*$CO_2$ Critical point dryer*

CdS

Post-annealing up to 500 °C

# Effect of Drying on Gel Morphology



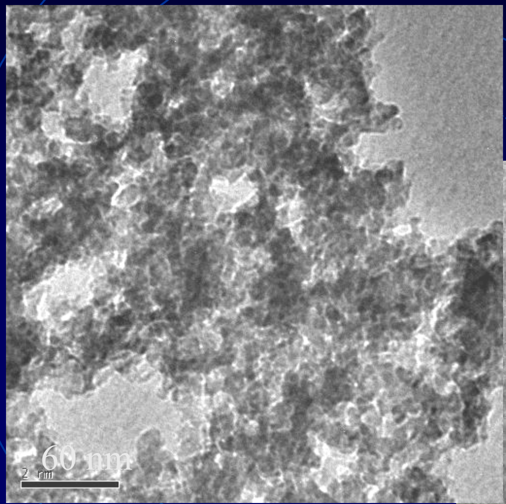

$\rho_{\text{bulk monolith}} \sim 0.07$ g/cc vs. $\rho_{\text{CdS crystal}} \sim 4.825$ g/cc

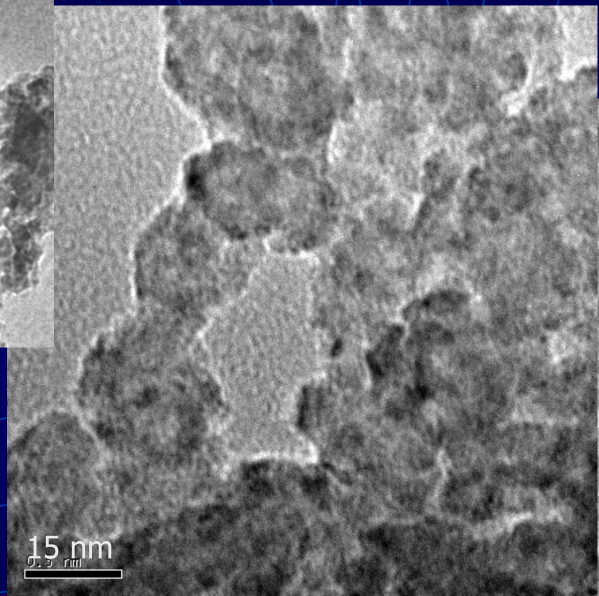
*CdS aerogels have 1.5% the density of crystalline CdS!*

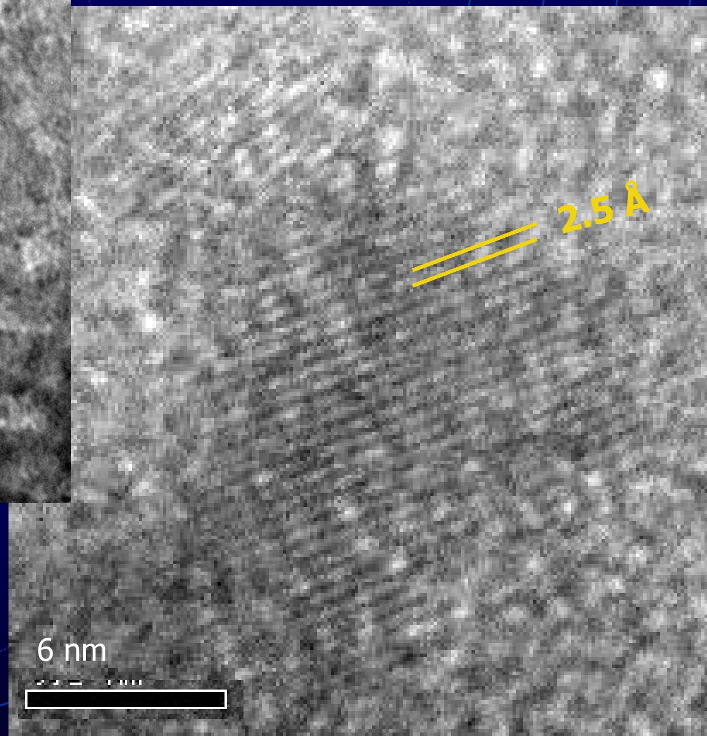
Mohanan; Brock, *J. Non-Cryst. Solids* (special issue from the 7th Int. Symp. on Aerogels), **2004**, *350*, 1-8.
Mohanan; Arachchige; Brock, *Science*, **2005**, *307*, 397-401.

# Electron Micrographs of CdS Aerogels

*annealed under vacuum, 100 °C*



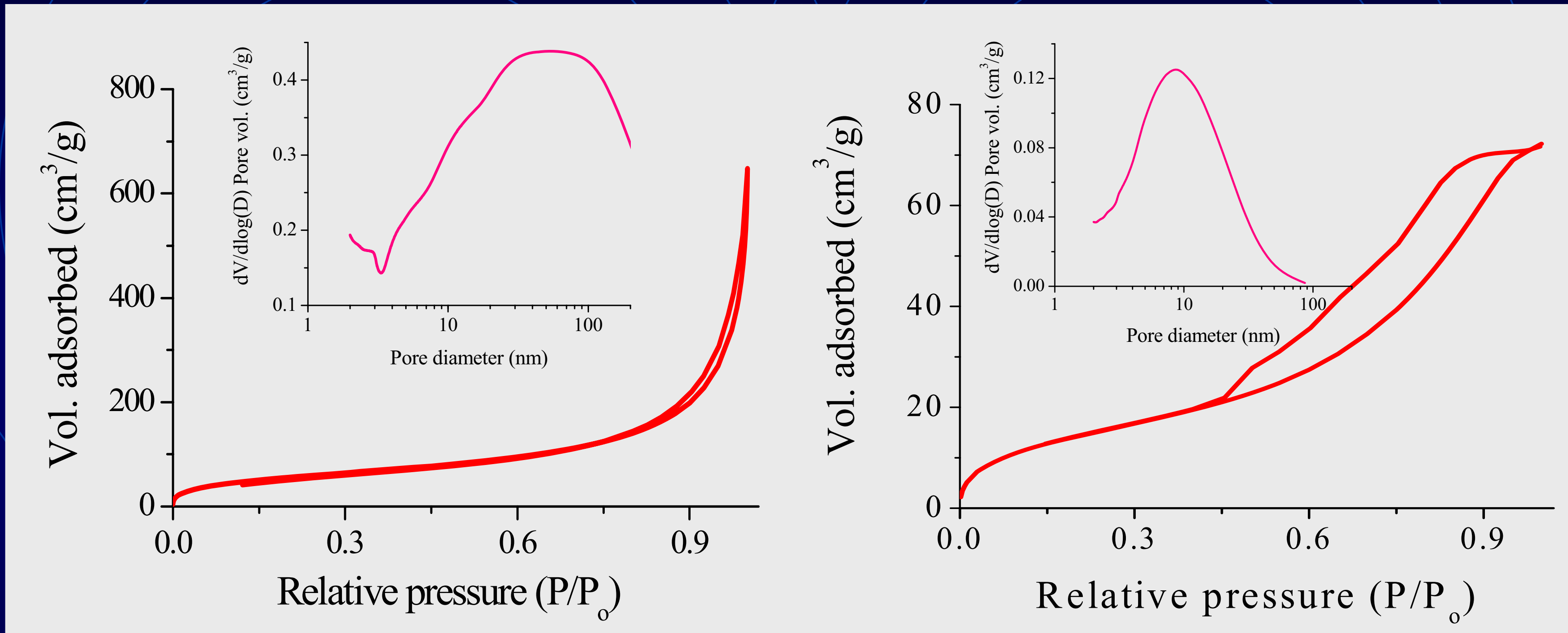




Cd/F ratio in aerogel product: 24/1 (relative to 4/1 in precursor)—no change upon annealing at 100 °C

*Hexagonal CdS (102) = 2.452 Å*

# Surface Area and Pore Size

Aerogel 100 °C degassed 30 h Xerogel




BET Surface Area: 250 $m^2/g$
(600 $m^2/g$ silica equivalents)

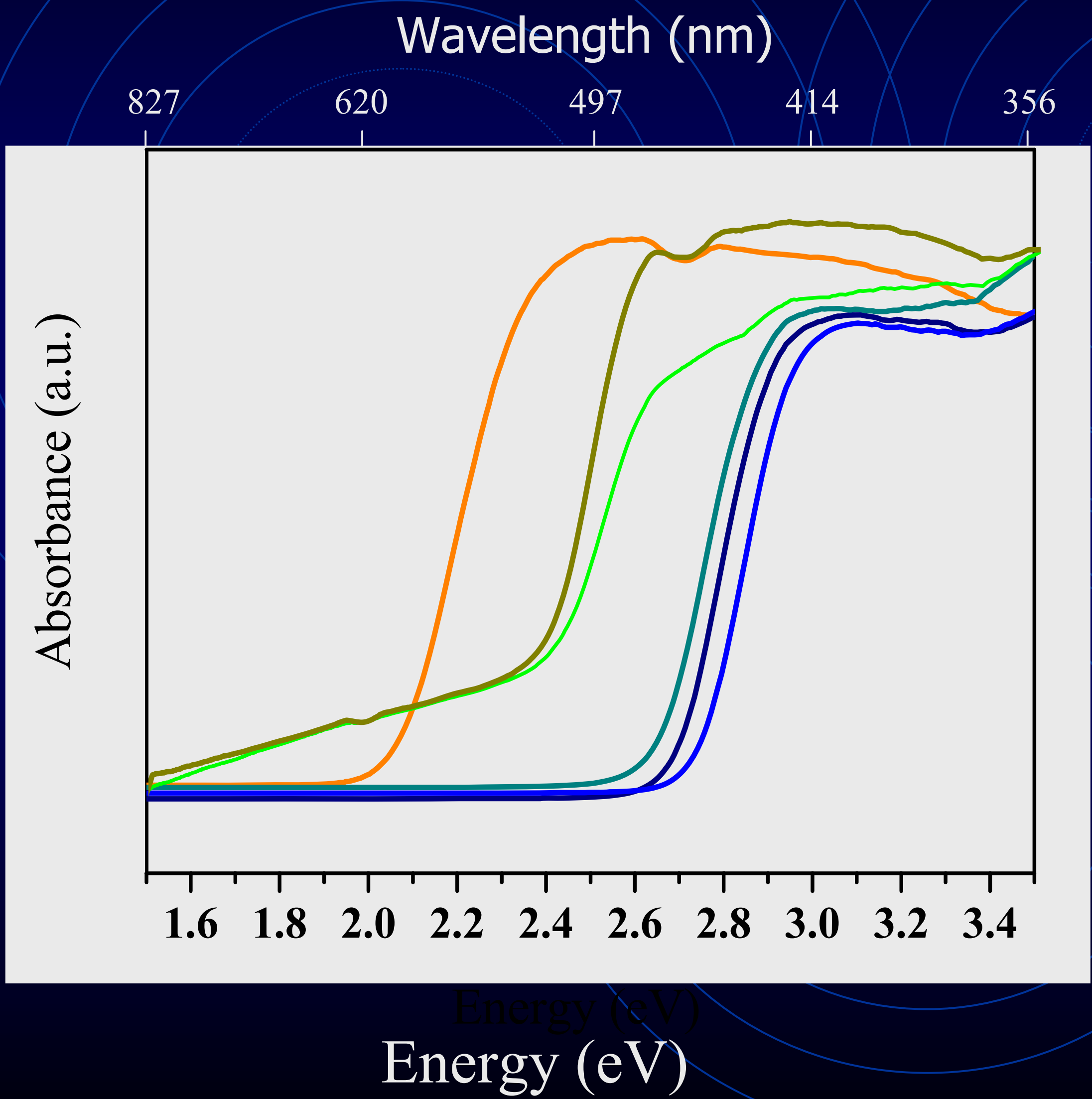
Ave pore diameter: 14 nm
Pore volume 0.78 $cm^3/g$

BET Surface Area: 55 $m^2/g$
(132 $m^2/g$ silica equivalents)

Ave pore diameter 8 nm
Pore volume 0.11 $cm^3/g$

Mohanan; Brock, *J. Non-Cryst. Solids*, **2004**, *350*, 1-8. Mohanan; Arachchige; Brock, *Science*, **2005**, *307*, 397-401.

