UV-vis Analysis of the Effect of Sodium Citrate on the Size and the Surface Plasmon Resonance of Au NPs

Eman Mousa Alhajji

North Carolina State University

Department of Materials Science and Engineering

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Patrick Snyder

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Abstract

The objective of this experiment was to analyze four samples of synthesized gold nanoparticles (Au NPs) using sodium citrate as a capping agent to control the size of the NPs. The tools used for Au NPs analysis were Cary 10 Scan UV-Visible Spectrometer and Malvern Zetasizer Nano-ZS Dynamic Light Scattering (DLS). The Au NPs solutions were synthesized using 25, 50, 75, 150 µL of sodium citrate as well as one which contained 50 µL of sodium citrate and NaCl (reducing agent). It was concluded that the capping agent, sodium citrate, caused the size of Au NPs to be smaller in the synthesis process. In fact, it stopped the NPs from growing. The surface plasmon resonance phenomenon was used to compare the sizes of Au NPs. Optical absorbance. The diameter of the Au NPs from these solutions were determined to be 97.08, 49.26, 32.40, and 20.69 nm, respectively. Adding NaCl to the solution containing 50 µL shifted the diameter from 49.26 to 797.0 nm, indicating agglomeration. Cary 10 Scan UV-Visible Spectrometer and Malvern Zetasizer Nano-ZS Dynamic Light Scattering (DLS) were suitable characterization techniques to show phenomena happening in the scale of nanometer of gold as a noble metal.

Introduction

In nanotechnology**,** a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties. [1] Particles between 1 and 100 nanometers in size are scientifically known as nanoparticle. Nanoparticles are considered a discovery of modern science in which development is progressively vital due to a wide variety of potential applications in biomedical, optical and electronic fields. Nanoparticles are unique because they are a bridge between bulk materials and atomic or molecular structures. [1,2] A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. Certain properties of NPs can be attained by controlling the size such as optical properties.2

One of the first explored nanoparticles are gold nanoparticles (Au NPs). [3] Au NPs have been used in bio-sensors, biological tags, imaging and are being investigated for use in cancer treatment. Generally, gold nanoparticles are produced in a liquid ("liquid chemical methods") by reduction of chloroauric acid (H $[AuCl_4]$). After dissolving chloroauric acid, the solution is rapidly stirred while a reducing agent is added. This causes Au^{3+}ions to be reduced to Au^{+}ions. Then a disproportionation reaction occurs whereby 3 Au^{+} ions give rise to Au^{3+} and 2 Au^{0} atoms. The Au^{0} atoms act as center of nucleation around which further Au^{+} ions gets reduced. To prevent the particles from aggregating, some sort of stabilizing agent that sticks to the nanoparticle surface is usually added. In the Turkevich method of Au NP synthesis, citrate initially acts as the reducing agent and finally as the capping agent which stabilizes the Au NP through electrostatic interactions between the lone pair of electrons on the oxygen and the metal surface.[2] In Turkevich method, citrate controls the driving force of nanoparticle agglomeration. To yield larger particles, less sodium citrate should be added (possibly down to 0.05%, after which there simply would not be enough to reduce all the gold).[3] The reduction in the amount of sodium citrate will reduce the amount of the citrate ions available for stabilizing the particles, and this will cause the small particles to aggregate into bigger ones (until the total surface area of all particles becomes small enough to be covered by the existing citrate ions).[2]

The surface plasmon resonance (SPR) phenomenon occurs when incident light strikes an electrically conducting Au layer at the interface between a negative and positive permittivity material. In other words, SPR phenomenon occurs when a gold nanoparticle is smaller than the wavelength of incident light. Given that Nanoparticles absorb different wavelengths in the ultraviolet and visible light based on their size and shape, UV-vis spectroscopy is a very useful tool to allow the estimation of Au NPs size, concentration, and aggregation level.[2,3]

The objective of this experiment was to analyze four samples of synthesized gold nanoparticles (Au NPs) using sodium citrate as a capping/reducing agent to control the size of the NPs. The tools used for Au NPs analysis were Cary 10 Scan UV-Visible Spectrometer and Malvern Zetasizer Nano-ZS Dynamic Light Scattering (DLS). The Au NPs solutions were synthesized using 25, 50, 75, 150 μL of sodium citrate as well as one which contained 50 μL of sodium citrate and NaCl (reducing agent).

