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Preparation of Gold Nanoparticles with the Plant Secondary Metabolite Catechin

Zach Gilbert

Sarah Mitchell

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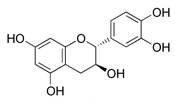
Zach Gilbert*, Sarah Mitchell*, Murielle Watzky

Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, CO 80639

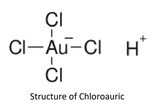
Department of Chemistry and Biochemistry

INTRODUCTION

The role of biocompatible nanoparticles is an emerging concept with a promising future. Biocompatible nanoparticles are small in size and can be utilized as vehicles for drug delivery, catalysis, optical sensing, and many other novel applications. The preparation of these nanoparticles often involves toxic chemicals, but the use of a plant secondary metabolite such as catechin as stabilizing and reducing agent reacting with a gold(III) solution ($HAuCl_4$) creates an environmentally friendly bottom-up synthesis that can be made to be reproducible and efficient. In solution, catechin reduces gold(III) ions to gold atoms and stabilizes the nanoparticles by coating the surface to prevent agglomeration.



Structure of Catechin



Structure of Chloroauric Acid

A bottom-up synthesis is used to stack atoms on a nanoscale into crystalline planes, which then forms nanostructures. It is the most accessible preparation method and follows a path of reduction, nucleation, and then growth.

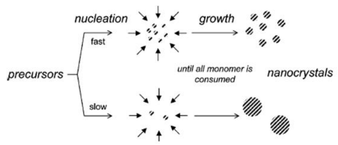


Diagram of a bottom-up synthesis

In order to observe the formation of gold nanoparticles in solution, the surface plasmon resonance (SPR) properties of gold nanoparticles were used, which can give insight into the shape and size of the nanoparticles produced. Modifying the reaction pH conditions with the addition of sodium hydroxide (NaOH) resulted in a decrease of the size of the nanoparticles produced, and a shorter reaction time.

EXPERIMENTAL

Stock solutions used in this project, which were prepared in nanopure water, include 1mM $HAuCl_4$, 2mM catechin extract, 10mM and 20mM sodium hydroxide. Reactions in this project consisted of two main standard methods, in which 2.5 mL of 1mM catechin were added to 10 mL of 0.5mM $HAuCl_4$. The addition was performed as a single purge (a dropwise addition gave similar results). In the first standard method ("standard pH"), the stock solutions were diluted in nanopure water prior to addition. In the second standard method ("1 mM NaOH"), the catechin stock solution was diluted in 10mM NaOH (or 1mM NaOH in the final reaction mixture). In a modification of this standard method, the catechin stock solution was diluted in 20mM NaOH (or 2mM NaOH in the final reaction mixture). The reaction was run at room temperature with stirring over one hour.

UV-vis spectra were measured at the end of each reaction. Aliquots were also collected during the reaction (at 5, 10, 20 and 60 minute intervals) to follow the reaction progress. To take UV-vis spectra, a 0.750mL aliquot of the reaction mixture was diluted with 1.5mL of nanopure water and placed in a 1cm cuvette. (One trial required further dilution of the reaction mixture for the UV-vis spectra, to a 1:3 dilution ratio. The absorbance results were then corrected to account for the increased dilution ratio.)

To prepare scanning electron microscopy (SEM) samples, 1.5mL aliquots of reaction mixture were placed in centrifuge tubes then centrifuged until solid pellets could be observed at the bottom of the tubes. The aqueous supernatant was removed from the tubes and the leftover solid was then redispersed with nanopure water. A few drops of the redispersed solution were placed onto double-sided carbon tape on aluminum supports. These were left to drying in open air for a few days prior to SEM and energy dispersive x-ray (EDX) data collection.

For dynamic light scattering (DLS) data, the reaction mixture solutions were used without further dilution or filtration. Nanoparticle average dynamic size (which includes the metal core and stabilizer layer) and surface zeta potential (an indicator of nanoparticle stability) were measured.

RESULTS AND DISCUSSION

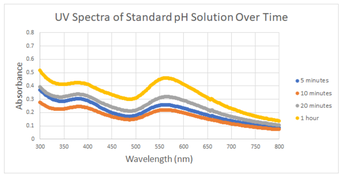


Figure 1: UV-vis spectra for synthesis of standard pH solution over one hour.

Figure 1 corresponds to a synthesis performed under "standard pH" conditions. The large peak around 560 nm indicates the production of gold nanoparticles, while an increase in its absorbance over time represents an increase in the amount of nanoparticles produced, until the reaction has mostly completed at the one hour mark.

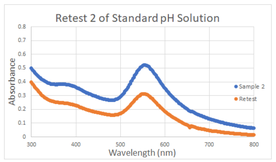


Figure 2: UV spectra of another sample of standard pH solution tested and then retested after two weeks.

Figure 2 shows UV-vis spectra for a sample prepared under "standard pH" conditions, then re-tested after two weeks. The sample was stored in an airtight container in the refrigerator, then brought to room temperature prior to taking the spectrum. The decrease in peak absorbance over two weeks points to some instability of nanoparticles prepared under "standard pH" conditions.

