Examining the Structure of Gold Nanoparticle Monolayers Based on Variable Dodecanethiol Concentration

Ariana Correia[1], Samuel Darr[1], Amber Dellacqua[1], Darshan Desai[1], Parita Shah[1], Shraddha Zina[1], Wayne Oras[1], Mrinal Kanti Bera[2], Wei Bu[2], Morgan Reik[2], Jake Walsh[2], Binhua Lin[2], Elena Shevchenko[3]
[1]Hoffman Estates High School, Hoffman Estates, IL 60169, [2]NSF's ChemMatCARS, University of Chicago, Chicago, IL 60637, [3]Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL 60439

Abstract

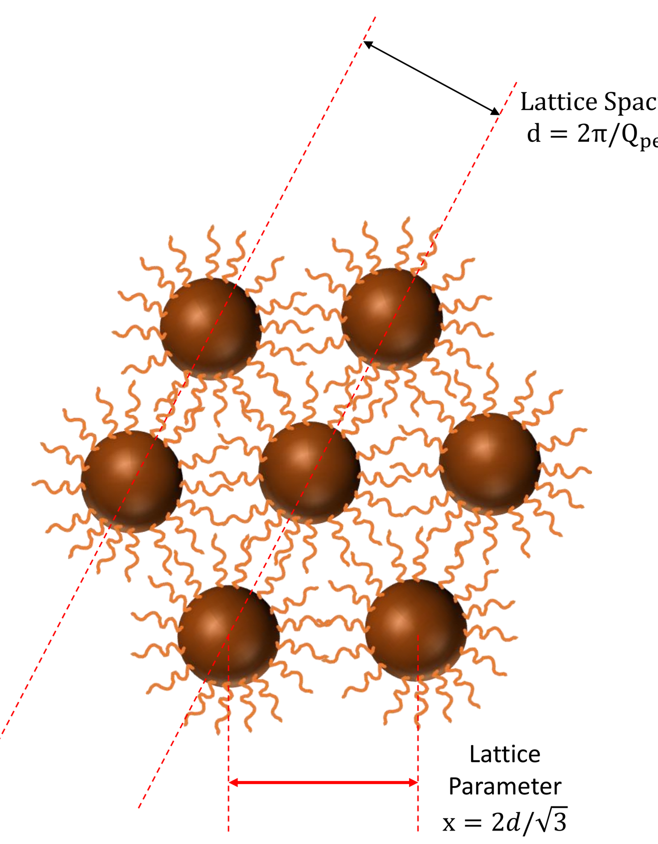
It is imperative to understand how nanomaterials and nanoparticles respond to changes in their environments. Inorganic nanoparticle (NP) films have a wide range of applications that involve sensors, transistors, photovoltaic cells, and filtration devices; however, their assembly is still being explored. NP films have unique properties that include superparamagnetism, surface plasmon resonance and quantum confinement. Analyzing the properties of self-assembled nanoparticle films and tunable nanoscale crystal structures will open up mankind to a series of inventions and innovations in the field of materials science and nanoelectronics.
Our objective is to observe how variable dodecanethiol concentration affects the structure of Gold nanoparticle monolayers. Understanding the structures of NP arrays will provide more information regarding NP monolayers as well as plasmon response changes. Data regarding surface coverage is key in the development, manufacturing, quality control and regulatory approval of nanobiomaterials for therapeutic use. Furthermore, surface coverage measurements will aid in the ability to predict the behavior and long-term impacts of nanomaterials.

