



Structural characteristics of crosslinked gold nanoparticle networks formed at an air-water interface



Tayo A. Sanders II, Mariah N. Saucedo, & Jennifer A. Dahl
Materials Science ❖ University of Wisconsin-Eau Claire

Abstract

The structural dynamics of thin films of surfactant molecules can be characterized by their behavior in a Langmuir trough, where the molecules reside at the air-water interface. Parameters such as molecular order, film density, and surface pressure are easily addressed, and multilayer superstructures can be fabricated using this classic surface science strategy. Less common is the use of a Langmuir trough for the fabrication of organized two-dimensional arrays of alkanethiol-capped gold nanoparticles. Here, hydrophobic nanoparticles are introduced to the air-water interface as a solution in hexanes; as the solvent evaporates, the floating nanoparticles can be compressed into a monolayer within the Langmuir trough. Preliminary studies have explored the relationship between film morphology and the length of the hydrocarbon chain; it has been found that nanoparticles functionalized with alkanethiols having chain lengths < C16 form poorly organized films with low collapse pressures. We are reporting the use of a dithiol crosslinking ligand to improve film morphology. We have found that the addition of alkanedithiols prior to film compression yields covalently bound soft networks of nanoparticles with greatly improved collapse pressures, evident by Langmuir isotherm measurements and structural analysis of the films by transmission electron microscopy.

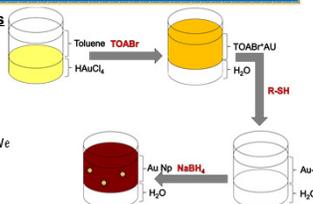
General Synthetic Scheme

B Brust synthesis of 4 nm Au cores

- Nanoparticle size is dependent upon the thiol: gold ratio.
 - Chain lengths vary from C₆-C₁₈
 - Nanoparticle size: 3-8 nm

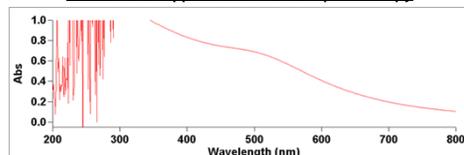
Extensive purification required

- Elimination of excess thiol and phase transfer reagent is key to isolating the surface effects of the nanoparticles. We employ the method of Soxhlet extraction for this purpose.



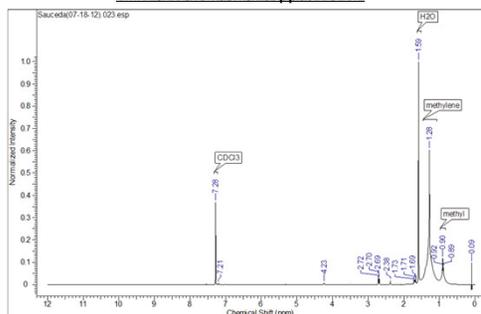
Nanoparticle Characterization

Hexanethiol-capped Au-NP UV-Vis Spectroscopy

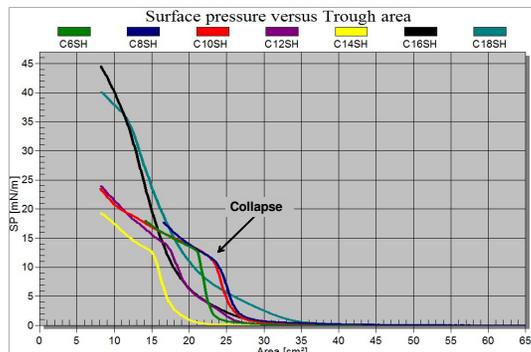


- Peak at ~522 nm consistent with average core diameter of 4 nm.
- Absence of peaks at ~650-700 nm indicates little aggregation in solution.
- Average core size confirmed by transmission electron microscopy (TEM).

