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Chem 69a

Lab 4

Gold Nanoparticle Synthesis

Experimental

Materials:

Synthesis A:

- Au(III) chloride hydrate
- Tri-sodium citrate
- Ultra pure water

Synthesis B:

- Au(III) chloride hydrate
- Tetraoctylammonium bromide
- Dodecanethiol
- NaBH₄
- Toluene
- EtOH
- DI water

Procedure A:

1. Boil 10 mL of 1 mM aqueous 30 mM HAuCl₄ using maximum heat setting. Add 1 mL of 38.8 mM aqueous tri-sodium citrate while stirring vigorously. The citrate salt acts as a reducing agent, changing Au(III) to Au metal as the reaction proceeds. The Au atoms eventually reach a supersaturation point as their concentration increases in solution; when this occurs, the Au atoms form into nanoparticles via a nucleation process.
2. Boil the solution for 15 minutes and observe a color change from yellow, to blue, to red. The red color indicates the presence of gold nanoparticles.
3. Remove solution from heat and add to 5 mL ice water, then centrifuge (in a 10 cm radius, 4000 rpms centrifuge, 1788.8 Gs applied) for 15 minutes. Wash particles twice with water centrifuging for 15 minutes after each wash.

Observations A:

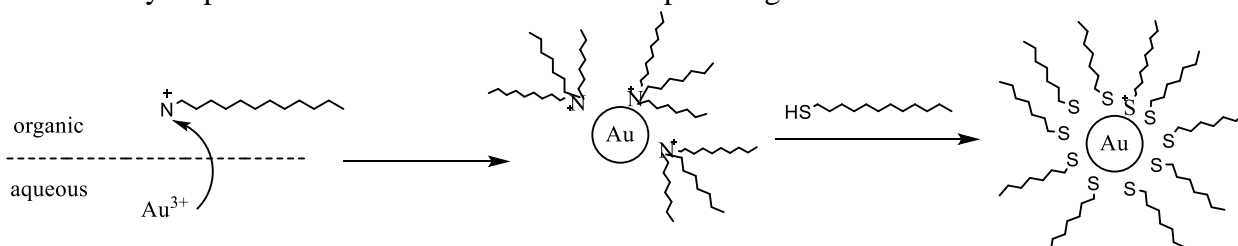
1. HAuCl₄ is clear, light yellow solution
2. Au solution is clear and light blue after 1 min of heating
3. Soln light brown after 5 min of heating
4. Soln light orange after 8 min of heating

- Soln light yellow after 10 min of heating
- Citrate solution is clear and colorless liquid
- Addition of citrate solution turned Au solution dark, clear purple
- Ruby red color was not observed- purple still indicated presence of nanoparticles
- Solution was clear, purple when put in centrifuge
- Very small amount of dark purple precipitate remained on bottom of centrifuged tube after washing

Procedure B:



- Prepare aqueous solution of NaBH_4
- Mix 15 mL, 30 mM aqueous HAuCl_4 with tetraoctylammonium bromide in toluene (40 mL, 50 mM). The ammonium in the organic layer draws the Au ions out of aqueous solution, creating a hydrophobic layer of hydrocarbon chains suspending the Au particles.
- Stir the two phase mixture vigorously until the organic phase becomes red and aqueous phase is colorless
- Add 85 mg of dodecanethiol to the organic phase. The thiol suspends the gold nanoparticles in organic solution as the polar heads are attracted to the gold particles, while the hydrophobic tails are attracted to the non-polar organic solution.

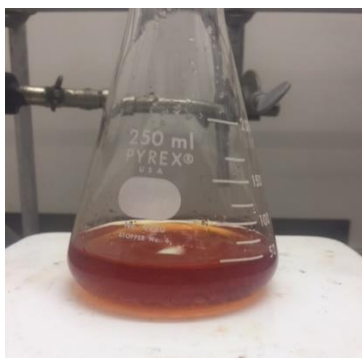


- Add 12.5 mL of NaBH_4 solution dropwise to organic solution while stirring. NaBH_4 acts as the reducing agent, reducing the Au^{3+} to Au(metal) throughout the reaction.
- Stir mixture for 2.5 hours
- After stirring, remove organic phase and reduce volume to 10 mL in rotovap
- Transfer concentrated solution with 200 mL ethanol to beaker and leave at -18°C for 1 week
- Upon return, filter off dark precipitate and rinse with 50 mL of toluene to redissolve precipitate. Toluene dissolves the nanoparticles due to the hydrophobic thiol coating, allowing them to be cleaned again when re-mixed with ethanol.
- Mix toluene soln with another 200 mL ethanol to re-precipitate the nanoparticles, then filter again.

