Silver Nanoparticle Synthesis, Characterization, Properties

A Thesis
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By

G.M. Asik Bayazid	11210007
Shahla Samim Shamma	11321054
Alim Al Razy	12121112
Rajib Bosu	11210011

Supervised by
Md. Anamul Hoque
Lecturer
Department of Electrical and Electronic Engineering
BRAC University, Dhaka.

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DECLARATION

We hereby declare that thesis work titled “Applications, Synthesis and Characterization of Silver NanoParticles” is our own work. The work has not been presented elsewhere for assessment. Where materials used from other sources have been properly acknowledged and referred.

Signature of
Supervisor

……..

Md. Anamul Hoque

Signature of
Authors

……

G.M. Asik Bayazid

.....

Shahla samim shamma

.....

Alim Al Razy

.....

Rajib Bosu

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ABSTRACT

Nanoparticle is a part of ultrafine particle and it has at least one dimension with lengths in between 1nm to 100nm, which shows different properties to the bulk materials for its greater surface area per weight. Now a day, nanoparticle is using immensely in many fields, such as electronics, medicine, manufacturing, environment to improve our lifestyle. Silver nanoparticles is a common substance using in nanotechnology. Due to the Surface Plasmon Resonance, their band gap and color vary for different frequency of energy. In this thesis, we are planning to explore the synthesis process of silver nanoparticles ,characterize it and observe different changes occurs with changed parameter.

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ABBREVIATIONS

AgNPs- Silver Nanoparticles

Silver Nitrate – $AgNO_3$

trisodium citrate dehydrate ($C_6H_5O_7Na_3.2H_2O$)

SPR- Surface Plasmon Resonance

TEM- Transmission Electron Microscope

SEM- Scanning Electron Microscope

UV-Vis- Ultraviolet-Visible light

FWHM- Full Width Half Maximum

Chapter 1

Introduction

1.1 Nanoparticle

At the titled “There is plenty of room in the bottom”, the speaker Richard Feynman talked about the technology and engineering at atomic scale. That speech of him is considered as the first spotlight of nanotechnology which made the scientists realize the increasing scopes of nanotechnology [1].

Nanoparticles are usually the particles of size 1 nm to 100 nm. Physiochemical properties of nanoparticles such as mechanical, chemical, magnetic, optical or electrical properties are different compared to bulk materials for the volume to surface ratio [2]. Nano technology is now a day’s spreading rapidly and researchers are focusing more on nanoscience due to increasing usage and applications of nano materials based on their various properties. There is quite possibility that in future Nanotechnology can take over significant area in technological field.

1.2 Silver

The element stated at period 5 and group 11(b) of the periodic table is named as silver (Ag). This is a chemical element with chemical number of 47 and also listed to have highest electrical and thermal conductivity as well as highest reflectivity among the entire metallic element. Pure form of silver is originated from mines of metals like copper, zinc, gold and this stays as the alloy with other metals.This soft, shiny white metal has been a member of the mostly valued metal family for so long. This worldwide famous metal is primarily known for the material of jewelries, coins as well as for its highest conductive nature. Besides, silver has many significant usages such as in electronics, energy production, photography, mirrors and glass production, brazing and soldering, electroplating of engine bearings etc. moreover, Silver has been used in many medical conditions and also for purifying and protecting the water and food hygiene. Though silver grabs a huge importance in our life, it has some threatening facts too. For example, a skin disease known as Argyria is the result of inhalation of silver compounds. [3][4]

1.2.1 Silver Nanoparticles

Nano-particles of silver (Ag-NPs) are tiny silver components of size 1nm to 100nmin Nano-Scale. It is often said that, silver comes as nanoparticles but sometimes they are composed of the Oxides of silver. According to the usage and applications the nanoparticles are built in different shapes. In random spherical, diamond octagonal shaped and then sheets of silver nanoparticles

are used. In today's nano science and nanotechnology the nanoparticles of silver is contributing equally with the other nano materials of several matters. Nanoparticles of silver are now widely being used in different cases such as food, cosmetics, medicines, health care and industrial usage. Ag-NPs are being used in Nano-medical science particularly in treatment of cancer and killing the tumor cells. Moreover, in optical sensors; drug and pharmaceutical industries, textile mills etc.There are significant rolesof silver nanoparticles. [5][6]