Experimental Procedure

Four Au NPs samples were synthesized with the following different combinations: 25, 50, 75, and 150 μL of sodium citrate as well as one which contained 50 μL of sodium citrate and

NaCl. . Each sample was then analyzed using Cary 10 Scan UV-Visible Spectrometer and Malvern Zetasizer Nano-ZS Dynamic Light Scattering (DLS).

A. Synthesis

Four small clean beakers were used to hold 10 mL of 0.12 molar HAuCl4•3H2O. The beakers were placed on a hot plate and heated until they began to boil (100 °C). A magnetic stir bar was added to each beaker. A different amount of sodium citrate (0.25 molar $C_6H_5Na_3O_7$) was added to each of the four beakers with a micropipette. The amount of sodium citrate added was 25 μL, 50 μL, 75 μL, and 150 μL to beakers 1-4 respectively. A fifth solution was created with 50 μL of sodium citrate and with 0.89 molar NaCl from salt water. The solutions were heated until a color change was observed and then heated for an additional five minutes. As the solutions were heated, water from the solutions began to boil off and additional deionized water was added to maintain a solution volume of approximately 10 mL. It might be necessary to quantitatively dilute the solutions in order to obtain absorbance values below 1.

B. Analysis

After the solutions have cooled to room temperature, they were dispensed into four individual disposable polystyrene latex cuvettes, type DTS0012. The cuvettes were filled to about the half. Before placing the cuvettes in the Cary 100 Scan UV-Visible Spectrometer to obtain an absorption spectrum for the samples, the baseline transmittance values were found. A 100% transmittance baseline was obtained by using a cuvette full of tap water as the sample and then a 0% transmittance baseline was obtained by blocking the beam with a piece of paper. Once the baseline was obtained the four Au NP samples were analyzed. The spectrometer scan range was 900-200 nanometers (nm). The light source switched from visible light to a UV source at 400 nm. The spectral bandwidth (SBW) was 2 nm. The data interval was 0.5 nm and the scan rate was 350 nm per minute. The beam mode used was double reverse. The data mode used was % transmittance. After the baselines were set, the samples spectra were taken. After the UV-Vis scan was complete, the samples were placed in a Malvern Zetasizer Nano-ZS with Zetasizer software version 6.20 to measure the size of the Au nanoparticles. The samples were analyzed at a temperature of 25°C and the equilibration time for the Zetasizer was 20 seconds.

Results

It was observed with the eye that the four samples, with 25 μL, 50 μL, 75 μL, and 150 μL of sodium citrate as shown in Figure 1, are ranged from the most red to the most blue, showing a blue shift.

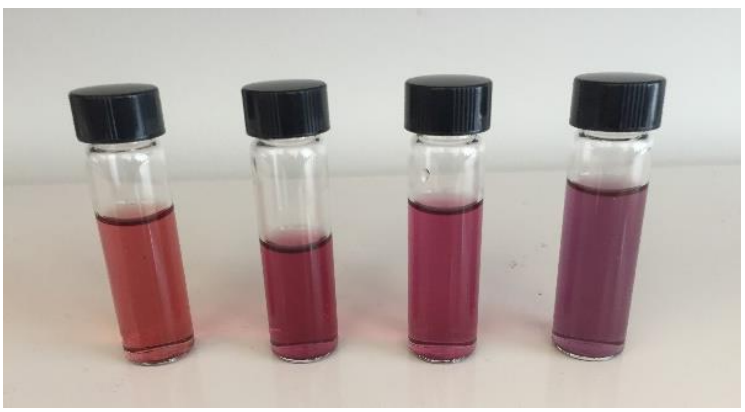

Figure 1. Au NPs Sample 1, 2, 3 and 4 respectively, showing a blue shift with the increase of sodium citrate.