# Optical Band-Edge Measurements




**Bulk : 2.05 eV**

**25 °C : 2.73 eV**

**50 °C : 2.68 eV**

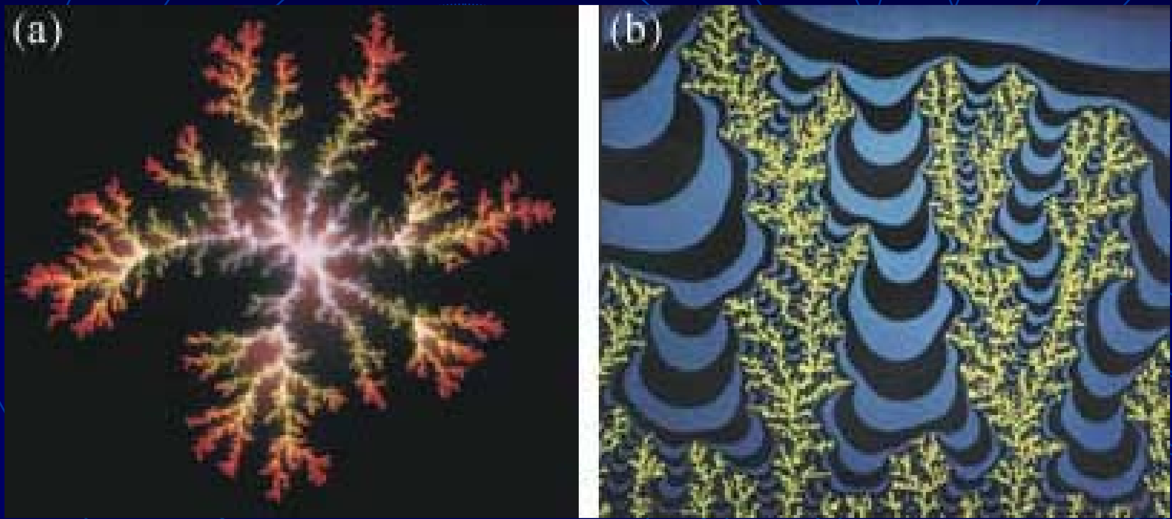
**100 °C : 2.64 eV**

**200 °C : 2.25 eV**

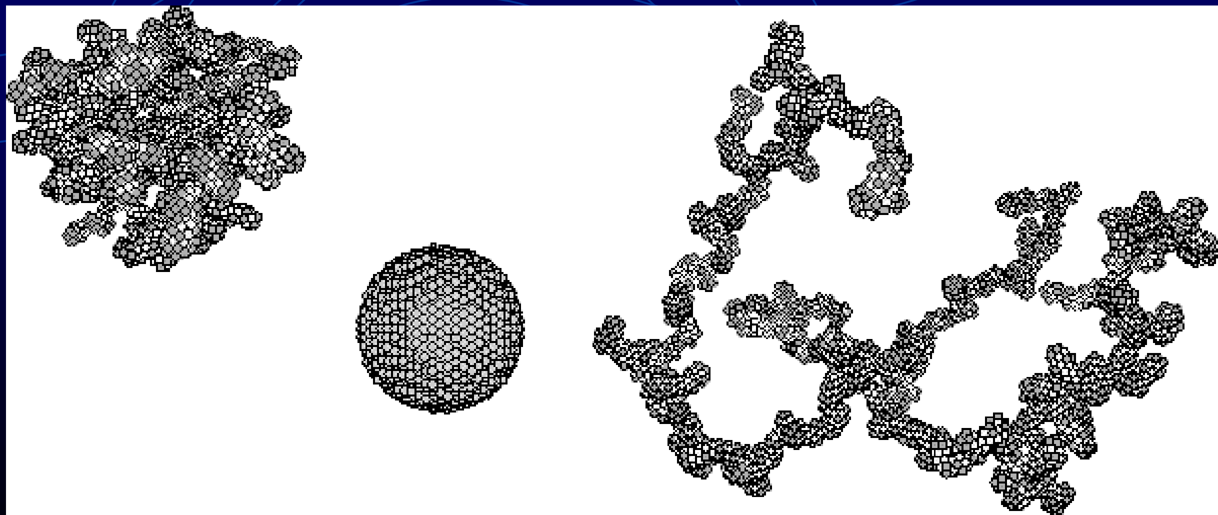
**300 °C : 2.22 eV**

*How is it that a 3-D linked structure remains quantum confined?*

# Gels as Fractal Networks…an Example of Diffusion Limited Aggregation (DLA)




***DLA fractals***
Halsey, Physics Today 11/01
http://www.aip.org/pt/vol-53/iss-11/p36.html

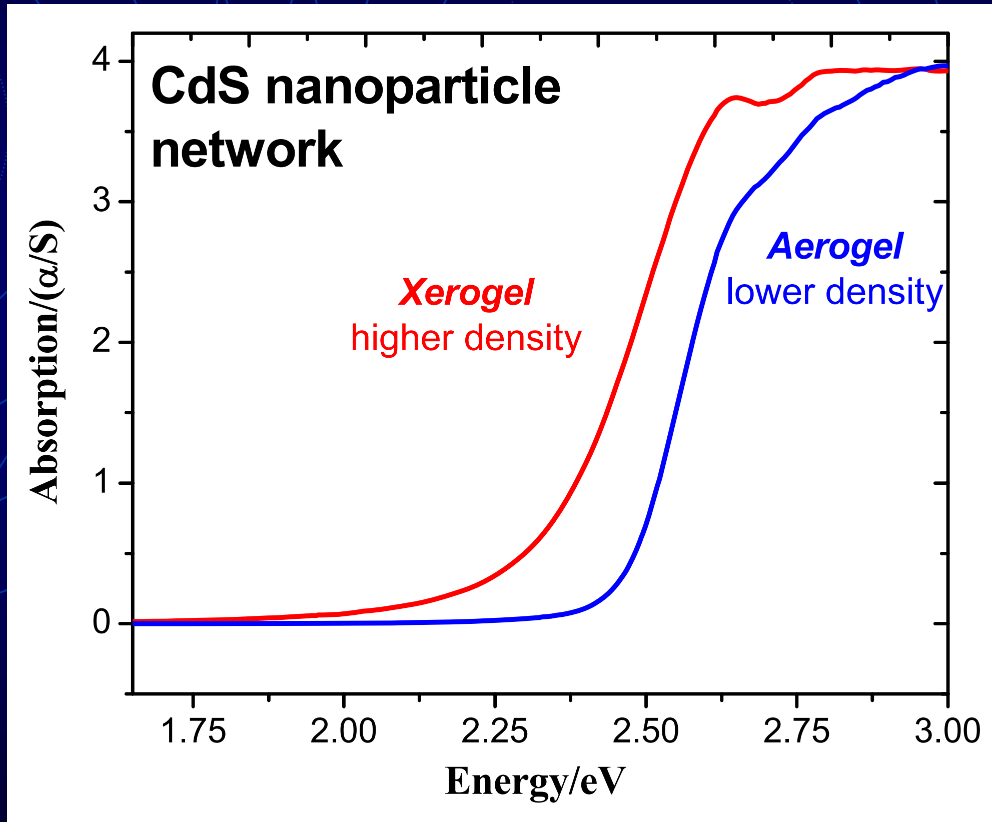


***DLA fractal, sphere and CL fractal, all with the same volume***
http://www.astro.ucla.edu/~wright/dust/

# Influence of Dimensionality on Quantum Confinement Effects in Nanoparticle Networks

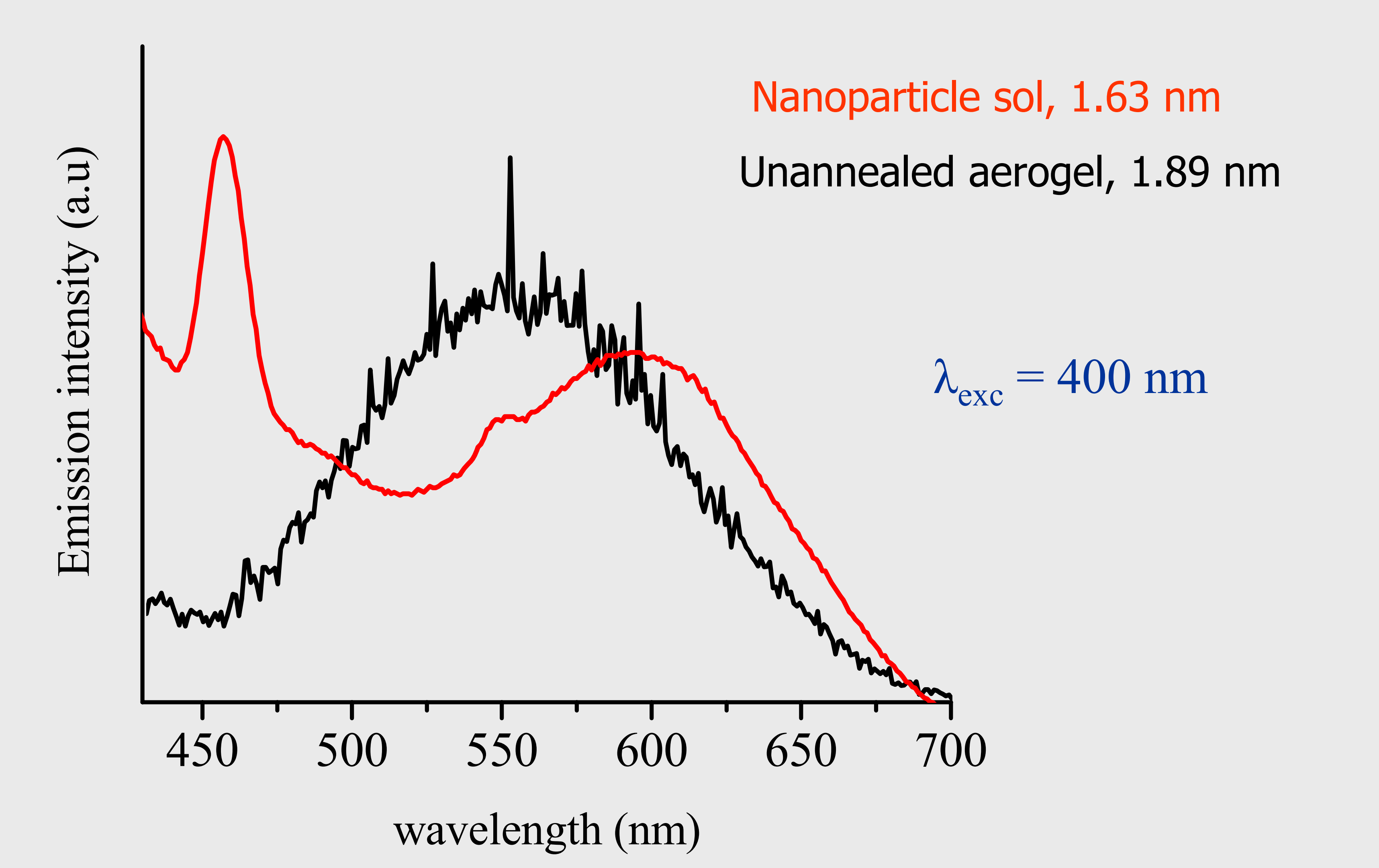
Low temperature processed networks-

no change in crystallite size as probed by X-ray powder diffraction




*The dimensionality of the network, and hence the extent of quantum confinement, can be tuned by density!*

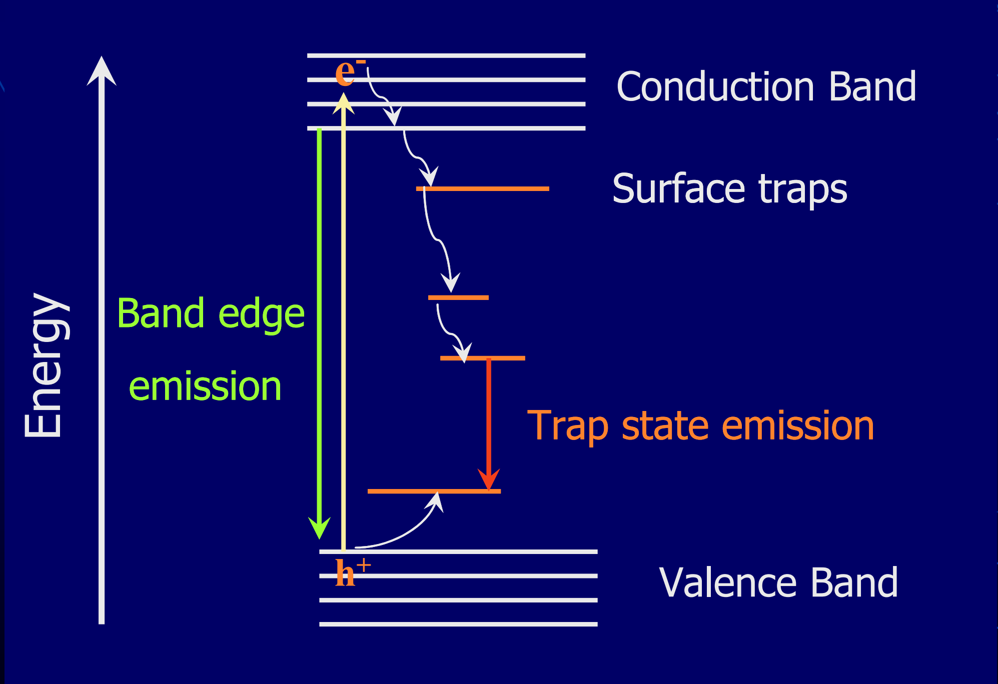
# Photoluminescence of CdS Nanoparticles & Aerogels



# Size-Dependent Bandgap and Photoluminescence from Semiconductor Nanoparticles

Intense band-edge PL in quantum dots-narrow & very intense

But defects provide a site for electron-hole recombination

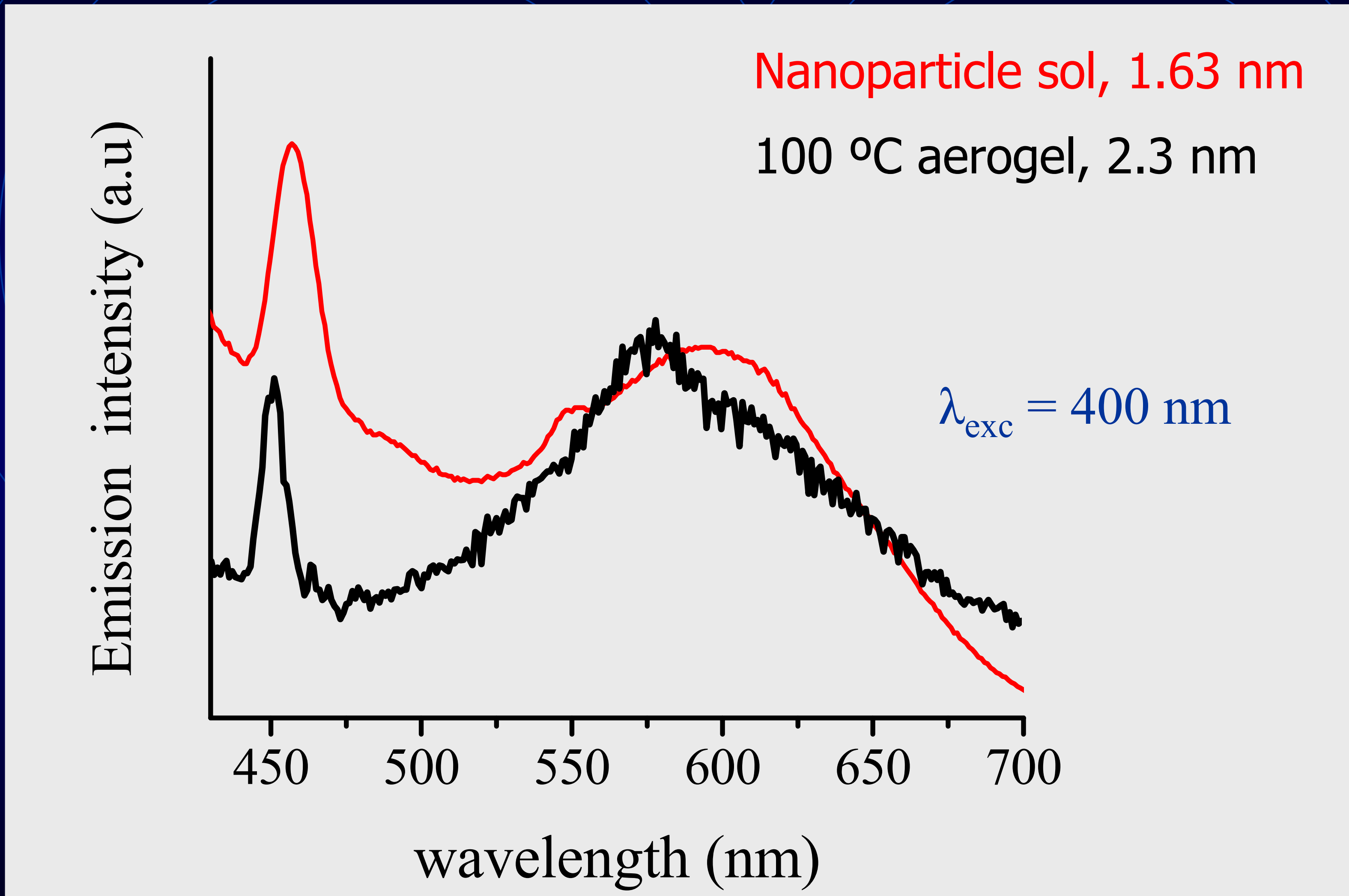



Result: broad PL red-shifted from band-edge PL

Defects due to poor crystallinity & surface sites for non-radiative recombination…especially for thiolate capping groups

http://www.evidenttech.com/products/quantum-dot-nanomaterials.php

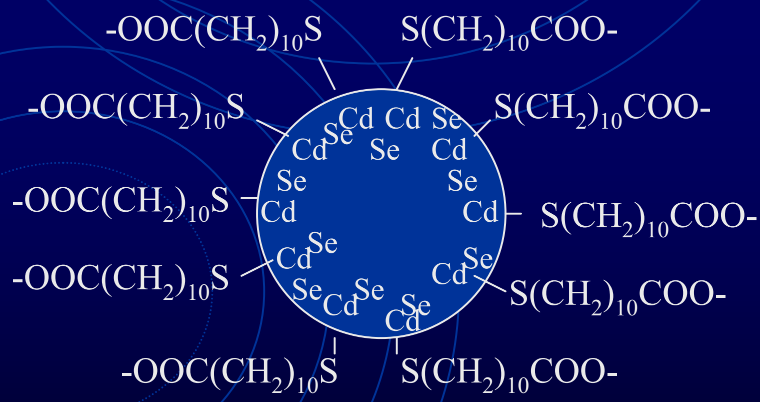
# Photoluminescence of CdS Nanoparticles & Aerogels



# Upping the Lumens: CdSe Nanoparticle Precursors by High Temperature Routes

CdO + TDPA* $\xrightarrow{300\ °C}$ $\xrightarrow[Se/P(octyl)_3]{270\ °C}$ CdSe nanoparticles (hexagonal, TDPA capped)

↓ 25 °C MUA*/TBAOH



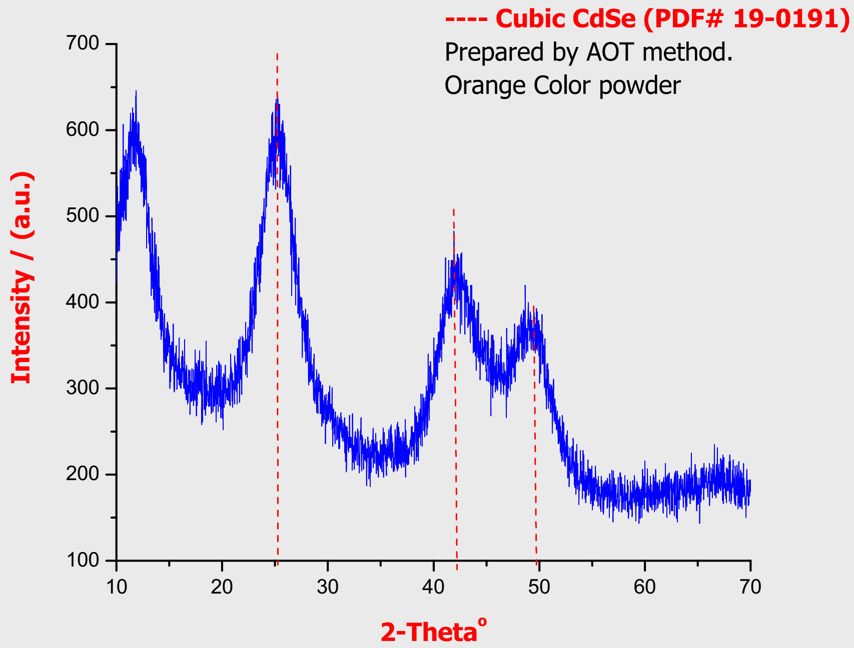

← Bz-O-O-Bz

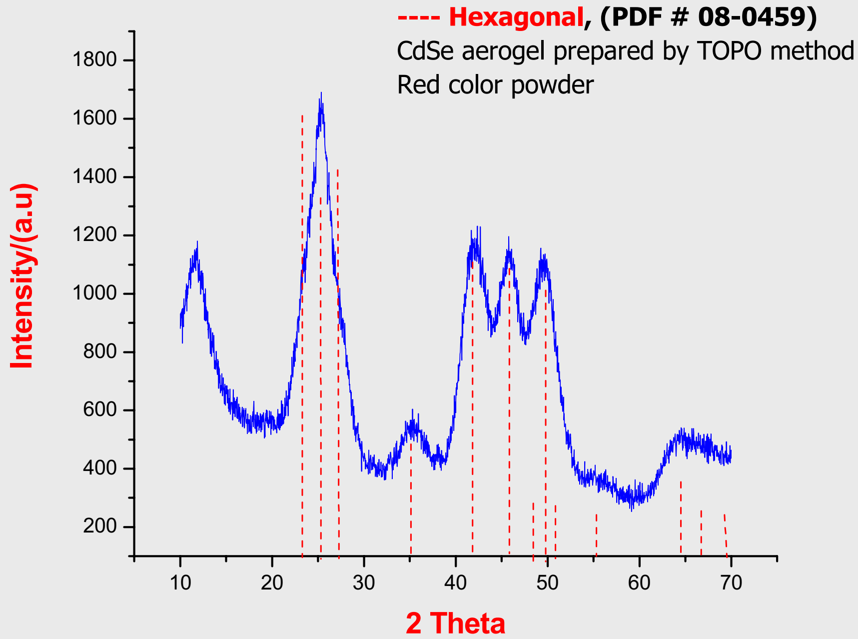
← $C(NO_2)_4$

← hν, $O_2$

*TDPA: $(OH)_2P(O)(CH_2)_{13}CH_3$; MUA: $HS(CH_2)_{10}COOH$ Xiaogang Peng, U Arkansas