1.3 Properties of Silver Nanoparticles:

1.3.1 Surface Plasmon Resonance:

When we incident light to silver nanoparticles, free electrons of its outer shell start to vibrate for the oscillating electric field. For this vibration it needs a specific energy, which the electrons get from the incident light. That's why the nanoparticlereflects all the color of light except that specific color. This phenomenon is called Surface Plasmon Resonance. Silver Nanoparticles shows different color for different environment, size and shape.

1.3.2 Different Shapes and Crystallinity:

Silver nanoparticles can form different shape for different fabrication techniques. Generally, anisotropic shapes are produced in the presence of stabilizing polymer that specially ties to one crystal face causing one crystal direction growing faster than others. Different fabrication process creates nanoparticles which different size of the crystalline domains.

1.4 Properties of Silver:

Some properties of Silver Nanoparticles are shown in below [7]

Properties	Value
Density	10.47 g/cm^3
Molar mass	107.86 u
Boiling point	2162°C
Melting point	961.78°C

Table 1: properties of silver

1.5 Topic covered in this paper

In this thesis we mainly focus on synthesis the silver($AgNO_3$) nanoparticles and characterization and properties of the silver nanoparticles. This paper cover the synthesis process of silver nanoparticle. In our thesis we use the chemical reduction method of synthesis. This method is easy and cost effective. AgNPs can be characterized in different way. In our paper we describe about UV-Uis spectroscopy, scattering of leaser light through nanoparticle solution ,polarization property of silver nanoparticles and resistance property.When we indicate light to silver nanoparticle the free electrons of it outer shell start to vibrate this property of nanoparticle is call surface Plasmon resonance, we discus about this property in this paper. We also cover the different shape and crystallinity of AgNPs and implementation of AgNPs.

1.6 Summery

In the second chapter of this paper we described about the apparatus we needed for the experient and the calculation which we need to make the solustion of the $AgNO_3$, trisodium citrate dehydrate($C_6H_5O_7$ $Na_3.2H_2O$) . The steps of the experiment of synthesizing silver Nanoparticle are studied in the next chapter. We also discus about different other synthesizing process in that chapter. The forth chapter describes the parameters we changed while doing experiment. In the fifth chapter , advance characterization thechniques are covered . The chapter also covers the brief description of the instruments and the product to carry out the test. Chapter six is about the application of Silver Nanoparticle. This chapter show some advance application of Silver Nanoparticles. Silver Nanoparticls has a huge opportunity of application. In capter six we give the description of few of them . Chapter seven is the last chapter of this thesis it contains future application scope of the silver nanoparticles . This final chapter of the paper concluded the result of the synthesis and some limitations. We also added the pictures to the relevant chapters which we took through the successful synthesis process.

Chapter 2

Applications of Silver Nanoparticles

2.1 Introduction

Current research indicates a comprehensive assortment of Silver Nanoparticle. From the preceding era some of the AgNps application has concerned a huge amount of devotion in medicine, optical, electronics and chemical fields. Silver Nanoparticle has electrical, organic, optical, non-cytotoxic prominence which consent to various applications for Silver Nanoparticle.

2.1.1 Applications in Medicine & Biology

Though all of the applications of silver nanoparticle are important perhaps the need is most desired in medical field. Biomedical applications of silver nanoparticle include water purification, artificial joint replacement, biosensor, silver coated medical devices etc.

