Synthesis and Processing of Metallic Nanomaterials using CO_2 eXpanded Liquids as a Green Solvent Medium

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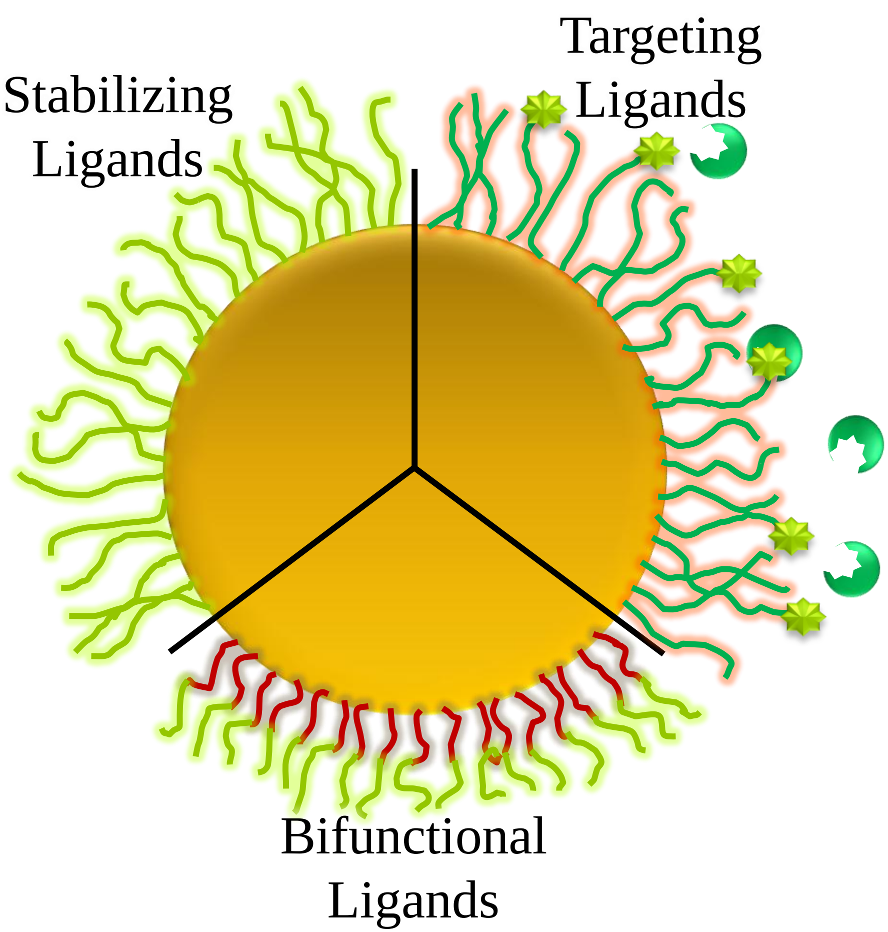
Engineered Nanoparticles



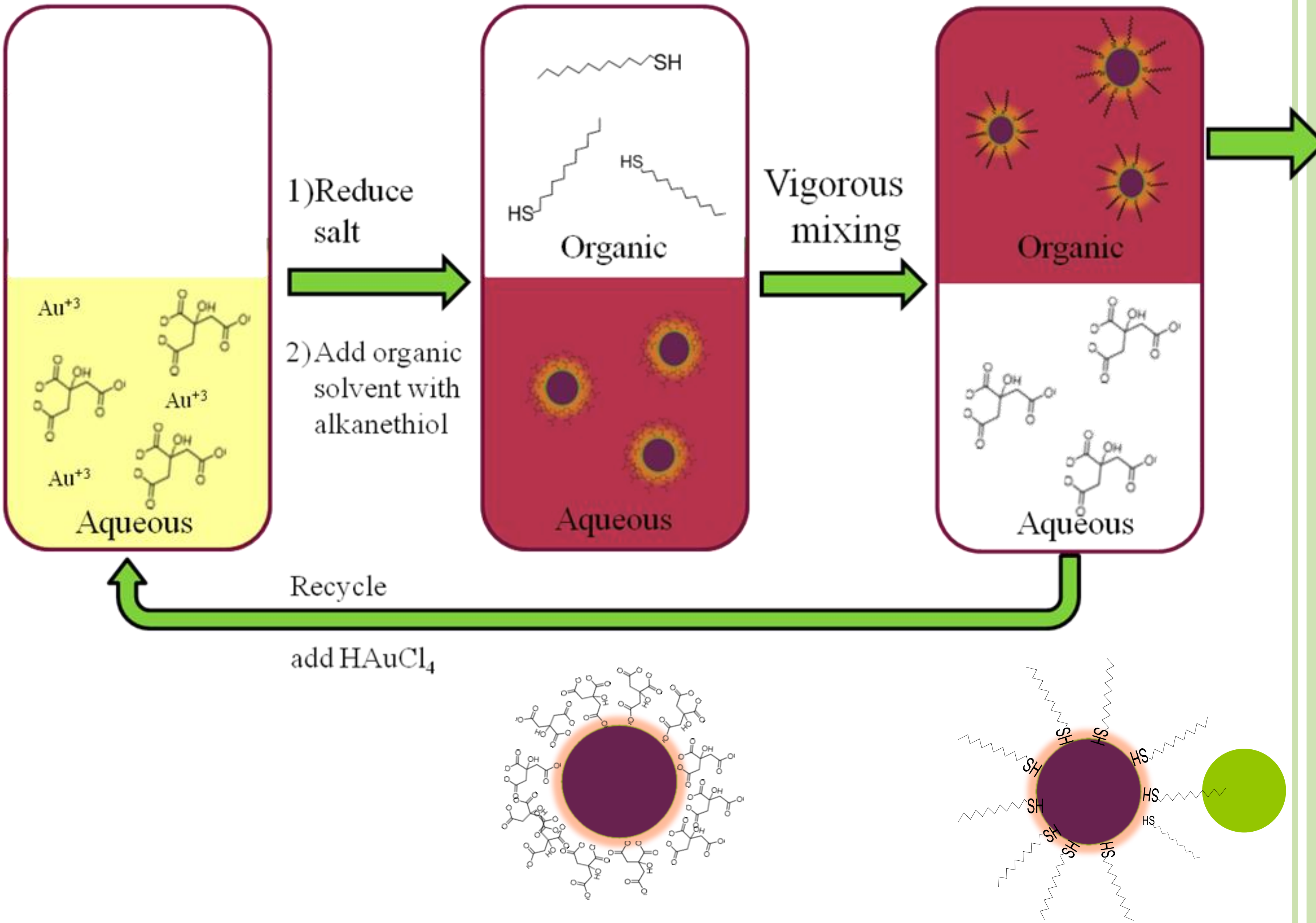
Role of Surface Chemistry

- Stability
- Size and Shape Control
- Compatibility
- Reactivity
- Functionality
  - Targeting
  - Sensing

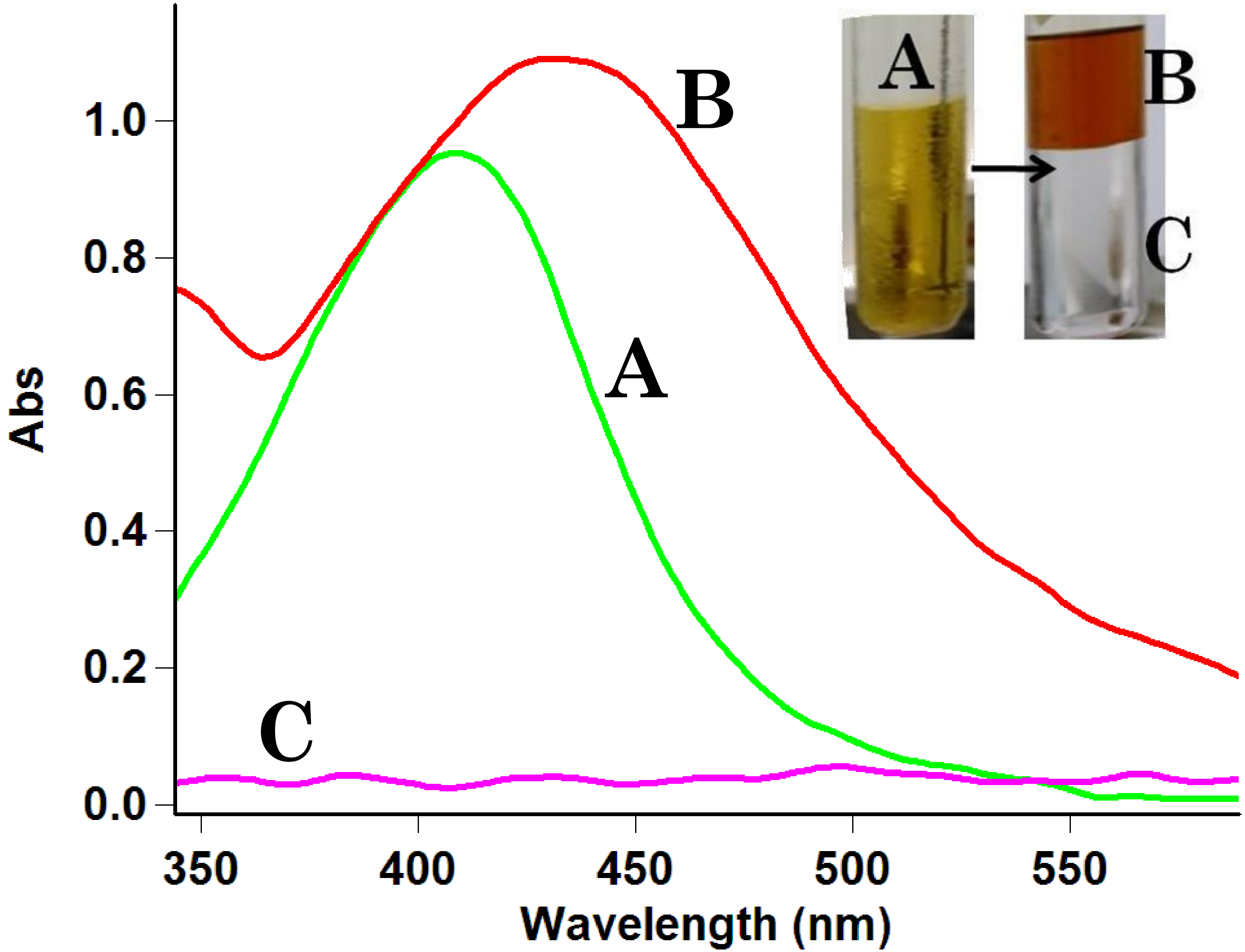
Outline

- Greener Synthesis of Metal Nanoparticles
- Processing of Gold Nanoparticles and Nanorods using Gas eXpanded Liquids (GXLs)
- Tunable Nanoparticle Synthesis in GXLs
- Organic Aqueous Tunable Systems

Synthesis and Ligand Exchange



Ligand Exchange (Silver Nanoparticles)



Tunable Organic-CO_2 Mixtures: Gas eXpanded Liquids (GXLs)

- CO_2 Miscibility
- Tunability
- Reversibility
- Advantages over Solvents
  - Better Transport Properties
  - Better Gas Solubility
- Advantages over SCFs
  - Lower Pressures
  - Better Solubility