# Low-T vs. High-T Prepared Nanoparticles: Structural Consequences for the Aerogel



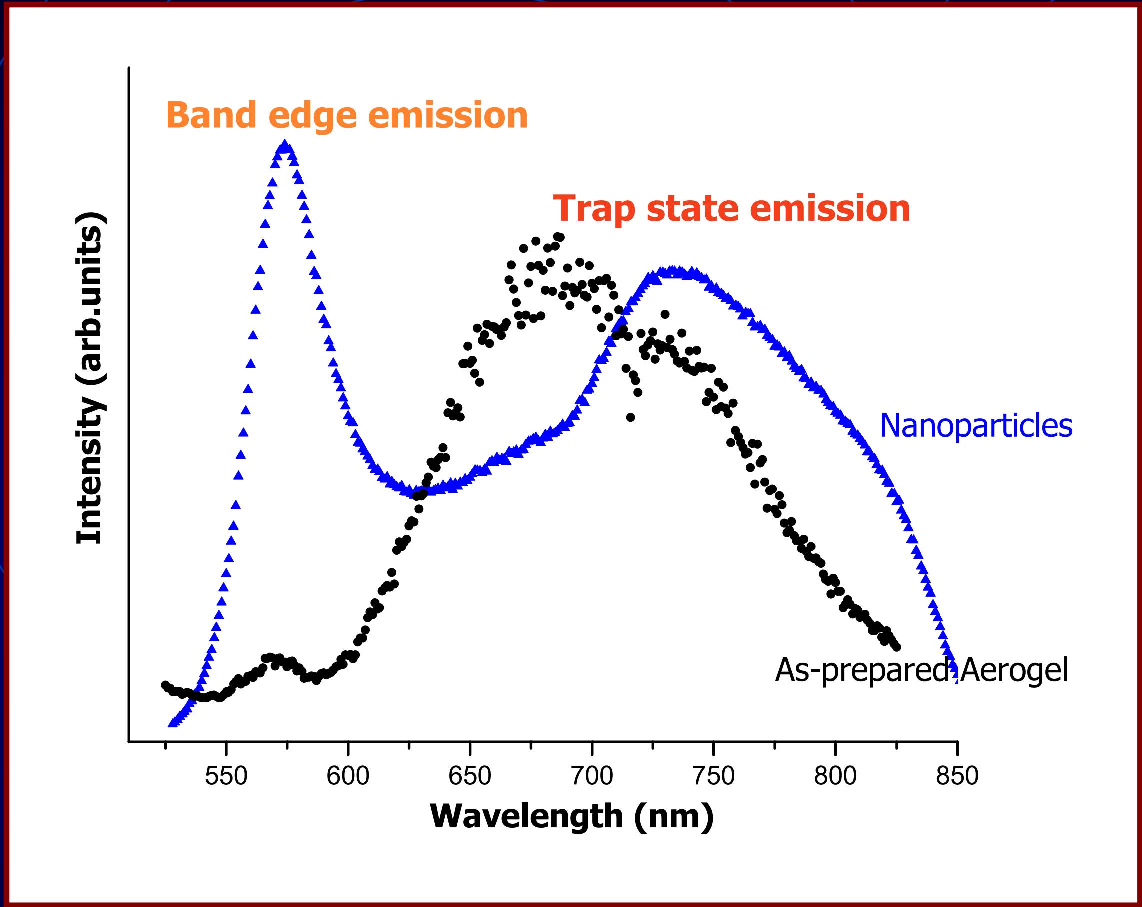

Cubic, $E_g$ = 2.0 eV

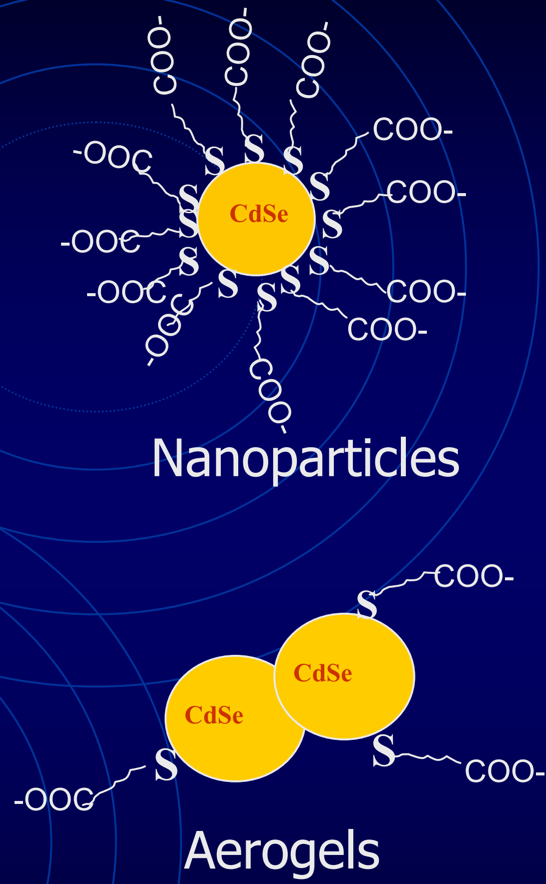
SA = 161 $m^2/g$

Hexagonal, $E_g$ = 2.2 eV

Mohanan; Arachchige; Brock, *Science*, **2005**, *307*, 397-401.

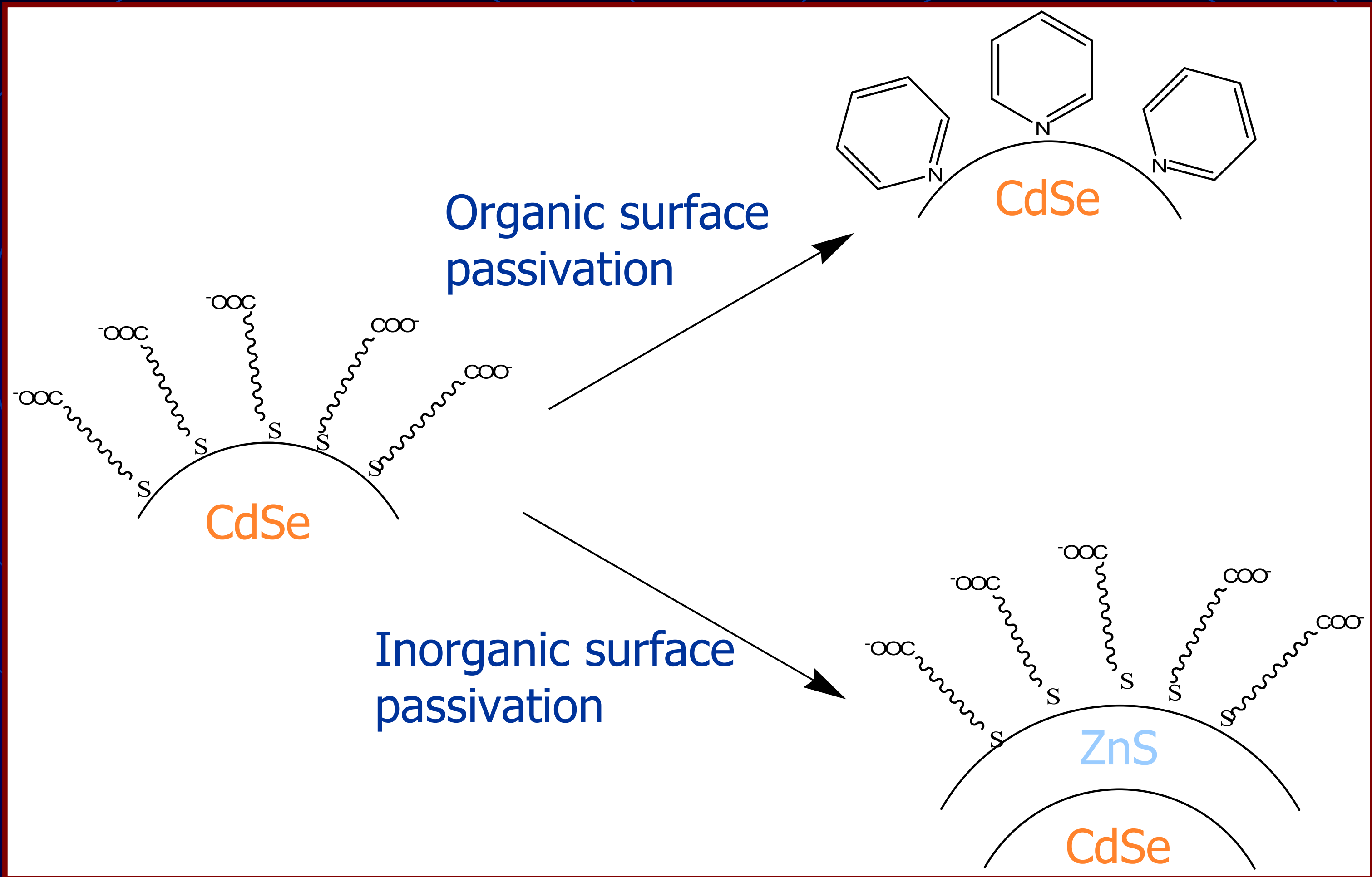
# Photoluminescence Spectra




Weak band-edge emission can be attained in as-prepared aerogels!

# Surface Chemical Passivation



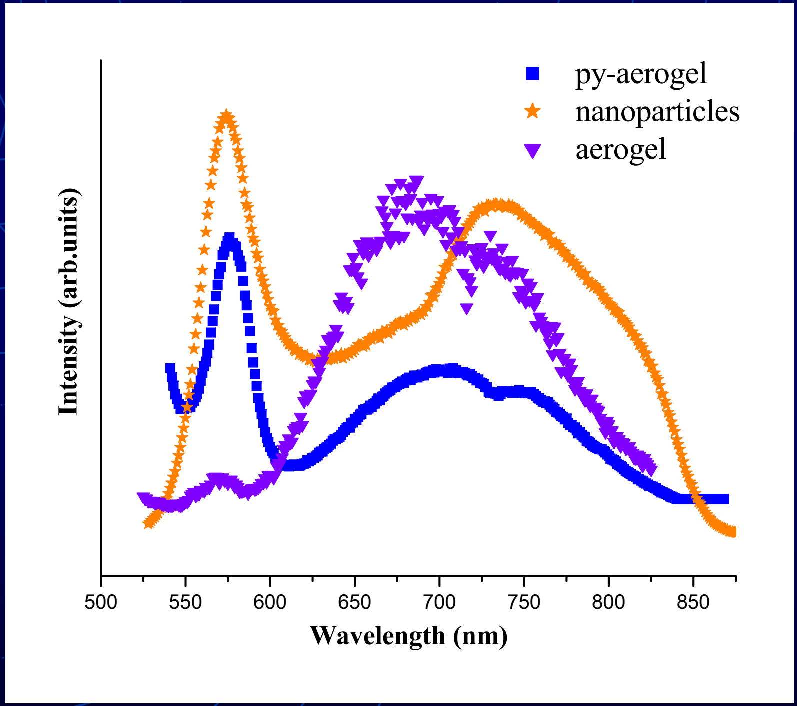

Surface passivation can minimize the surface defects, augmenting band-edge photoluminescence.

*Trindade, T.; O'Brien, P.; Pickett, N. L., Chem. Matter. 2001, 3843-3858*

# Upping the Lumens II: Organic Surface Modification

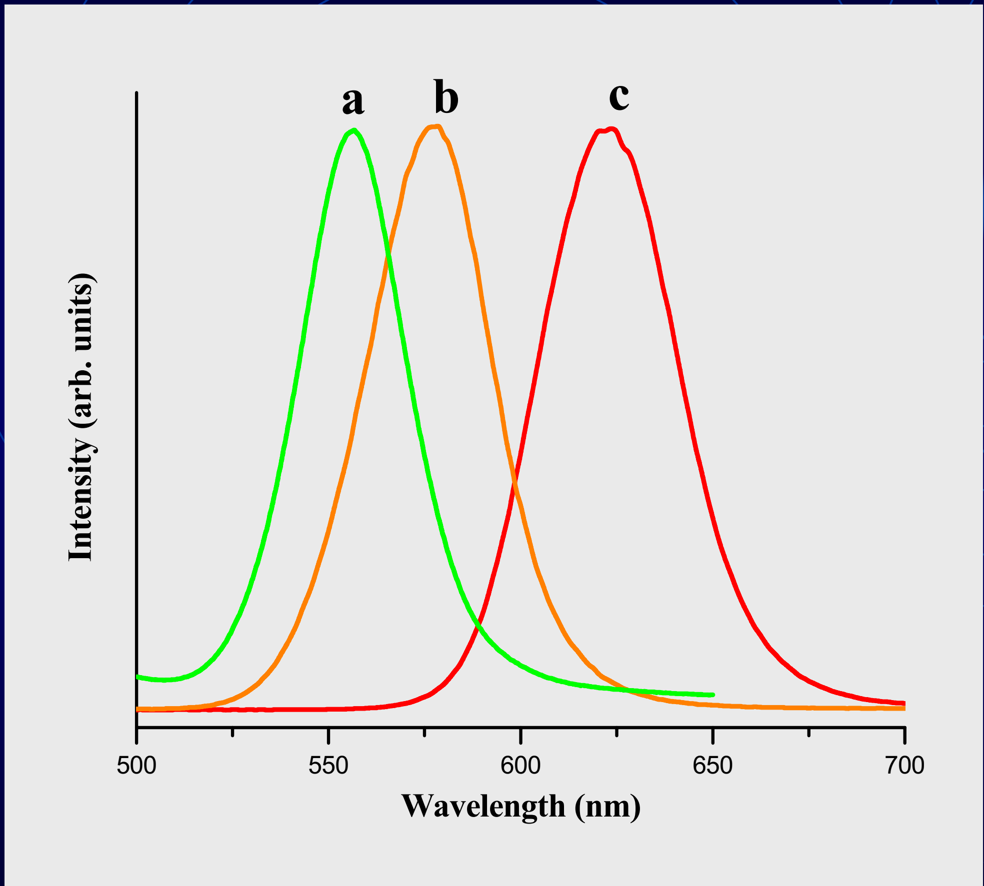
*Exchange of surface thiolates with pyridine at the wet-gel stage*

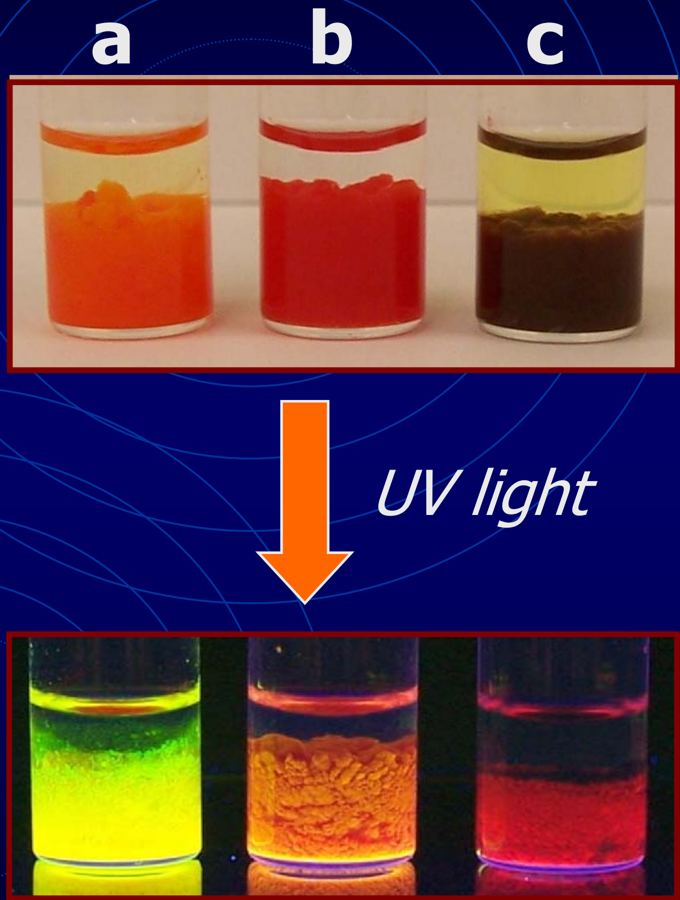
| Sample | Cd % | Se % | S % | P % |
|---|---|---|---|---|
| CdSe (TOPO) Nanoparticles | 41 | 41 | 0 | 18 |
| CdSe-MUA Nanoparticles | 38.9 | 38 | 19 | 4 |
| CdSe Aerogel (wet gel was exchanged only with acetone ) | 42 | 41 | 14 | 4 |
| CdSe Aerogel (wet gel was exchanged with pyridine and acetone ) | 43 | 50 | 6 | 2 |




