Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Gold Nanoparticle Microwave Synthesis

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Abstract

At the nanometer scale, numerous compounds display different properties than those found in bulk material that can prove useful in areas such as medicinal chemistry. Gold nanoparticles, for example, display promise in newly developed hyperthermia therapies for cancer treatment. Currently, gold nanoparticle synthesis is performed via the hot injection technique which has large variability in final particle size and a longer reaction time. One underdeveloped area by which these particles could be produced is through microwave synthesis. To initiate heating, microwaves agitate polar molecules creating a vibration that gives off the heat energy needed. Previous studies have used microwaves for gold nanoparticle synthesis; however polar solvents were used that partially absorbed incident microwaves, leading to partial thermal heating of the sample rather than taking full advantage of the microwave to solely heat the gold nanoparticle precursors in a non-polar solution. Through this project, microwaves were utilized as the sole heat source, and non-polar solvents were used to explore the effects of microwave heating only as pertains to the precursor material. Our findings show that the use of non-polar solvents allows for more rapid heating as compared to polar solvents, a reduction in reaction time from 10 minutes to 1 minute, maximizes the efficiency of the reaction, and allows for reproducibility in the size/shape of the fabricated nanoparticles.

Introduction

Many small chemical compounds can display multiple interesting properties at the nanometer scale compared to that of the bulk material. This is due to the larger surface area, and the fact that many biological processes occur at this small scale. Gold nanoparticles (GNP) specifically have displayed promise in hyperthermia treatment for cancer due to their ability to absorb infrared light. These nanoparticles can play a role in catalysis and are cheaper than the platinum alternative. With this need for gold nanoparticles, various ways to synthesize them have been studied. The most common method, the Turkevich method involves hot chloroauric acid and trisodium citrate which acts as a reducing agent. On average, the Turkevich method takes 10 minutes to produce monodisperse spherical particles. These particles range in size of 10-20 nm in diameter [J. Phys. Chem. C 111, 6281-6287,(2007)]. While this method is fairly simple, it can be difficult to reproduce consistent particles with identical shape and size. In addition, this method depends directly on the scientist executing the reaction, and can therefore vary from person to person. The speed and point during the reaction in which the chloroauric acid is injected, can both result in varied final particles as well.

Another commonly used method for gold nanoparticle synthesis is the Brust method. This method is best for reactants that aren't soluble in water. In this reaction, chloroauric acid, tetraoctylammonium bromide (TOAB), and sodium borohydride are combined in toluene. Just like the

Turkevich method, the chloroauric acid provides the gold cations, while TOAB acts as an anti-coagulant and sodium borohydride the reducing agent. Since TOAB acts as an anti-coagulant, it is important that it does not bind too tightly or else the final particles will aggregate too slowly and the reaction can take up to weeks. This is prevented by the addition of a thiol which protects the gold from binding too tightly to the TOAB. The Brust method yields very small nanoparticles with a diameter size of 5-6 nm [Chem. of Mater. 15, 20-28, (2003)].

One minimally to unexplored method for gold nanoparticle synthesis that has potential to yield more consistent results is via microwave synthesis. Utilizing the microwave requires a closed system and therefore eliminates heat loss and variation in injection rate. In addition to consistency, the microwave can heat and cool faster thus improving the reaction time and maximizing throughput.

Microwaves heat compounds by agitating the polar molecules (i.e. water) in the complex. This agitation then creates a vibration that produces heat waves. Therefore, polar compounds heat very rapidly while non-polar compounds heat tremendously slower. Through this project, scientists utilized microwaves to heat the precursor gold nanoparticles to synthesize the final desired nanoparticle product. In order to make the reaction as efficient as possible and not lose any heat energy, non-polar solvents were explored. By using a non-polar solvent rather than polar, ideally the only thing being heated would be the reactants, thus no heat would be absorbed by the solvent. This method almost combines both the Turkevich and Brust methods by using trisodium citrate as a reducing agent and an organic non-polar solvent rather than water.