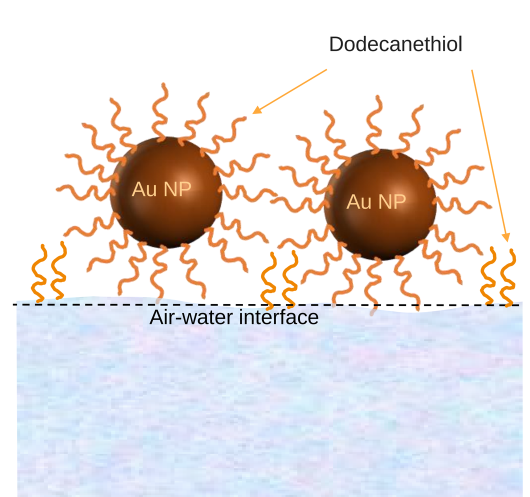
Background

Studies have shown that the presence of dodecanethiol can increase the stability of Gold nanoparticle films. Specifics on how dodecanethiol concentration affects the structure and stability of Gold nanoparticles enables a greater understanding of nanoparticle film structures and open up a variety of possible uses.

Grazing Incidence Diffraction (GID) is a technique used to examine the change in interparticle spacing formed by the interactions between crystalline structures. Reflectivity scans are collected from nanoparticle interfaces based on reflected X-ray intensity beams as a function of different incident angles.

Observing the effect of variable dodecanethiol concentration on in-plane structures using GID in combination with reflectivity analysis will facilitate a greater understanding of the film structure's optical properties and the electron density of Gold nanoparticles.





Nanoparticle interaction at the liquid-surface interface

Intensity peaks in the GID plots correspond to Lattice Spacing (d).

The Lattice Parameter (x) can then be determined.

Images courtesy of Mrinal Kanti Bera, NSF's ChemMatCARS, University of Chicago

Goals

- Observe the packing of Gold nanoparticle films with variable dodecanethiol concentrations.
- Determine the relationship between dodecanethiol concentration and nanoparticle superlattice structures.

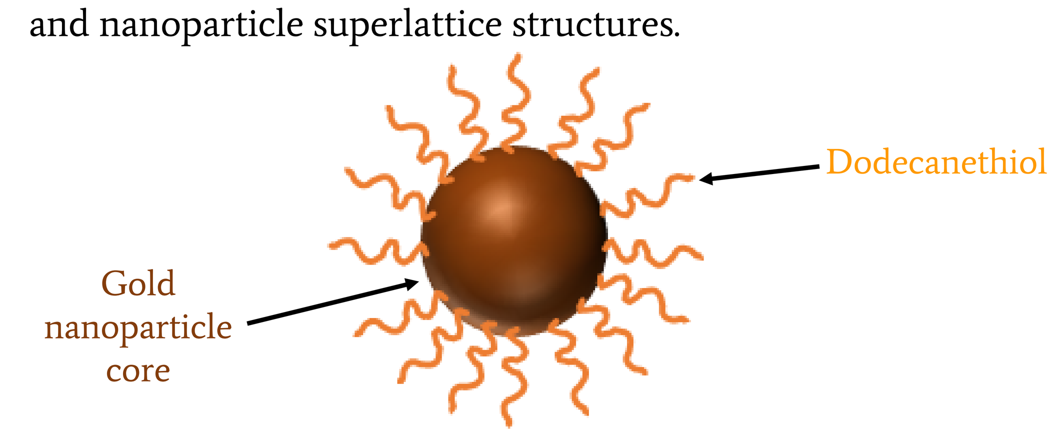
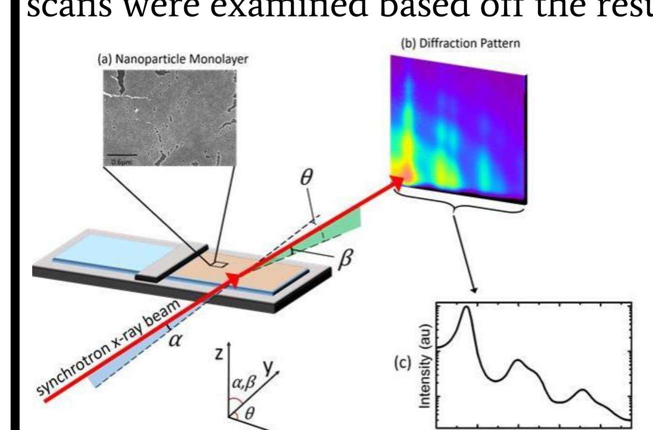