*Arachchige, I. U.; Brock, S. L. J. Am. Chem. Soc. 2006, 128, 7964-7971*

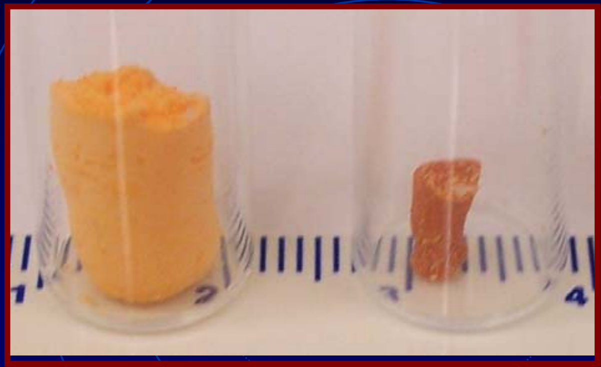
# Highly Luminescent Wet Gels



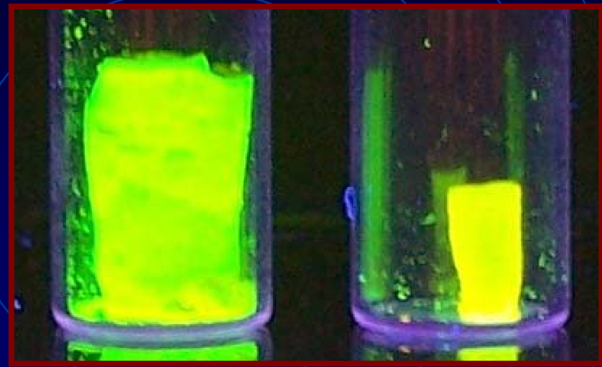




*Arachchige I. U.; Brock S. L., J. Am. Chem. Soc. (submitted)*

# Highly Luminescent Quantum Dot Monoliths



**UV light** →



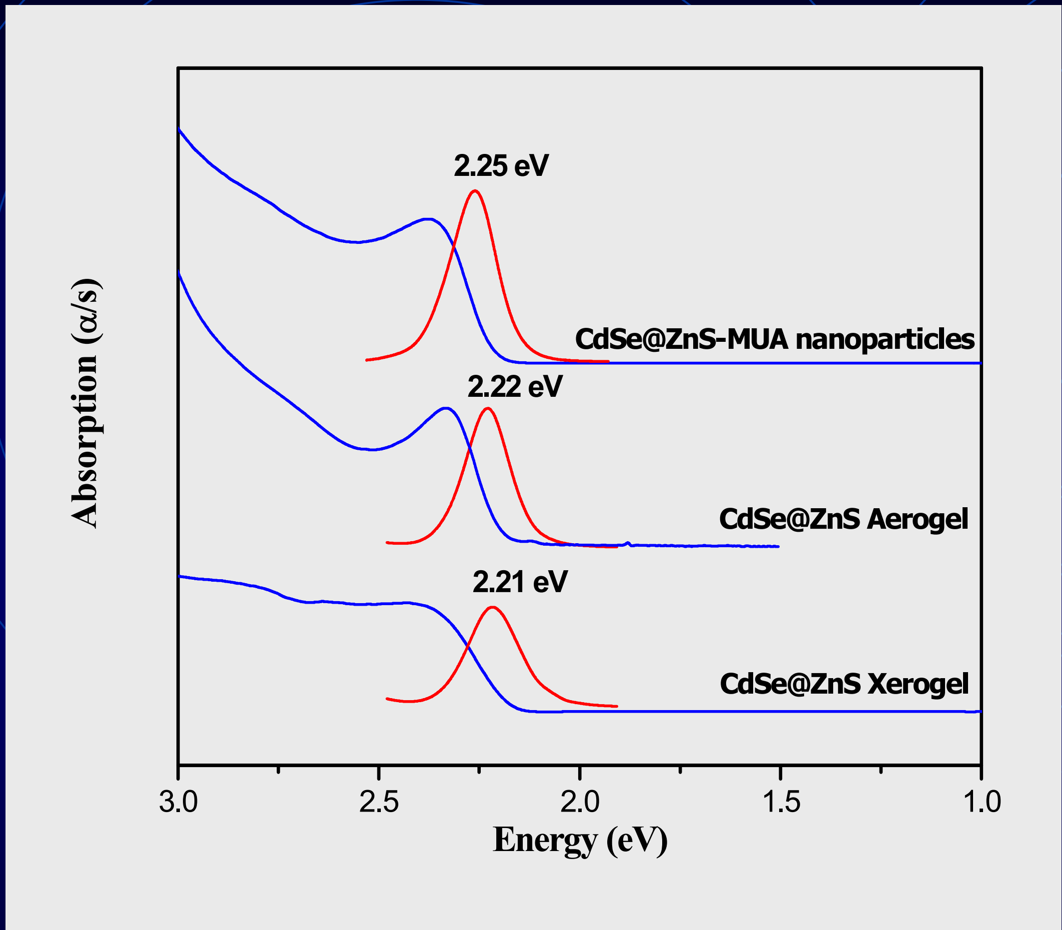
- First report on large (cm-mm size ) free standing CdSe nanoparticle networks without intervening ligands.
- Effect of drying on the compaction of nanoparticle network is clearly evident from the apparent densities of these networks,

***Aerogel ~ 0.08 g/cm$^3$***

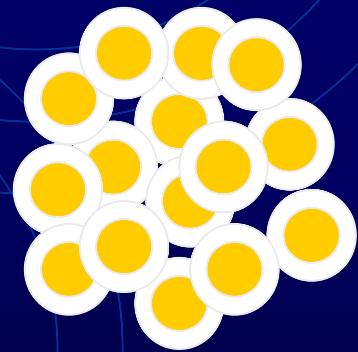
***Xerogel ~ 1.7 g/cm$^3$***

***Arachchige I. U.; Brock S. L., J. Am. Chem. Soc. (submitted).***

# Optical Absorption and Emission Properties




| Sample | Band gap onset |
|---|---|
| Nanoparticles | 2.20 eV |
| Aerogel | 2.18 eV |
| xerogel | 2.15 eV |
| CdSe (bulk) | 1.73 eV |

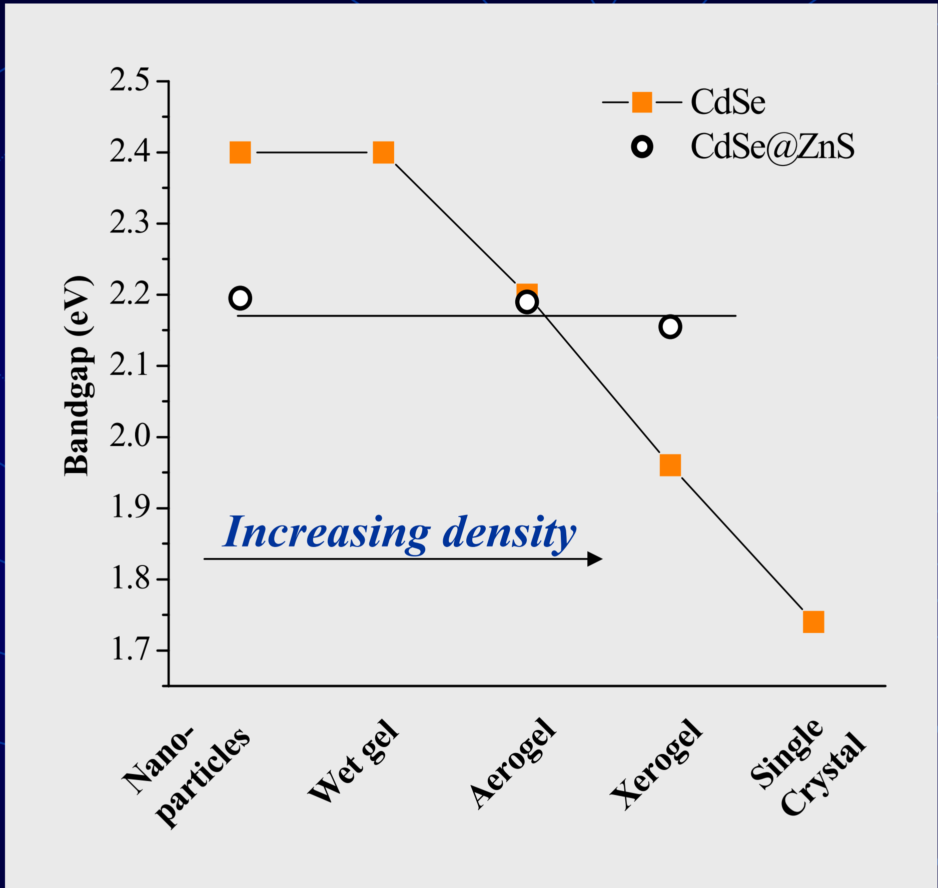


CdSe@ZnS Xerogel

- CdSe@ZnS aerogel and xerogel essentially retain the quantum confined opto-electronic properties of the nanoparticle building blocks.

***Arachchige I. U.; Brock S. L., J. Am. Chem. Soc. (submitted).***

# Influence of Dimensionality on Quantum Confinement Effects: "Naked" vs. Core/Shell Structures




The presence of a ZnS barrier layer preserves the quantum confinement of the precursor nanoparticle, regardless of network density

*Arachchige, I. U.; Brock, S. L. J. Am. Chem. Soc. (submitted)*

# A Closer Look at CdSe-Influence of Oxidant on Aerogel Properties

Sol formation:

$Cd(NO_3)_2 + Na_2Se$ —(AOT/water, heptane)→ CdSe sol/AOT (red colloid)

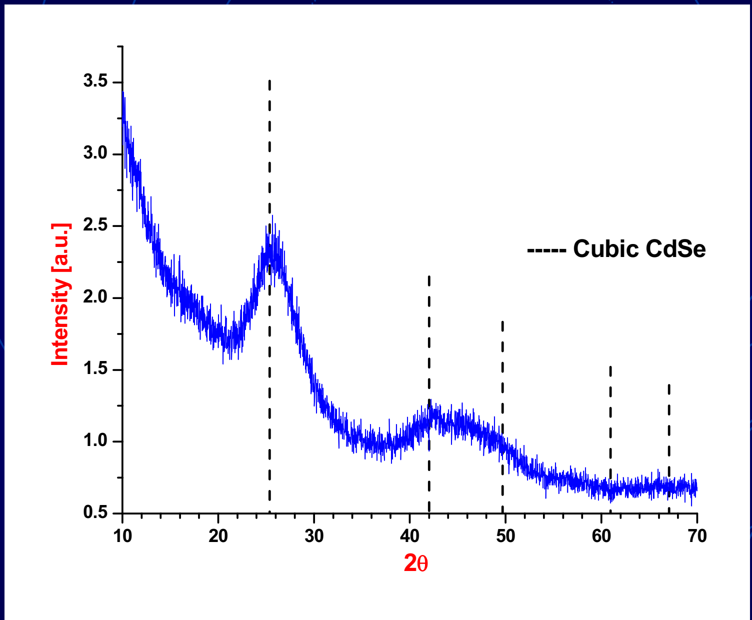
↓ HS-ϕ-F + TEA

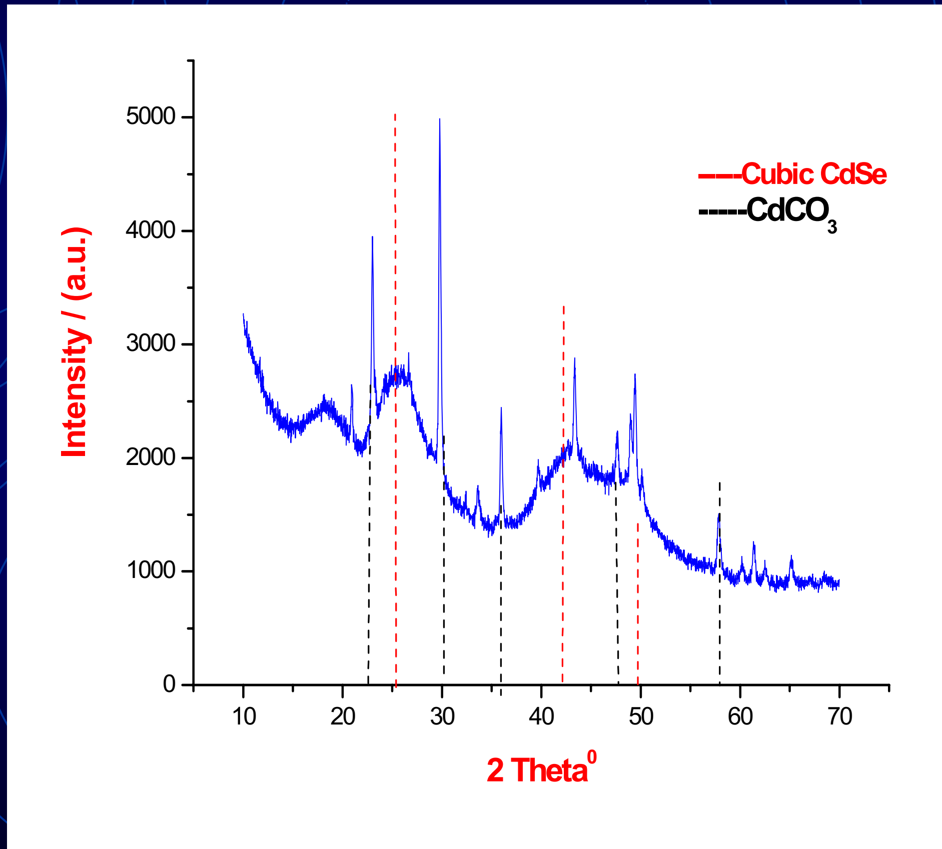
Isolate/redissolve in acetone

CdSe sol/S-ϕ-F capped —($H_2O_2$)→ *immediate color change (yellow)*

*CdSe gel formation*

# CdSe Gels and Aerogels



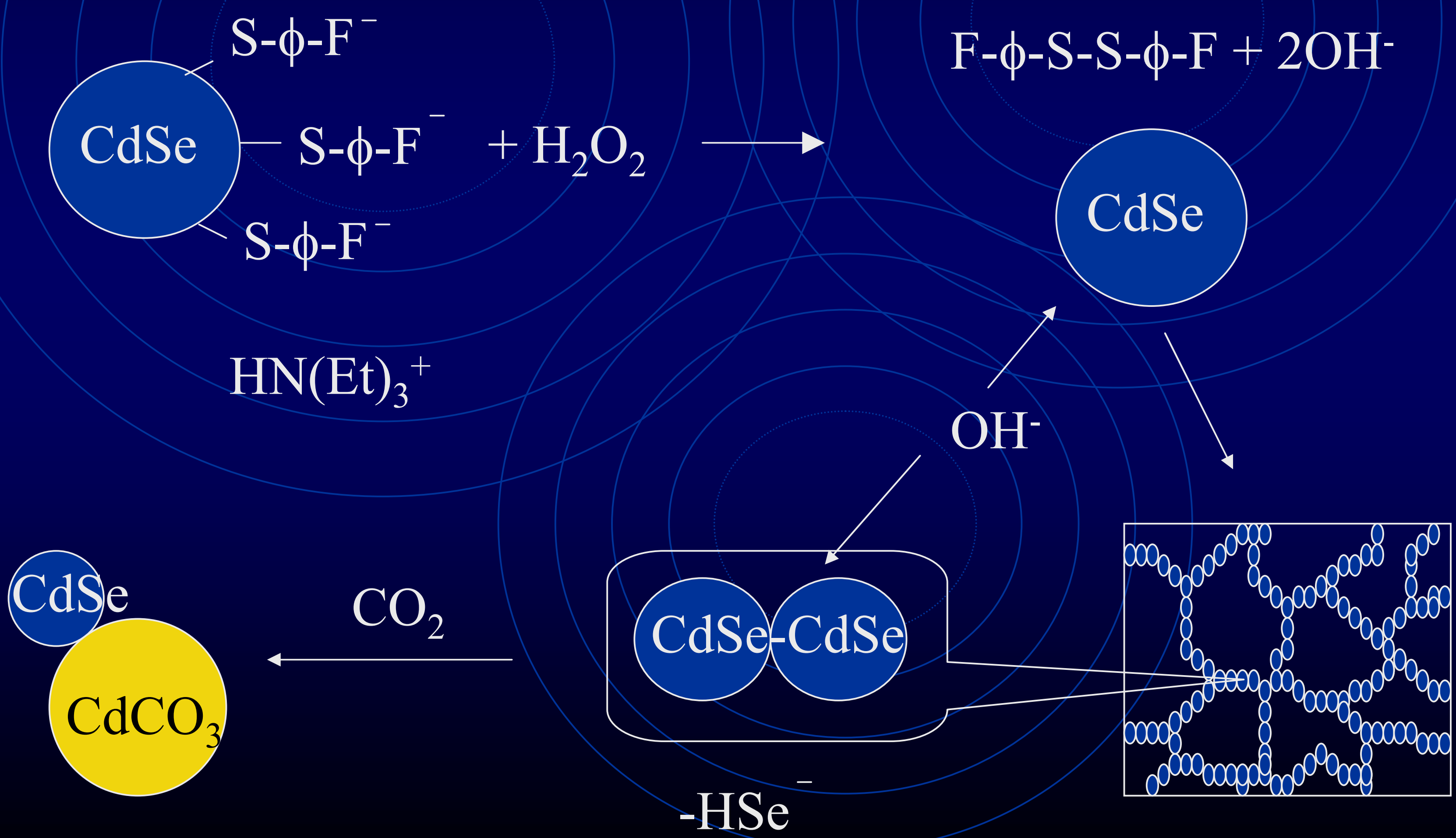




CdSe Xerogel

Benchtop drying

CdSe Aerogel, SC $CO_2$ Drying

# Carbonate Formation in CdSe Aerogels



# Avoiding Carbonate Formation by Neutralization

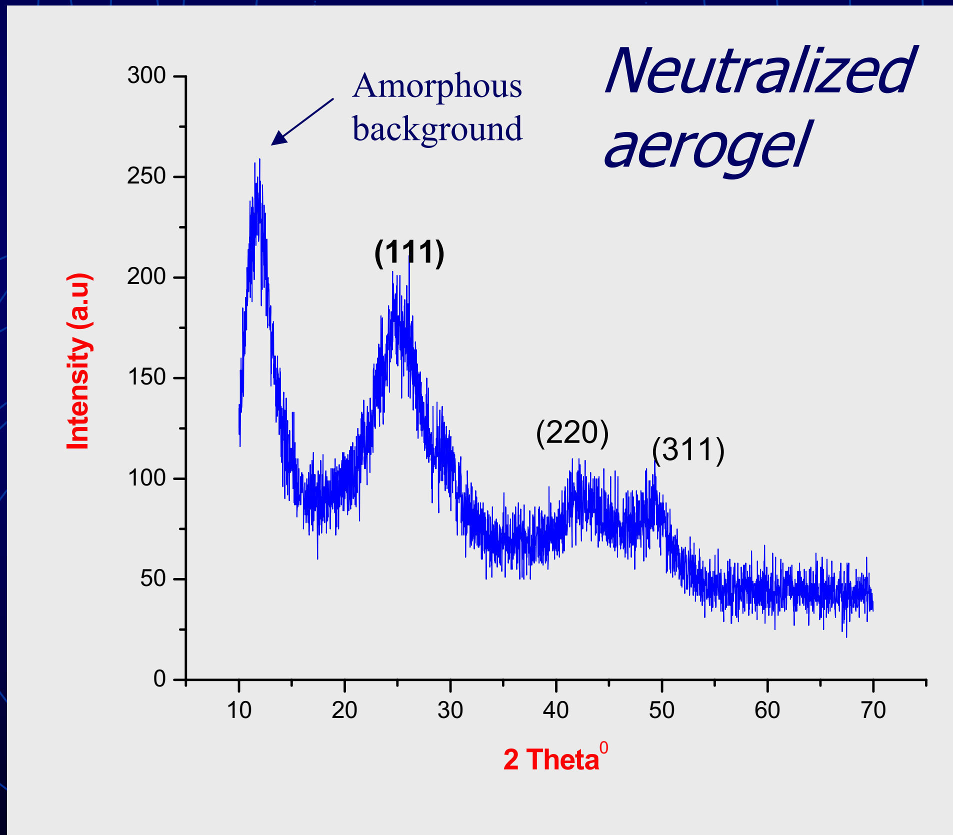
*If hydroxide is the problem, is neutralization the solution?*