Experimental

All reactions were executed using a Discover CEM SP microwave (Figure 1.). To begin this project, preliminary solubility tests were performed in the microwave. The solvents undecane and butanol were tested to see how solid trisodium citrate, a trisodium citrate solution (34 mM), and a chloroauric acid solution ($2.5x10^{-4}$ M) dissolved in them. Undecane was selected as an initial solvent because a long chain non-polar solvent was desired. Unfortunately, the reactants were more polar compounds so they did not dissolve very well into undecane. Therefore butanol, slightly more polar solvent, was selected. Consequently, the trisodium citrate was still not soluble in the butanol however it did slightly disperse in the solution. Solutions with both butanol and undecane as solvents were then heated separately to 100 °C at 300 watts to see how fast they heated, and if they boiled too rapidly. For complete synthesis of the gold nanoparticles, reactions were run using undecane, butanol, and water as solvents. The purpose for this was to obtain final particle images to see how the size and shapes compared to each other.

Figure 1: Discover CEM SP microwave used for GNP synthesis.

Each reaction was heated inside the microwave using 10 mL thick walled glass test tubes. These tubes were sealed with a rubber cap and the system was closed to air. Air flow to the reaction vessel cooled the microwave at the end of synthesis (Figure 2).

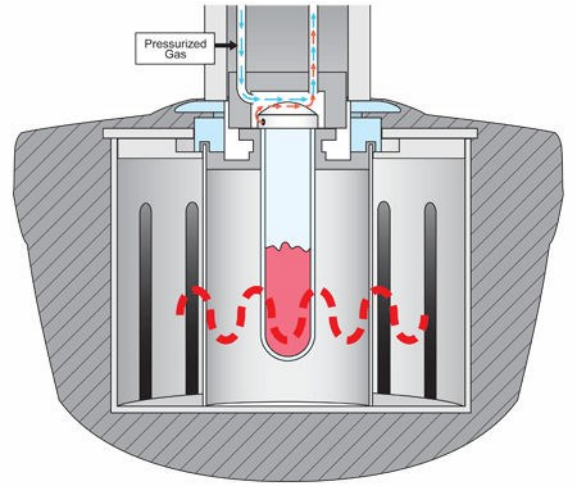

Figure 2: Schematic showing the reaction vessel inside the microwave.

Synthesis of Au Nanoparticles Using Undecane as Solvent:

A solution of undecane (8 mL), trisodium citrate (8 mg), and $HAuCl_4$ was sonicated then heated in the CEM microwave to 100 °C at 300 watts for one minute. Final product was filtered and rinsed.

Synthesis of Au Nanoparticles Using Water as Solvent:

A solution of water (6 mL), trisodium citrate solution (600 µL, 34 mM), and $HAuCl_4$ (150 µL, $2.5x10^{-4}$) was sonicated and then heated in the CEM microwave to 100 °C at 300 watts for one minute. Final pink colored product was filtered and rinsed.

Synthesis of Au Nanoparticles Using Butanol as Solvent:

A solution of butanol (6 mL), trisodium citrate solution (600 µL, 34 mM), and $HAuCl_4$ (150 µL, $2.5x10^{-4}$) was sonicated and then heated in the CEM microwave to 100 °C at 300 watts for one minute. Final product was filtered and rinsed.

Results

Through this study, gold nanoparticle aggregates were synthesized using a microwave and with much faster reaction times. By using a microwave that heats and cools tremendously faster than the hot plate alternative, our reaction times were reduced from 10 minutes to 1 minute. This made for a much more efficient reaction and will then allow for the synthesis of more

particles. Reaction times were tremendously shorter however; final products were large aggregates with a non-uniform morphology (Figures 3-5). This was most likely due to the precursors not quite dissolving in the undecane and butanol solvents, therefore the reactants conglomerated.