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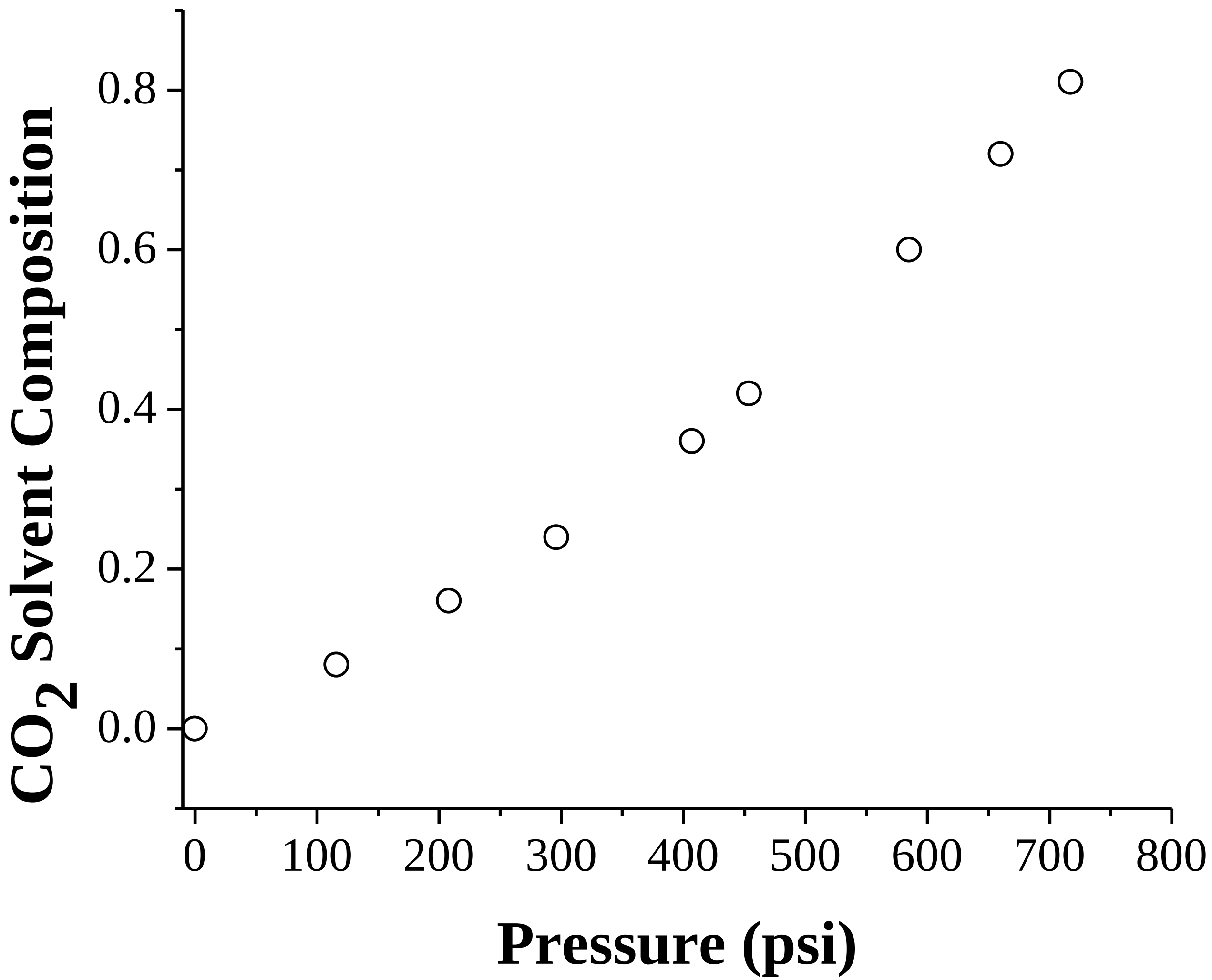
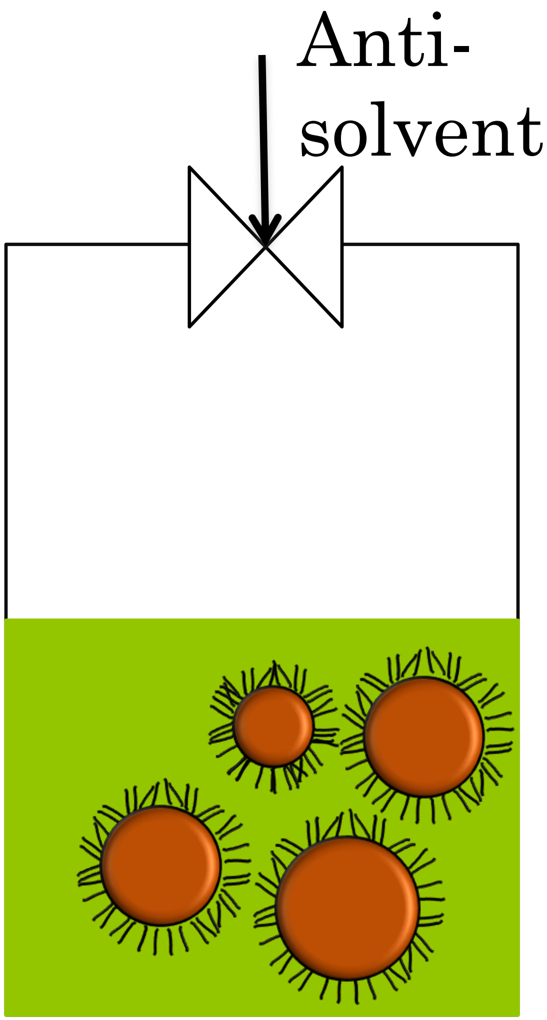
COMPOSITION OF N-HEXANE, D14 WITH CO_2

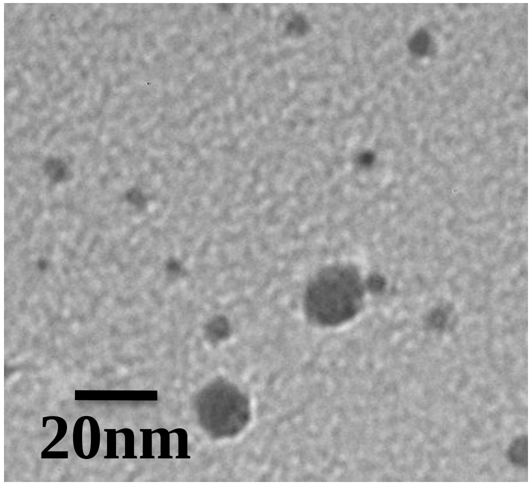


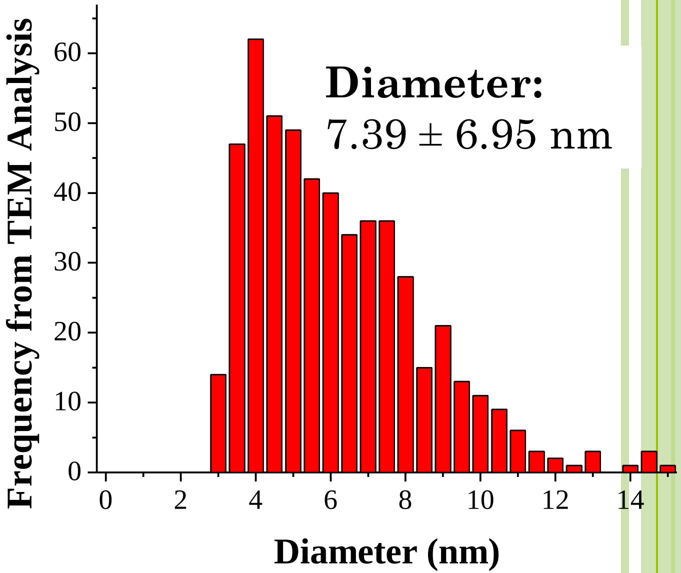
POST-SYNTHESIS PROCESSING



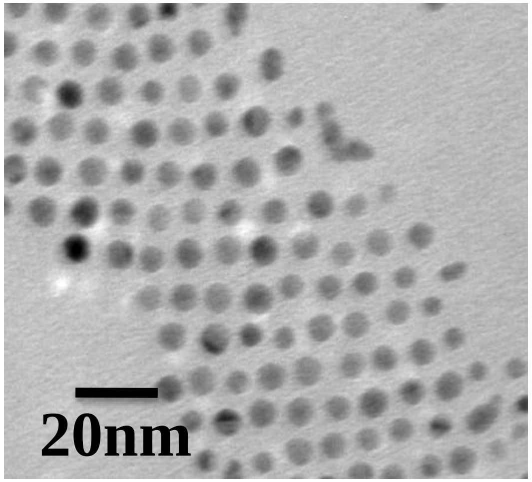
n-hexane

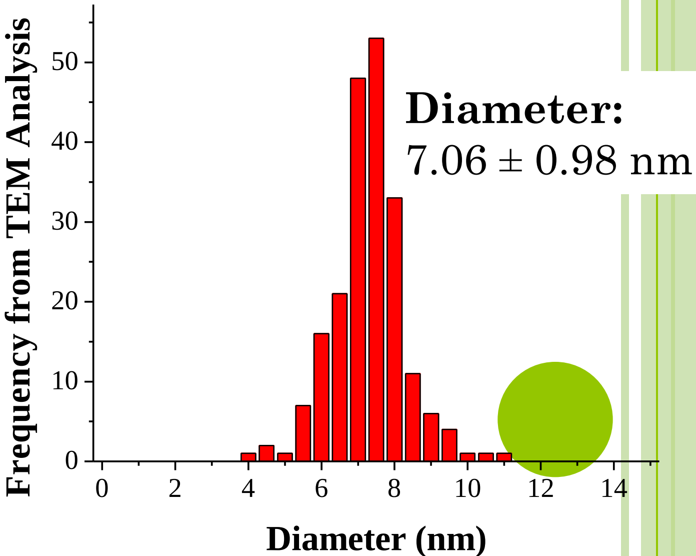
Polydisperse



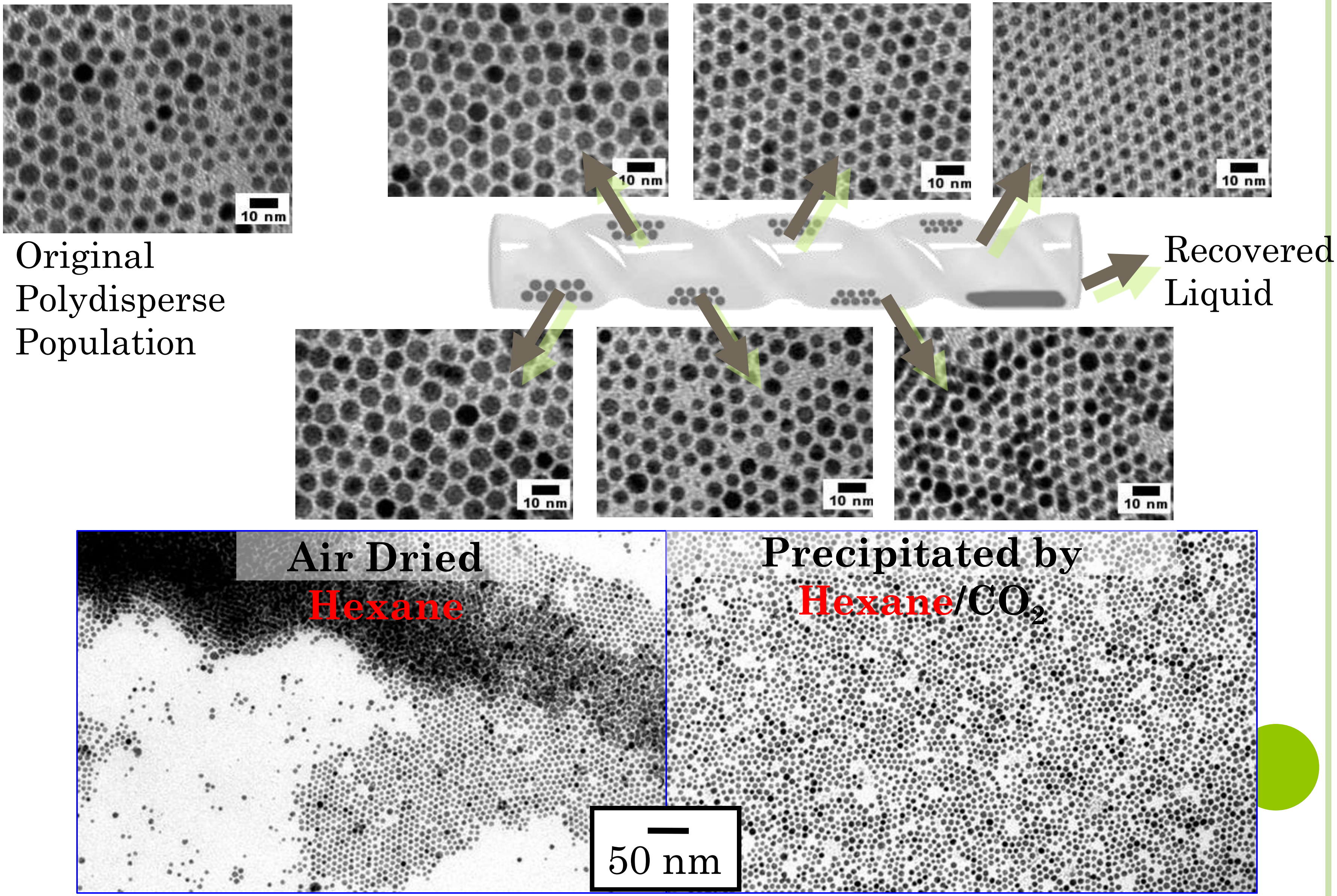


Monodisperse



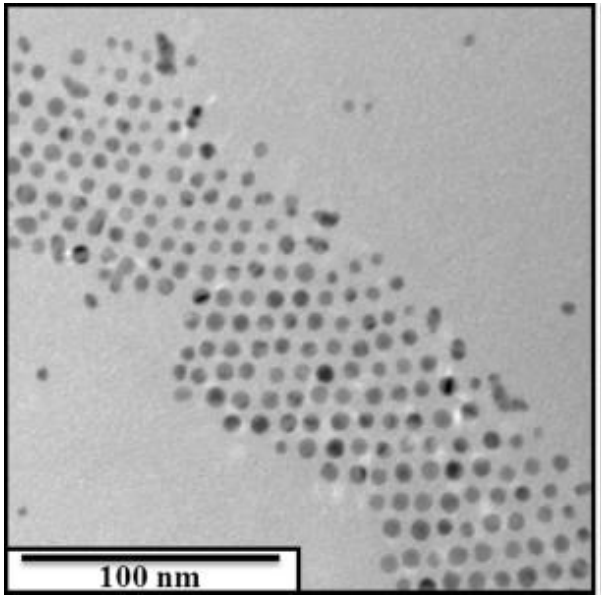


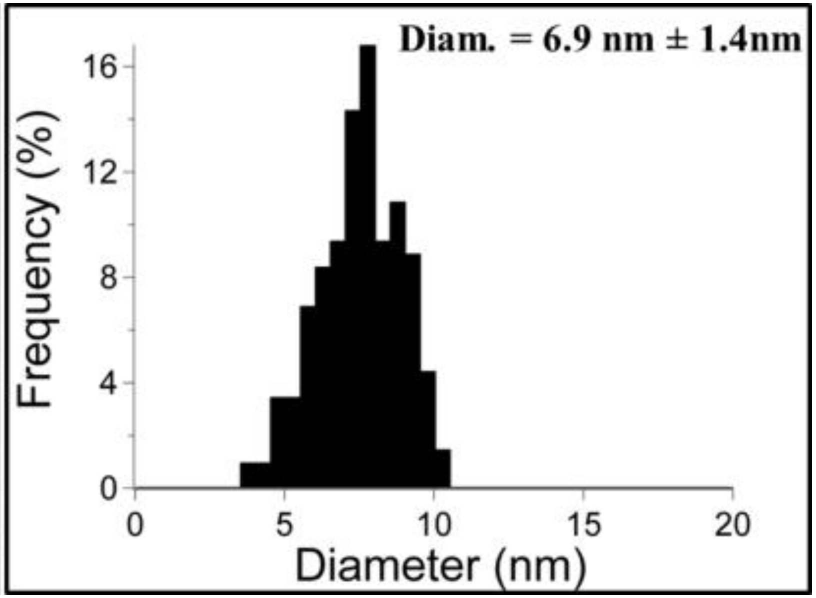
Silver Nanoparticle Size Fractionation and Uniform Deposition