Water Purification

Now-a-days drinking contaminated water is a severe civic apprehension. Waterborne diseases spectacularly rise as a consequence of microbiological contamination [17-19]. It is a universal encumber especially in developing countries [20-23] and approximately 1.7 million deaths per year occur for this reason [24]. Many scientists and countrywide Governments are going through to discover a process to condense waterborne illness by purification of fresh water [25]. Some of the researches are showing excellent outcome. One of the most innovative researches is water purification by Silver Nanoparticle. Fibrous membrane allow to purify water by removal of microorganism from the waste-water [26-28]. Electrospun fibers serve as fibrous membrane. It is fabricated by electrospinning (ELSP). It has some advantages like simple, cost-effective [29-31] but one of its shortcoming is it acts like a physical barrier only and no other properties. So to enhance antimicrobial activity researchers have developed hybrid membranes by incorporating

with AgNps [32-33]. Earlier Jain and Pradeep established that AgNps coated onto Polyurethane (PU) foam can serve to avert bacterial pollution of drinking water. To get PU nanofiber first they dissolved PU in a mixed solvent system of DMF/THF (v/v=5:5) to get the ELSP solution. After that, ELSP solution was loaded into a syringe equipped with 20 gauge metal blunt tip needle. They covered the collector with aluminum foil with rotating mandrel and the machine operate with the rate of 1mL/h and the distance between needle and collector should be 15cm. After drying it overnight in vacuum at room temperature then the PU fiber was mounted on digital printing paper and silver ink was injected in cartridge. After that direct printing take place and the achieve result were again dried overnight at room temperature. As silver nanoparticle is a excellent tool widely useful to eliminate bacteria. There are some mechanisms to eliminate bacteria from water. One system is silver nanoparticle attach to the negatively charged bacteria surface and alter the cell membrane. Another mechanism they discovered that silver ions can thwart DNA reproduction. As a outcome one can get fresh drinking water from impure water. These mechanisms can participate in a key function in tumbling water pollution and infectivity [61].

Artificial Joint Replacement

Silver nanoparticles are used in bone cement that is used as artificial joint replacement. Polymethyl methacrylate laden with nano silver is being measured as the bone cement as the nano silver can stimulate antimicrobial action [34]. Polyethylene has been model choice for joint replacement but it has a downside of inclined to wear and tear. To trounce this, AgNPs were added and significantly condensed the shortcoming of polymer [35]. Surgical meshes are used to bridge wound and tissue repair. These meshes are effective but highly risky to microbial infection. Silver nanoparticle coated with polypropylene mesh is 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.

Anticancer Activity

One out of three people has possibilities to widen cancer in their natural life. Even if various chemotherapeutic agents are presently being used on different types of cancers, the side effects are colossal, and predominantly, administrations of chemotherapeutic agents by intravenous infusion are a dreary procedure [36]. As a result, it is obligatory to build up technologies to evade systemic side effects. On this stage, lots of researchers are engrossed in developing nanomaterials as an substitute tool to produce formulations that can mark tumor cells particularly. at this point they summarized the toil from diverse laboratories exposure anticancer activity using both in vitro and in vivo model systems. Gopinath et al. [37] investigated the molecular system of AgNPs and establish that involuntary cell bereavement was concentration-dependent under circumstances. Additionaly, they observed a synergistic outcome on apoptosis by using uracil phosphoribosyltransferase (UPRT)- expressing cells and non-UPRT-expressing cells in the presence of fluorouracil (5-FU). They observed that AgNPs not only provoke apoptosis but also sensitize cancer cells in this tentative situation. The anticancer property of starch-coated AgNPs was studied in normal human lung fibroblast cells (IMR-90) and human glioblastoma cells (U251). AgNPs induced modifications in cell morphology, reduced cell capability and amplified oxidative stress leading to mitochondrial dent and enlarged assembly of Reactive Oxygen Species (ROS), ending with injured DNA. Between these two cell types, U251 cells proved additional sensitivity than IMR-90 [38]. The equivalent assemblage also confirmed that the cellular uptake of AgNPs came about generally throughout endocytosis. AgNP-treated cells exhibited various abnormalities, as well as downregulation of major actin binding protein, upregulation of metallothionein, [39]. The morphology scrutiny of cancer cells implied that biologically synthesized AgNPs could induce cell death very notably. Jun et al. [39] sophisticatedly primed multifunctional silver-embedded magnetic nanoparticles. The first type contain of silver-embedded magnetic NPs with a magnetic core of average size 18 nm and an additional type consist of a bulky silica shell with silver having an usual size of 16 nm; the consequential silica-encapsulated magnetic NPs (M-SERS dots) fabricate sturdy surface-enhanced Raman scattering (SERS) signals and have magnetic chattels, and these two significant