Observations B:

- NaBH_4 is white powder, aqueous soln is clear and colorless
- HAuCl_4 is clear and light yellow liquid

3. Addition of toluene to Au solution turns solution dark red/orange



4. Tetraoctylammonium bromide is a white, flaky crystal, aqueous soln is clear and colorless
5. Addition of tet. Br solution turns Au soln to light yellow (from dark red), then almost clear
6. Addition of NaBH_4 immediately turns solution dark brown, then black



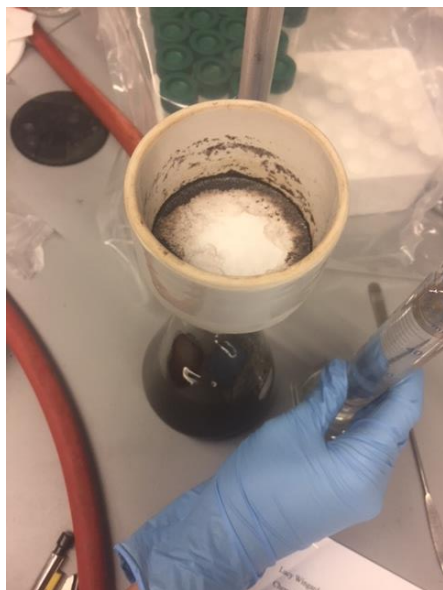
7. Solution dark black and slightly viscous after rotovap



8. Solution had no change in appearance over week in freezer
9. Precipitate is black, leaving clear and colorless filtered soln



10. Addition of toluene redissolves precipitate, turning soln dark grey



11. Many particles remain in solution after filtering- nanoparticles are too small for the pores of this filter paper and easily pass through

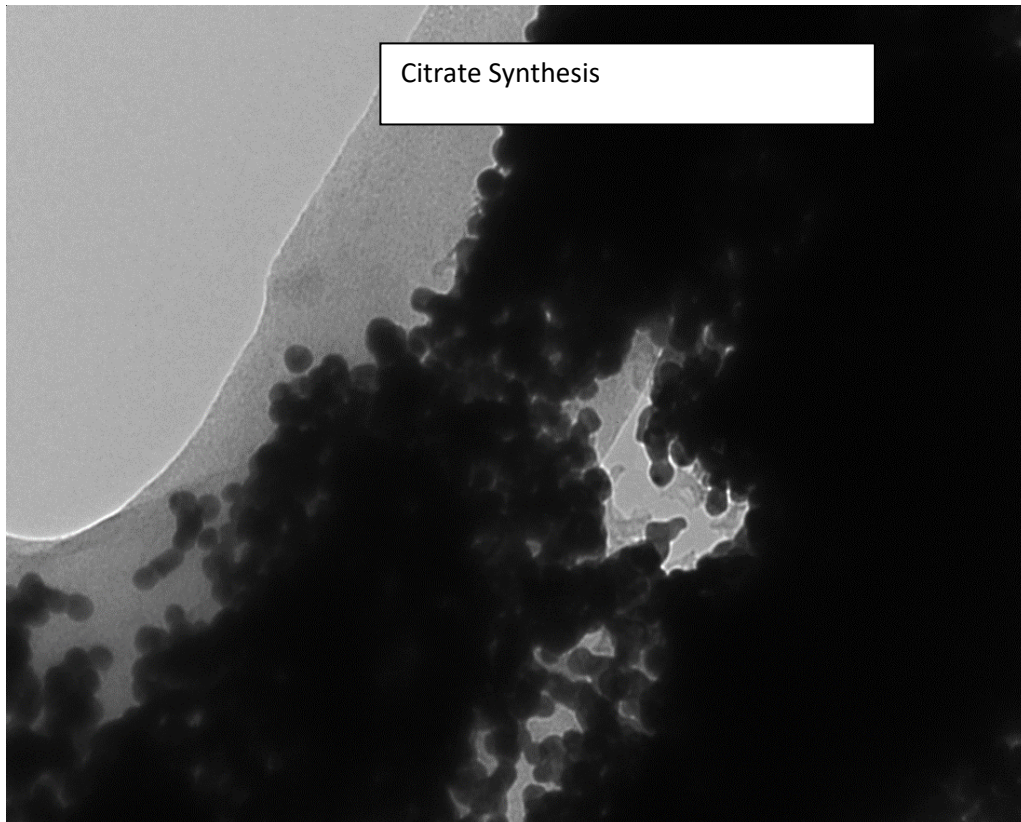


Results & Discussion

Gold nanoparticles can serve a variety of functions dependent on their size; during this lab we followed two synthesis routes and used TEM imaging to compare the sizes produced. In the first procedure, we used citrate reduction to synthesize the nanoparticles. When examining the particles under TEM imaging, we see heavy clustering (as indicated by the dark circular clusters) of particles on the 100 nm scale. The heavy clustering matches what was expected based on the color of the nanoparticles; while red particles would have aligned with smaller nanoparticles (less clustering i.e. nucleation), purple particles indicate slightly larger clusters, evident in the TEM image.