CO_2 anti-solvent fractionation of AgNPs in n-hexane,d14

Fraction (psi)	CO_2 Fraction of GXL	Mean (nm)	Standard Deviation (nm)	Surface Coverage
400 to 450	37 to 44%	7.2 (7.1*)	1.4(1.5*)	44%
450 to 500	44 to 51%	7.0(6.9*)	1.3(1.4*)	55%
500 to 550	51 to 58%	6.6	1	62%
550 to 600	58 to 66%	5.9	0.9	60%





Curvature Effects and Surface Coverage (Determined by SANS)

Diameter (nm)	Curvature ($Å^{-1}$)	Surface Coverage	Ligand Solvation	L_o (Å)	L_f (Å)
7.1	0.282	44%	19%	13.0	7
6.9	0.29	55%	19%	13.6	7
6.6	0.303	62%	17%	12.3	7
5.9	0.339	60%	27%	9.4	7

- Fractionation with Increasing CO_2 Pressure
- Similar Curvature, Varying Surface Coverage
  - ↑Surface Coverage = ↑ Shell Thickness, ↓ Ligand Solvation
- Similar Surface Coverage, Varying Curvature
  - ↑ Curvature = ↑ Ligand Solvation

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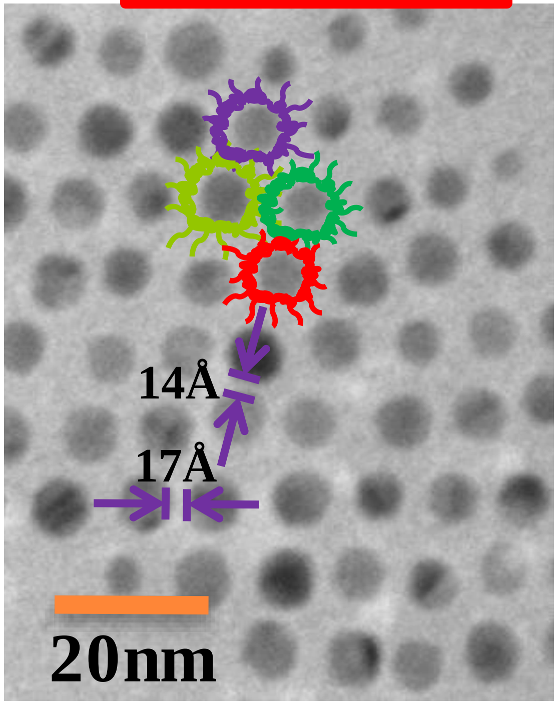
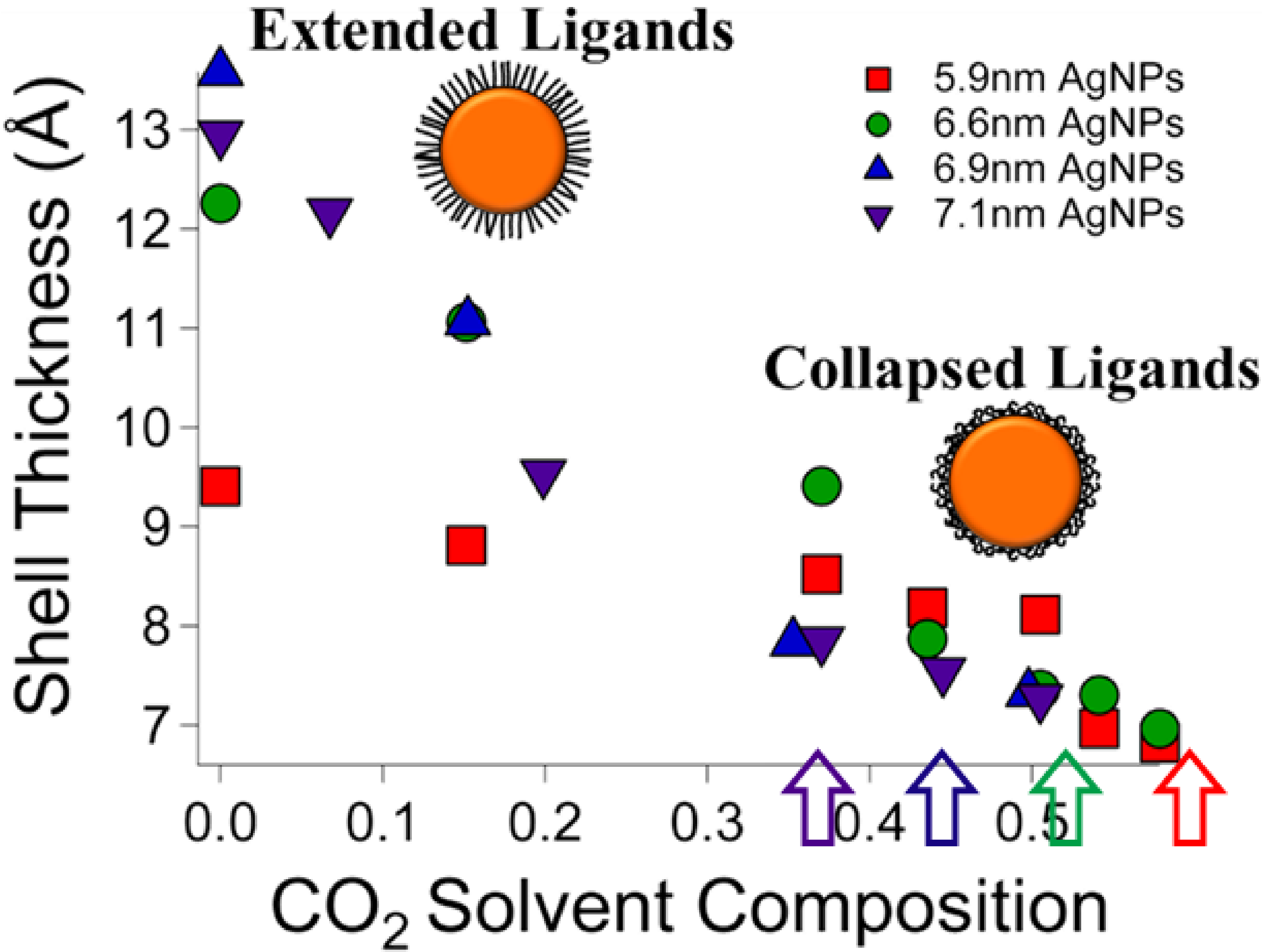
- Thin Film Interparticle Spacing
- Ligand Collapse

  vs

  Ligand Interdigitation

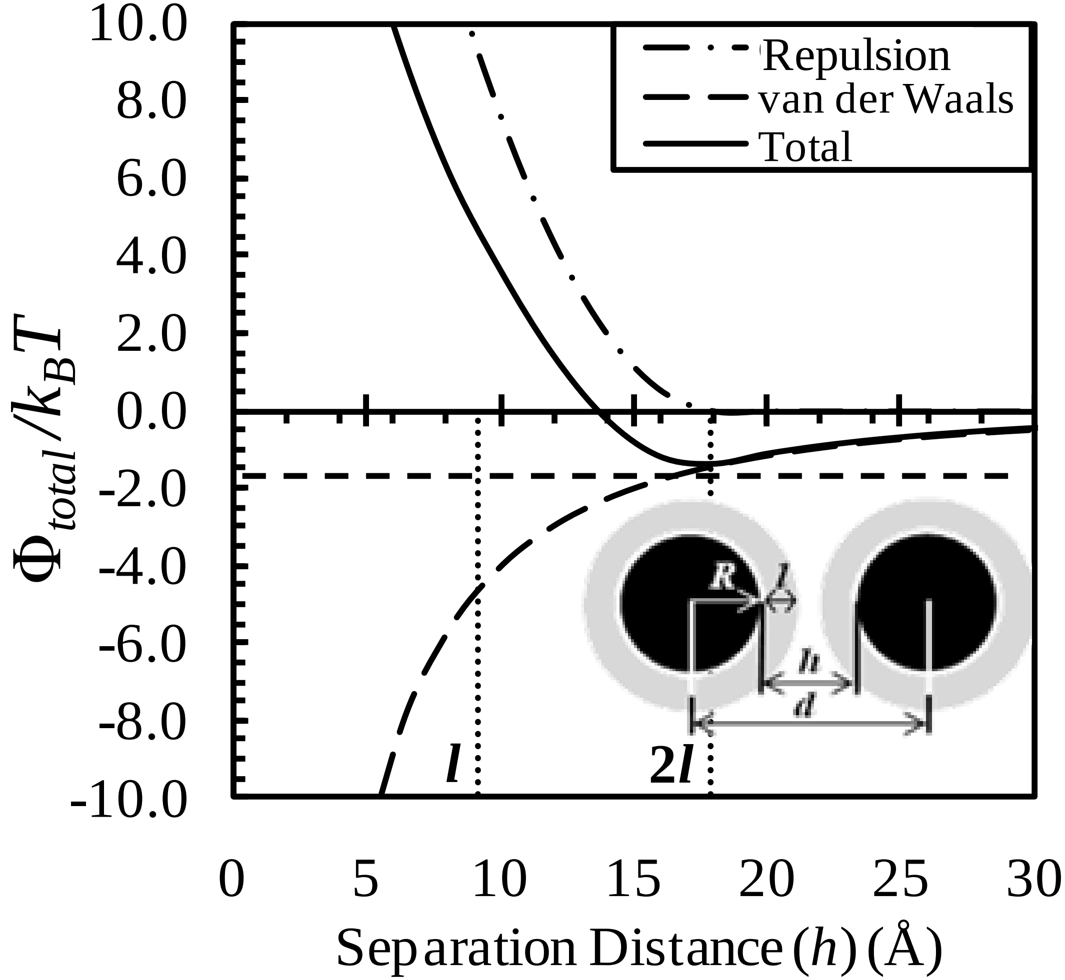


Shell Thickness of Dodecanethiol



Prediction of Nanoparticle Dispersion – Interparticle Potential

$$\Phi_{total} = \Phi_{vdW} + \Phi_{Repulsion}$$



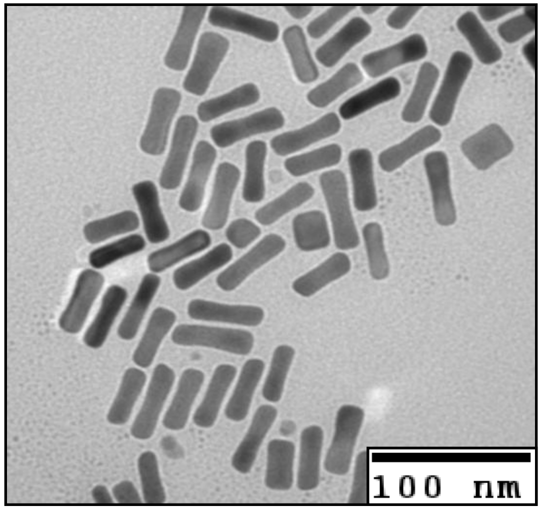
- Repulsion forces dependent on ligand:
  - **Shell Thickness***
  - **Solvation***
  - **Surface Coverage***
  - Electrostatics
- *Measured by SANS

Post-Synthesis Processing

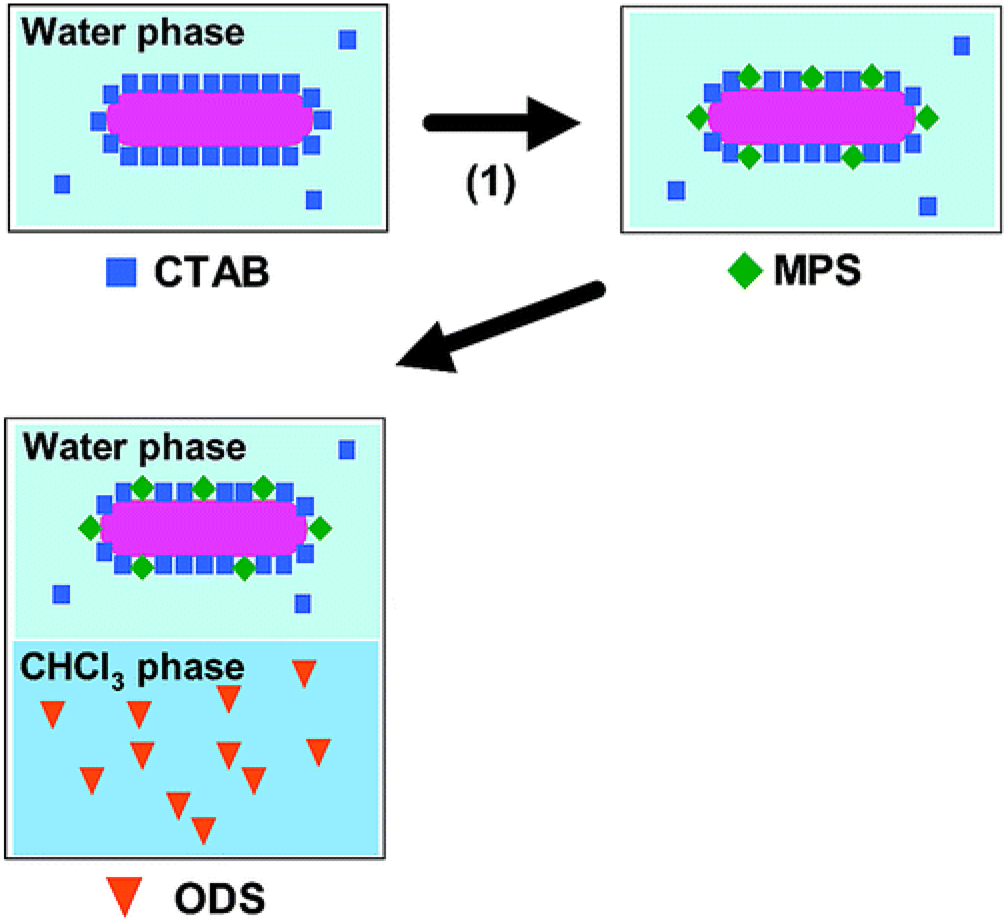
- Liquid Anti-Solvent Precipitation
  - Ethanol
  - Requires large amounts of anti-solvent and centrifugation
  - Effective for lab-scale volumes
- CO_2 Anti-Solvent Precipitation
  - Non-toxic, abundant, moderate pressures required
  - High miscibility with organic solvents
  - Highly tunable with pressure
  - Facile solvent recovery
  - Enhanced transport properties
  - Elimination of liquid/vapor interface for NP deposition
  - **Fractionate NPs based on Size, Surface Chemistry, and Shape**