Figure 2 shows the absorbance spectra of the four Au NPs samples using the UV-Vis spectrometer. It was observed that Au NPs absorbed visible length most strongly between 520 and 540 nm. It was also observed that the absorbed wavelength decreases with the increase of sodium citrate. The UV/Vis Spectra for the Au NPs sample 2 with Na citrate before and after adding NaCl (aq) shows a red-shift (a blue shift to the eye). The addition of NaCl (aq) shifted the peak from 529 nm to 532, as shown in Figure 3.

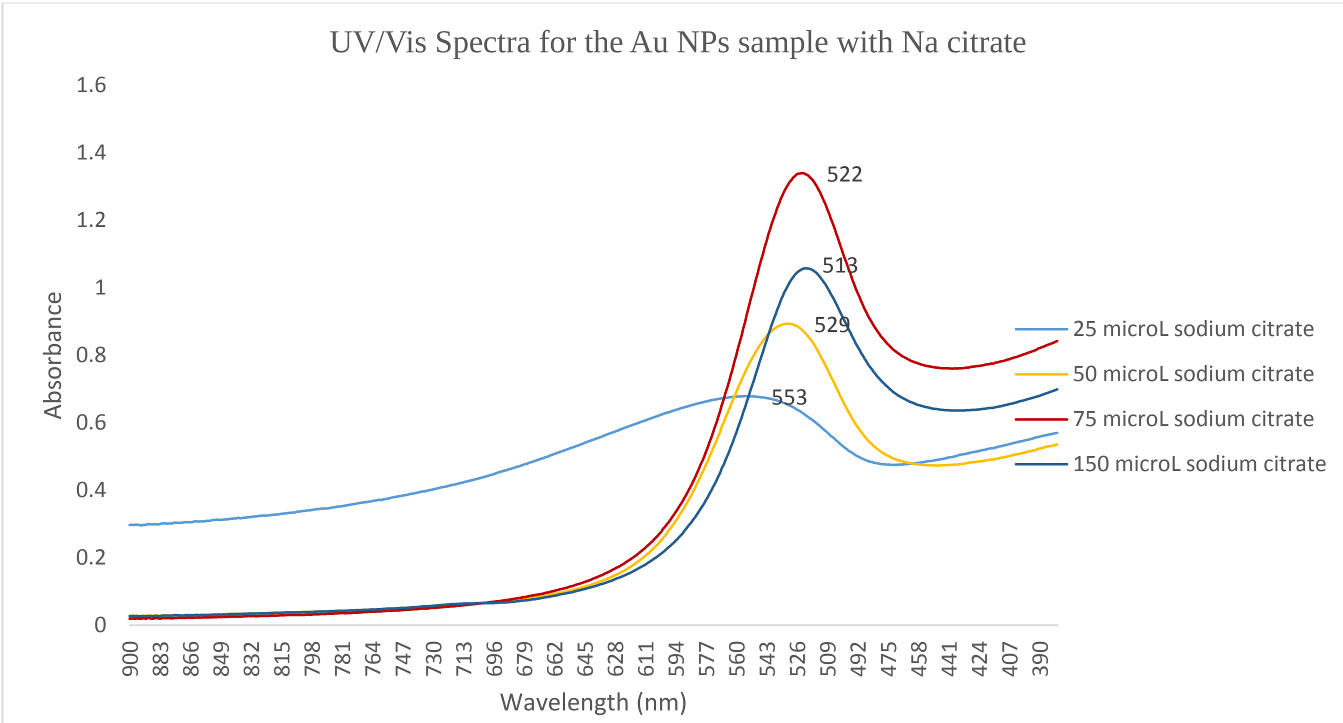

Figure 2: UV/Vis Spectra for the Au NPs samples at different concentration of sodium citrate (the reducing agent).

