Silver nanoparticle synthesis, UV-Vis spectroscopy to find particle size and measure resistance of colloidal solution

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Abstract. It is an important part in nanotechnology to produce nanoparticles with specific properties like particle size or resistance. To produce colloidal silver nanoparticles with specific size and resistance by Turkevich method, it is needed to synthesized silver nanoparticle with various molarity of AgNO₃ and concentration of Trisodium citrate. UV-Vis spectrum was taken for the colloidal silver nanoparticle and analysed to roughly measure the particle size. That value was also cross checked by the optical theorem and weighed the resistance of colloidal solution for different parameters.

1. Introduction
Nanoparticles are usually the particles of size between 1 to 100 nanometer in which physicochemical properties such as mechanical, chemical, magnetic, optical or electrical properties are different to bulk matter for the volume to surface ratio [1]. Using these properties, it is possible to utilize in various applications. One of these is plasmonic oscillation. Plasmonic resonance frequency depends on shape, size and dielectric environment of nanoparticles. Nanoparticles band gap between valence band and conduction band is higher than the bulk material. This higher band gap changes the absorbance of the particle. So the colloidal solution can scatter in different frequencies than the bulk particle would scatter. Electrons can’t move freely in nanoparticles. These things change some electrical properties of the particles. Silver nanoparticle (AgNP) has various types of application in the medical field. It can be used for water purification, artificial joint replacement, anticancer activity, cancer therapy and silver coated medical devices. On the other hand, as an electronic application AgNP can be used for flexible electronics. In the research it is tried to synthesize AgNP and find some of its properties, which can be helpful for future research.

2. Literature review
From the Feynman lecture, “There’s plenty of room at the bottom” first idea about nanotechnology came from. After that many researchers worked on it and day by day it developed. Now nanotechnology has a lot of branches like nanoparticles. Silver nanoparticles have wide scope to use in catalyst and photonics with unique electrical, optical and thermal properties. This is the reason silver nanoparticle synthesis is so important in recent times. There are many methods to synthesize silver nanoparticles, which can be classified as physical, chemical and biological routes. All of these processes have some advantages and disadvantages. They are briefly described in table 1: [2]
Table 1. Difference between three types of synthesis.

| Chemical method                                      | Physical & Mechanical method                                                                 | Biological method                                                                 |
|-------------------------------------------------------|---------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Made by reducing AgNO₃ by a reducing agent            | Different methods like condensation and evaporation.                                        | Made by using green plants which can be used as naturally reducing agents.         |
| This process is simple to prepare and cost effective. | It's time consuming and needs high energy, temperature and pressure.                        | This process is not much simpler as chemical synthesis.                             |
| Shape and size of particle depends on molar ratio of AgNO₃ and PVP. | Nearly 10 nm size.                                                                         | Less than 15 nm and spherical shape.                                               |
| Common in researcher for future implementation.       | Common for bulk production                                                                | Also common in medical research.                                                   |

Using UV Vis spectroscopy is very common to find the information about the plasmonic resonance of nanoparticles. Confirmation of silver nano-particle formation and plasmonic resonance can be found by analyzing the absorbance data of UV-VIs spectroscopy. It can also roughly estimate the size of a particle. But SEM, TEM can give better measurement of particle size. Rather than these, Energy dispersive x ray spectroscopy (EDS), X Ray photoelectron spectroscopy (XPS), X Ray diffractometry (XDM), Fourier transform infrared spectroscopy (FTIR) are also used to characterize nanoparticles.

There are some factors which can affect the size of the nanoparticle. The first thing that changes the size of nanoparticles is the influence of dispersant by polyvinylpyrrolidone (PVP). When PVP is added a little amount, it cannot coat the AgNP fully. In that time some other particle comes closer and makes a larger particle. On the other hand, if PVP is much more, it also prevents the particle to stay smaller. It is best to use a specific amount of PVP in synthesis. Secondly, The Amine can change the size of the particle. Amine reduces the silver ion in aqueous solution, which leads the particle to be larger in size. Lastly, when synthesizing nanoparticles with high temperature, it tends to have larger and non-spherical particles in colloidal solutions. In low temperature it shows the opposite [3].

In the Turkovich method, Trisodium citrate is used as a reducing agent as well as stabilizing agent, while AgNO₃ is used as a silver precursor. This process makes the silver nanoparticle, which are between 30 to 60 nm in size in average [4]. To find estimated particle size, the optical theorem is used in this paper. This theorem states that how much light a particle scatters in forward direction depends on the cross section of the particle. As the cross section depends on nothing but size it can be determined the particle size from the scattered light [5].

3. Synthesis process
Between some different methods, the Turkevich method of chemical synthesis was selected. By this method different size and shaped nanoparticle can be synthesized. Firstly, Silver nitrate (AgNO₃) and Trisodiumcitratedihydrate (C₆H₅O₇Na₃.2H₂O) was needed to synthesized colloidal solution of AgNP. As both of them are in solid form, it is important to make a solution with different molarity of AgNO₃ and different percent of concentration for Trisodium citrate dihydrate. For AgNO₃, 250mL distilled water was used for each solution.