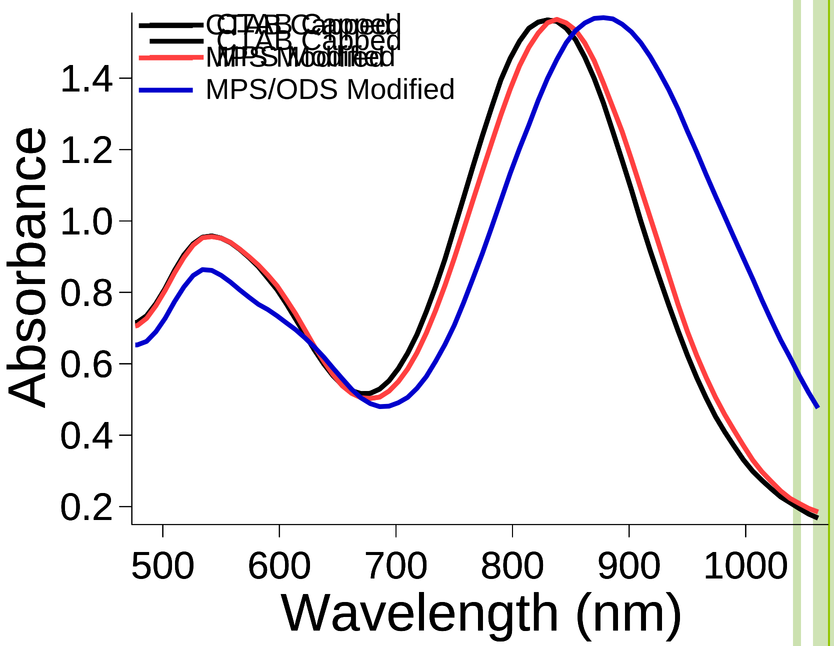
Gold Nanorods (GNRs)

- Nanorod Applications
  - Sensors and Electronics
  - Biomedical Contrast Agents
  - Thin Film Optical Limiters
  - Polymer Fillers
- *GXL Fractionation?*
- Drawbacks
  - Difficult to Redisperse CTAB Stabilized GNRs in Organic Solvents
  - No High Yield Wet-Chemical Synthesis Protocols for GNRs with Hydrophobic Surface Chemistry



GNR Surface Modification

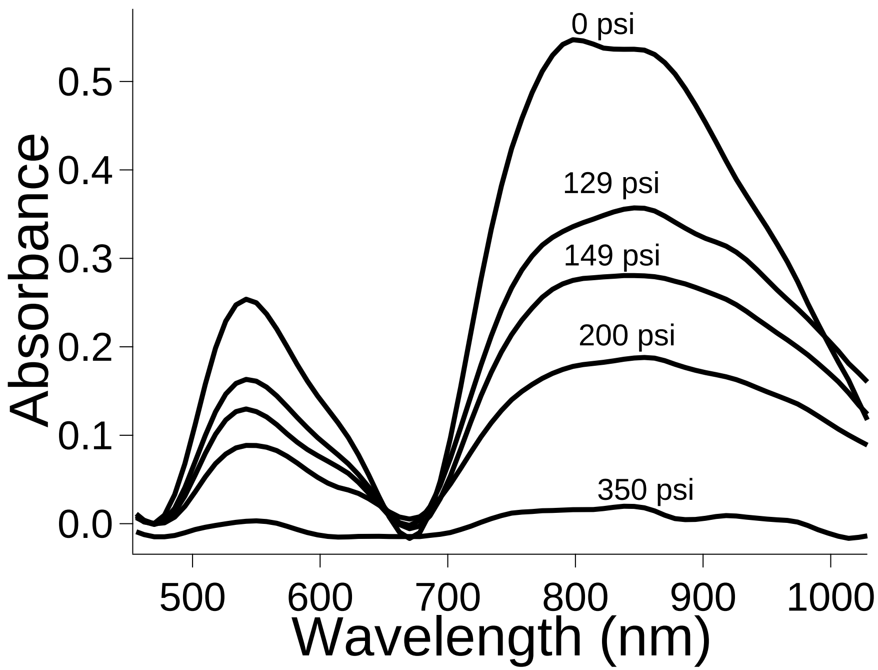




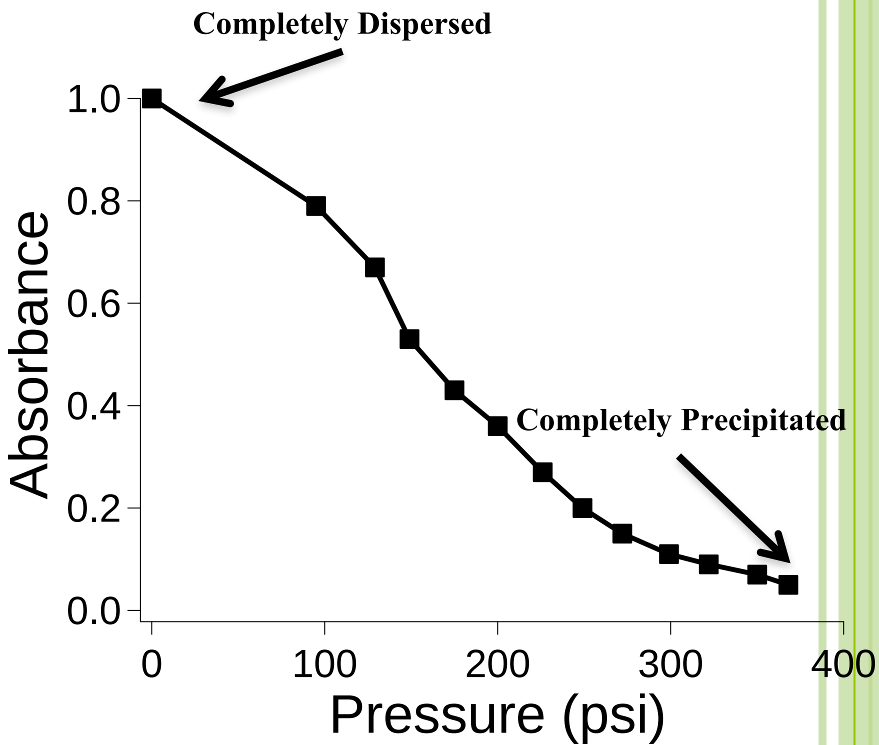
*DDS can be substituted for ODS. GNRs stabilized by either ODS or DDS must be co-stabilized by either dodecanethiol or octadecanethiol

Mitamura et al. J. Phys. Chem. B, Vol. 111, No. 30, 2007

Dispersibility of GNRs



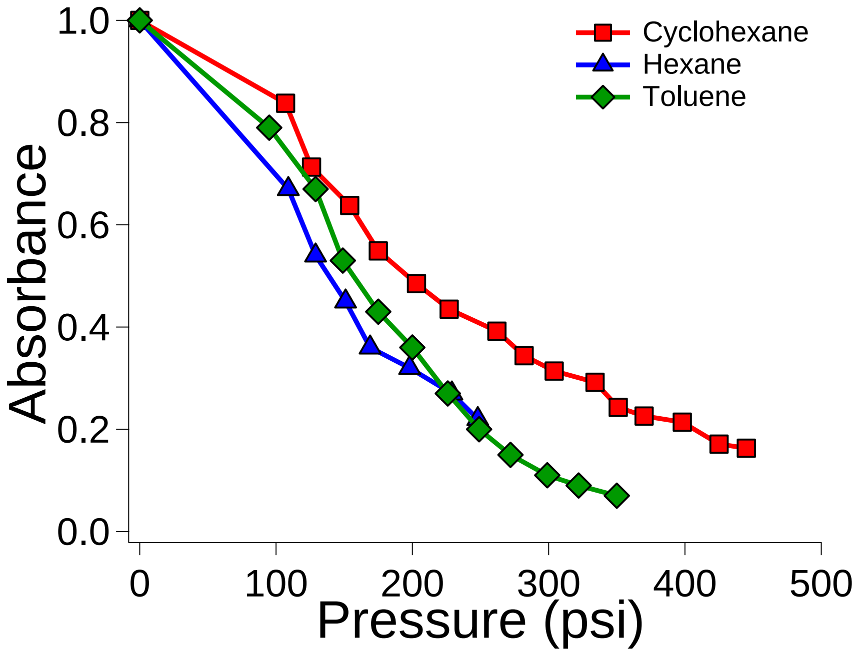
GNRs capped by ODS/C18SH in CO_2-Expanded Toluene (aspect ratio ~3)



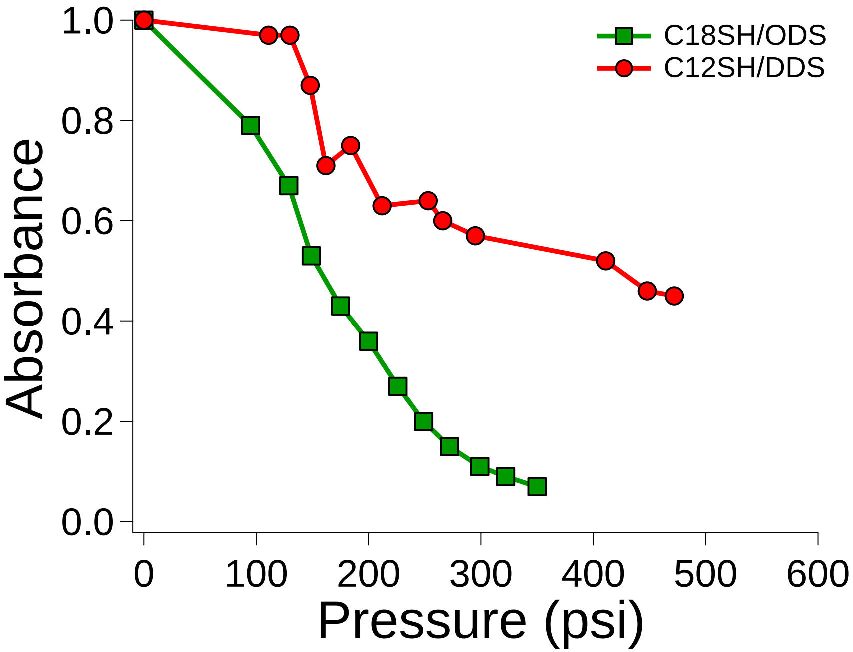
Max UV-VIS with varying CO_2 Pressure

GNRs were reversibly precipitated out of CO_2-Expanded Toluene at 350 psi

Dispersibility of GNRs



GNRs capped by ODS/C18SH in CO_2-Expanded Solvents

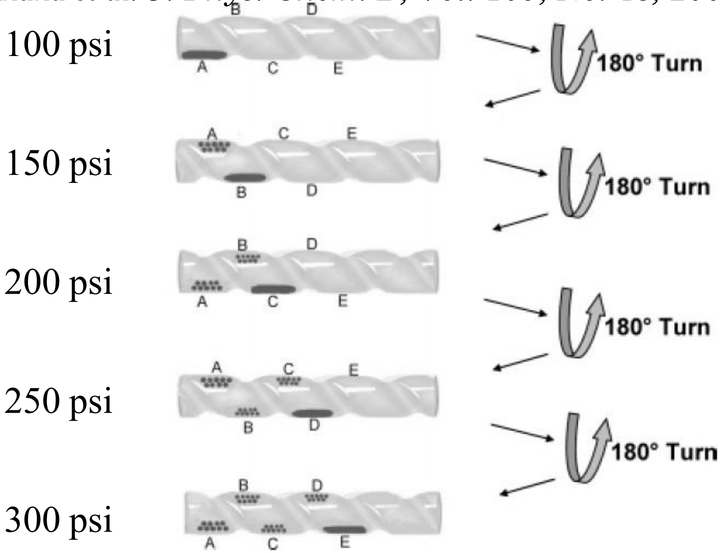


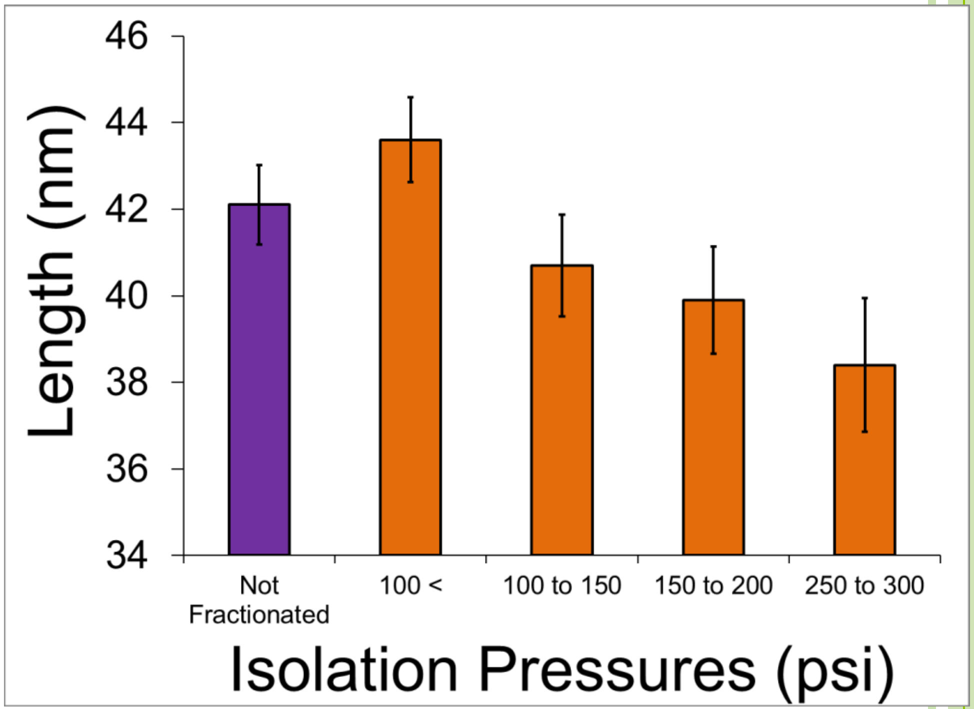
GNRs in CO_2-Expanded Toluene Capped by Varying Ligands