properties were used for targeting breast-cancer cells (SKBR3) and hovering leukemia cells (SP2/O).

Cancer therapy

The medical application of AgNPs in cancer is alienated into diagnostic and therapeutic reasons. 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. For illustration, Lim et al. [40] synthesized plasmonic magnetic nanoparticles to augment MRI contrast consisting of various apparatus of various nanoparticles in a single dais containing silver monolayer-gold-coated magnetic nanoparticles. These encrusted materials showed exceedingly competent carnage of SKBr3 cells within 3 min of near-infrared laser at the comparatively low exposure of 12.7 W/cm at 808 nm. To deal with the competence of photothermal therapy, Huang et al. [41] deliberate an aptamer-based nanostructure which combines the high absorption efficiency of Au–Ag nanorods screening tremendous hyperthermia efficiency and selectivity. The amalgamation of AgNPs with ligands stalwartly influences the toxicity and cellular uptake into the cells. Photo-based nanomedicine has achieved much substance for cancer healing amid some looms [42]. Khlebtsov et al. [43] extended multifunctional NPs which appreciably induced cell death in HeLa cervical cancer cells. Wang et al. [44] expanded folic acid (FA)-coated AgNPs with a typical size of 23 ± 2 nm showing tremendous receptor-mediated cellular uptake; with this compound (FA-AgNPs), they conjugated the chemotherapeutic medicine doxorubicin (DOX) by electrostatic bonding. Cell death was observed after 8 h when DOX was released proficiently. They completed that AgNPs can be used as nanocarriers for preferred drugs for cancer treatment.

Silver coated Medical Devices

Silver Nanoparticles are also considered as a candidate for coating medical devices. On the other side, medical devices coated with metallic silver are proved disappointing in the clinical test because of the inactivation of metallic silver when it comes in contact with blood plasma and the lack of durability of the coating. It also fails to develop antimicrobial bustle [riley]. Researchers demonstrated the use of AgNPs for impregnation of polymeric medical devices to amplify antimicrobial efficiency. Silicon discs of 0.45mm width were used as a biomaterial for impregnation, the silver polyester non woven.

2.1.2 Electrical Applications

In current days, AgNPs have diverse electrical functions such as photovoltaic cells, light-emitting diodes (LEDs), organic thin film transistors, displays, smart clothing, sensors and etc. Silver Nanoparticles Inkjet technology is used for some of these types of applications. It is digital, non- contact and also a mask-less additive pattern process is used to deposit very wide range of materials. The advantages o this technology is cheap costly, stable in big area manufacturing and flexible electronics.

Flexible Electronics

The conductive material is the most important constituent of Inkjet printing of AgNPs electrical applications. There are some other conductive materials such as, polymers [45-46], graphene [50-51], carbon [47-49] and metal NPs [52]. But in the case of conductive polymers, carbon and grapheme the conductivity ($10\text{-}10^2$ s. cm^{-1}) which is 2-4 order lower magnitude than metal NPs ($10^4\text{-}10^5$ $s.cm^{-1}$). Because of some of these downsides, metal NPs are considered most capable

