SYNTHESIS AND PROCESSING OF METALLIC NANOMATERIALS USING CO₂ 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

Stabilizing Ligands

Targeting Ligands

Bifunctional Ligands
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**

1. Reduce salt
2. Add organic solvent with alkanethiol

Vigorous mixing

Recycle

Add HAuCl₄
Ligand Exchange (Silver Nanoparticles)
Tunable Organic-CO$_2$ Mixtures: Gas eXPanded Liquids (GXLs)

- Add CO$_2$
- CO$_2$ Miscibility
- Tunability
- Reversibility
- Advantages over Solvents
  - Better Transport Properties
  - Better Gas Solubility
- Advantages over SCFs
  - Lower Pressures
  - Better Solubility
Tunable Organic-CO$_2$ Mixtures: Gas eXPanded Liquids (GXLs)

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COMPOSITION OF N-HEXANE, D14 WITH CO₂
**POST-SYNTHESIS PROCESSING**

- **Anti-solvent**
  - Polydisperse
  - Monodisperse

- **n-hexane**

**Frequency from TEM Analysis**
- **Diameter:** 7.39 ± 6.95 nm
- **Median:** 5.71 nm

**Diameter:** 7.06 ± 0.98 nm
- **Median:** 7.06 nm
Silver Nanoparticle Size Fractionation and Uniform Deposition

Original Polydisperse Population

Recovered Liquid

Air Dried Hexane

Precipitated by Hexane/CO₂
**CO\textsubscript{2} ANTI-SOLVENT FRACTIONATION OF AgNPs IN n-HEXANE, d14**

<table>
<thead>
<tr>
<th>Fraction (psi)</th>
<th>CO\textsubscript{2} Fraction of GXL</th>
<th>Mean (nm)</th>
<th>Standard Deviation (nm)</th>
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<tr>
<td>400 to 450</td>
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![Image of AgNPs](image1.png)

Diam. = 6.9 nm ± 1.4nm

![Histogram of Diameter](image2.png)
CURVATURE EFFECTS AND SURFACE COVERAGE (DETERMINED BY SANS)

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Curvature (Å⁻¹)</th>
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<th>Ligand Solvation</th>
<th>L₀ (Å)</th>
<th>Lᶠ (Å)</th>
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<tbody>
<tr>
<td>7.1</td>
<td>0.282</td>
<td>44%</td>
<td>19%</td>
<td>13.0</td>
<td>7</td>
</tr>
<tr>
<td>6.9</td>
<td>0.29</td>
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<td>7</td>
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<tr>
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<td>12.3</td>
<td>7</td>
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<td>5.9</td>
<td>0.339</td>
<td>60%</td>
<td>27%</td>
<td>9.4</td>
<td>7</td>
</tr>
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- Fractionation with Increasing CO₂ Pressure
- Similar Curvature, Varying Surface Coverage
  - ↑Surface Coverage = ↑Shell Thickness, ↓Ligand Solvation
- Similar Surface Coverage, Varying Curvature
  - ↑Curvature = ↑Ligand Solvation
**Curvature Effects and Surface Coverage (Determined by SANS)**

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- Thin Film Interparticle Spacing
- Ligand Collapse vs Ligand Interdigitation
Shell Thickness of Dodecanethiol
Prediction of Nanoparticle Dispersion – Interparticle Potential

\[ \Phi_{\text{total}} = \Phi_{\text{vdW}} + \Phi_{\text{Repulsion}} \]

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

*Measured by SANS
Liquid Anti-Solvent Precipitation
- Ethanol
- Requires large amounts of anti-solvent and centrifugation
- Effective for lab-scale volumes

CO\textsubscript{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

*DDS can be substituted for ODS. GNRs stabilized by either ODS or DDS must be co-stabilized by either dodecanethiol or octadecanethiol
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 CO₂-Expanded Solvents