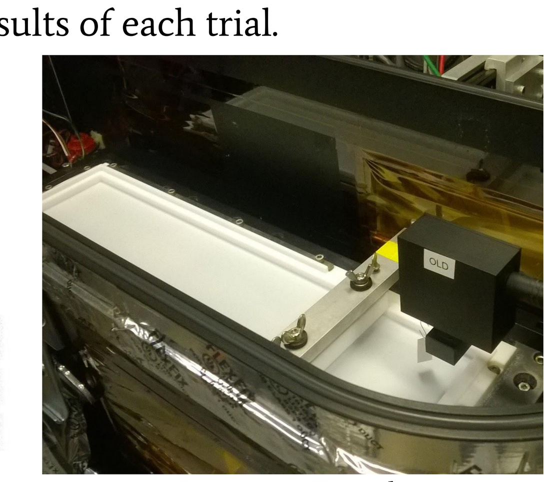
Image courtesy of Mrinal Kanti Bera, NSF's ChemMatCARS, University of Chicago

Sample Preparation Procedure

Gold nanoparticle samples with varying concentrations of dodecanethiol were deposited on the water surface. The Langmuir trough was first cleaned with chloroform and then used to increase surface pressure, causing in and out plane packing of the nanoparticles. GID was then used to measure the in-plane structure of the gold nanoparticles. Gold nanoparticles and their respective dodecanethiol concentration amounts were filled into syringes and deposited into the trough for each trial. Through computer software, GID and reflectivity scans were examined based off the results of each trial.