entrant for Inkjet printing objects and most metal NPs ink are standing on AgNPs. Bulk silver has the lowest resistivity than other metallic elements. Furthermore, it is inexpensive than gold and oxygen control is not needed in this method as like as copper [53]. The researchers accounted that AgNPs is fine conductive when they are sintered at approximately 200-350℃ [54-57]. However, in these temperatures AgNPs ink is incompatible with many plastic, paper substrate used in flexible electronics and biomedical devices. If AgNPs ink arranged by the reactive Inkjet printing approach [58-59] it can be sintered at low temperature and it demonstrates superior conductivity. Shen et al. [60] to acquire AgNPs ink they primed it simply. Firstly, they added diverse quantity of silver to de-ionized water (8g) and ethylene glycol (2g). Ethylene glycol was used to regulate the ink viscosity and surface tension. Then they kept it in ultrasonic treatment for 20 minutes. The upshot of this method is brown and highly stable powder. By Inkjet printing system it can be printed 2D- pattern and it can be premeditated by Microsoft Office. The width of the ink lines can be controlled by shifting silver quantity or number of printing cycle. Now the printed silver lines were sintered at 50℃ for 15 minutes and amplify the size of NPs. After that it was dried for 24hours and then it was scrutinized by SEM. It showed AgNPs were not in contact with the surface of printed substrate. AgNPs melt and enclosed large area at 80℃. It stays incessant but there may be several splits. But at 140℃, the precincts of AgNPs fade away and become smoother and more incessant which abridged electrical resistivity. Finally, the electrical applications of AgNPs are cost effective; it needs short procedures, durable and most importantly highly conductive.

Chapter 3

Apparatus and Calculation

3.1 Introduction

There are so many method of synthesis silver nanoparticle . To create different size and shape of nanoparticle these methods are used. Among many methods we use chemical reduction method. This method is simple and cost effective and also it gives the desire shape of silver nanoparticle. In this method we use Silver Nitrate($AgNO_3$) and trisodium citrate dehydrate($C_6H_5O_7$ Na_3.2H2O). Both of them are available in solid form. We have to make solution from solid form of these two salts. For Silver Nitrate($AgNO_3$) we make the solution of different mMole concentration and for trisodium citrate dehydrate($C_6H_5O_7$ $Na_3.2H_2O$) we make the solution of different parentage(%) concentration.

3.2 Apparatus and Chemicals

3.2.1 Chemicals

1. Silver Nitrate($AgNO_3$)
2. Trisodium citrate dehydrate($C_6H_5O_7$ $Na_3.2H_2O$)
3. Distilled water

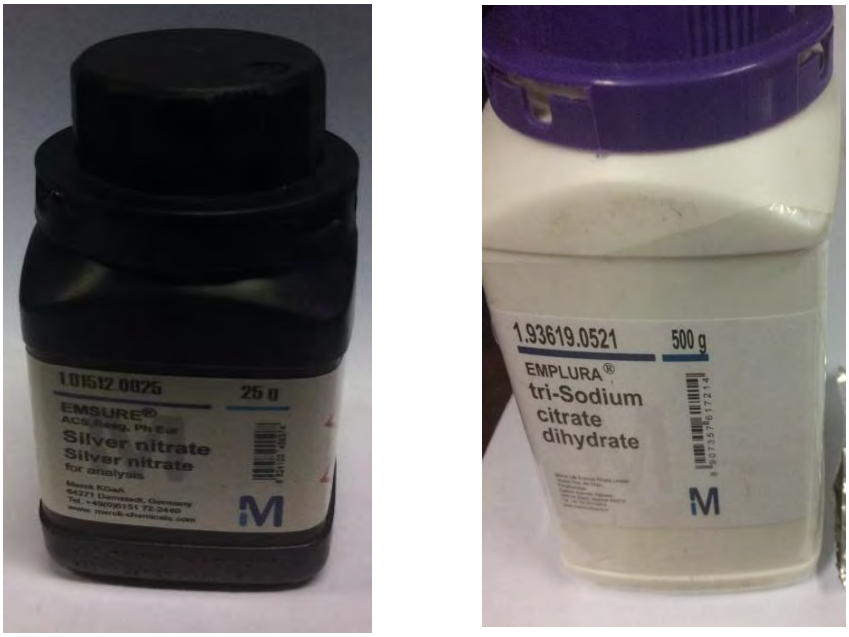


Figure 1: Chemicals of Silver Nitrate and Trisodium citrate dehydrate

3.2.2 Apparatus:

1. Beaker
2. Test Tube
3. Conical Flask
4. Pipette
5. Burette
6. Measuring Cylinder
7. Glass Funnel
8. Dark glass bottle with stopper
9. Erlenmeyer Flask
10. Magnetic Stirrer and hotplate combination
11. Digital thermometer
12. Aluminum Foil