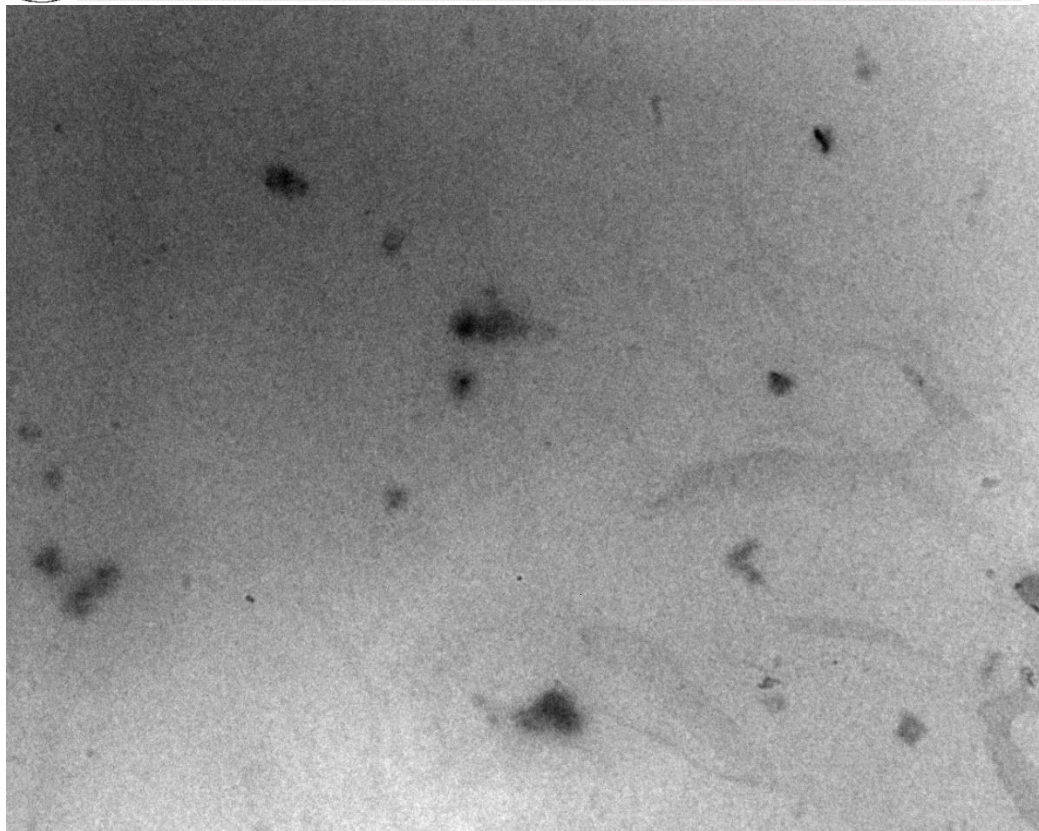
In procedure B particles were synthesized via NaBH_4 reduction, with a suspension in the organic phase by attachment of thiol tails. The resulting precipitate was not red, as predicted, but grey/dark black; this indicated that the nanoparticle synthesis did not create particles of the expected scale (as red correlates with smaller particles). Examination under TEM shows sparse individual particles without clustering at the 500 nm scale. This indicates error throughout the experiment; possibly an incorrect molar ratio of thiol was used in reaction, limiting the number of particles that could have ultimately been reduced.

Citrate Synthesis



bing xu.24937
Gold1
Print Mag: 298000x @ 7.0 in

100 nm
HV=80.0kV
Direct Mag: 36000x
AMT Camera System



bing xu.24950
Gold2
Print Mag: 44300x @ 7.0 in

500 nm
HV=80.0kV
Direct Mag: 5600x
AMT Camera System

Conclusion

This lab examines the synthesis of gold nanoparticles through two synthetic routes: citrate and sodium borohydride reduction. This exploits the useful property of gold nanoparticles; that their size can be easily controlled via different synthesis routes. Along with an easy synthesizability, this lends gold nanoparticles many uses and applications in biotechnology. For instance, gold nanoparticles can be conjugated with a variety of biological molecules, including DNA, some sugars, and some proteins. Because these nanoparticles are visible under various imaging techniques, they can be delivered alongside these biological molecules and then their movement/bonding tracked. This lends great insight into pathways and functions of various biomolecules. Additionally, gold nanoparticles can be used to transport drugs through targeted delivery methods, which can be relatively easily controlled based on the well-established properties of gold nanoparticles at different sizes and shapes. Furthermore, because of their established color-size dependency, gold nanoparticles offer an interesting material for optic research.