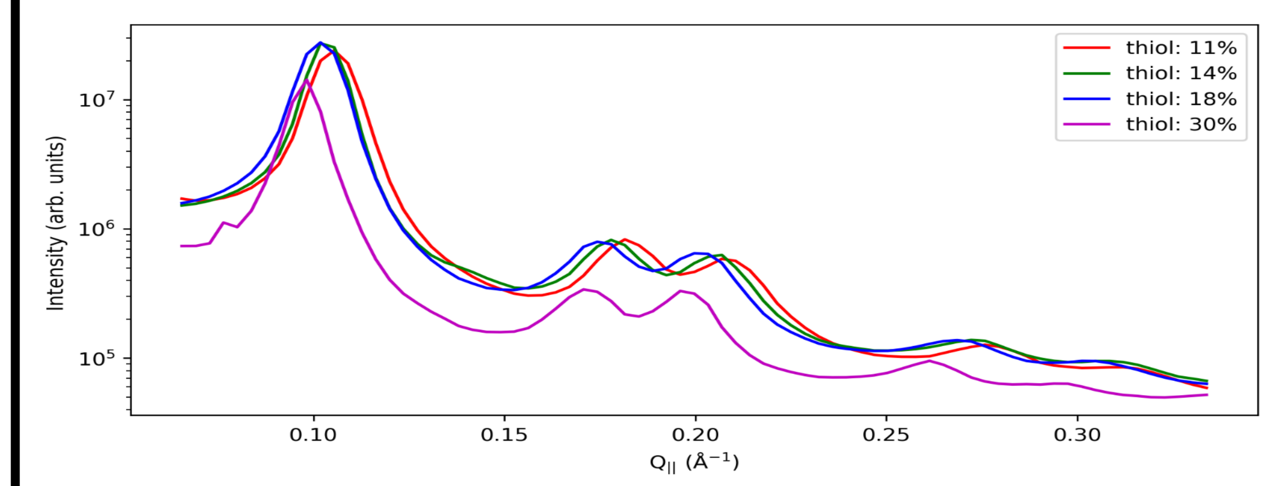


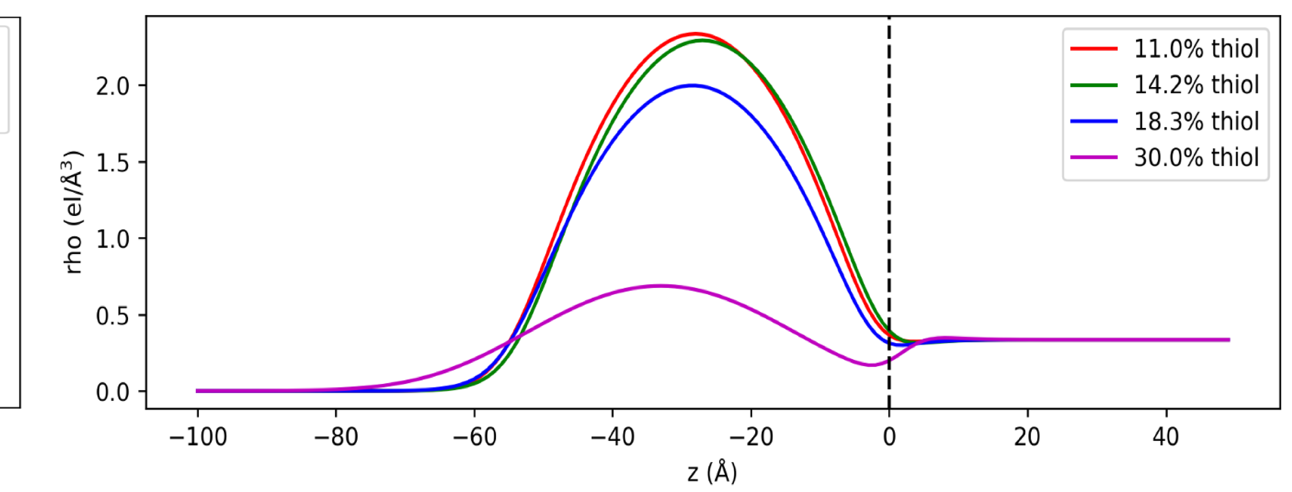
Schematic of Liquid Surface X-ray Scattering
Image courtesy of Dr. Leandra Boucheron, University of New Mexico.



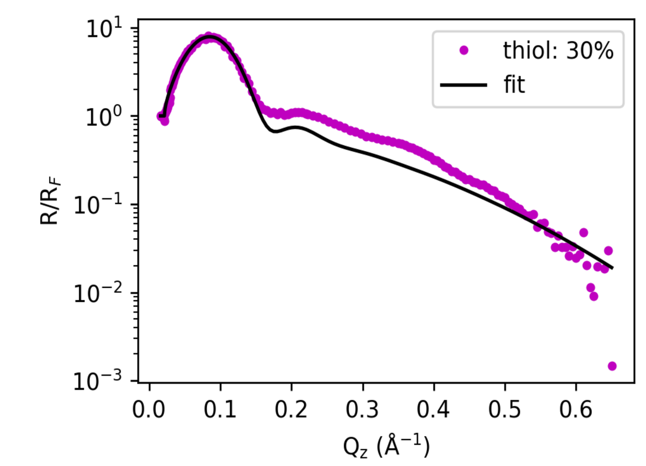
Langmuir Trough
Image courtesy of Wayne Oras, Hoffman Estates High School.