Yellow CdSe gel

+ 0.2 mL HCl (0.1 M)

↓

Red CdSe gel —wash / CPD→



# Avoiding Carbonate Formation: Choice of Oxidant

*How about a non-oxygen transferring oxidant?*

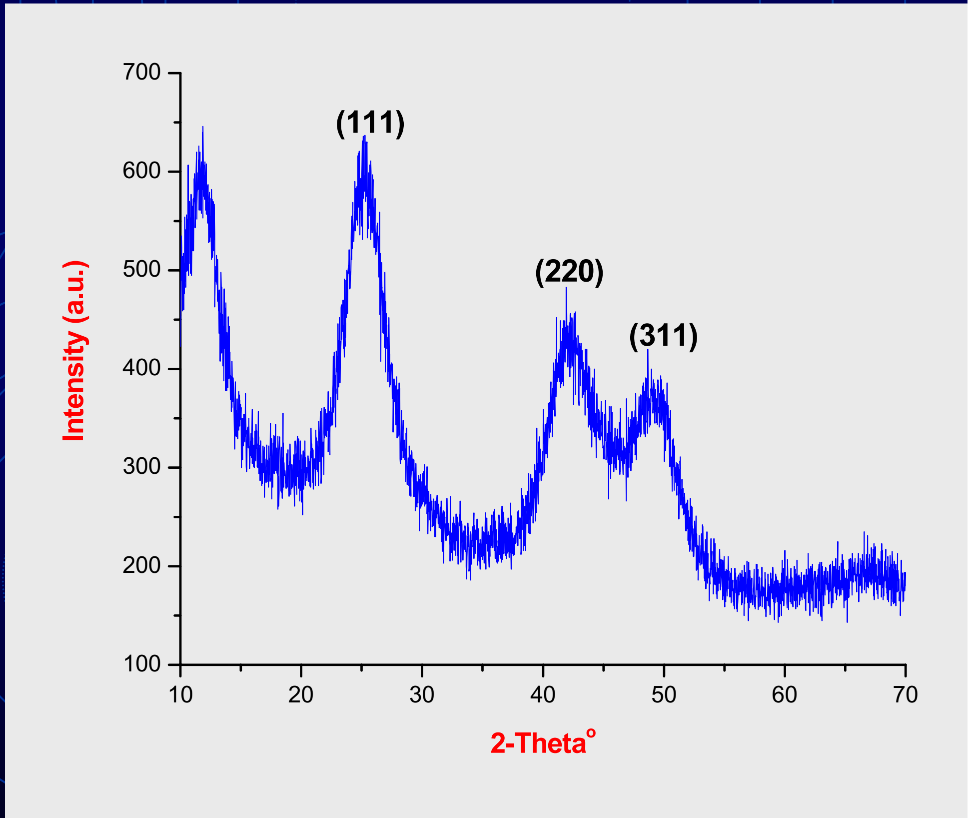
$RSH + C(NO_2)_4 \rightarrow RSNO_2 + HC(NO_2)_3$

$RSNO_2 + RSH \rightarrow RSSR + HNO_2$

CdSe sol/S-ϕ-F capped (red)

↓ 0.1 mL $C(NO_2)_4$ 3%

CdSe gel (red) → SCD




Evans, B. J.; T. D., J.; Musker, W. K. J. Org. Chem. 1990, 55, 2337-2344.

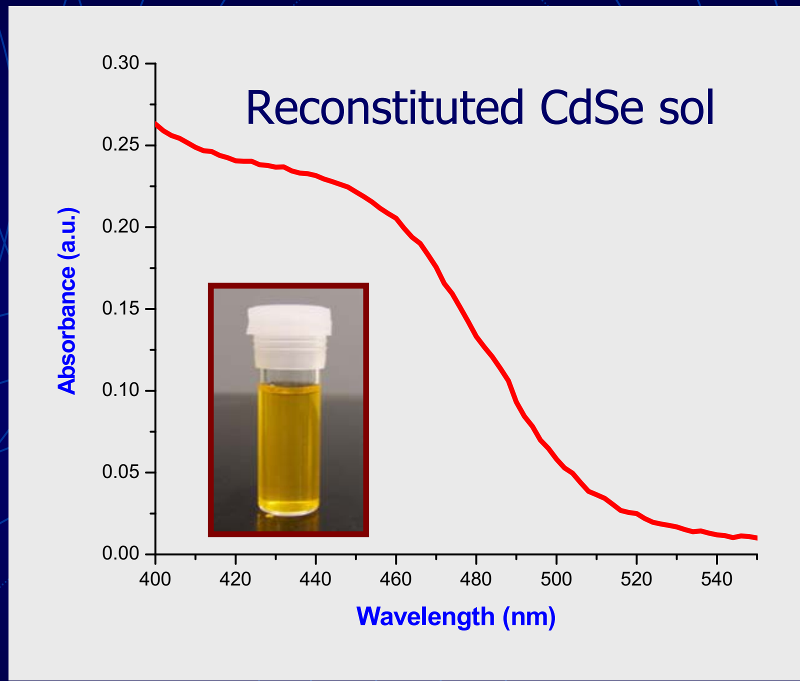
# Treatment of CdSe Wet Gels with Thiols

Red CdSe gel

+ 0.1 mL F-ϕ-SH

↓

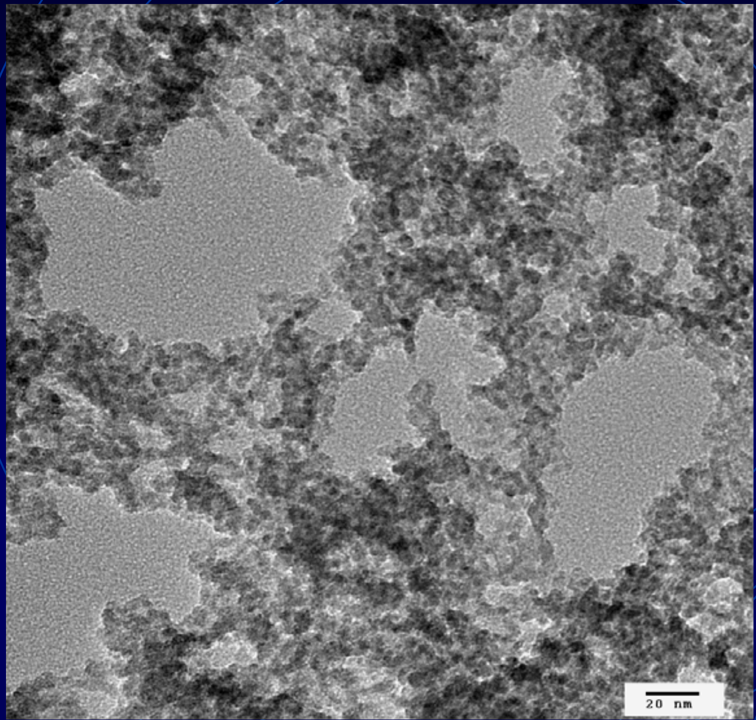
Red CdSe colloid →



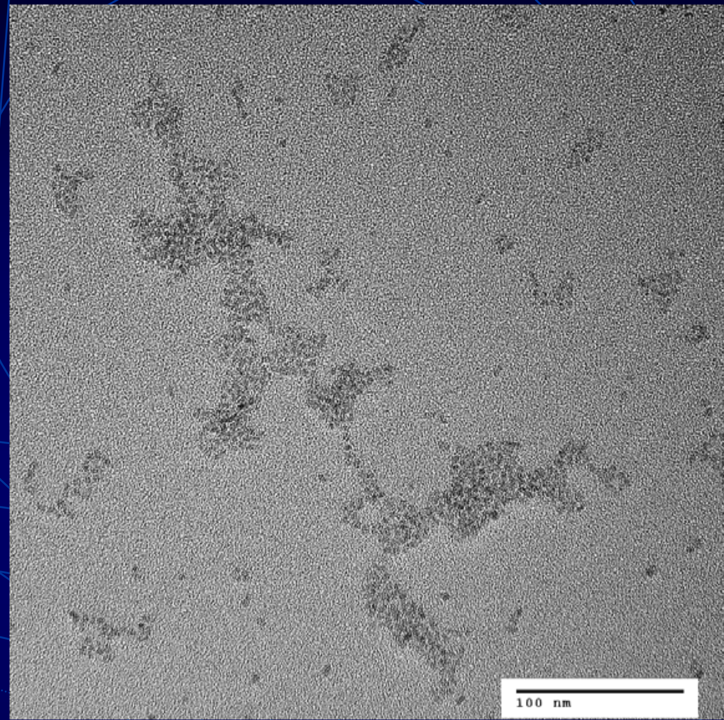

Gelation is reversible!

Aerogels and xerogels can also be dispersed, and the whole process is cyclable!

# Dissolution of Gels




**MUA/TMAH**




As-prepared Aerogel

**Particle size ~ 4.0 ± 0.5 nm**

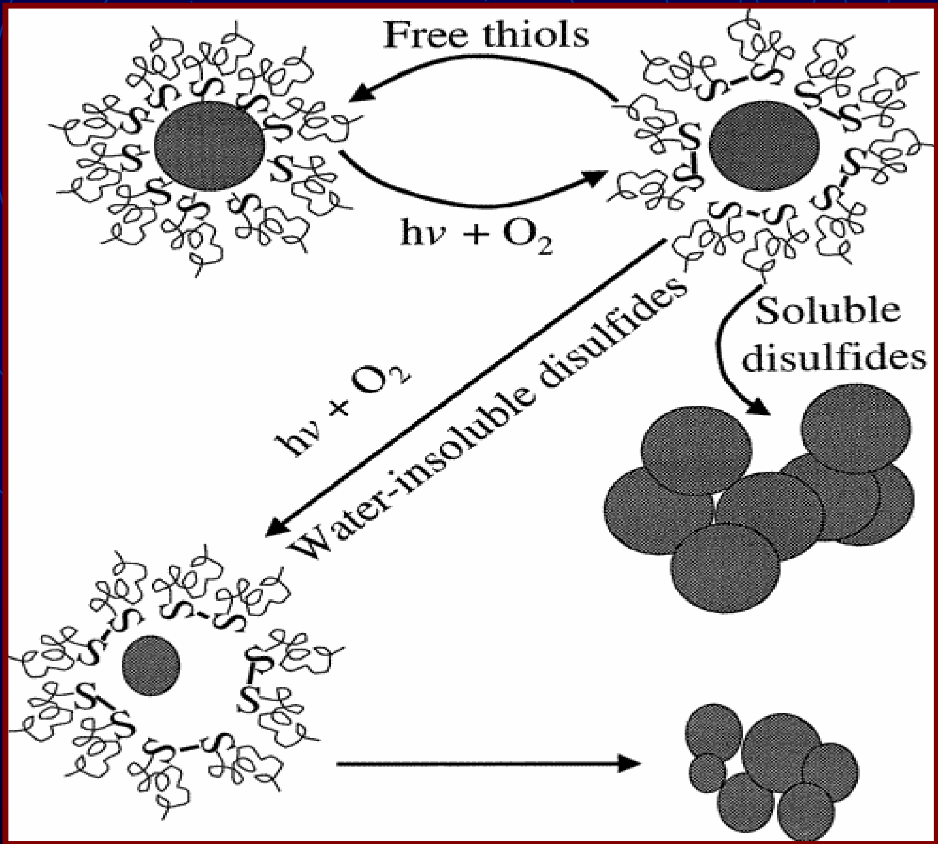
Dispersed Aerogel

**Particle size ~ 3.8 ± 0.5 nm**

- *Dispersed aerogel shows small aggregates and individual nanoparticles.*
- *Dissolution breaks the gel network structure.*

# Dispersing Aggregated Nanoparticles

- Peng et al reported the instability of thiolate on CdSe nanoparticle surfaces.
  - *Free thiols can replace the disulfides and keep nanocystals in solution*

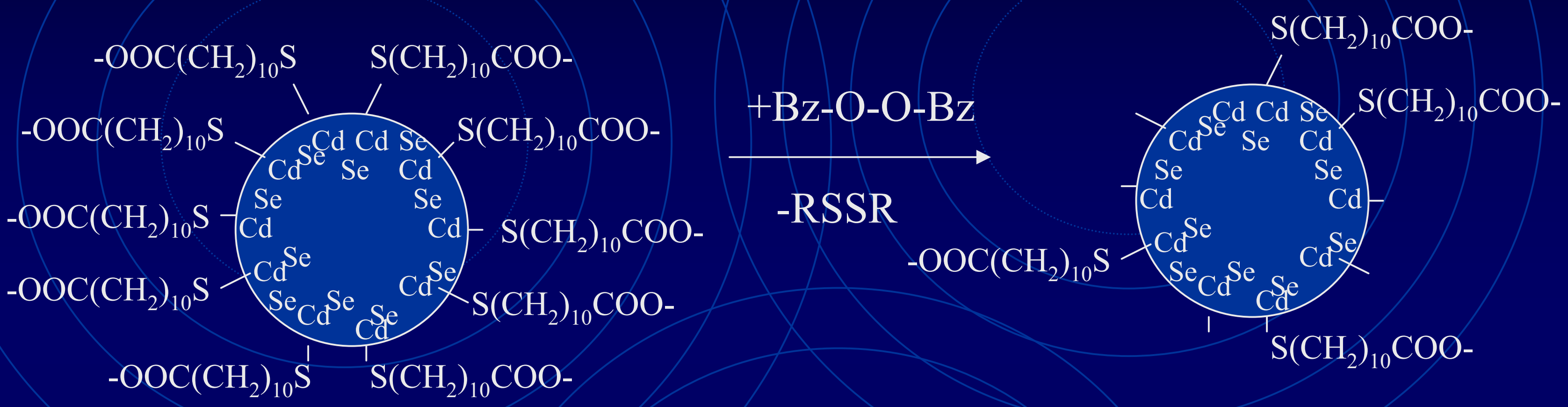


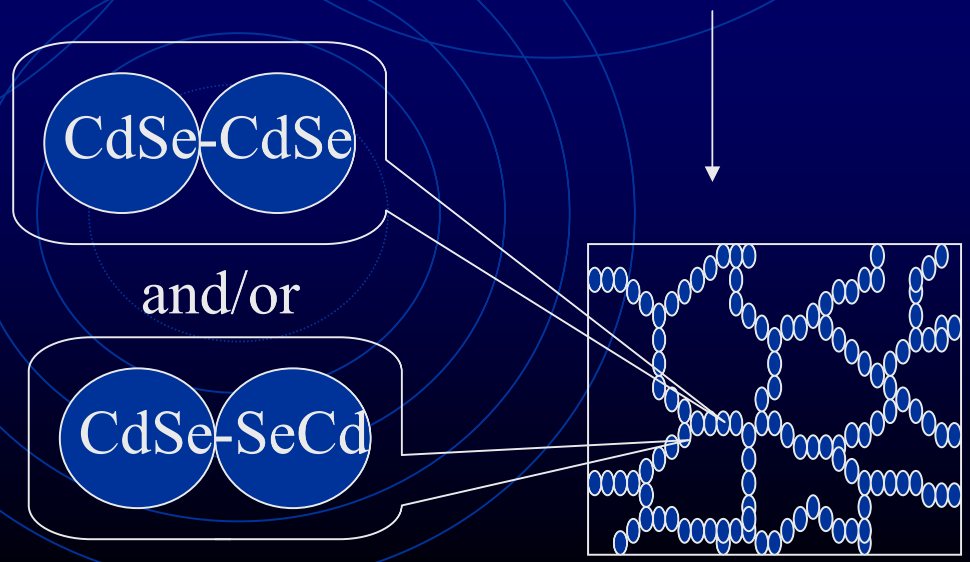

***Is this the process for gel dissolution that we are observing?***

*Treatment with a variety of solvents (including Lewis Bases) has no effect on the gel*

***Aldana, J.; Wang, Y. A.; Peng, X., J. Am. Chem. Soc. 2001, 123, 8844-8850***

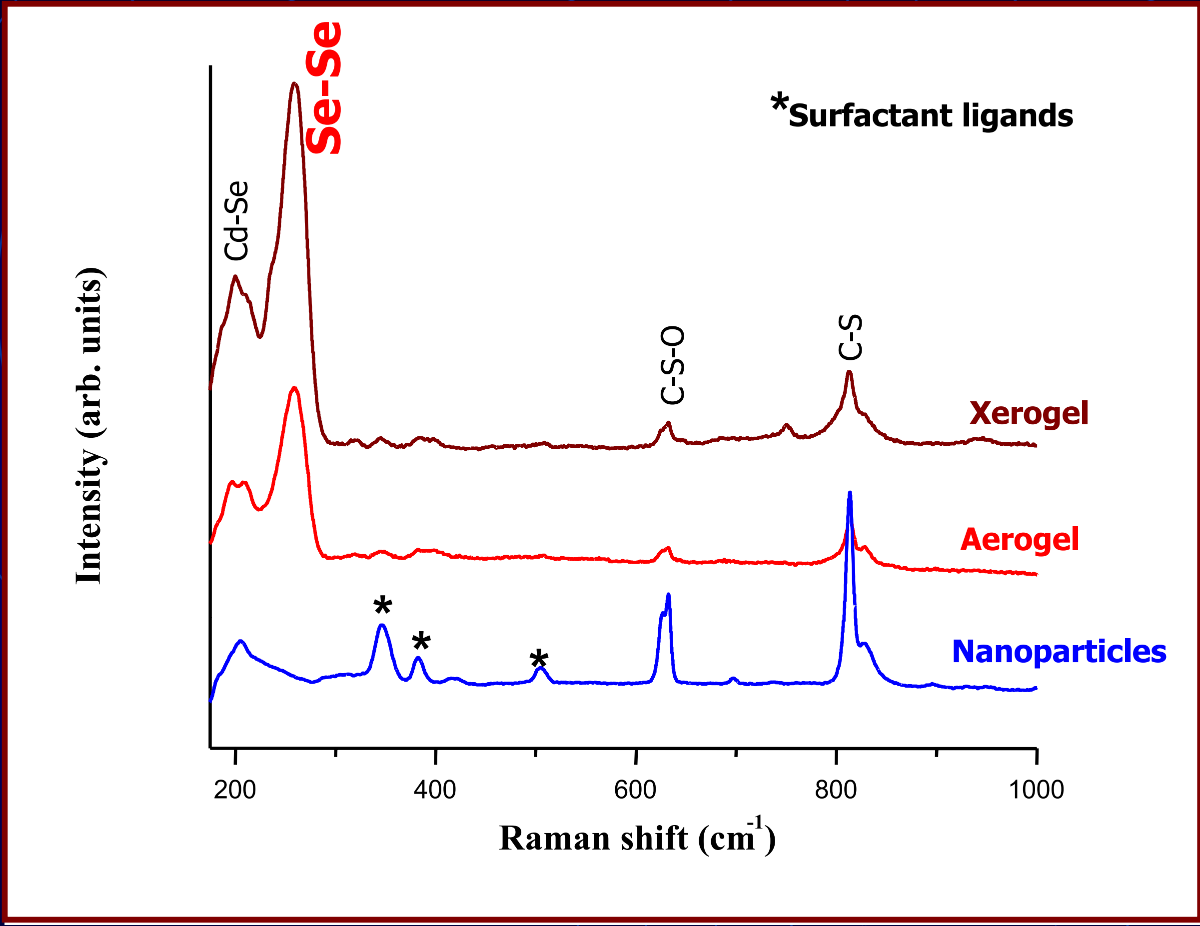
# What is the Mechanism of Interparticle Linkage Formation?

