Preparation of Gold Nanoparticles in Novel Thioether-Functionalized Ionic Liquids

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Introduction

- Gold nanoparticles have found a range of applications in the biomedical field as chemical and biochemical sensors, which take advantage of the nanoparticles' plasmonic properties
- The project looks at optimizing the synthesis, synthetic reproducibility, and isolation of the gold nanoparticles prepared with these novel thioether-functionalized ionic liquids.
- The reaction was followed with UV-visible spectroscopy, and the nanoparticles were characterized using scanning electron microscopy with energy-dispersive X-ray.

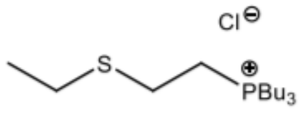

Figure 1. 2-(ethylmercapto)ethyl-tributylphosphonium chloride

Research Goals

- Lack of stability can result in the formation of bulk metal when preparing and isolating these nanoparticles.
- Focusing on the molar ratio, reaction time, and reaction conditions can heavily impact the reaction outcome and help avoid the formation of bulk metal.
- Goal is to develop an efficient and reproducible method to prepare and isolate these nanoparticles.

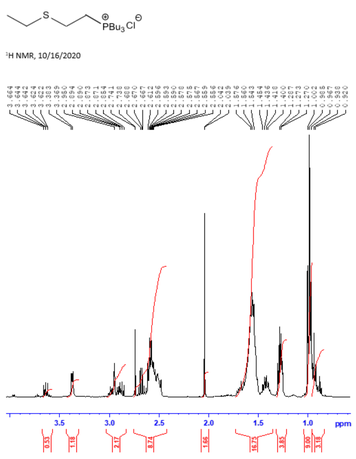

Figure 2. ^{1}H NMR of 2-(ethylmercapto)ethyl-tributylphosphonium chloride

Methods

- $HAuCl_4$ stock concentration 3.0*10^{-3} M, 100 mL, stored chilled
- IL-2 stock solution concentration 20*10^{-3} M, 100 mL, stored on benchtop
- $NaBH_4$ stock solution made with 0.003 – 0.007 g solid $NaBH_4$ in 25 mL water
- Nanopure water is only water used; glassware is inspected for scratches
- Starting concentrations for $HAuCl_4$ and IL-2: 0.762mM; $NaBH_4$ used in changing ratio
- Each reactant is added in its specific concentration to an individual 10 mL volumetric flas
- Add stir rod and 10 mL gold solution to 100 mL beaker, start plate at 220 RPM.
- Then add IL-2 dropwise over 80 seconds
- Turn down RPM to 200 RPM. Immediately add $NaBH_4$ dropwise over 75 seconds
- Stir until bubbling subsides, about 15 minutes
- Continue stirring an additional 10 minutes
- Take UV Visible spectrum of reaction mixture immediately after the reaction and after 7 days

Results

- Molar ratio of 1.1.1 ($HAuCl_4$: IL-2: $NaBH_4$) presented a better data set compared to molar ratios of 1.1.2, or 1.1.4
- Bulk metal was formed with higher concentrations of $NaBH_4$
- The 1.1.1. molar ratio displayed a more narrow peak for the gold nanoparticles compared to the other ratios tested.
- After 7 days, the peak showed a higher absorbance than in the freshly made nanoparticle solution.
- Bulk metal appeared to form after the seven day period, yet the peak for the gold nanoparticles had increased drastically.

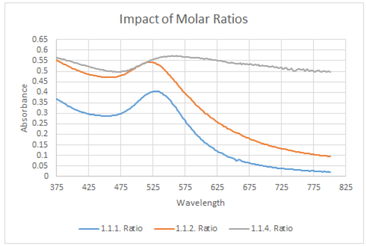

Figure 3. Impact of molar ratios as shown by UV Vis spectra

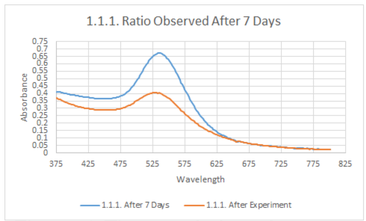

Figure 4. Time evolution of the UV Vis spectrum from the 1.1.1. molar ratio

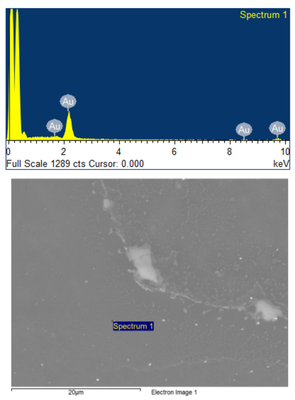

Figure 5. SEM and EDX of the reaction mixture at a 1.1.1. molar ratio

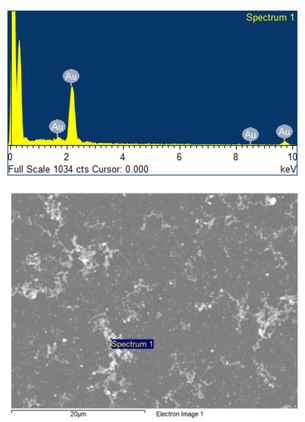

Figure 6. SEM and EDX of the 1.1.1. reaction mixture centrifuged for 20 min then redispersed in nanopure water

Discussion and Conclusions

- A higher concentration of $NaBH_4$ in solution gave a more convoluted data set for the UV Vis spectra, as more bulk metal was found in solutions with a higher concentration of $NaBH_4$.
- An extended period of time spent in the refrigerator gave rise to a more narrow peak for the gold nanoparticles, in addition to a higher absorbance.
- Over time, more bulk metal formed in solution regardless of the temperature at which it was kept, but when taking UV Vis spectra, we took care to collect the solution without bulk metal.
- Variability in nanoparticle formation seen after time spent in the fridge could possibly be used in the future as a form of moderation of nanoparticle synthesis.
- Observations were also made to optimize the amount of time spent stirring the reaction mixture in the beaker: The longer we had the solution under stirring, the more bulk metal would form. With shorter times of stirring of the solution, less bulk metal formed and a narrower peak was observed in the UV Vis spectrum.
- We believe time plays a part in the formation of nanoparticles, but we are still isolating variables, i.e. time in cooler temperatures, light exposure, and cooler temperature vs. room temperature.

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References

Games, Joie, "The Synthesis and Characterization of Gold Nanoparticles Prepared with Novel Thioether- Ionic Liquids" (2020). Master's Theses. 167.
https://digscholarship.unco.edu/theses/167