Figure 2: Apparatus needed for experiment

3.3 Calculation:

For make the solution at first have to do the calculation of the salts. Different concentrations need different amount of salt.

3.3.1 Calculation for Silver Nitrate($AgNO_3$):

Molar Mass,$AgNO_3$→[107.8628+14.067+(3*15.4994)]→169.87g

This is state that if 169.87g of Silver Nitrate ($AgNO_3$) dissolved into 1L of distilled water ,1L of Silver Nitrate ($AgNO_3$) which concentration is 1M.

In this experiment we need different concentration of Silver Nitrate ($AgNO_3$) like .5mM,1mM,2mM,3mM,4mM,5mM,6mM,7mM,8mM,9mM,10mM,20mM.

At first we have to covert the 1M to 1mM and we also have to change the amount of distilled water from 1L to 250mL.

For 1mM concentration and amount of water is 250mL need→$(\frac{169.87*250}{1000*1000})$g of $AgNO_3$

→0.0424675g

We keep the amount o distilled water constant 250mL

To make the other Moler concentrations solution we follow an equation. The equation is given bellow.

Amount of $AgNO_3$ needed→(.0424675*x)g

x→ Concentration of Moles

For .5mM:

Amount of $AgNO_3$ needed→(0.0424675*x)g

→(0.0424675*0.5)g

→0.021233g

By dissolving 0.021233g of $AgNO_3$ into 250mL of distilled water, we get the AgNO solution of concentration of 0.5mM.

For 2mM:

Amount of $AgNO_3$ needed→(0.0424675*x)g

→(0.0424675*2)g

→0.084935g

To make the $AgNO_3$ solution of $AgNO_3$ of concentration of 2mM we have to dissolve 0.084935g $AgNO_3$ into 250mL of distilled water.

For 3mM:

Amount of $AgNO_3$ needed→(0.0424675*x)g

→(0.0424675*3)g

→0.1274g

To make the $AgNO_3$ solution of $AgNO_3$ of concentration of 3mM we have to dissolve 0.1274g

$AgNO_3$ into 250mL of distilled water.

For 20mM:

Amount of $AgNO_3$ needed→(0.0424675*x)g

→(0.0424675*20)g

→0.84935g

By adding 0.84935g of $AgNO_3$ into 250mL of distilled water we make the solution of $AgNO_3$ which concentration is 20mM.

Using that equation we find out the other amount of $AgNO_3$ we needed to make the solution of $AgNO_3$ of different mMs.

3.3.2 Calculation for Trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$) :

In this experiment we also use the different concentration of trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$). We have the solid from of trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$) ,we dissolved it into distilled water and thus we make the solution of the trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$).

To calculate the concentration of solution we use the weight/volume percentage method.

$\frac{w}{v}$%= [mass of solution(g)/volume of solution(mL)]*100%

For obtain 0.5% of trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$) solution

(0.25g/50mL)*100%=0.5%

Therefore we need to dissolve 0.25g of trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$)into 50mL of distilled water to get 0.5% of trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$) solution.