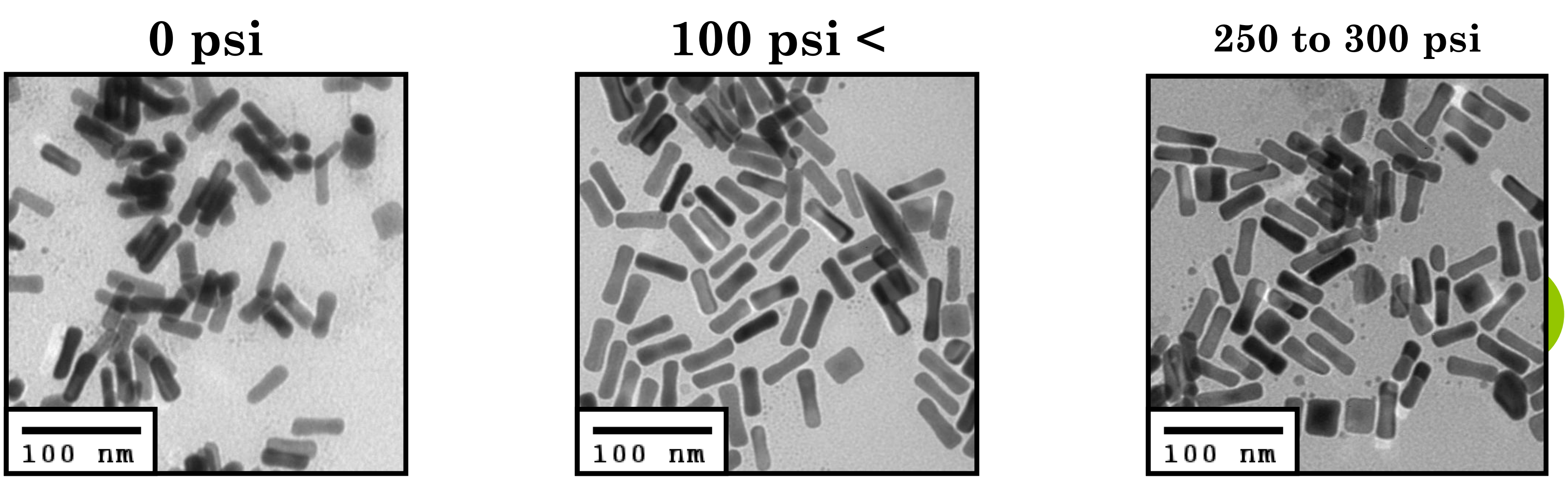
GNRs have an aspect ratio of 3.3 0.6, Width = 42.1 nm, Length = 14.7 nm

GNR Fractionation

Anand et al. J. Phys. Chem. B, Vol. 109, No. 48, 2005





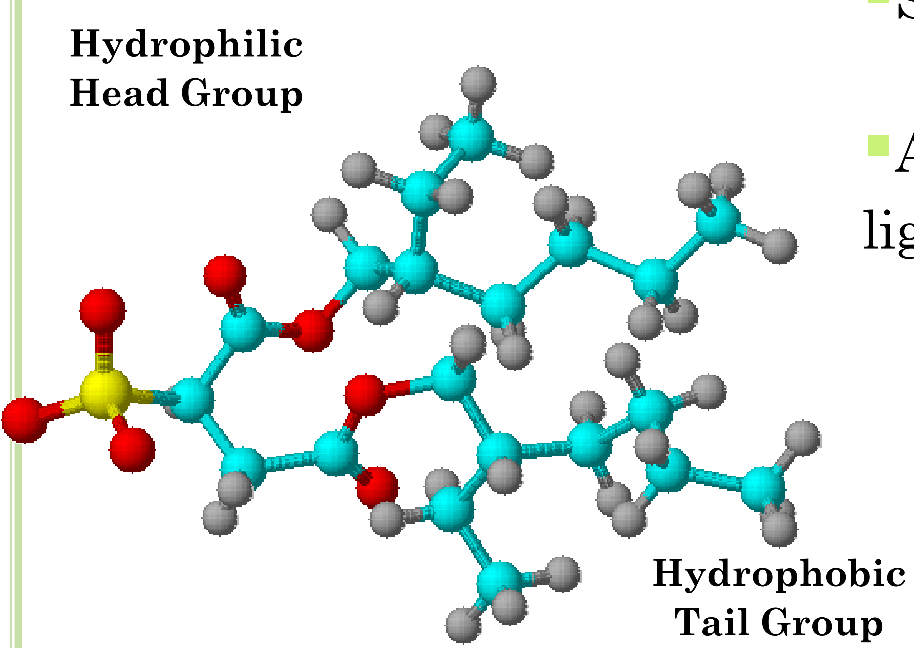


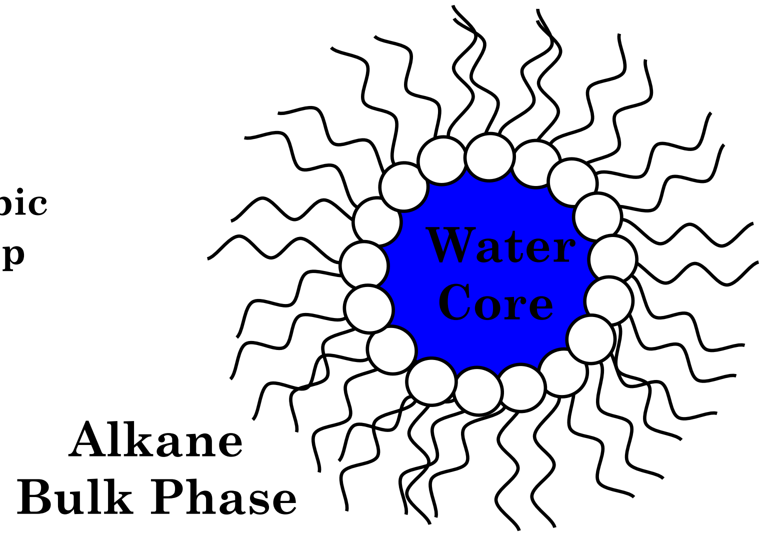
Nanoparticle Synthesis in GXL

Surfactants and reverse Micelles

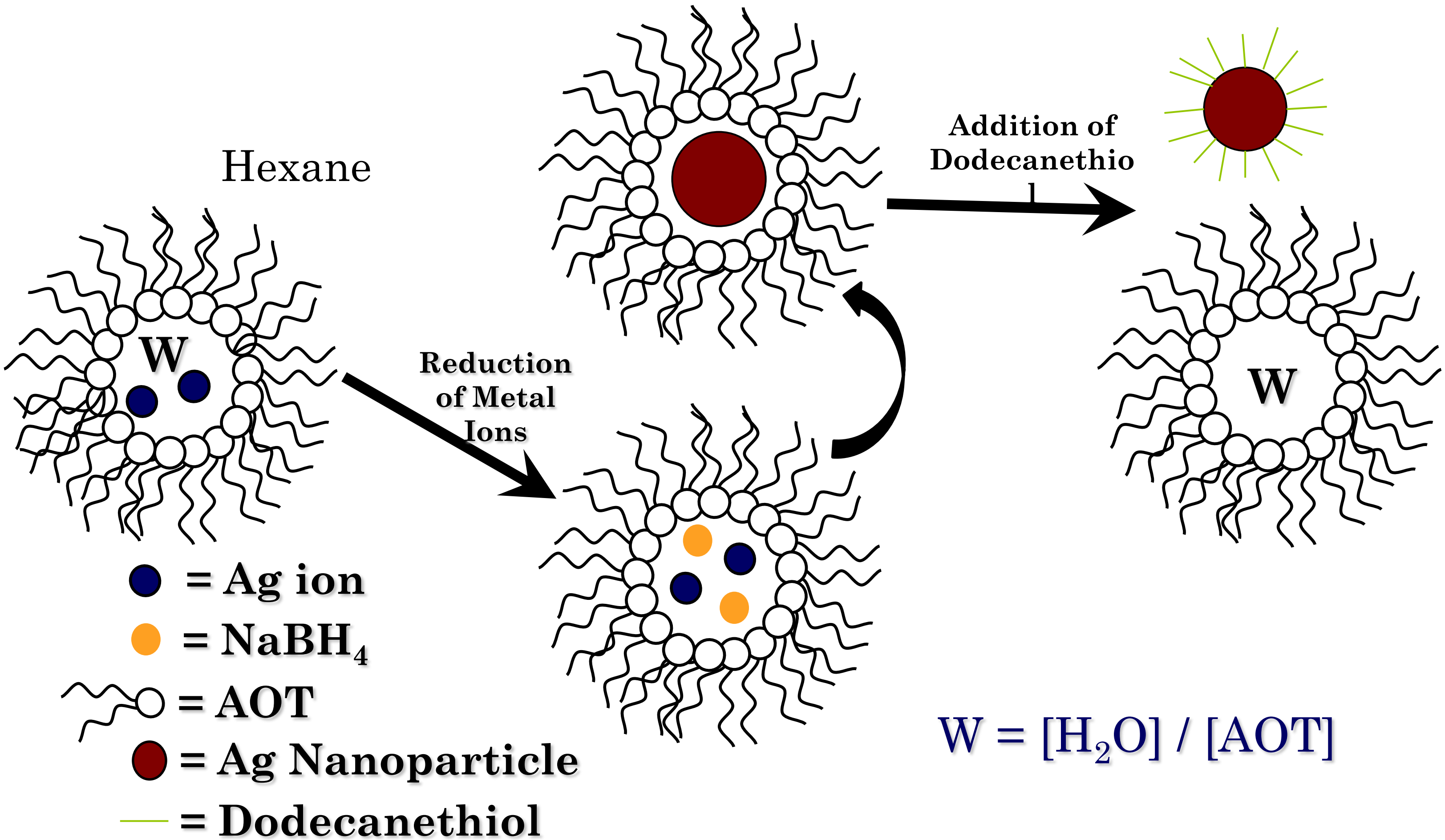
- AOT: sodium bis(2-ethylhexyl) sulfosuccinate
- Size of Micelle Determined by W

  $W = [\text{Moles } H_2 0] / [\text{Moles AOT}]$
- Act as stabilizing agents until ligand is introduced