Amount of salt for each bottle = MxWxx

Where, M is the molar mass of AgNO₃. Value of M is 169.87. W is the amount of water in litter. As it used 250mL distilled water for each solution, this case W will be 0.25 and x is the concentration that is wanted.
On the other hand, for Trisodium citrate dihydrate, Concentration percentage = \( [\text{mass of the solution (g)}/\text{volume of the solution (mL)}] \times 100\% \).

To store this solution, it was needed to keep the solution away from light and a high temperature. Dark glass bottle was being wrapped by aluminum foil to protect the solution from sunlight and air.

It was 20 ml Silver nitrate (AgNO\(_3\)) on a 50 ml beaker, which was heated with a continuous stirrer until it reached boiling temperature. 2 mL Trisodium citrate dihydrate (C\(_6\)H\(_5\)O\(_7\)Na\(_3\).2H\(_2\)O) was added drop by drop using burette until it changed to the greenish yellow color. This change in color represents the production of AgNPs. For the reducing agent amount of silver nanoparticles increase with respect to Ag\(_3^+\). Different concentrations of citrate make different colored solutions as well as different sized nanoparticles. Picture of these colloidal solution is given in figure 1.

It was synthesized various times by changing the molarity of AgNO\(_3\) and Trisodium citrate. Every time when it was done synthesis, kept the data about color and whether sediment was found or not during synthesis. All this information is given in table 2 and 3.

The data were taken during the synthesis in table 2 and 3:

![Figure 1. Top 7 bottles: Colloidal solutions had the molarity of AgNO\(_3\) kept 1mM and Bottom 8 bottles: Colloidal solutions of AgNP has constant concentration of Trisodium citrate as 3%](image)

### Table 2. Information for constant citrate percentage colloidal solution.

| Molarity (mM) for 3% Trisodium citrate constant | Color     | Sediment |
|-----------------------------------------------|-----------|----------|
| 0.5                                           | Yellow    | No       |
| 1                                             | Orange    | No       |
| 2                                             | Red       | No       |
| 3                                             | Green     | No       |
| 4                                             | Light Orange | No   |
| 5                                             | Yellowish | No       |
| 10                                            | Transparent | Yes   |
| 20                                            | Transparent | Yes   |

### Table 3. Information for constant molarity of silver nitrate with different citrate concentration.

| Concentration (%) for AgNO\(_3\) molarity (mM) | Color       | Sediment |
|-----------------------------------------------|-------------|----------|
| 1                                             | Orange      | No       |
| 2                                             | Orange      | No       |
| 3                                             | Deep Orange | No       |
| 4                                             | Deep Orange | No       |
| 5                                             | Yellowish   | No       |
| 7                                             | GreenishYellow | No   |
| 10                                            | Transparent | Yes     |
After that, the liquid was being cooled and stored. Approximately 5 days after synthesis, UV-Vis spectroscopy was measured with a long range of wavelengths.

4. Application
Current research shows in future nanotechnology will make a huge change in our life. Silver nanoparticle has its application in the medical, electronics and many other sectors. Though all of the applications of silver nanoparticles are important perhaps the need is most desired in the medical field. Biomedical applications of silver nanoparticle include water purification, artificial joint replacement, biosensor, silver coated medical devices etc. While inkjet printing can make the electronics world simpler in future.

Now-a-days drinking contaminated water is a severe civic apprehension. Many people have died from water related diseases in mostly developing countries. Many scientists are trying to reduce waterborne illness by purifying water and some of them are getting excellent outcomes by using AgNP. Fibrous membranes can purify water by removing microorganisms, which can be developed by AgNP. This process is famous to the new researcher for its cost effectiveness [6].

Silver nanoparticles are used in bone cement that is used as artificial joint replacement. As nano silver can stimulate antimicrobial action, Polymethyl methacrylate laden with silver particles is being measured as the bone cement. Surgical meshes are used to bridge wound and tissue repair. These meshes are effective but highly risky to microbial infection. Silver nanoparticles coated with polypropylene mesh are said to have good antimicrobial activity. Some other medical treatment such as wound dressing, bone cement, and dental fillings can all make use of nano silver to prevent microbial infection [7].

Cancer is now a serious and common disease worldwide. Though chemotherapy is used to destroy the cancer cell for patients, it destroys a lot of healthy cells too. Numerous laboratories have addressed the enhancement of the therapeutic usage of AgNPs as nanocarriers for targeted delivery, chemotherapeutic agents, and as enhancers for radiation and photodynamic therapy. They summarized the probable therapeutic looms for cancer via AgNPs in cancer cell lines or animal representation [8].

Textile industry is encouraged to use silver nanoparticles inside the fabric. AgNP will help to prevent bacterial effect for its antibacterial activity against E coli. This can drastically reduce some diseases like pneumonia or urinary infection. [3]

The conductive material is the most important constituent of Inkjet printing of AgNPs electrical applications. Though there are some other conductive materials such as polymers, graphene and other things, metal nanoparticles like silver and gold nanoparticles have a higher conductivity than others. And AgNP is the best option here for its cost effectiveness. AgNP is a good conductor when it is sintered at 200-300 degree Celsius. This process needs short procedure, durable and highly conductive [9].