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


100 psi

150 psi

200 psi

250 psi

300 psi

0 psi

100 psi <

250 to 300 psi
NANOPARTICLE SYNTHESIS IN GXL
SURFACTANTS AND REVERSE MICELLES

- AOT: sodium bis(2-ethylhexyl) sulfosuccinate
- Size of Micelle Determined by $W$
  \[ W = \left[ \text{Moles H}_2\text{O} \right] / \left[ \text{Moles AOT} \right] \]
- Act as stabilizing agents until ligand is introduced
**Reverse micelle Nanoparticle Synthesis**

\[ W = \frac{[\text{H}_2\text{O}]}{[\text{AOT}]} \]

- \(W\) = Water
- \(\text{W} = \frac{[\text{H}_2\text{O}]}{[\text{AOT}]}\)

- \(\text{W}\) = Ag Nanoparticle
- \(\text{NaBH}_4\)
- \(\text{AOT}\)
- \(\text{Ag ion}\)
- \(\text{Dodecanethiol}\)

Hexane
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

<table>
<thead>
<tr>
<th>W-Value</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total H$_2$O (mL)</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>0.1M AOT, (mL)</td>
<td>5.55</td>
<td>5.55</td>
</tr>
<tr>
<td>NaBH$_4$, (mL)</td>
<td>0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>AgNO$_3$, (mL)</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>NaBH$_4$ Conc., (M)</td>
<td>0.25</td>
<td>0.1</td>
</tr>
<tr>
<td>AgNO$_3$ Conc., (M)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Metal:NaBH$_4$</td>
<td>0.04</td>
<td>0.04</td>
</tr>
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TEM IMAGES w = 20

A) Ambient

B) 7 bar

C) 14 bar

D) 21 bar
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
RESULTS

![Graph showing particle diameter (nm) vs. pressure (Bar) under w = 20 and w = 40 conditions. The x-axis represents pressure in Bar, ranging from Ambient to 41.4 Bar. The y-axis represents particle diameter in nm, ranging from 3 to 8 nm. The graph includes error bars indicating variability.]

- Pressure values: Ambient, 6.9, 13.8, 20.7, 27.6, 34.5, 41.4 Bar
- Particle Diameter values for w = 20: 6.9, 13.8, 20.7, 27.6, 34.5, 41.4, 5.5 nm
- Particle Diameter values for w = 40: 6.9, 13.8, 20.7, 27.6, 34.5, 41.4, 5.5 nm
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 – Aqueous Tunable Solvents (OATS)

THF + H₂O + CO₂

20 bar CO₂  →  1 bar CO₂

Organic Reactants/Products

Water Soluble Catalyst Ionic Reactant
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

Diameter = 8.41 ± 0.99nm
Median = 8.51 nm
1690 Particles Counted

TEM Image

Scale: 20 nm

Frequency

Diameter (nm)
**SMALL-ANGLE NEUTRON SCATTERING (SANS) INTRODUCTION**

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

<table>
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<th>Material</th>
<th>SLD (Å⁻²)</th>
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<tr>
<td>Gold</td>
<td>4.50E-06</td>
</tr>
<tr>
<td>Dodecanethiol</td>
<td>-3.67E-07</td>
</tr>
<tr>
<td>1-Octadecanethiol</td>
<td>-3.49E-07</td>
</tr>
<tr>
<td>n-hexane, d14</td>
<td>6.14E-06</td>
</tr>
<tr>
<td>n-hexane</td>
<td>-5.71E-07</td>
</tr>
<tr>
<td>toluene, d8</td>
<td>5.66E-06</td>
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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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![Image of nanoparticles and histogram](image-url)
Diameter of Silver Nanoparticles vs CO$_2$ Composition
Shell Thickness of Dodecanethiol
DODECANETHIOL LIGAND SOLVATION

Fraction of Solvent in Shell

CO₂ Solvent Composition

- 5.9nm NIST
- 6.6nm NIST
- 6.9nm ORNL
- 7.1nm ORNL