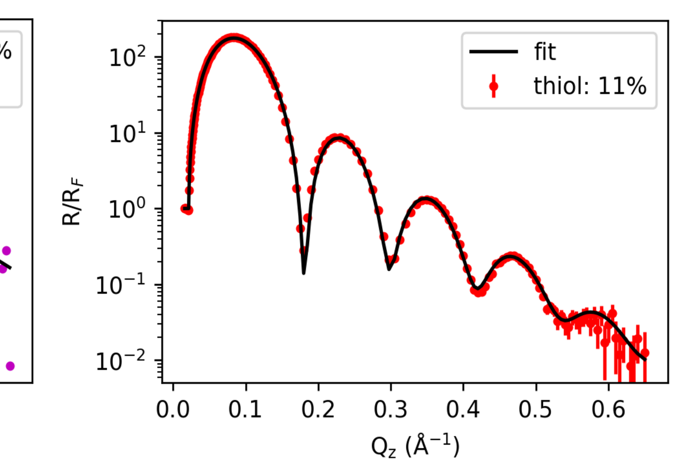
Results





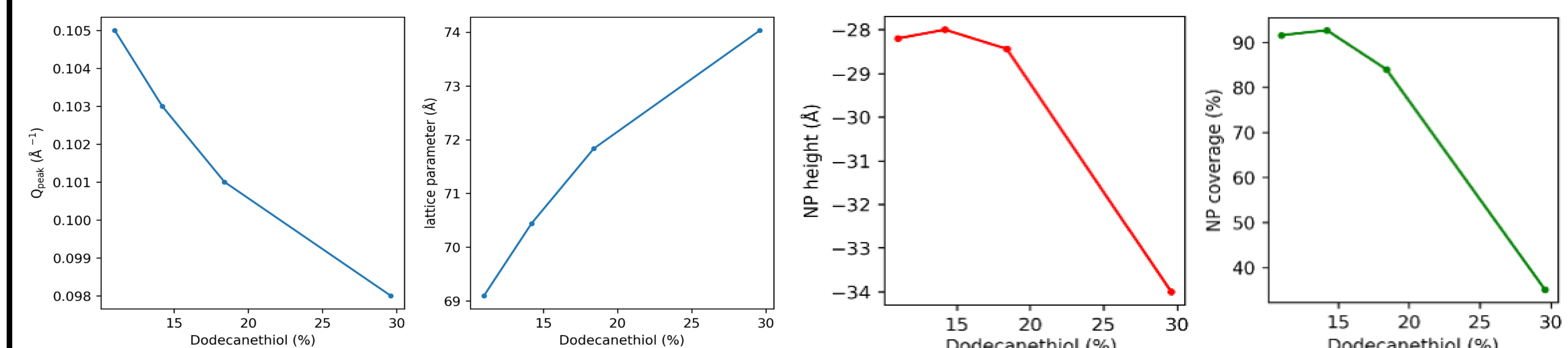
The results from GID analysis above show the peaks shifting toward lower Q values as the dodecanethiol concentration is increased, though it was observed that it remained a hexagonal lattice. An increase of ligand coverage inhibits the free movement of dodecanethiol and hence makes them rigid, which is directly proportional to the increased distance between the particles and the lattice parameters. Accordingly, with less ligands attached to the particle, the solution is less dense. Therefore, by changing the ligand concentration, we can directly change equilibrium coverage.





The dramatic decrease in NP coverage with an increase of ligand concentration is due to the greater availability of free dodecanethiol in the solution. Since the ligands covered a significant amount of the air-water interface, the nanoparticle coverage is reduced and the dodecanethiol coverage is increased.

The patterns obtained from the reflectivity scans, as shown above, produce oscillations of Q that provide information concerning electron density. From analyzing these profiles, it can be concluded that the height of the nanoparticles between the air-water interface increases and is proportional to dodecanethiol concentration.



Images coutesy of Dr. Mrinal Kanti Bera and Dr. Wei Bu, NSF's ChemMatCARS, University of Chicago

Conclusions

- The concentration of dodecanethiol in a nanoparticle solution is a critical factor in varying lattice parameters.
- Change in dodecanethiol concentration is directly related to interparticle spacing.

Future Directions

The ability to fine-tune properties of self-assembled nanostructures will continue to be a leading goal of materials science research.

Further research must be done to better understand the interaction of ligands and nanoparticles during the self-assembly process as well as the effect that it has on nanostructure.

Acknowledgements

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