For 1% ——————→0.5g was dissolved into 50mL of distilled water

For 1.5% ——————→0.75g was dissolved into 50mL of distilled water

For 2% ——————→1g was dissolved into 50mL of distilled water

For 3% ——————→1.5g was dissolved into 50mL of distilled water

For 4% ——————→2g was dissolved into 50mL of distilled water

For 5% ——————→2.5g was dissolved into 50mL of distilled water

For 6% ——————→3g was dissolved into 50mL of distilled water

For 7% ——————→3.5g was dissolved into 50mL of distilled water

For 8% ——————→4g was dissolved into 50mL of distilled water

For 9% ——————→4.5g was dissolved into 50mL of distilled water

For 10% ——————→5g was dissolved into 50mL of distilled water

For 11% ——————→5.5g was dissolved into 50mL of distilled water

For 12% ——————→6g was dissolved into 50mL of distilled water

For 13% ——————→6.5g was dissolved into 50mL of distilled water

For 14% ——————→7g was dissolved into 50mL of distilled water

For 15% ——————→7.5g was dissolved into 50mL of distilled water

3.4 Storage:

Storing both the Silver Nitrate($AgNO_3$) and Trisodium citrate dehydrate($C_6H_5O_7Na_3.2H_2O$)solution proved to be a challenge. Proper storage would require the solutions to be kept completely away from sunlight and stored in a termperature controlled environment. We use dark glass bottle and stopper to protect the solution from sunlight and air. We also use aluminum foil to protect it from reacting with the air because silver is very reactive with the oxygen.

Figure 3: Storage of $AgNO_3$

Figure 4: Storage of Trisodium citrate dehydrate($C_6H_5O_7\ Na_3.2H_2O$)

Chapter 4

Synthesis of Silver Nanoparticle

4.1 Introduction

In our search we find different method to synthesis silver nanoparticle. To create different size and shape nanoparticle these methods are used. There are many other methods from these we find three processes are simple to use and picked a suitable and cost effective one. First two methods are used to create spherical shape silver nanoparticle. They are called chemical reduction methods. In first method aqueous Silver Nitrate ($AgNO_3$) and trisodium citrate dehydrate ($C_6H_5O_7Na_3.2H_2O$) were used. In another method aqueous $AgNO_3$ where reduced in the presence of $NaBH_4$. By using third method triangular nanoprism can be created. In this method PVP: $AgNO_3$ and hydrogen per oxide and sodium citrate where used. Size and shape of AgNPs can very because of synthesis process as well as parameters and concentration of chemicals. Parameters like temperature, percentage of chemical, reaction rate can produce different size AgNPs.

In this paper we are going to discuss about the first chemical reduction method which was introduced by John Turkevich (1951).We select this method as it is the simplest method and cost effective as well.

4.2 Synthesis process

In the citrate reduction method trisodium citrate dehydrate ($C_6H_5O_7Na_3.2H_2O$) where used as reducing agent as well as stabilizing agent and Silver Nitrate ($AgNO_3$) where used as precursor. In this method we took 20ml of $AgNO_3$on a 50ml beaker and heat the solution with continuous stirrer. After the solution reaches boiling temperature we add 2ml of trisodium citrate dehydrate

($C_6H_5O_7Na_3.2H_2O$) one drop per second by using a burette. We continue the heating and stirrer until the mixture turn into greenish yellow color. This change in color represents the production of AgNPs [8].

4.2.1 Common terminologies and definitions

Before we discuss farther about synthesis process of AgNPs we need to understand some basic terminologies for better understanding the process [9].

1. **Nucleation:** Nucleation is the process that determines how long an observer has to wait before the new phase or self-organized structure appears. It is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organization. In our case this is the formation of molecule.

2. **Crystal growth:** It is a major stage of a crystallization process, and consists in the addition of new atoms, ions, or polymer strings into the characteristic arrangement of a crystalline Bravais lattice. The growth typically follows an initial stage of either homogeneous or heterogeneous (surface catalyzed) nucleation, unless a "seed" crystal, purposely added to start the growth, was already present.

3. **Aggregation:** Aggregationmeans formation of a number of things in a cluster.Aggregation occurs when particles contacts with each other and thermodynamic interactions allow for particle attachment to happen. There are two types of aggregation relevant to NPs homoaggregation and heteroaggregation. Homoaggregation means aggregation of two similar particles. Heteroaggrigation means aggregation between two different particles.