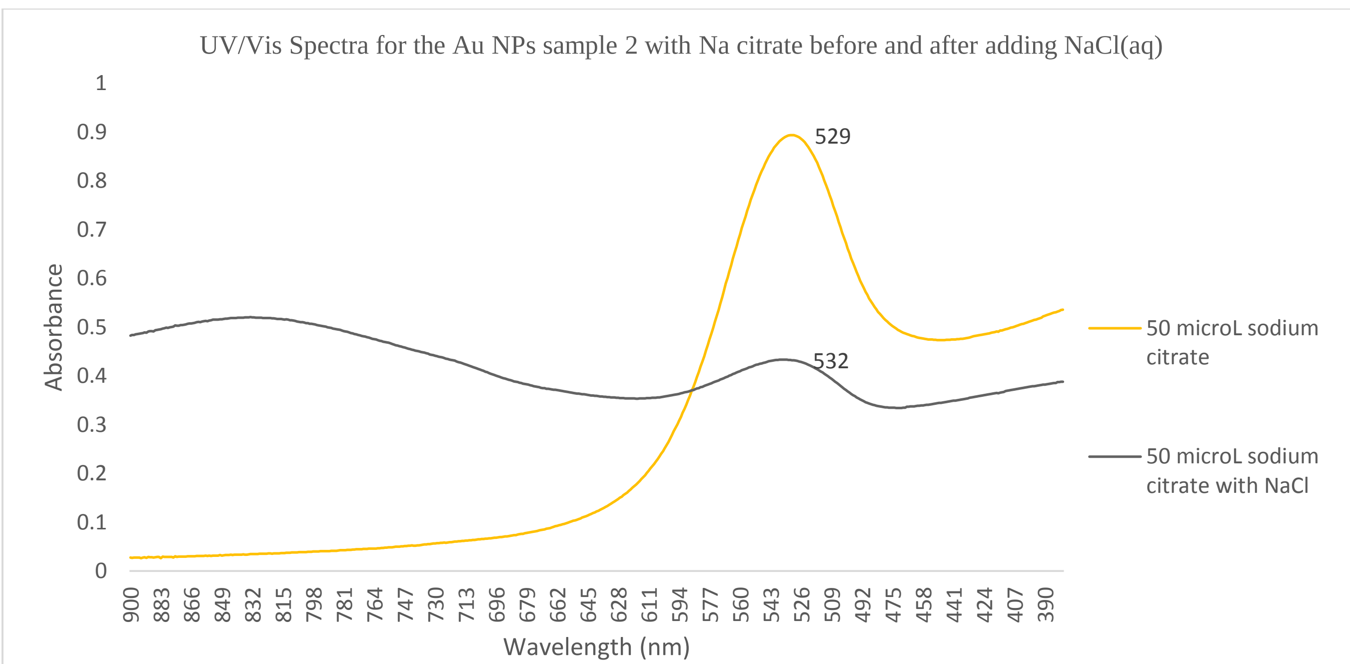

Figure 3. UV/Vis Spectra for the Au NPs sample 2 with Na citrate before and after adding NaCl (aq).

Figure 4 shows the distributions of Au NPs sizes in the four solutions at a different amount of sodium citrate added in each one as a reducing agent. The average diameter of nanoparticle in the 25 µL sodium citrate solution was 97.08 nm. The average diameter of nanoparticle in the 50 µL sodium citrate solution was 49.26 nm. The average diameter of nanoparticle in the 75 µL sodium citrate solution was 32.40 nm. The average diameter of nanoparticle in the 150 µL sodium citrate solution was 20.69 nm. A trend of increasing concentration leading to smaller Au NPs sizes was observed.