Reverse micelle Nanoparticle synthesis

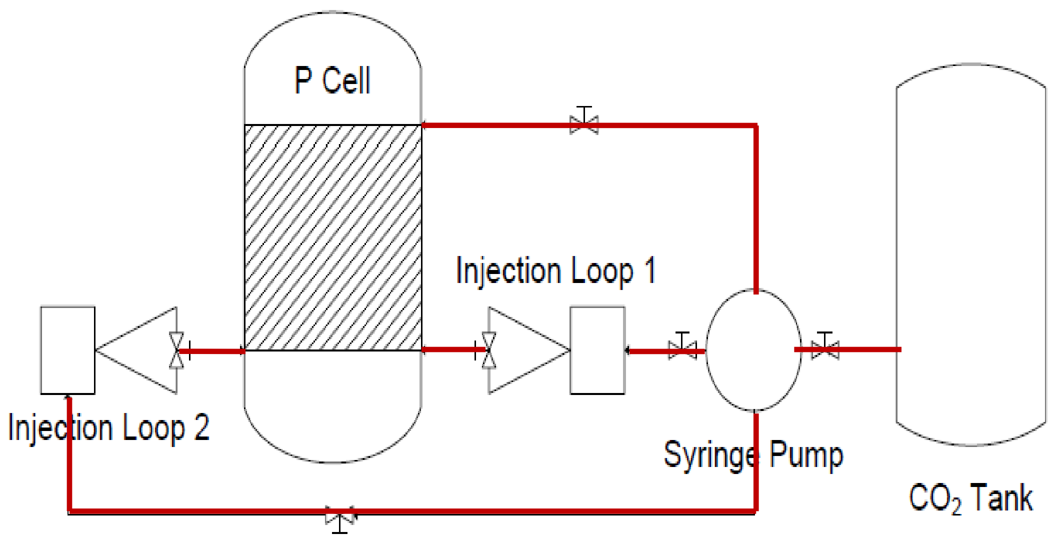


$W = [H_2O] / [AOT]$

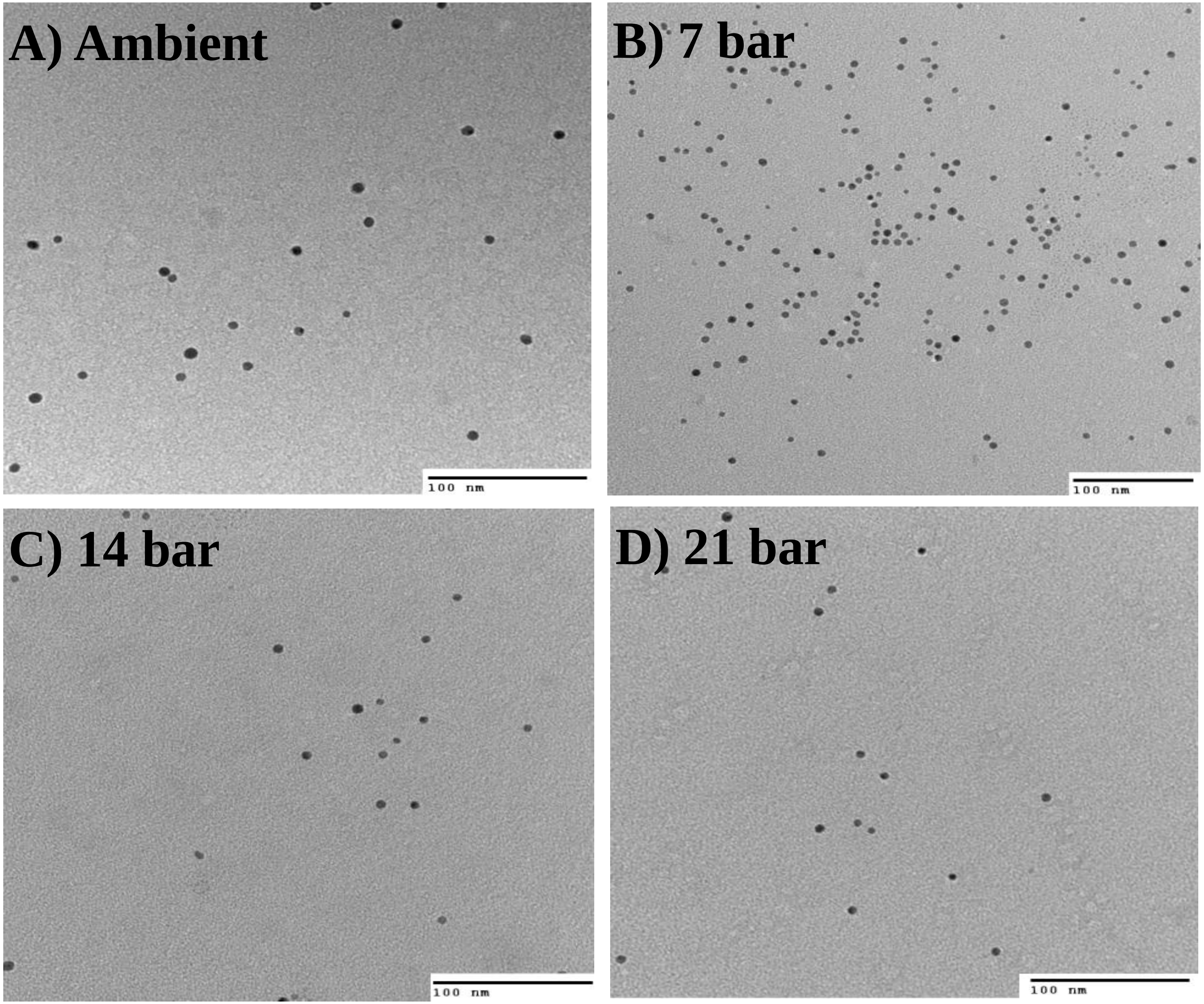
Synthesis and Characterization

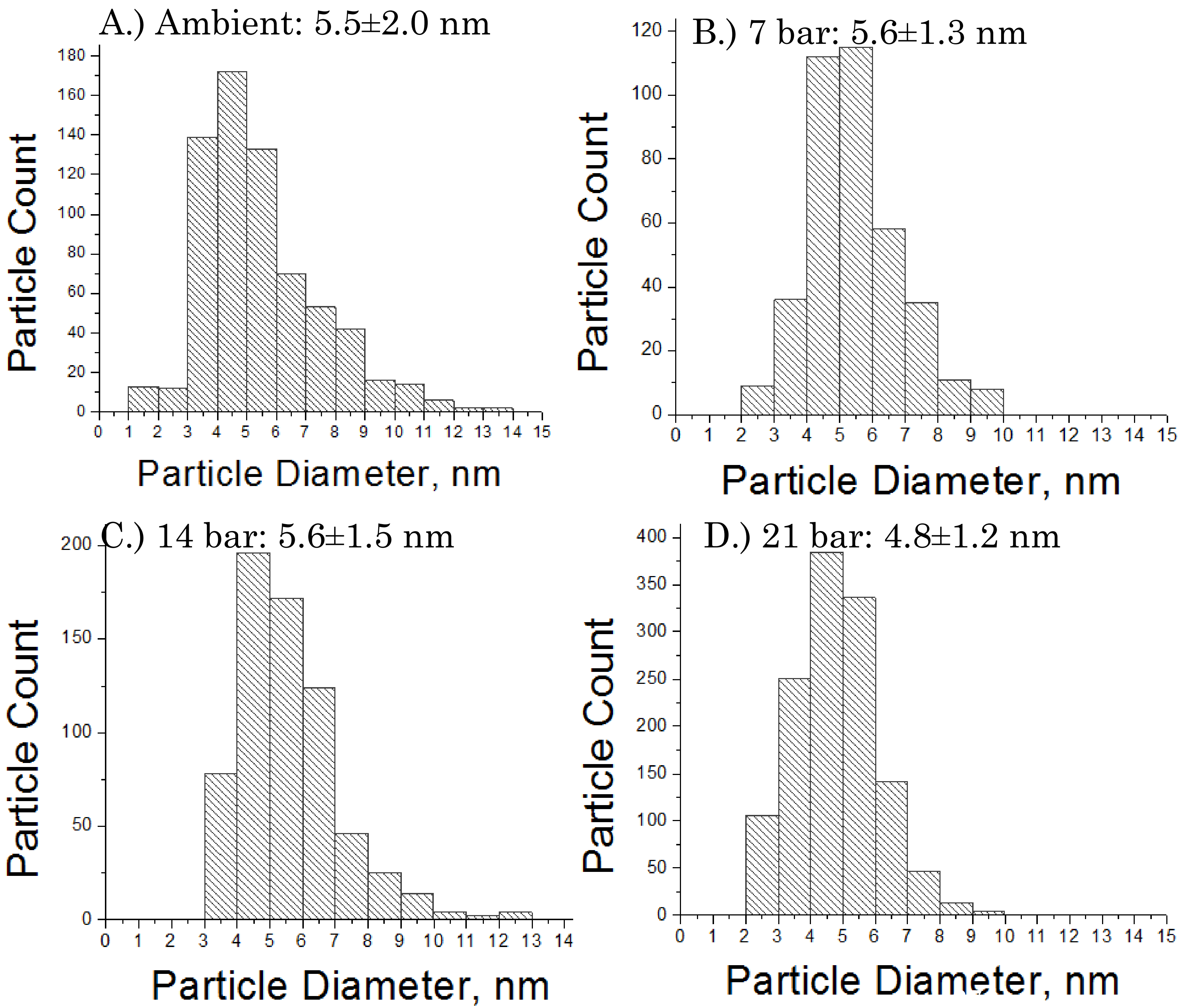
- Experimental conditions:
  - W = 20 and W = 40
  - Ambient Pressure to 41 bar
- Stabilized by dodecanethiol
- Washed 2x with ethanol
- TEM
- ImageJ analysis

W-Value	20	40
Total H_2O (mL)	0.2	0.4
0.1M AOT, (mL)	5.55	5.55
$NaBH_4$, (mL)	0.1	0.25
$AgNO_3$, (mL)	0.1	0.15
$NaBH_4$ Conc., (M)	0.25	0.1
$AgNO_3$ Conc., (M)	0.01	0.01
Metal:$NaBH_4$	0.04	0.04

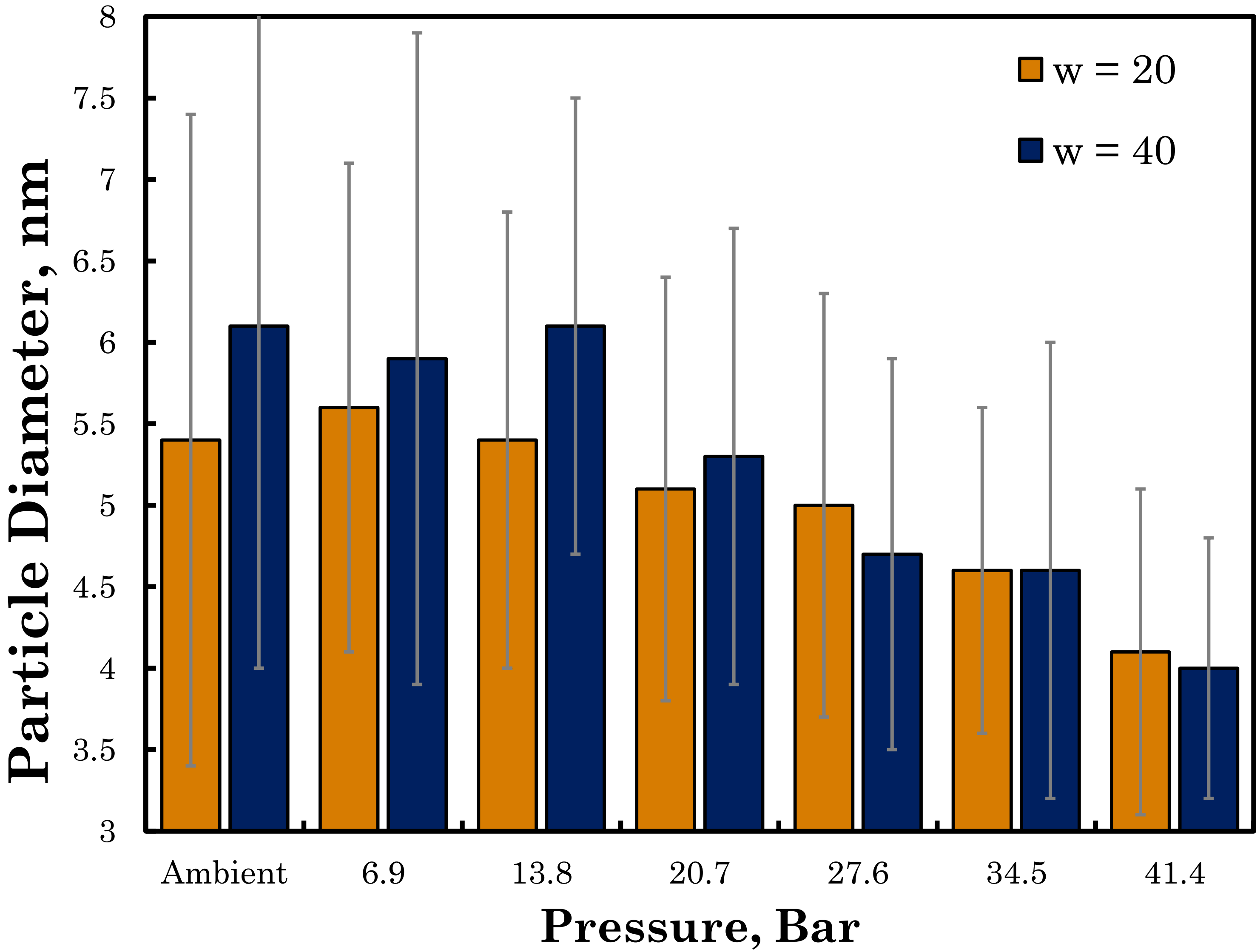


TEM Images w = 20




A.) Ambient: 5.5±2.0 nm
B.) 7 bar: 5.6±1.3 nm
C.) 14 bar: 5.6±1.5 nm
D.) 21 bar: 4.8±1.2 nm
Particle Count
Particle Diameter, nm

Results

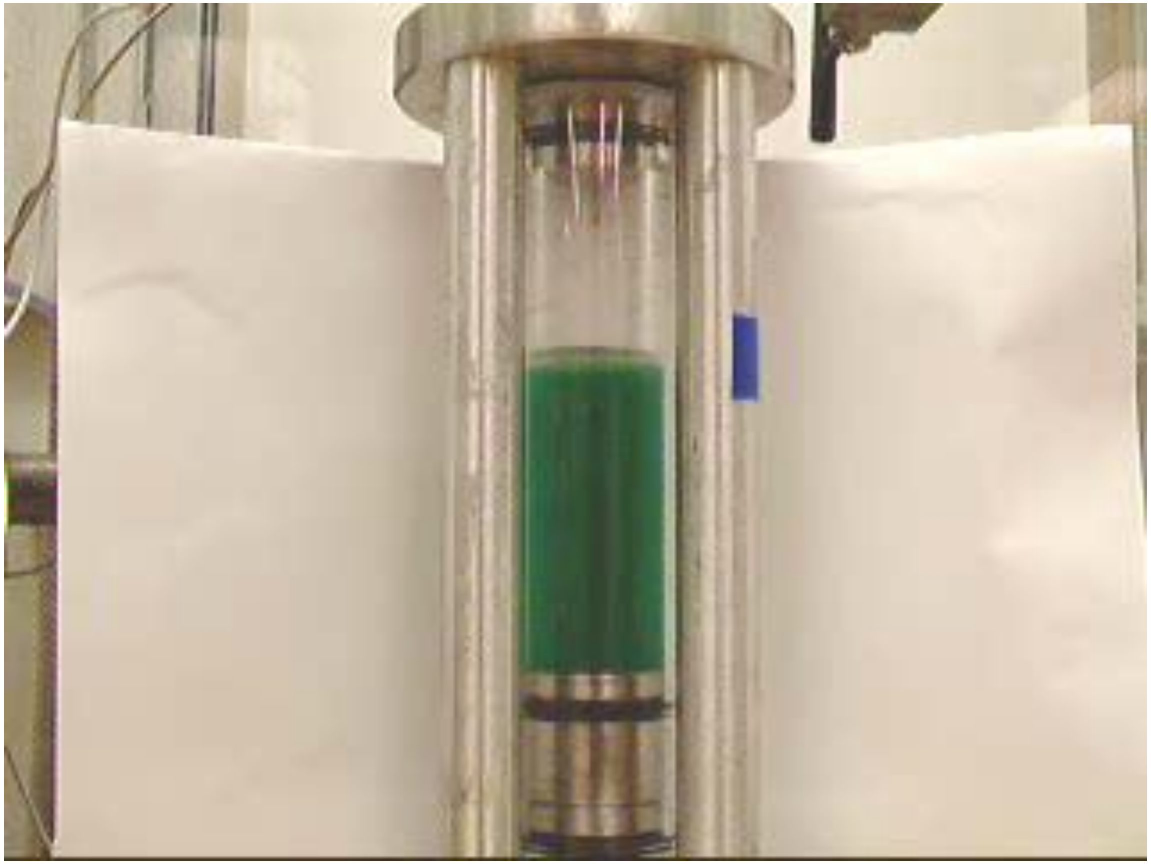


w = 20
w = 40
Particle Diameter, nm
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
Ambient
6.9
13.8
20.7
27.6
34.5
41.4
Pressure, Bar