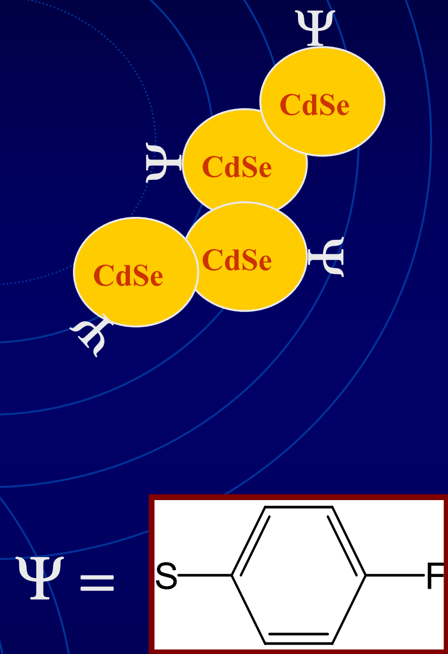



What is the nature of the bonding between the particles?

# Raman Spectra of Nanoparticles, Aerogels and Xerogels



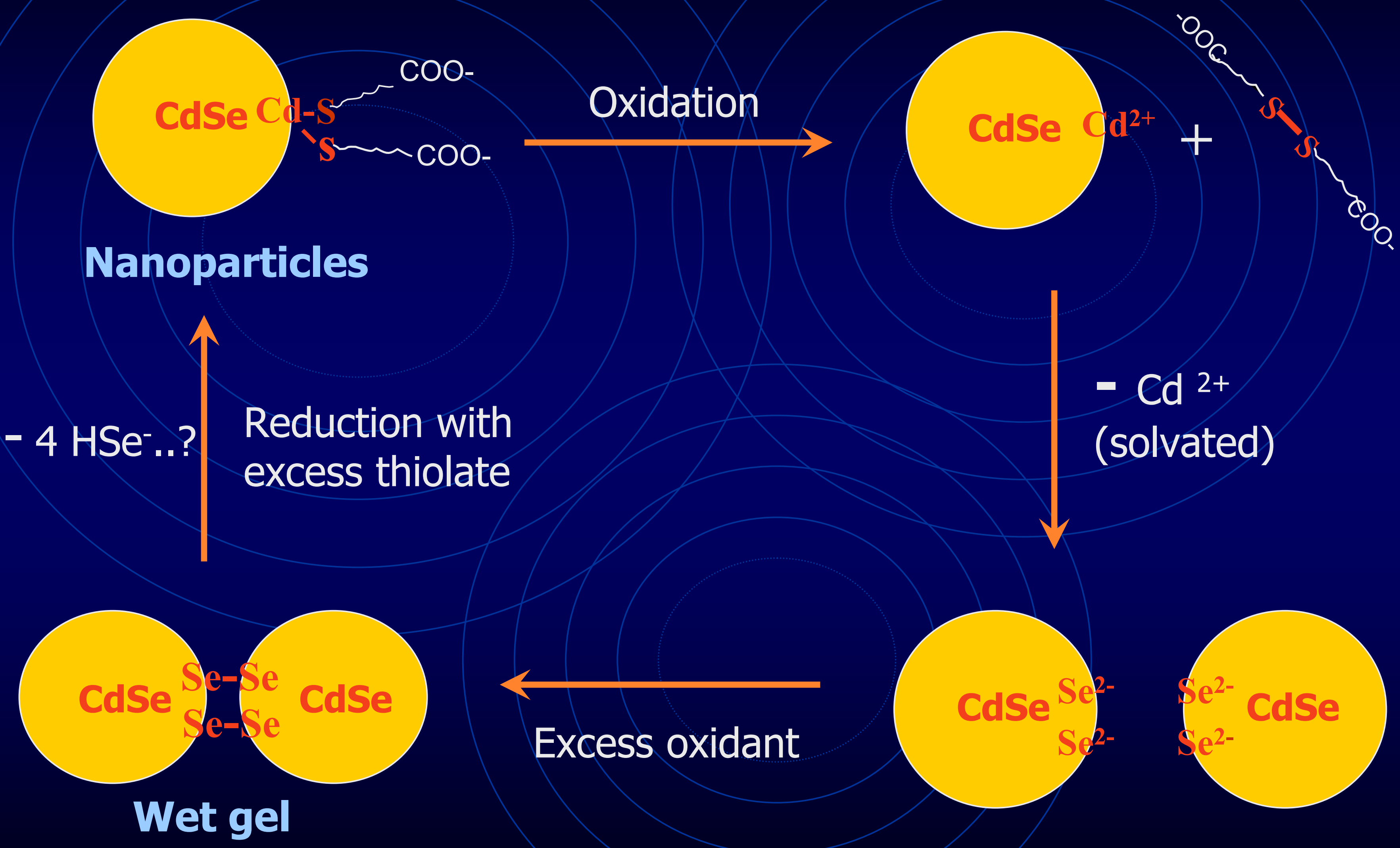




- Se-Se bonds may be responsible for the nanoparticle linkages

***-Need a reducing agent to cleave the Se-Se bonds***

*Edward et al, Vibrational Spectroscopy, 2000, 24, 213-234*

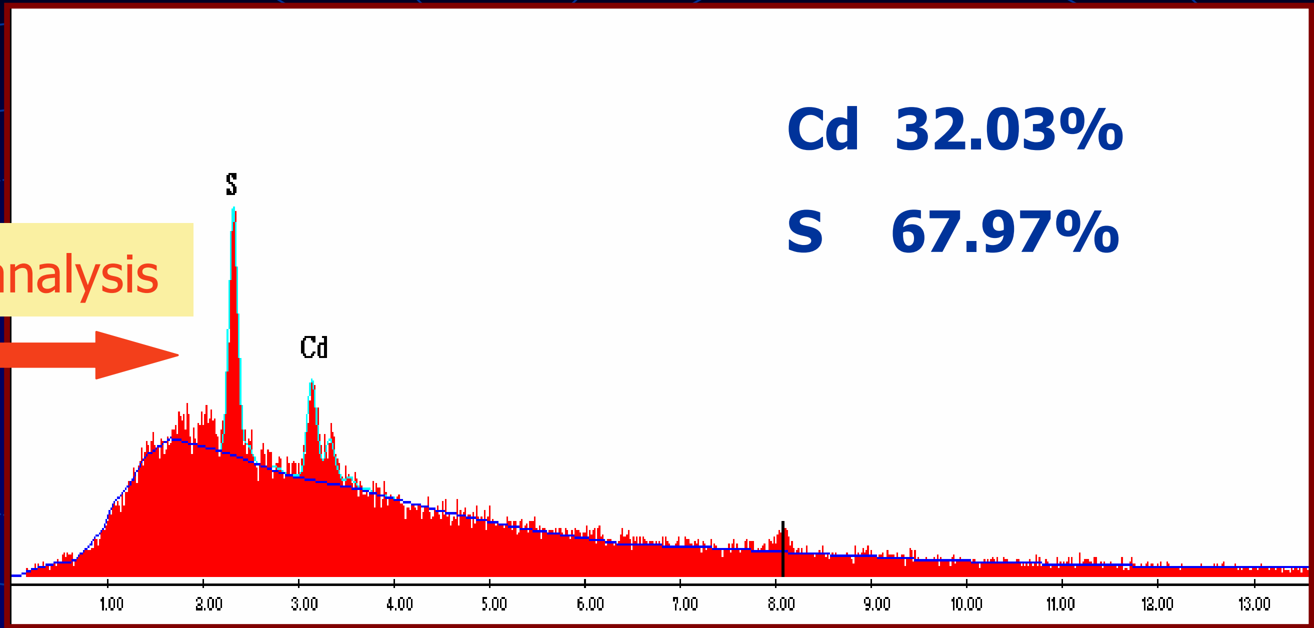
# Proposed Mechanism



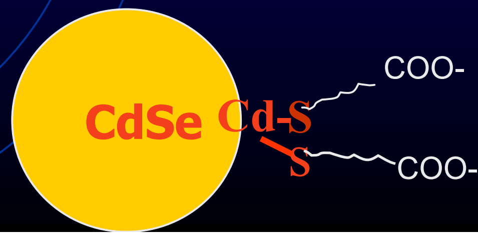
# EDS Spectra of Supernatant of the Wet Gel

EDS analysis

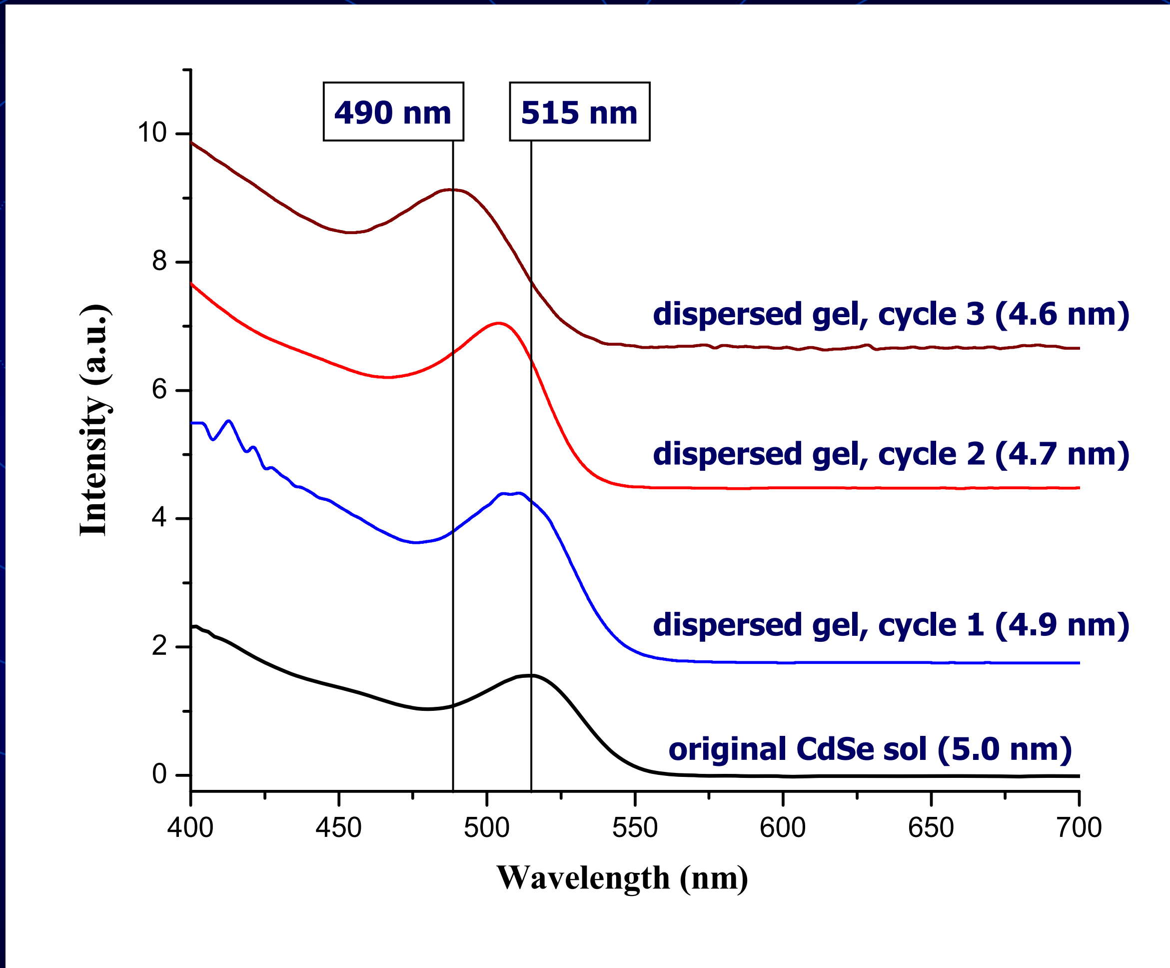
***CdSe wet gel***




- Semi quantitative EDS indicates the presence of sulfur and cadmium in the oxidized solution.
- Selenium is absent in the supernatant solution.
- Atomic ratio of Cd : S is 1 : 2.1 consistent with two thiolates binding to a surface $Cd^{2+}$ ion.



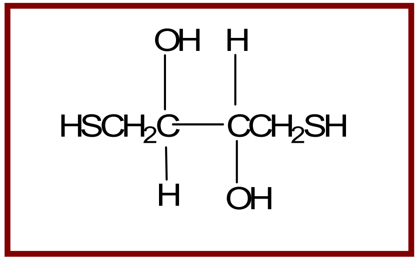
# UV-Visible Spectra of Precursor Nanoparticles, Dispersed Gels, Aerogels and Xerogels



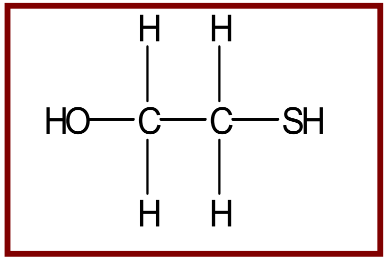

**Absorption spectra CdSe dissolved gels, aerogels and xerogels are blue shifted compared to that of precursor nanoparticles due to surface etching.**

# What About Other Reducing Agents..?

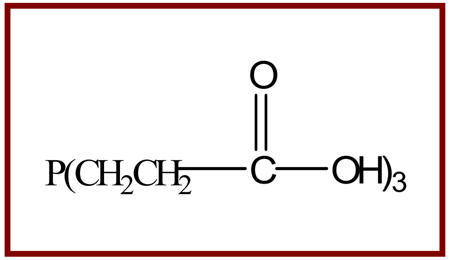
- DDT, ME and TCEP are used in biological systems to cleave disulfide bonds in proteins.




*DTT (dithiothreitol)*




*ME (mercaptoethanol)*




*TCEP (tris-(2-carboxyethyl) phosphine*

- Diselenide bonds are even easier to reduce than disulfide bonds.

***S-S bond energy ~ 226 kJ mol$^{-1}$***

***Se-Se bond energy ~ 172 kJ mol$^{-1}$***

- CdSe wet gels, aerogels and xerogels disperse into a sol after adding these reducing agents.