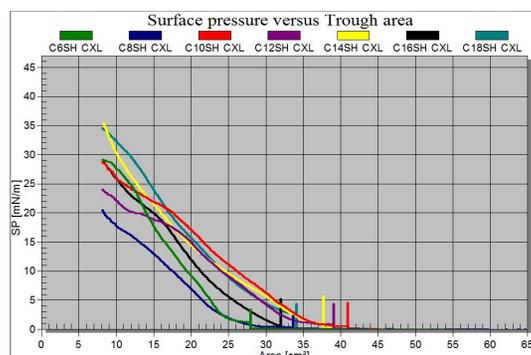
NMR of Hexanethiol-capped Au-NP



Impact of Crosslinking



Collapse for C₆, C₈, C₁₂, and C₁₄ occurred at a surface pressure of approximately 13mN/m while C₁₆ and C₁₈ collapsed at approximately 37mN/m. At room temperature C₆ – C₁₄ ligands exist in a fluid state due to their lower glass transition temperatures, resulting in low collapse pressures.

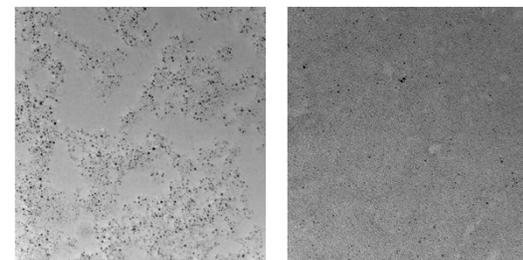


Collapse Pressure Comparison

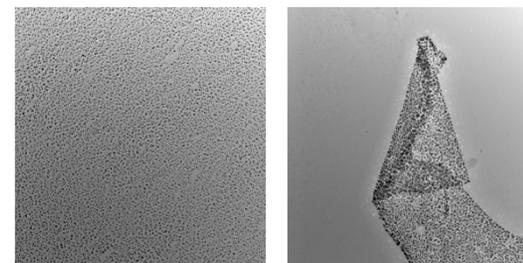
	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈
Original Collapse Pressure (mN/m)	13	11	12	14	12.5	34	36
Collapse Pressure with Linker (mN/m)	25	17	20	18	24	18	30
Δ Collapse Pressure (mN/m)	+12	+6	+8	+4	+11.5	-16	-6

Utilizing a 12 chain dithiol linker significantly increases the nanoparticle film collapse pressure in all cases except C₁₆ and C₁₈. Here, the rigid ligand shell does not allow crosslinking to occur with a linker of only 12 carbons.

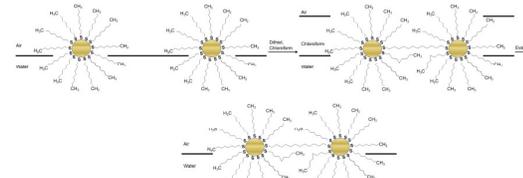
TEM Analysis



Analysis of Au nanoparticle deposition onto TEM grids shows both close packed and spacious "foam" arrangements. Greater consistency of the close packed film morphology can be obtained by isometric compression of the barriers to maintain surface pressure during deposition.



TEM images of C₆SH-capped Au nanoparticles with crosslinker reveal the formation of a densely packed film morphology. The flexibility and structural integrity of the film suggest successful crosslinking of the film.



Dithiol linkers lock nanoparticles in a more rigid arrangement that is held together by covalent bonds rather than Van der Waals interactions alone. This prevents diffusion of particles into nonpolar solvents and allows the particles to remain at the polar/nonpolar liquid interface. Because C₆-C₁₄ have T_m values below room temperature, the disordered chains can freely rotate. As a result, a linker needn't span twice the length of the ligand shell. A 12 chain dithiol linker can successfully connect two C₁₄SH-capped nanoparticles.

Acknowledgments

- WiSys Technology Foundation Prototype Development Fund
- WiSys Technology Foundation Applied Research Grant
- University of Wisconsin-Eau Claire Materials Science Center
- Wisconsin Alliance for Minority Participation
- Transmission Electron Microscopy - Dan Decato and Annie Laskowski, UWEC