Nanoparticle Processing in Organic – Aqueous Tunable Solvents (OATS)

Organic – Aqueous Tunable Solvents (OATS)

$THF + H_2O + CO_2$



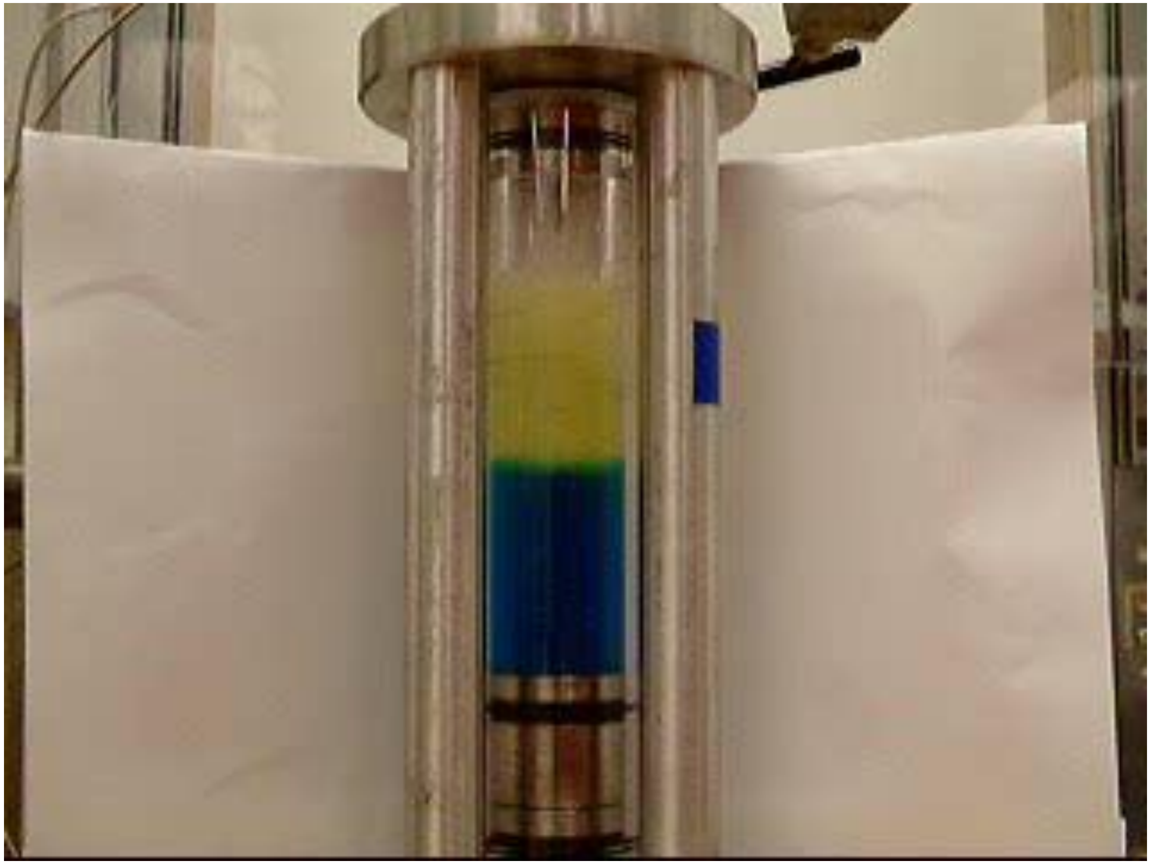
1 bar CO_2 → 20 bar CO_2

Organic Reactants/ Products

Water Soluble Catalyst Ionic Reactant

Organic – Aqueous Tunable Solvents (OATS)

THF + H_2O + CO_2

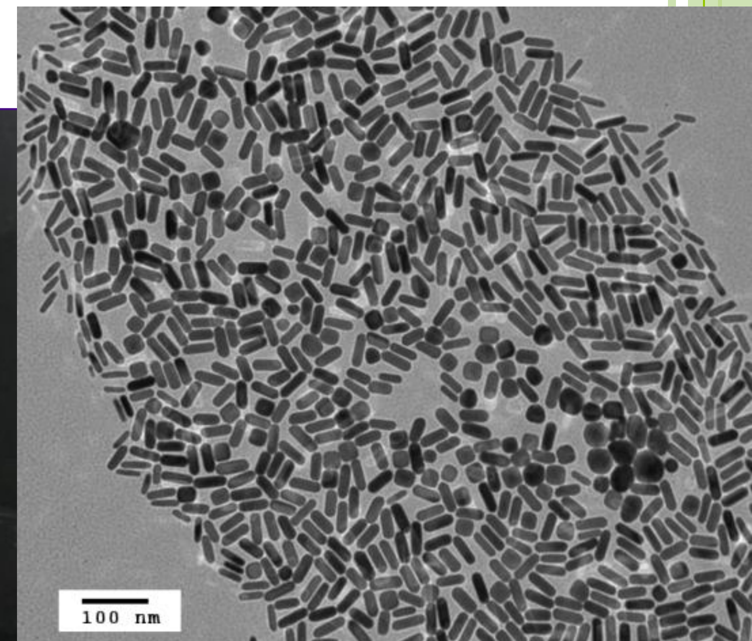


20 bar CO_2 ⟶ 1 bar CO_2

Organic Reactants/ Products

Water Soluble Catalyst Ionic Reactant

OATS For Nanoparticle Synthesis and Processing



Gold Nanorod synthesis and surface modification.

Conclusions

- GXL for effective fractionation of nanoparticles based on:
  - Size Shape Surface Chemistry
- Controllable with CO_2 pressure and completely reversible
- SANS to characterize stabilization ligands
- GXL to control silver nanoparticle size synthesized in AOT reverse micelle system
  - Decrease in particle size with increasing CO_2 composition
- Future work with OATS

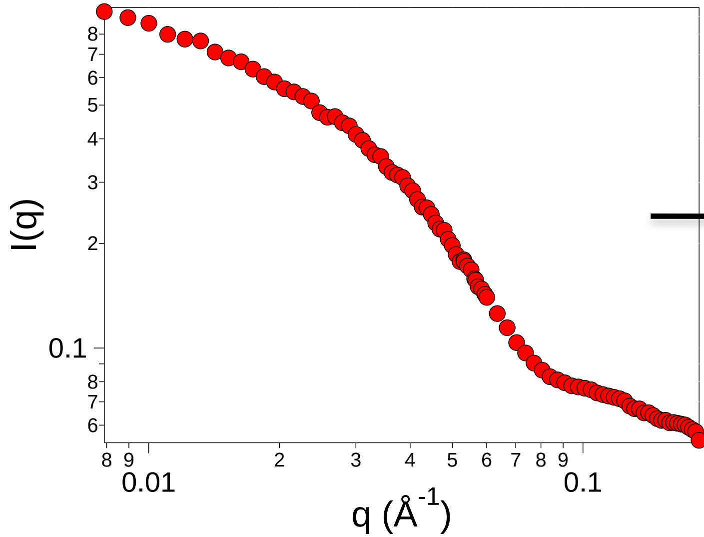
Acknowledgements

- National Science Foundation
- PSA-NGGF fellowship at Clemson University
- NIST Center for Neutron Scattering

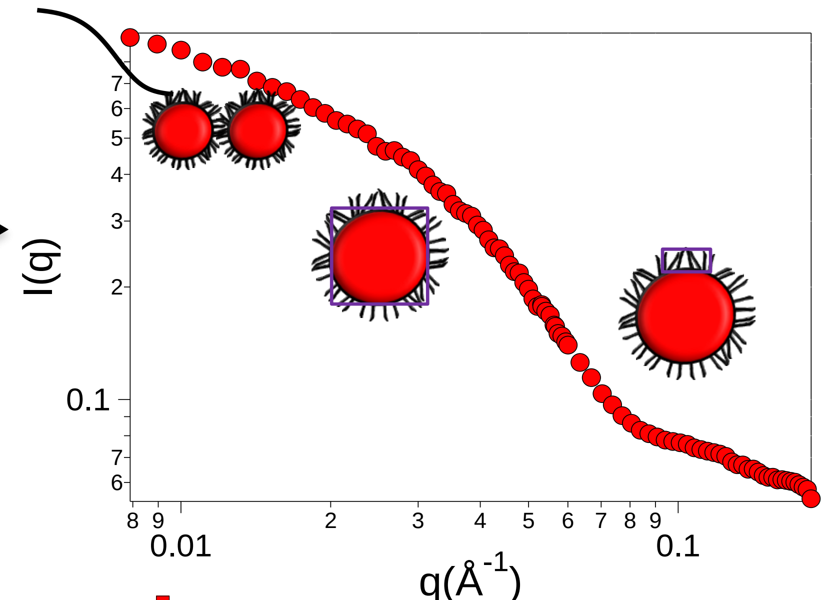
Ligand Behavior via. Small Angle Neutron Scattering (SANS)

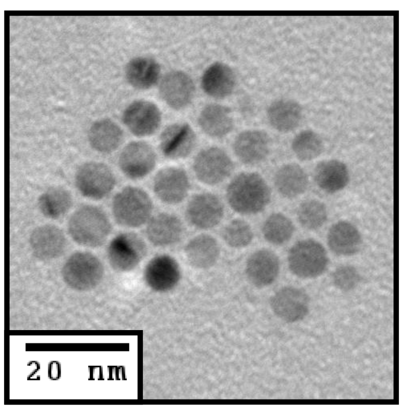
SMALL-ANGLE NEUTRON SCATTERING (SANS) INTRODUCTION

Reduced 1-D SANS Data

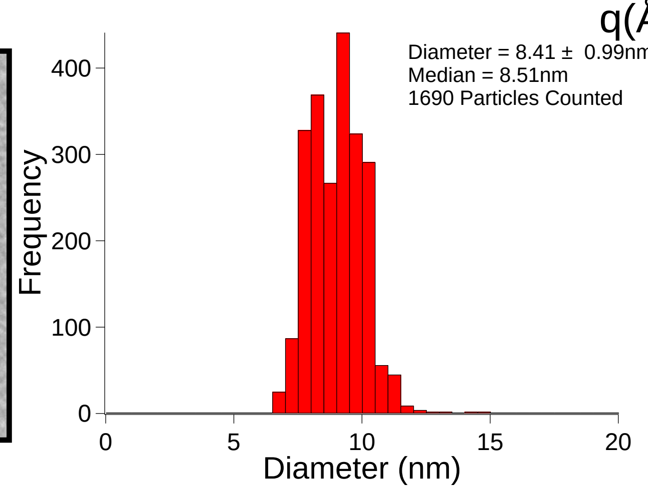


Fit 1-D SANS Data





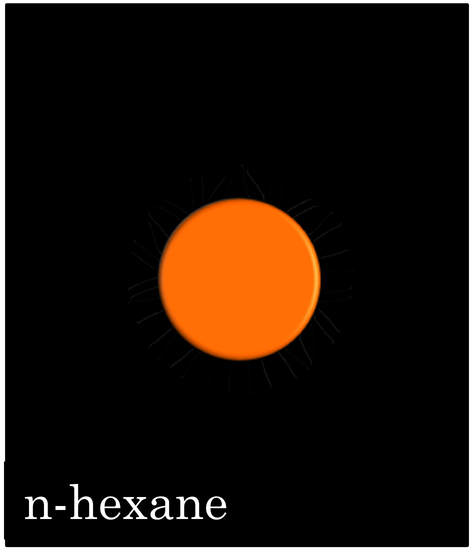
TEM Image

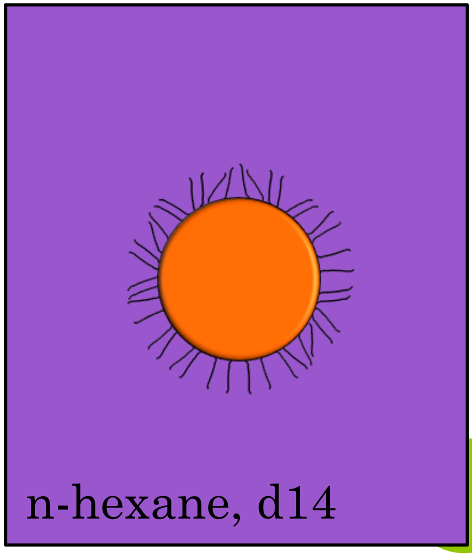


SMALL-ANGLE NEUTRON SCATTERING (SANS) INTRODUCTION

- Scattering Length Density (SLD)
  - Dependent on atomic number/composition
  - Allows for great contrast between hydrogen and deuterium