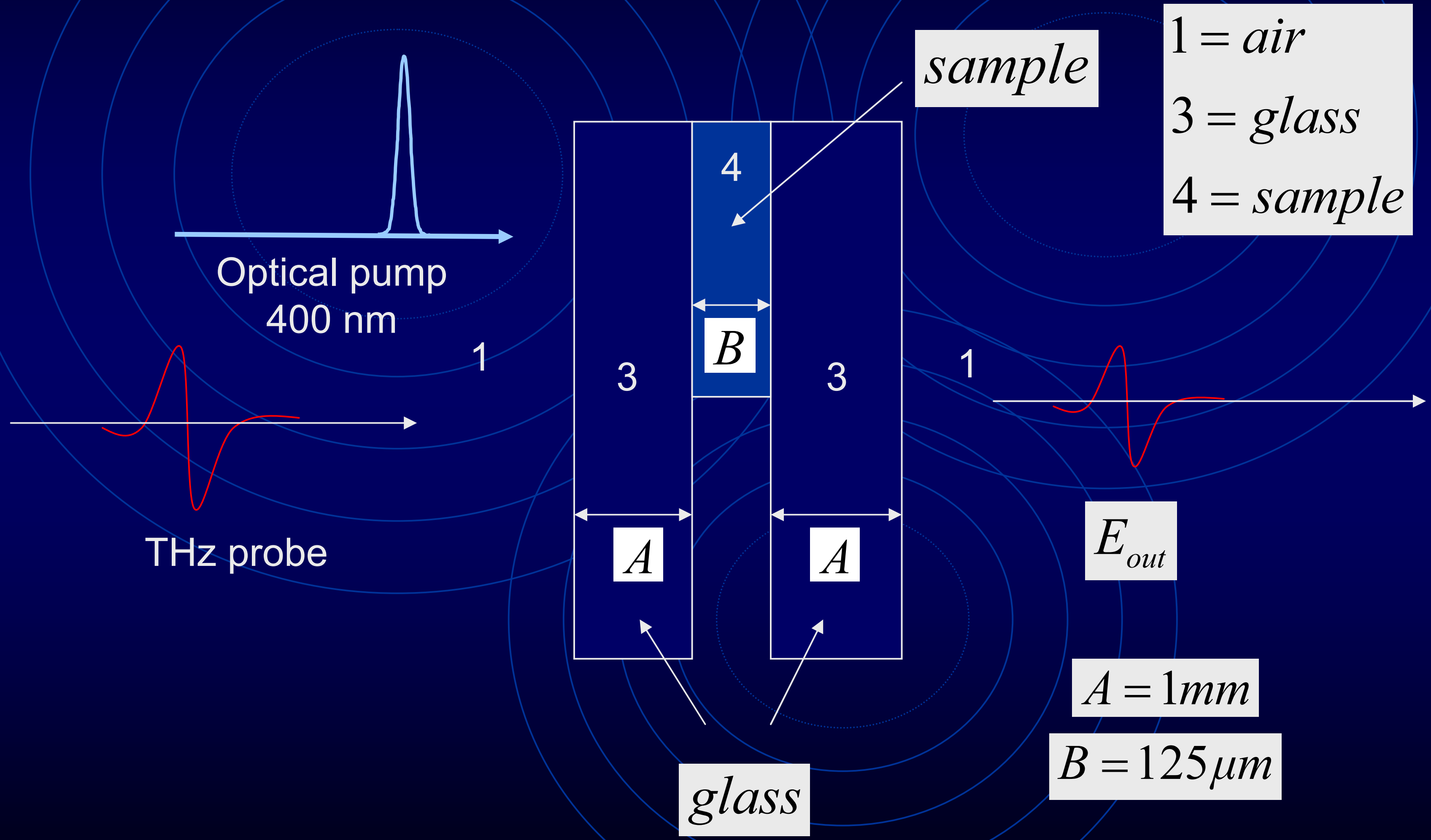
# Revisiting Potential Applications

What can be done with these aerogels and xerogels, anyway?

*Preliminary results with CdSe aerogels*

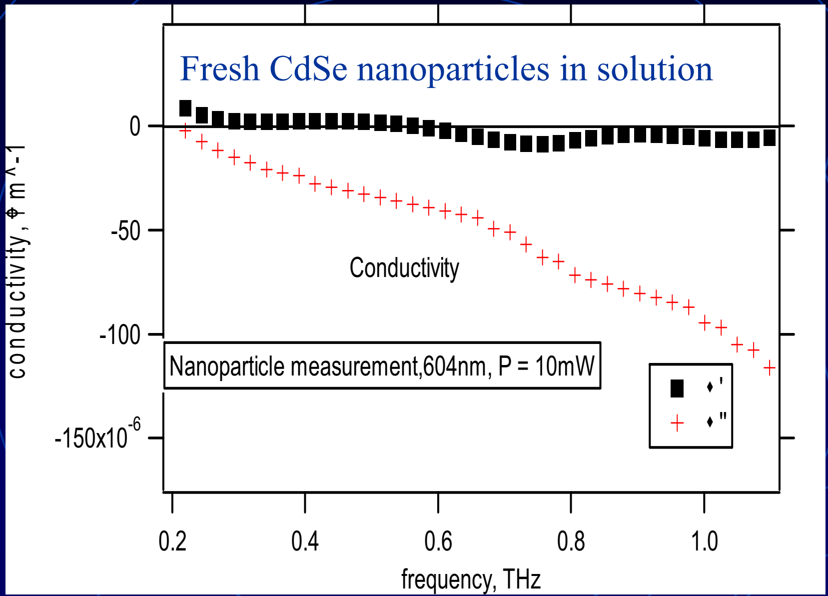
- Photovoltaic devices
  - *photoconductivity studies*
- Chemical sensing
  - *photoluminescence response to triethylamine*

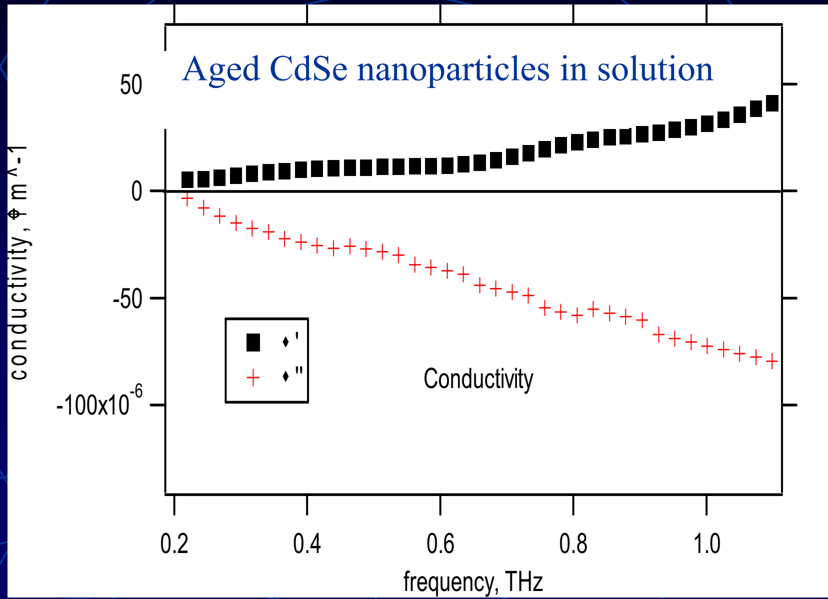
# Contactless Photoconductivity Measurements Using Terahertz Spectroscopy

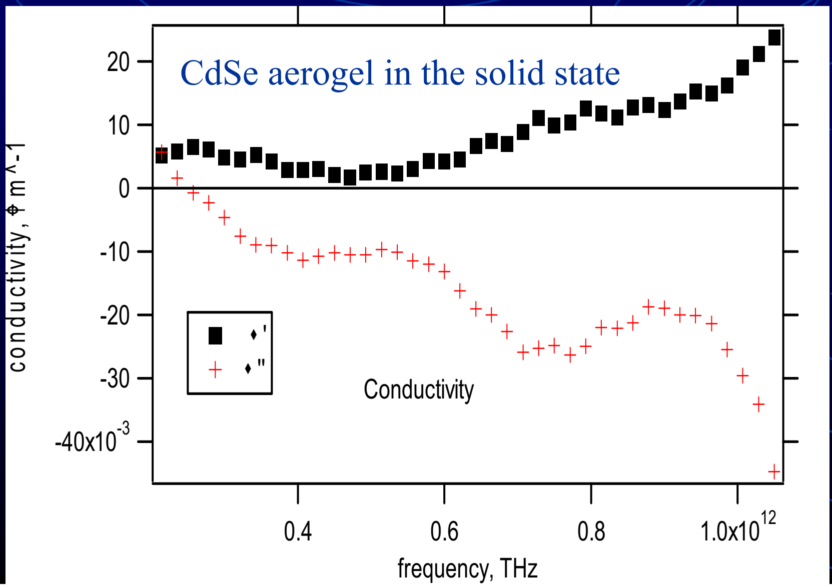



*Collaboration with Prof. Jie Shan, Physics, Case Western Reserve*

# Photoconductivity of CdSe Nanoparticles and Aerogels

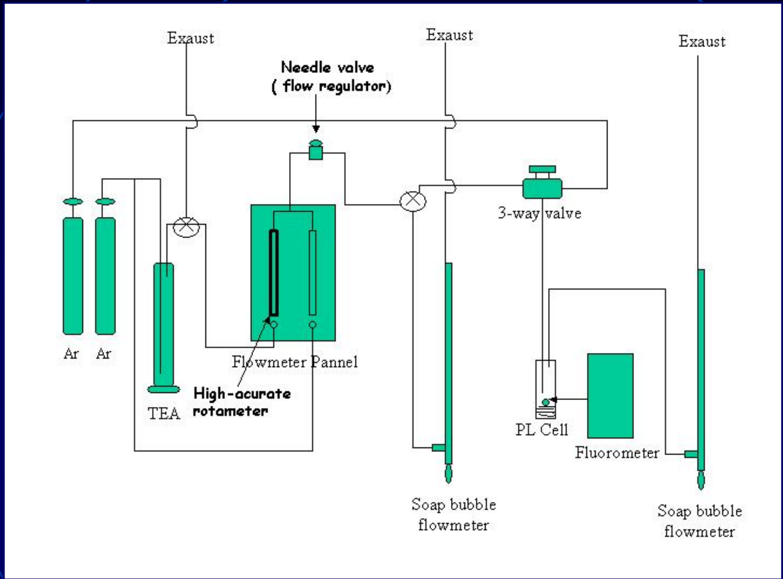


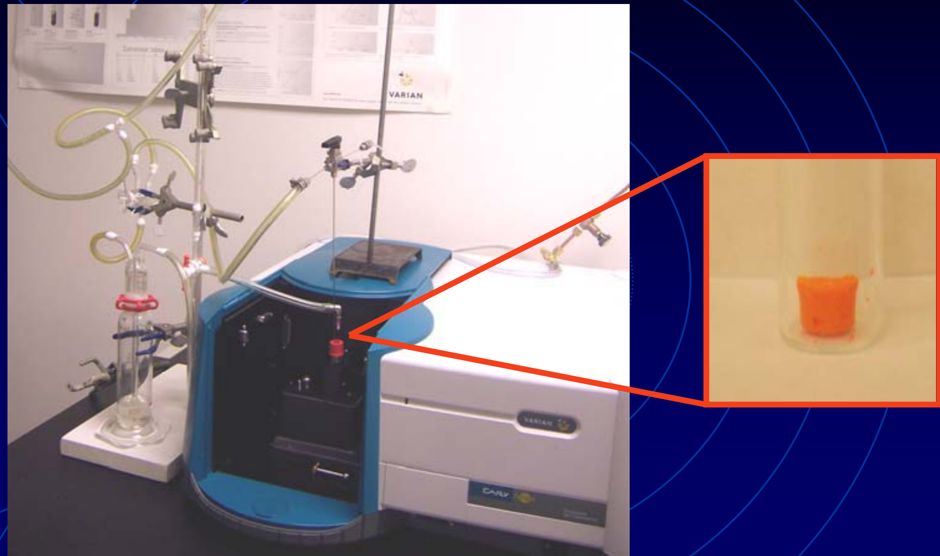



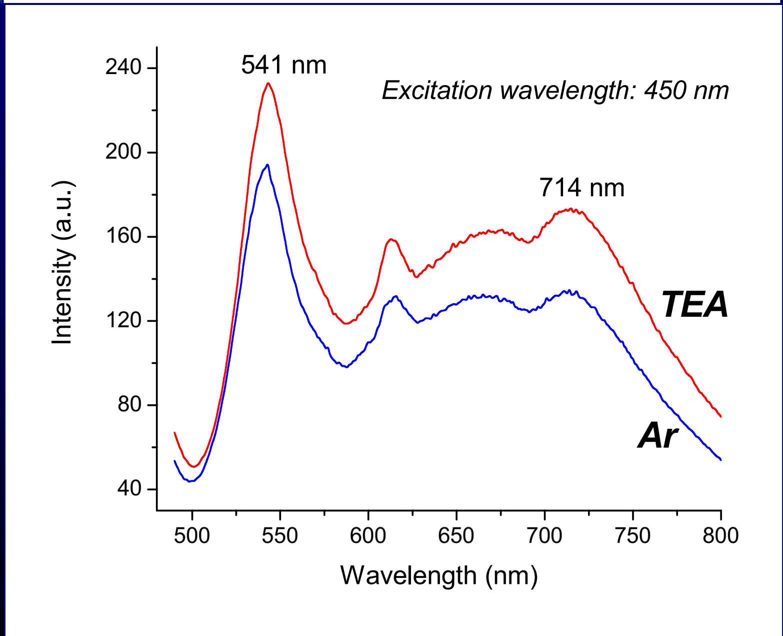



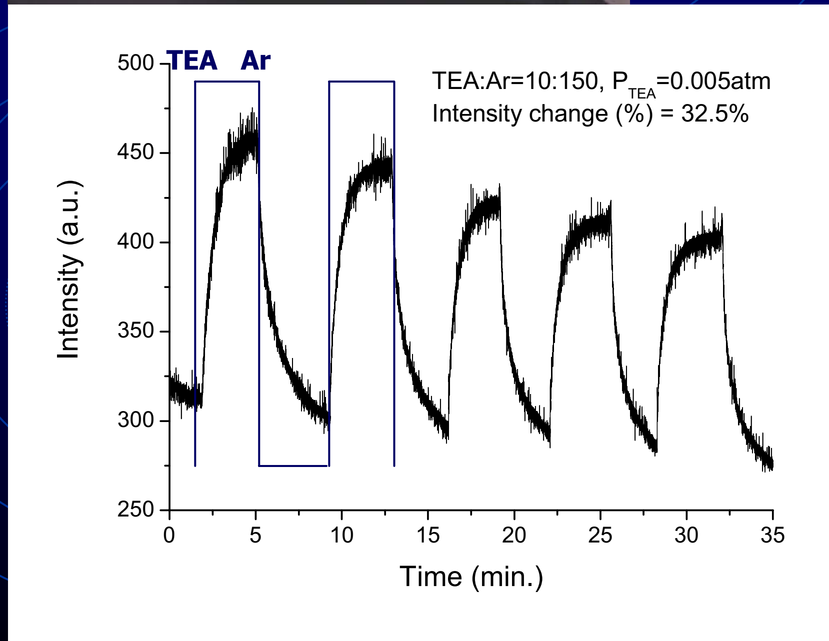

- Conductivity (ca. 50 x $10^{-6}$ $Sm^{-1}$) in aged CdSe nanoparticle solutions is attributed to aggregation
- Aerogels exhibit photoconductivity 1000x greater than aged nanoparticles

# PL Sensing of Triethylamine with CdSe Aerogels



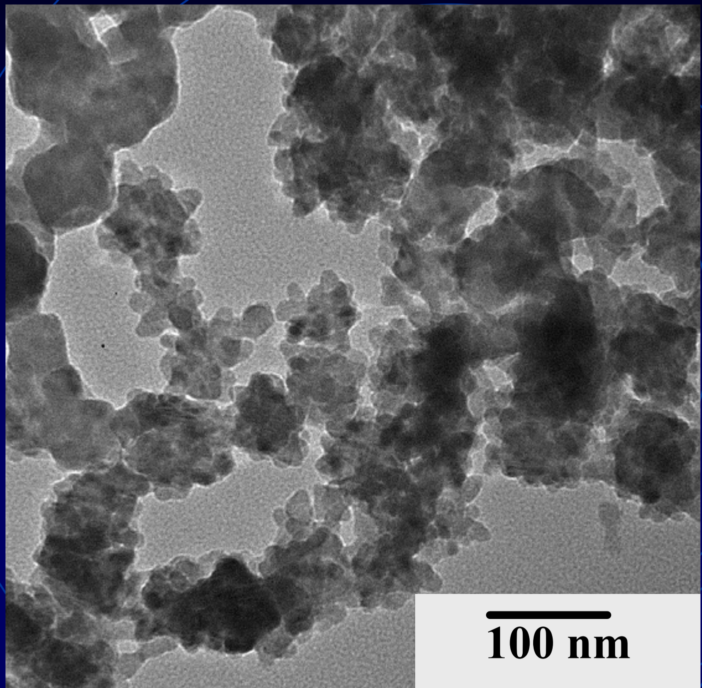


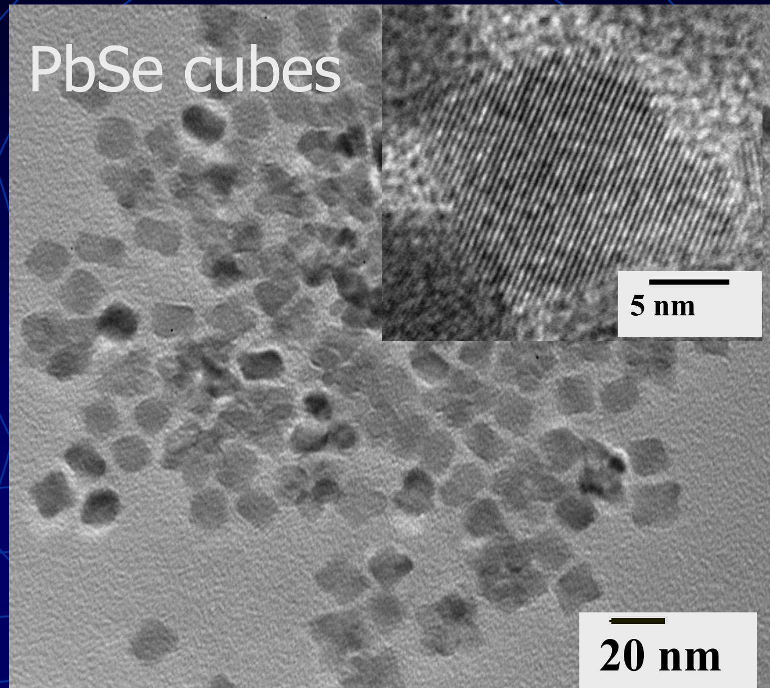
# Chalcogenide Aerogels: Generality

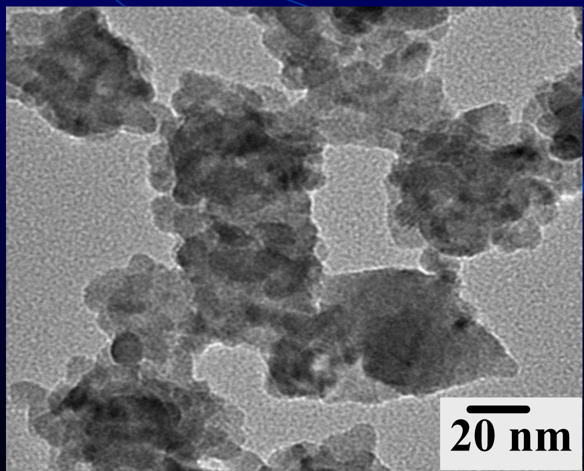
| Chalcogenides | PXRD | $E_g$ (eV) | BET Surface area (SA) ($m^2/g$) | BJH adsorption ave.pore diam. (nm) | BJH adsorption Cumulative pore vol. ($cm^3/g$) |
|---|---|---|---|---|---|
| ZnS | cubic | 3.85 | 202 | 15 | 0.86 |
| CdS | cubic | 2.72 | 212 | 14 | 0.78 |
| CdSe | cubic | 2.15-2.25 | 128-161 | 16-29 | 0.53-0.98 |
| CdSe | hex | 2.08-2.25 | 106-124 | 23-28 | 0.63-0.72 |
| CdSe@ZnS | hex | 2.21 | 188-234 | 21-23 | 1.57-0.96 |
| PbS | cubic | 0.95 | 119 | 45 | 0.94 |
| PbSe | cubic | 0.63 | 39 | 18 | 0.18 |

