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Synthesis of AuNP with the use of Bunte Salts

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Introduction:

Gold nano-particles (GNP) have a diverse range of application. From medical to optics, GNP are part of the latest and most advanced research. The role GNP takes determined by its functionality. This functionality can be a diverse array of compounds which are attached to the GNP via a Thiol group. For many years the major method for producing these particles has been the Brust Prep. Though this method is cheaper and more efficient than previous methods, it is our belief that a more productive method is to be found with the use of Bunte Salts ($RS_2O_3Na^+$).

Procedure:

Synthesis of the Bunte Salt:

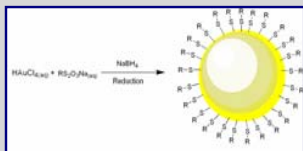
Before synthesizing the AuNP we must create the bunte salt. The reaction below was prepared in an aqueous solution and refluxed. We proceeded to rotovap the solution and pressure vaporize to ensure a dry product. The final product was washed with ethanol on a frit with the purpose of removing NaBr. A final analysis of the crystal product was done with ^1H-NMR .



Synthesis of AuNP:

The actual synthesis of the particles was done using a standard hutch lab procedure:

For the experiments discussed we used the bunte salt analog of the Mercaptohexanoic Acid



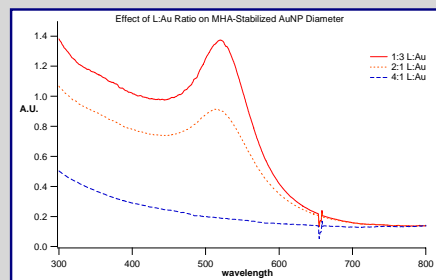
How Do Various Experimental Parameters effect the core diameter of AuNP?

Ligand to Gold Ratio:

Solutions were prepared using 1:3, 2:1, and 4:1 ligand to gold ratios. The spectrum to the right is the UV-Spectrum of the different solutions.

The peak in the middle indicates the particles plasmon. We can decipher whether the particles are large or small, but not the size. The absorbance of Smaller particles will more blue shifted from that of bulk gold than the larger particles.

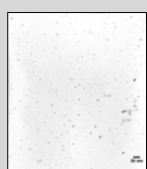
We found that the largest particles were produced by the solution using a 1:3 L: Au, whereas the 4:1 produced the smallest.



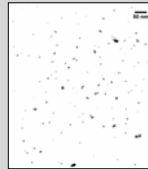
Conclusion: The higher L: Au ratios produce smaller particles than those with lower ratios. This is explained by the fact that excess ligand enables the reduced gold to be passivated before they are able to extensively congregate.

Temperature:

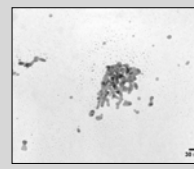
When looking at the cores dependance on the temperature in which the reaction takes place, we found it necessary to run the reaction at an even L: Au ratio. when ran with a high L: Au, the size distribution of the iced and the room temperature batches overlap. For this reason we ran these experiments at a 2:1 L: Au and reductant: Au ratio. The reductant was added using a .10 M solution a $NaBH_4$. As you can see the hot water batch produced particles which we were unable to run a proper size analysis on. The picture shows and aggregated cluster of AuNP.



Ice bath
 $d_{core} = 3.9 \pm 2.0$ nm



RT (old sample)
 $d_{core} = 6.5 \pm 3.1$ nm

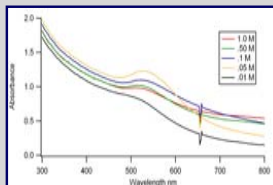


Hot water bath

Conclusion: Core size is proportional to temperature. This is due to the change in the leave to stay rate of the passivating ligand. At higher temperature there is more energy in the solution, enabling the ligand to dissociate from the Au. Thus allowing the Au to further congregate.

Rate of Reduction:

To control the rate of reduction we used various concentrations of reductant. We prepared 5 solutions prepared using reductants of various concentrations and ran them through UV-Vis analysis to determine the trend.

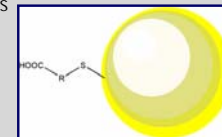


The particles generally increase in size as the concentration decreases. The only deviation we find is that of the .01 M solution and there are two possible explanations for this. First, since the solution is so dilute the reduction is occurring at a slow rate. This lowers the amount of particles that are reduced and thus the ability for them to aggregate before passivation.

Conclusion: more concentrated solutions produce smaller particles. Further more the more equivalents of reductant you add, the smaller the particles will be.

Ligands:

Ligands passivate the reduced gold atoms. Once completely shelled by the ligand core growth come to a halt. The ligand is where you will find the functionality (COOH), which determines what the Nanoparticles are used For.

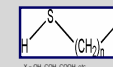


Core diameter is thus depended on the competition of two separate reactions. The reduction of the Au (and thus the conjugation of Au) and the passivation of these particles by the ligand

Why Bunte Salts:

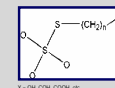
Thiols:

- Hard to store
- Narrow core diameter, 1.5-5.2 nm (Brust Prep.)*
- Multi-step organic synthesis



Bunte Salts:

- Easily stored
- Wide core range
- One step aqueous synthesis.



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References:

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