Material	SLD ($Å^{-2}$)
Gold	4.50E-06
Dodecanethiol	-3.67E-07
1-Octadecanethiol	-3.49E-07
n-hexane, d14	6.14E-06
n-hexane	-5.71E-07
toluene, d8	5.66E-06

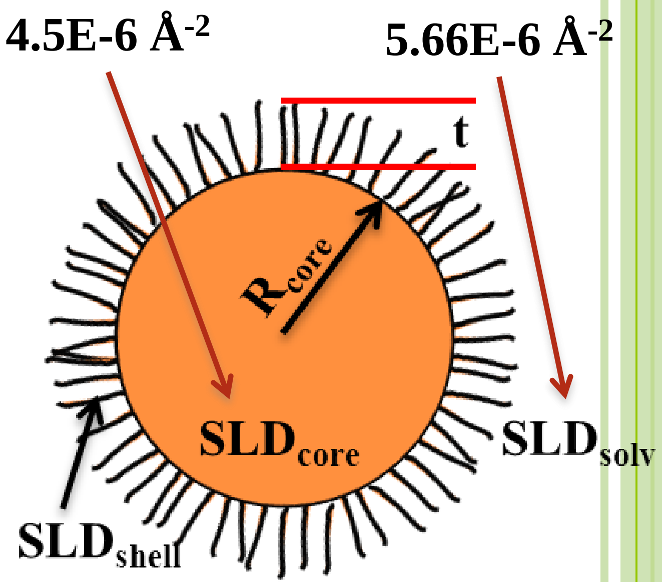


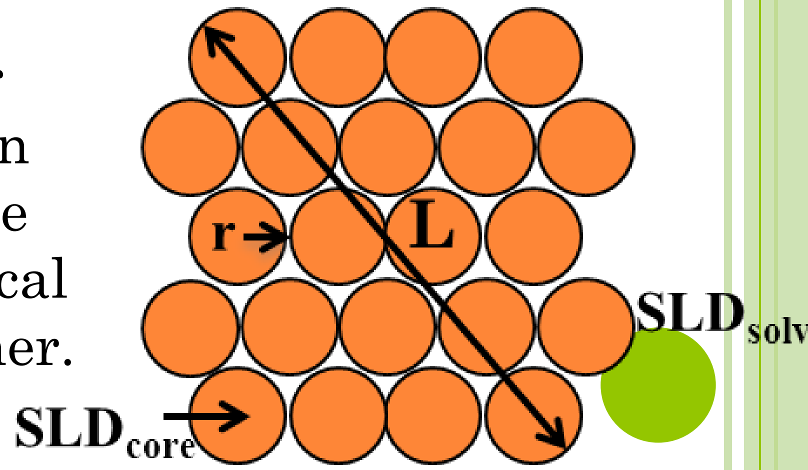


SANS DATA ANALYSIS

Two different Models were used to analyze the SANS Data

- Polydisperse Core-Shell Form
  - Calculates the form factor P(q) for polydisperse spherical particles with a core-shell structure.
- Fractal Model
  - Calculates the form factor P(q) for fractal like aggregates dispersed in solution. The aggregates are made up of randomly distributed spherical particles which have joined together.





NANOPARTICLES INVESTIGATED

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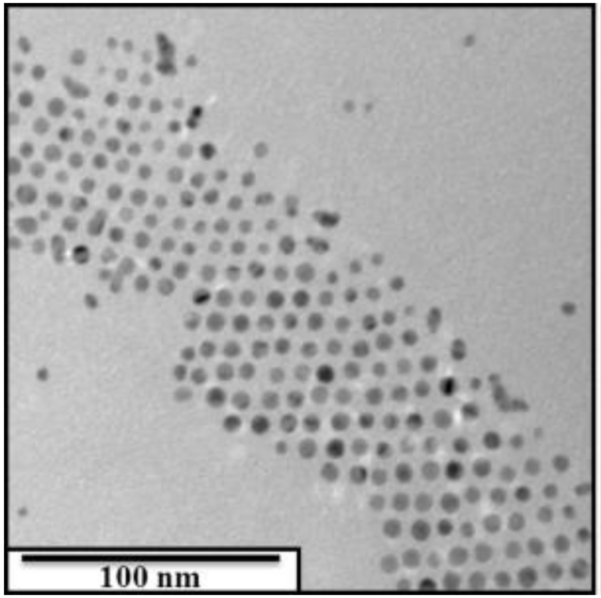
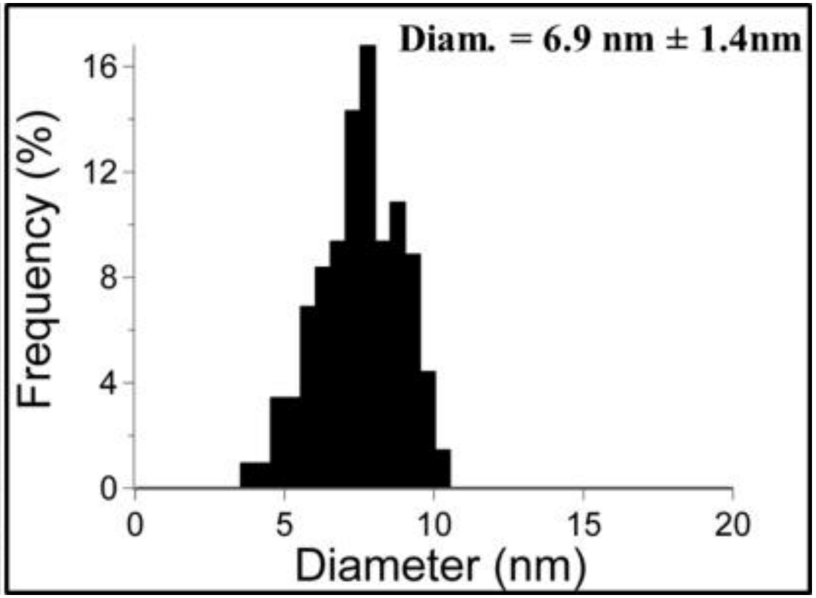
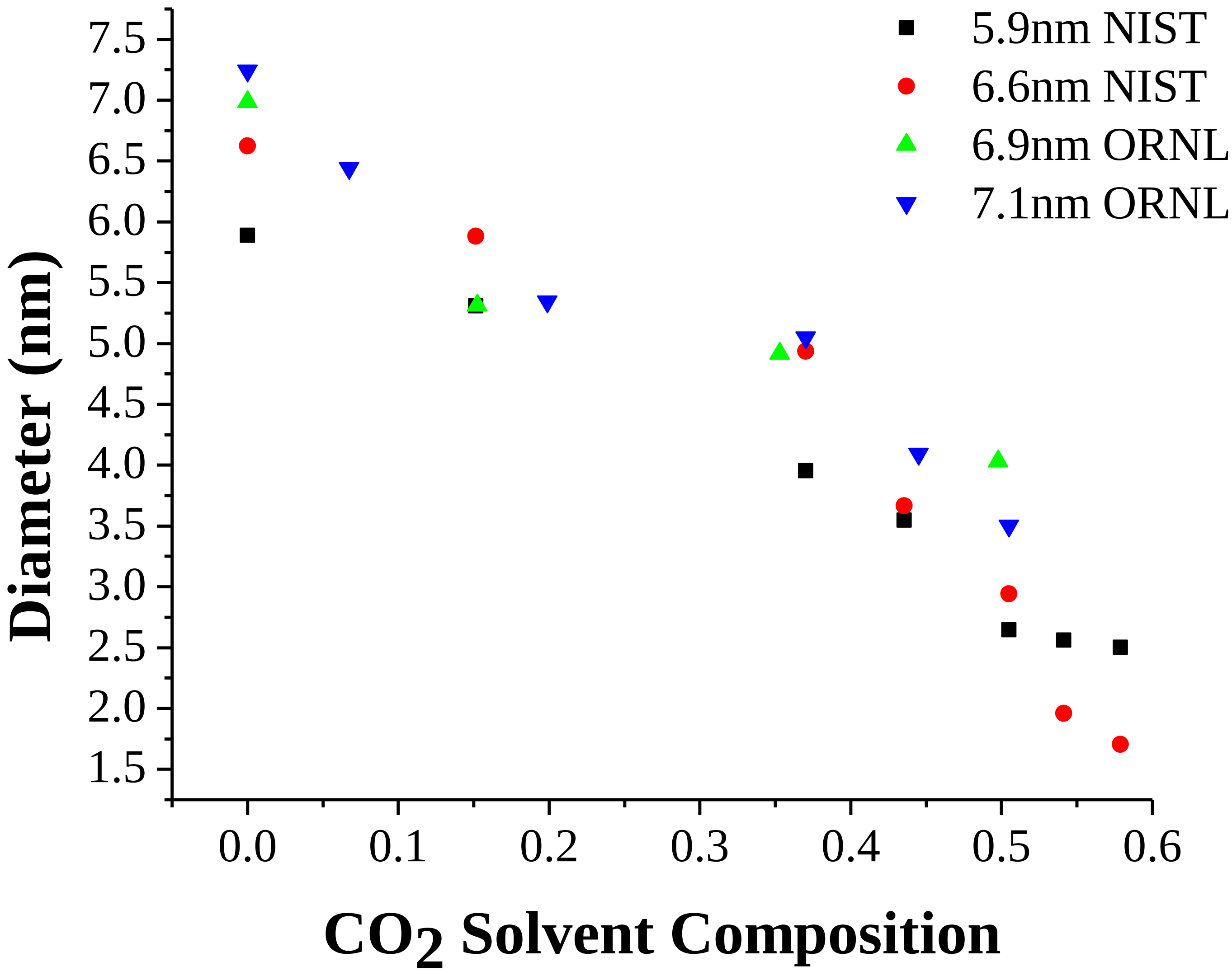
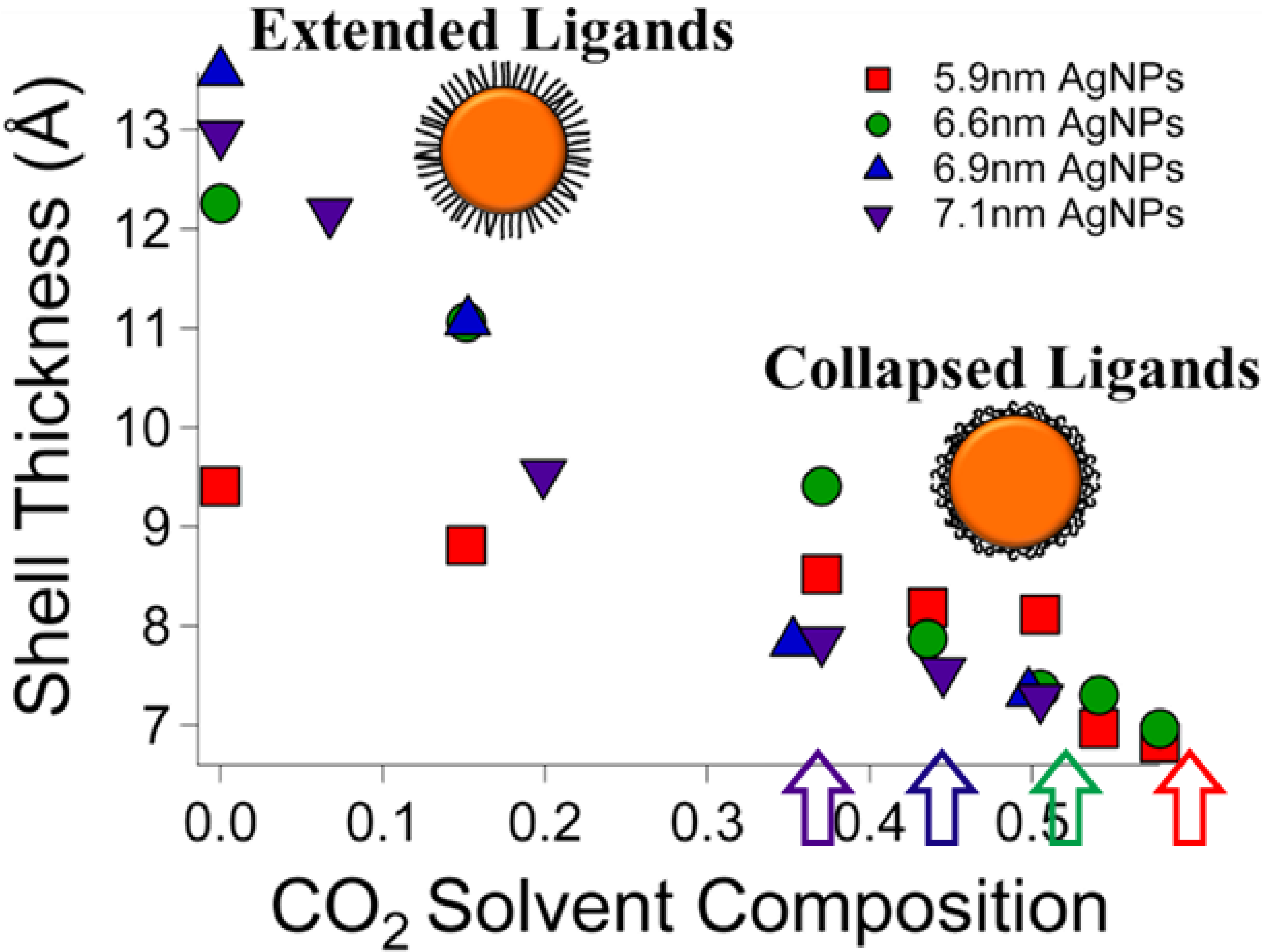




Diameter of Silver Nanoparticles vs CO_2 Composition



Shell Thickness of Dodecanethiol



DODECANETHIOL LIGAND SOLVATION