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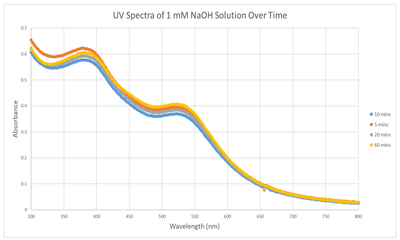

Figure 3: UV-vis spectra for 1 mM NaOH solution over one hour.

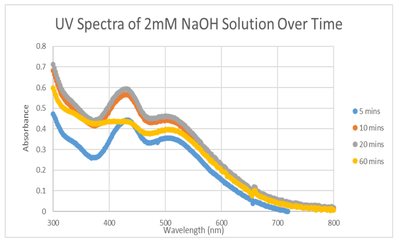

Figure 4: UV-vis spectra for 2 mM NaOH solution over 1 hour.

Figure 3 corresponds to a synthesis performed under "1 mM NaOH " conditions. The large peak around 540 nm indicates the production of gold nanoparticles, while an increase in its absorbance over time represents an increase in the amount of nanoparticles produced, until the reaction has mostly completed at the one hour mark.

Figure 4 corresponds to a synthesis performed under the modified "2 mM NaOH " conditions. The large peak around 520 nm indicates the production of gold nanoparticles, while an increase in its absorbance over time represents an increase in the amount of nanoparticles produced, until the reaction has mostly completed at the one hour mark. It is noticeable how altering the concentration of sodium hydroxide seems to affect nanoparticle formation and stability. It should be noted that the aliquots at 10, 20 and 60 mins were diluted to a 1:3 ratio rather than 1:2 due to oversaturation of the detector; the absorbances shown here were corrected for the difference in dilution.

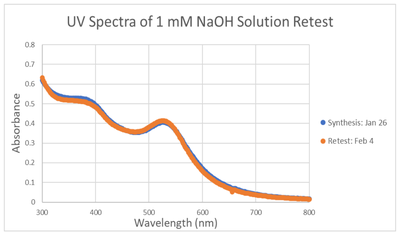

Figure 5: UV spectra for one sample of 1 mM NaOH solution tested and then retested after two weeks.

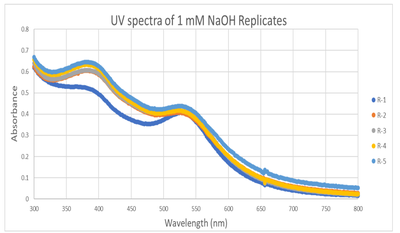

Figure 6: UV-vis spectra for replicate syntheses of 1 mM NaOH solution.

Figure 5 shows UV-vis spectra for a sample prepared under "1 mM NaOH" conditions, then re-tested after two weeks. The sample was stored in an airtight container in the refrigerator, then brought to room temperature prior to taking the spectrum. The two spectra almost completely overlap each other, showing a good stability of the nanoparticles prepared under "1 mM NaOH" conditions.

Figure 6 shows UV-vis spectra collected at the end of the reaction (one-hour) for replicates of the synthesis under "1 mM NaOH" conditions. The first replicate (dark blue) was carried out using an older $HAuCl_4$ stock solution. Overall, these spectra show good reproducibility between syntheses performed under "1 mM NaOH" conditions.

SEM/EDX

SEM and EDX techniques were used to view the gold nanoparticles and confirm their composition. SEM imaging was easier to perform on the larger nanoparticles prepared under "standard pH" conditions as seen in **Figure 7**. EDX results confirm the presence of gold in "standard pH" solution as seen in **Figure 8**. SEM imaging of "1 mM NaOH" solution depicts evidence nanoparticle formation in **Figure 9,** though it is more difficult to observe. EDX results confirm the presence of gold in "1 mM NaOH" solution as seen in **Figure 10**.

Standard pH solution

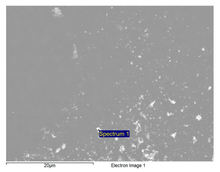

Figure 7: SEM image of "standard pH" solution

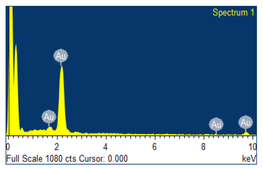

Figure 8: EDX of "standard pH" solution

1 mM NaOH solution

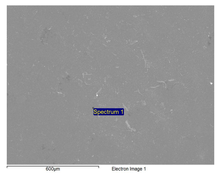

Figure 9: SEM image of "1 mM NaOH" solution

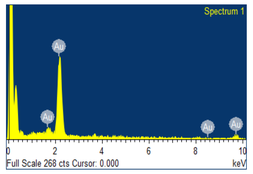

Figure 10: EDX of "1 mM NaOH" solution

DLS

DLS results showed a larger hydrodynamic size for nanoparticles prepared under "standard pH" conditions (average, 97 nm) compared to nanoparticles prepared under "1 mM NaOH" conditions (average, 42.5 nm). The zeta-potential values indicate moderate stability for the nanoparticles.

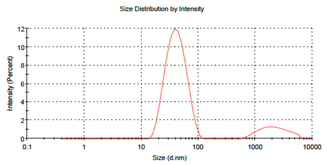

Figure 11: DLS results of "standard pH" solution

Reaction Mixture	Average Hydrodynamic Nanoparticle Size (nm)	Zeta Potential (mV)
"Standard pH" conditions	97.2	-35.2
"1 mM NaOH" conditions	42.5	-22.3

ACKNOWLEDGEMENT

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