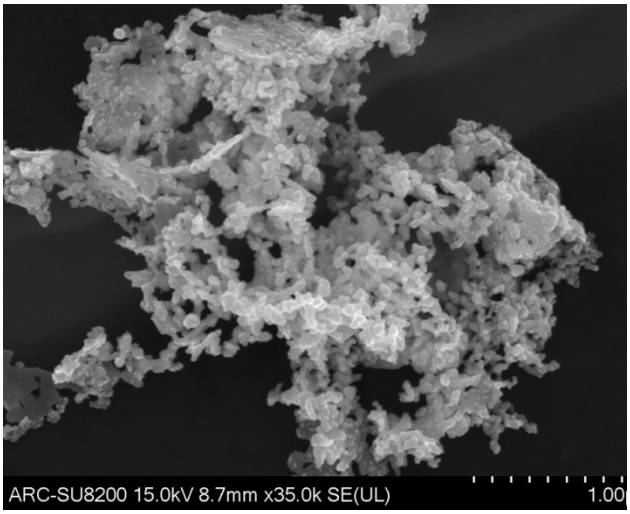

Figure 3: SEM image of GNP at 1.00 µm with undecane as the solvent.

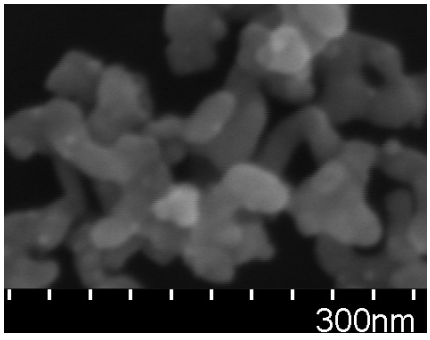

Figure 4: SEM image of GNP at 300 nm with undecane as the solvent.

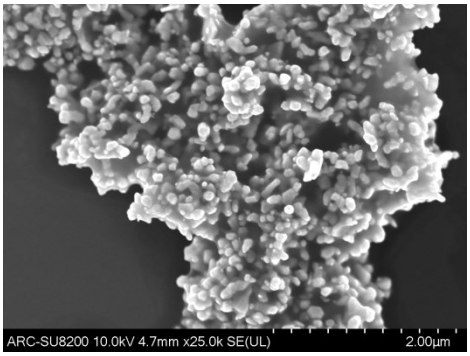

Figure 5: SEM image of GNP at 2.00 µm with butanol as the solvent.

Conclusions

After completing a few reactions, we were able to conclude that utilizing microwaves can significantly reduce reaction time for gold nanoparticle synthesis. While the final particles were not as uniform as desired, this gave us a better idea of what the microwave was capable of doing. Using the microwave allowed us to reduce overall reaction time by 9 minutes which was significant. We were also able to synthesize nanoparticle aggregates using a very non-polar solvent in which the precursors did not completely dissolve. This then opens the possibility of using different solvents that could potentially improve the final particle size.

Future Work

With this reduction in reaction time, it allows for more reactions to be conducted with varying conditions. In the future, we plan to continue synthesis varying reaction conditions such as, temperature, pressure,

reducing agent, and solvent. Additionally, we would like to eliminate all use of water if possible to utilize the microwave to its full potential and eliminate wasted heat. Furthermore, incorporation of thiols would increase biocompatibility and open the doors to more medical studies. In addition, the gold nanoparticles would need to be functionalized making them magnetic in order to be used for hyperthermia treatment. This functionality would be obtained by attaching the gold nanoparticles to iron oxide nanoparticles. Both the gold and the iron are biologically compatible and the incorporation of the two allows for both hyperthermia treatment for cancer cell death and magnetic resonance imaging for tumor detection.

Acknowledgements

This research project was funded by the DOE through the SULI program in which Natalie Ferguson organizes at SRNL. The undergraduate student intern was mentored by Aaron Washington, and had help from Jonathan Christian. Another student intern, Joshua Sparks, aided in the reaction synthesis.

Resources

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