5. Experiment
After synthesis, UV-Vis spectroscopy was taken for some colloidal solutions. From there the data of UV-Vis spectroscopy was found and those were analysed in this paper. It was kept 3% Trisodium citrate constant and analysed the graph was found from different AgNO₃ molar concentrations. Then the same thing was done for 1mM AgNO₃ constant and analysed for different Trisodium citrate concentration.

5.1 UV-Vis Spectroscopy
UV-Vis Spectroscopy gives much insight about synthesized AgNP. From the peak value of the solutions the molecular size of AgNP can be determined. It was seen that from 1mM to 3mM concentration the particle size increased and for 5mM it became lesser than the 1mM and went on.

![UV-Vis Spectroscopy Graph](image)

**Figure 2.** UV-Vis Spectroscopy of AgNP with different molarity of AgNP, when concentration of Trisodium citrate was 3%

| 3% Trisodium citrate | 1mM | 2mM | 3mM | 5mM | 10mM |
|----------------------|-----|-----|-----|-----|------|
| Peak value (nm)      | 444.5 | 481.5 | 505 | 436.5 | 420  |
| Particle size (nm) [10] | 70  | 95  | 110 | 65  | 50   |

Table 4. Peak value and estimated particle size when Trisodium citrate was kept constant.

From figure 2, the peak value was taken and list it in table 4. Particle size was measured in nanometer from the peak value. it can be shown that the pick value as well as the size of AgNP increase until 3mM and then it starts to decrease. To determine the shape, it is important to analyze the shape of the graph in figure 2 and particle size in table 4. Figure 2 and table 4 both are showing that AgNPs are much aggregated.
Figure 3. UV-Vis Spectroscopy of AgNP with different concentration of AgNP, when molarity of AgNO$_3$ was 1mM

Table 5. Peak value and estimated particle size when silver nitrate was kept constant.

| 1mM AgNO$_3$ | Pick value (nm) | Particle size (nm) [10] |
|--------------|----------------|------------------------|
| 1%           | 417            | 48                     |
| 3%           | 444            | 70                     |
| 7%           | 406            | 30                     |

In figure 3 and table 5, size of the particle increases until 3% and then decrease. The shape of graph and smaller particle size determines low aggregation. It can be said that when AgNO$_3$ is stays at 1mM, the aggregation is much less.

From the figure 2 and 3 and also table 4 and 5, it is seen that where the concentration of Trisodium citrate was 3%, the particles were more aggregated. This thing can be determined by the right side of the peak value of figure 2 and 3. On the other hand, when molarity of 1mM was constant, particles did not aggregate that much.

5.2 Scattering experiment

By relating figure 1, 2 and 3 it is shown that the colloidal AgNP with higher peak value at UV Vis spectroscopy or with larger particle looks darker than the particle with lower peak value or smaller one. Scattered light only can be shown by any detector, if the light scattered at the same angle with incident light in which angle the detector stays. It can be explained with the optical theorem. As larger particles don’t do backward scattering so much, the larger particle is shown darker if light source does not be at the opposite side to the camera with respect to the colloidal solution.

5.3 Resistance

Resistance of some synthesized colloidal solution of AgNP was measured by multimeter, which two probes were kept at the same distance during all measurements. For result, 5 measurements were taken
for each value and kept the average of all 5 values to reduce error. The graph of the resistance is given in figure 4 and figure 5.

![Graph](https://example.com/graph)

**Figure 4.** Resistance of colloidal solution of AgNP with different molarity of AgNO₃, when concentration of Trisodium citrate was 3%

At figure 4, where the concentration of Trisodium citrate dihydrate is kept as 3% and changes the molarity of AgNO₃, shows the resistance can be predicted as a linear straight line for increasing the concentration of AgNO₃.

![Graph](https://example.com/graph)

**Figure 5.** Resistance of colloidal solution of AgNP for different concentration of Trisodium citrate when molarity of AgNP was 1mM

In figure 5, where the molarity of AgNO₃ is 1mM and vary the concentration of Trisodium citrate (%) shows the graph was found as a curved line, with two peaks.

From the figure 4 and figure 5, it is seen that when citrate percentage was kept constant, it shows less resistance to the values where the molarity kept constant. It is thought that the reason for this
change is for aggregation. From the UV-Vis spectrum, it was shown that the colloidal solution with constant citrate aggregates more.

6. Conclusion
From the peak value of the UV-Vis spectroscopy it was shown how particle size varies for producing silver nanoparticles with different molarity and concentration. It is also possible to assume particle size by analyzing scattered light from colloidal nanoparticles. Using both information the estimation can be verified. Resistance of colloidal AgNP shows a linear relation when 3% citrate was constant, but a curve with two peaks shows when molarity of 1mM was constant. The data of resistance will help in inkjet printing. In future the plan is to measure resistance with more accurate way and using more various type of samples.

7. References
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