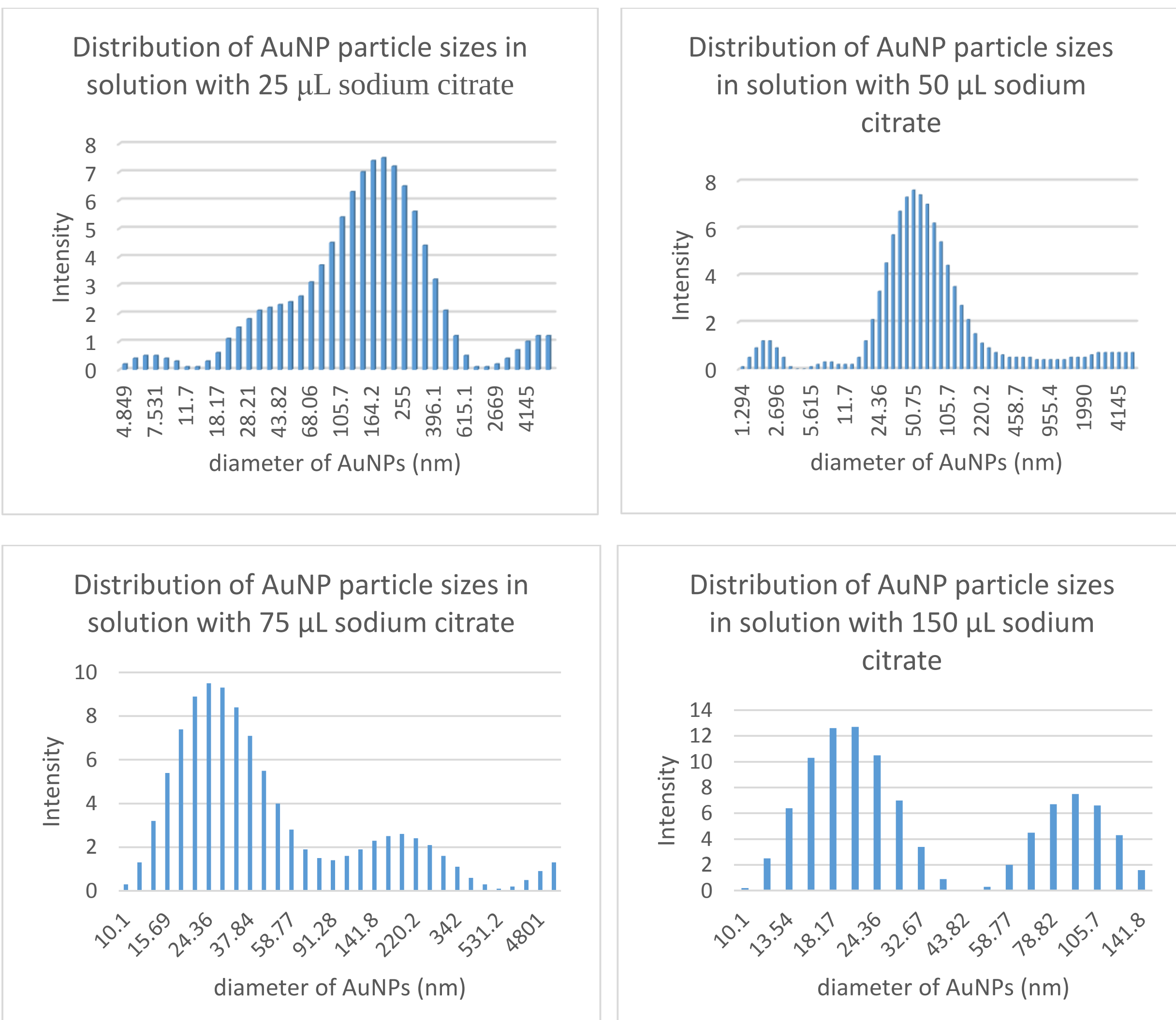

Figure 4. Distributions of Au NPs sizes in the four solutions at a different amount of sodium using Dynamic Light Scattering.

Figure 5 shows the distributions of Au NPs sizes in sample 2 with and without the addition of NaCl using Dynamic Light Scattering. The average diameter of Au NPs in this the 50 µL sodium citrate solution after the addition of NaCl increased to 797.0 nm.