# Effect of Nanoparticle Shape on Aerogel Morphology




gelation



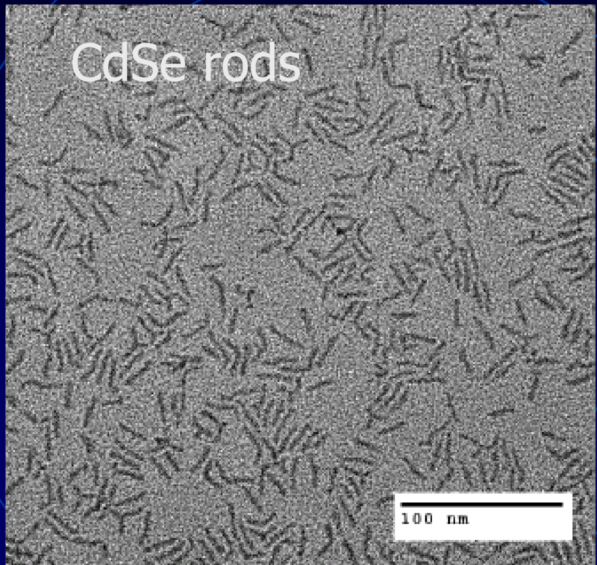

**Morphology: hierarchical structure**

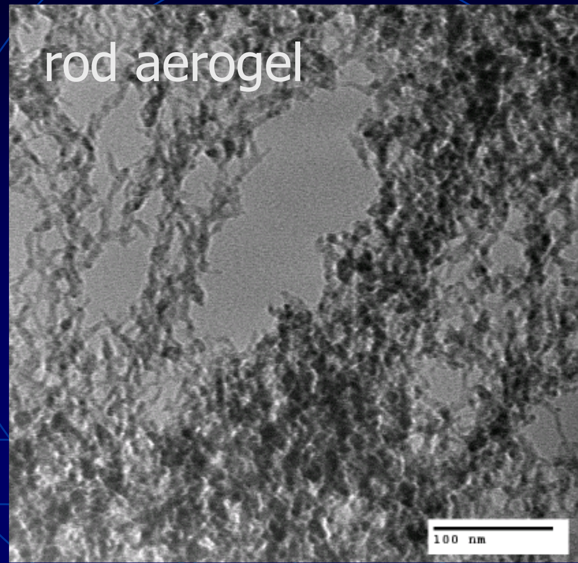
- **14 nm cubes linked into ~ 50 nm cubes**
- **Larger cubes form cluster-cluster links**

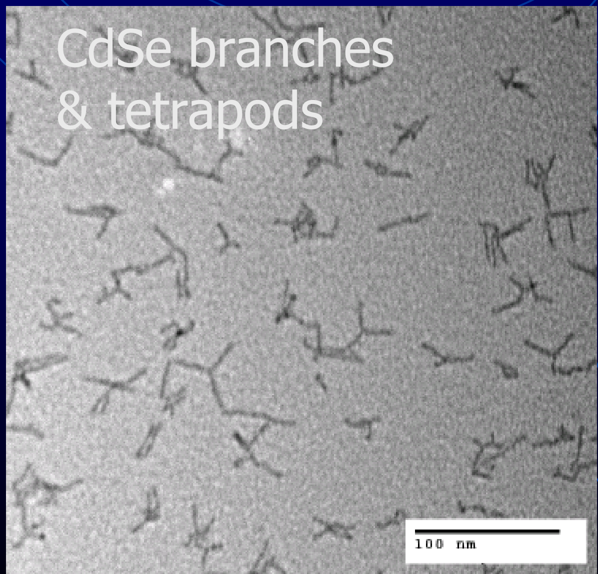
**Surface area:**

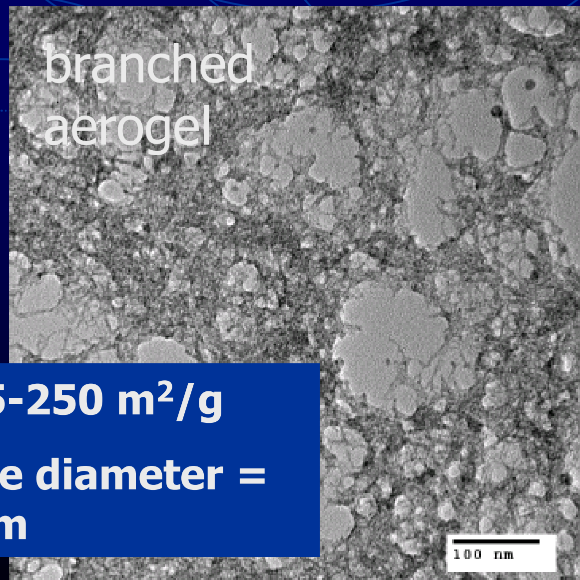
**61 $m^2/g$ (285 $m^2/g$ silica, per mole basis)**

# Effect of Nanoparticle Shape on Aerogel Morphology



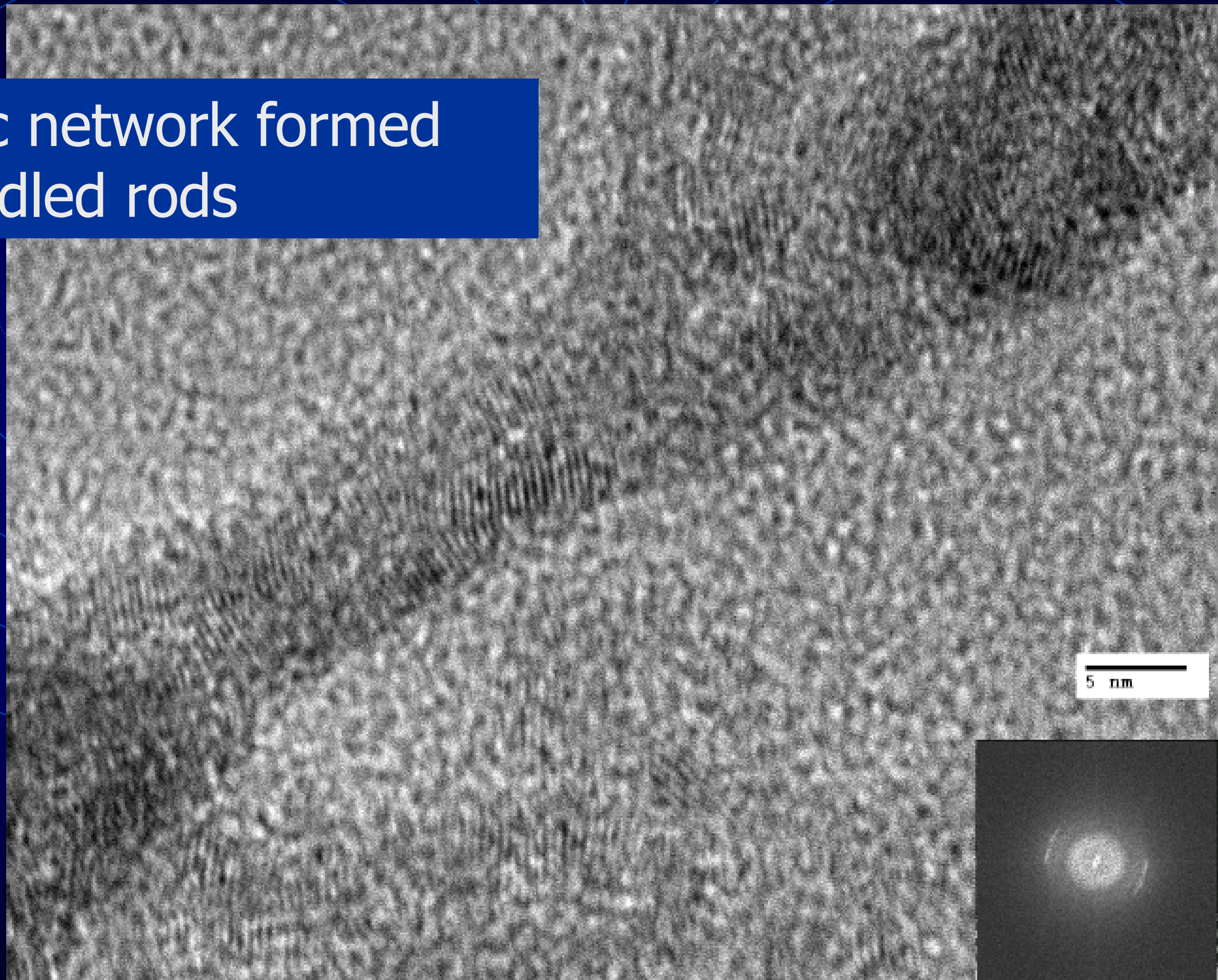




**SA= 215-250 $m^2/g$**

**Ave. pore diameter = 20-30 nm**

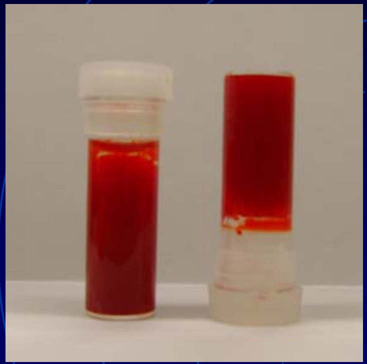
# High Resolution TEM Image of Rod Aerogel

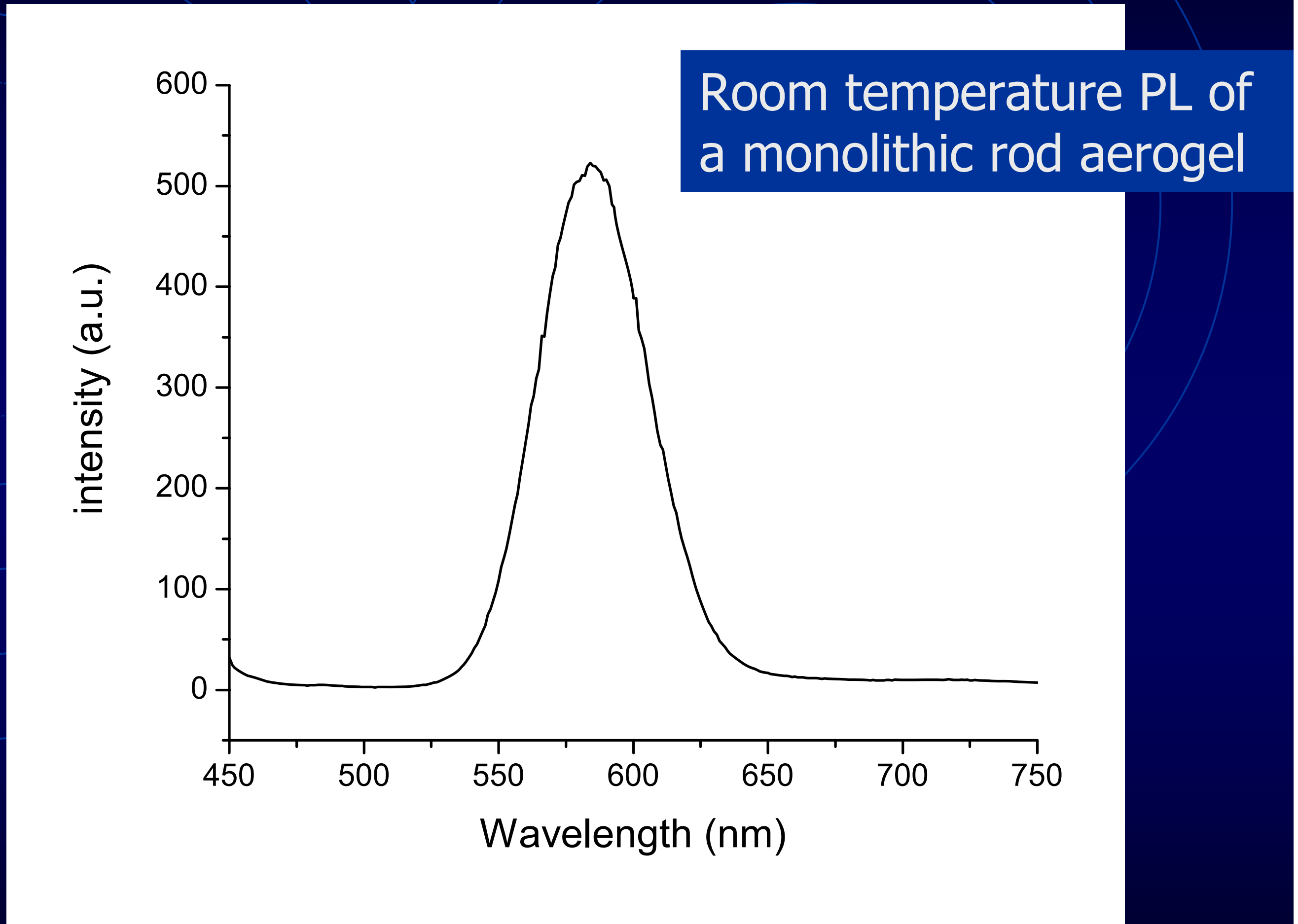
Polymeric network formed from bundled rods




**Lattice fringes = 2.00 Å ,value for (103) plane of CdSe = 1.98 Å**

# CdSe Rod Gels and Aerogels






Robust gels with high PL intensity, even at room temperature!

# Pushing the Envelope: What About Phosphides?

*$Ni_2P$ promising hydrocatalyst…can we prepare as high surface area aerogels?*

$NiCp_2$ + P(octyl)$_3$

TOPO ↓ 300 ºC

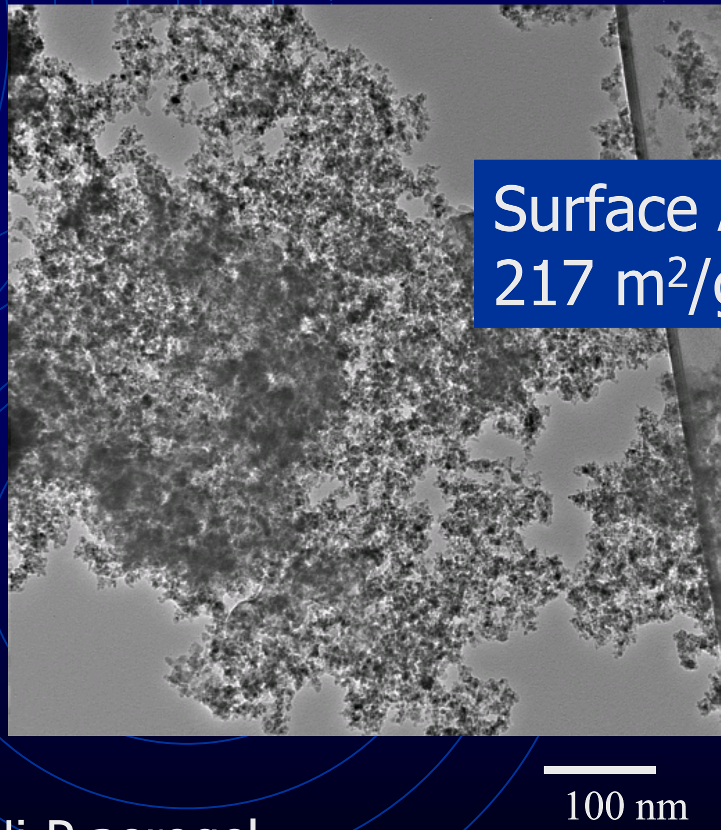
$Ni_2P$ nps (TOPO capped)

MUA ↓ TMAOH

$Ni_2P$ nps (MUA capped)

$H_2O_2$ ↓

$Ni_2P$ gel → (Acetone exchange; $CO_2$ supercritical drying)




Surface Area: 217 $m^2/g$

$Ni_2P$ aerogel

# Acknowledgements

## The Brock Research Group


*left to right*: Kennedy Kalebaila, Kristy Gregg, Valentina Ganzha-Hazen, Qinghong Yao, Indika Arachchige, Keerthi Senevirathne, Elayaraja Muthuswamy, Hongtao Yu; *Not pictured:* Albert Gjeluci, Mehul Barat

*Alumni:* Jaya Mohanan, Susanthri Perera, Kimber Stamm, Buddhi Jayasekera, Kanchana Somaskandan, Palaniappan "Pops" Arumugam, Dhammika Herath, Jen Aitken

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