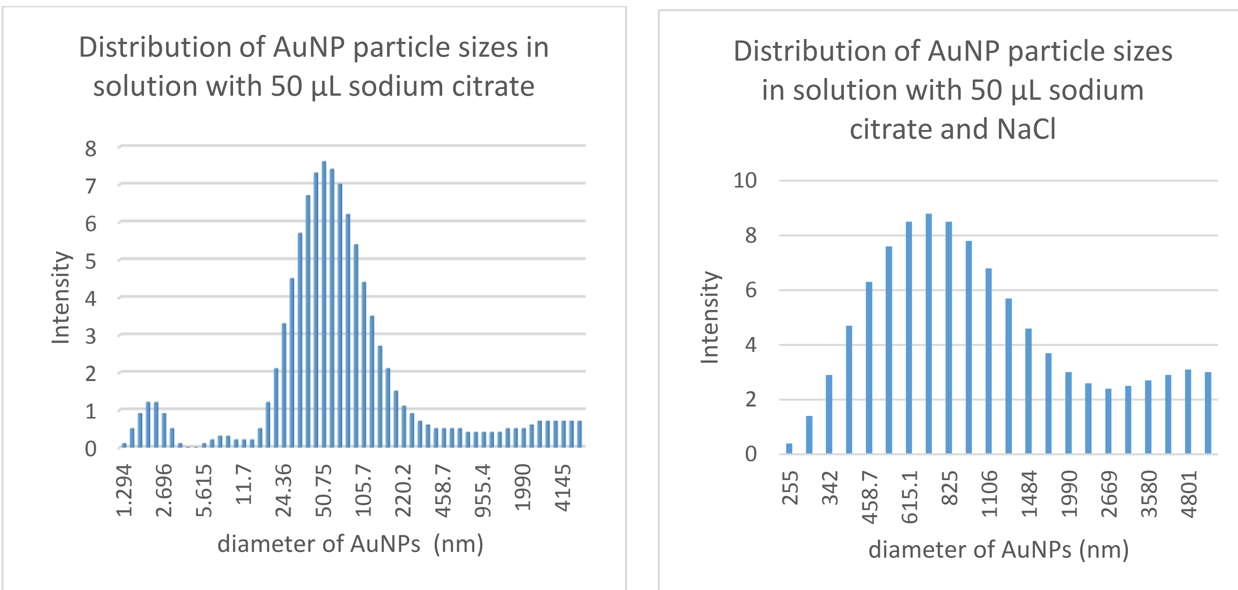

Figure 5. Figure 4. Distributions of Au NPs sizes in sample 2 with and without the addition of NaCl using Dynamic Light Scattering.

Discussion

The Au NPs solutions showed absorption peaks between 520 and 540 nm and were red to purple in color. These findings are consistent with the literature. [2, 3, 4] The results, agreeing with the research, suggest that increasing the amount of sodium citrate leads to an increase in the reduction rate of Au particles, yielding a smaller size of NPs. In other words, the increased concentration of sodium citrate caused the reaction to stay in the nucleation phase longer and form more particles rather than move into the growth phase where existing particles increase in size. Furthermore, the smaller the size of the Au NPs, the more red it appears to the human eye. [2] The phenomena of Au NPs optical properties is explained by the occurrence of surface plasmon resonance. In addition, adding NaCl to the solution containing 50 μL shifted the diameter from 49.26 to 797.0 nm, indicating agglomeration. [3,4] DLS measurements aided in interpretation of the data. It clearly showed a correlation between the size of Au NPs and the amount added to the solutions. [4]

Conclusion

The objective of this experiment was to analyze four samples of synthesized gold nanoparticles (Au NPs) using sodium citrate as a capping/reducing agent to control the size of the NPs. The tools used for Au NPs analysis were Cary 10 Scan UV-Visible Spectrometer and Malvern Zetasizer Nano-ZS Dynamic Light Scattering (DLS). The Au NPs solutions were synthesized using 25, 50, 75, 150 μL of sodium citrate as well as one which contained 50 μL of sodium citrate and NaCl (reducing agent).

This lab successfully demonstrated that the size of Au NPs can be controlled by the concentration of the capping and reducing agent during synthesis. The diameter of the Au NPs from these solutions were determined to be 97.08, 49.26, 32.40, and 20.69 nm, respectively. Adding NaCl to the solution containing 50 μL shifted the diameter from 49.26 to 797.0 nm, indicating agglomeration. Cary 10 Scan UV-Visible Spectrometer and Malvern Zetasizer Nano-ZS Dynamic Light Scattering (DLS) were suitable characterization techniques to show phenomena happening in the scale of nanometer of gold as noble metal.

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