4. **Super saturation:** is a state of a solution that contains more of the dissolved material than could be dissolved by the solvent under normal circumstances. Normally we cannot see the material in the solution if it is fully dissolved, but in super Saturation we can see the material.

4.2.2 Formation of AgNPs

We add trisodium citrate one drop per second on the $AgNO_3$. The citrate acts as a reducing agent and reduce Ag^{3+} ion to Ag atoms. Nucleation happens. The solutions then become super saturated due to strirring. Due to aggregation silver atoms collide and form stable silver nucleus and crystal growth stars to form after a few minutes. The color of the solution starts to change into reddish yellow then greenish yellow. This color change confirms the formation of AgNPs.

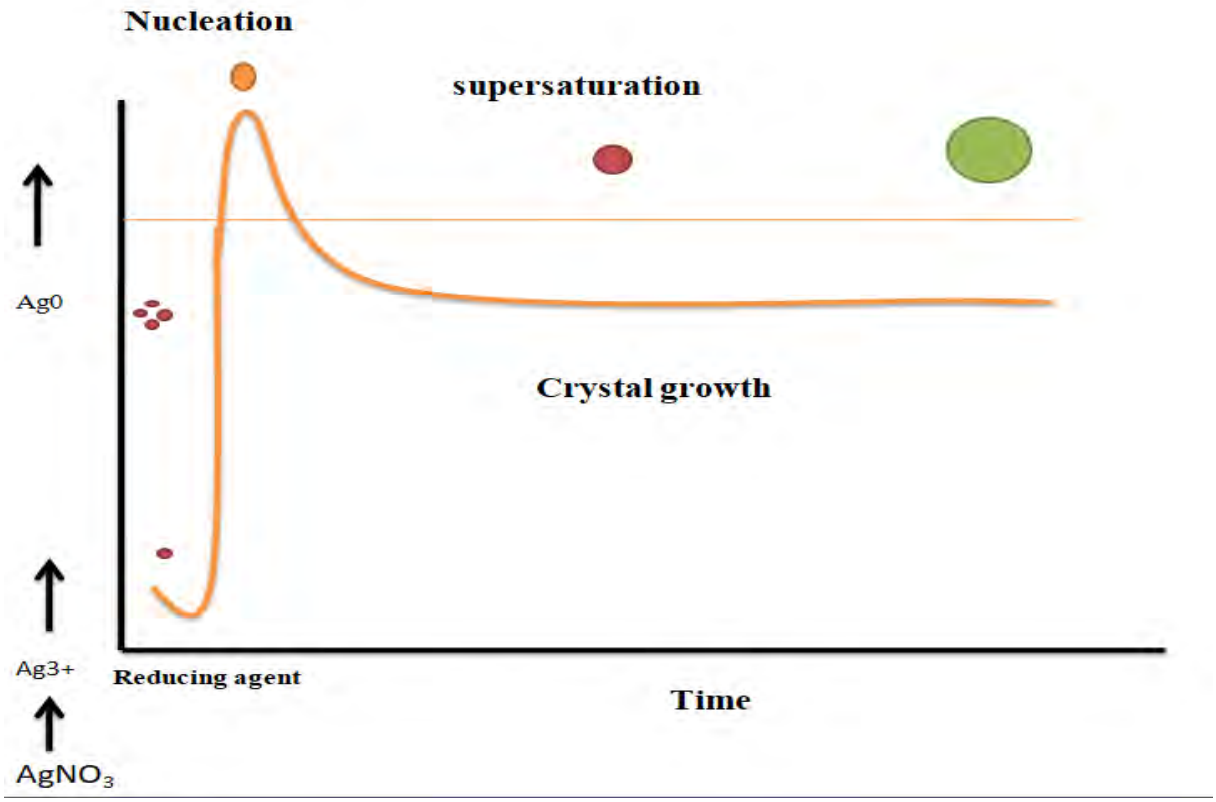


Figure 5: Formation of AgNPs

4.2.3 Flowchart of Synthesis process

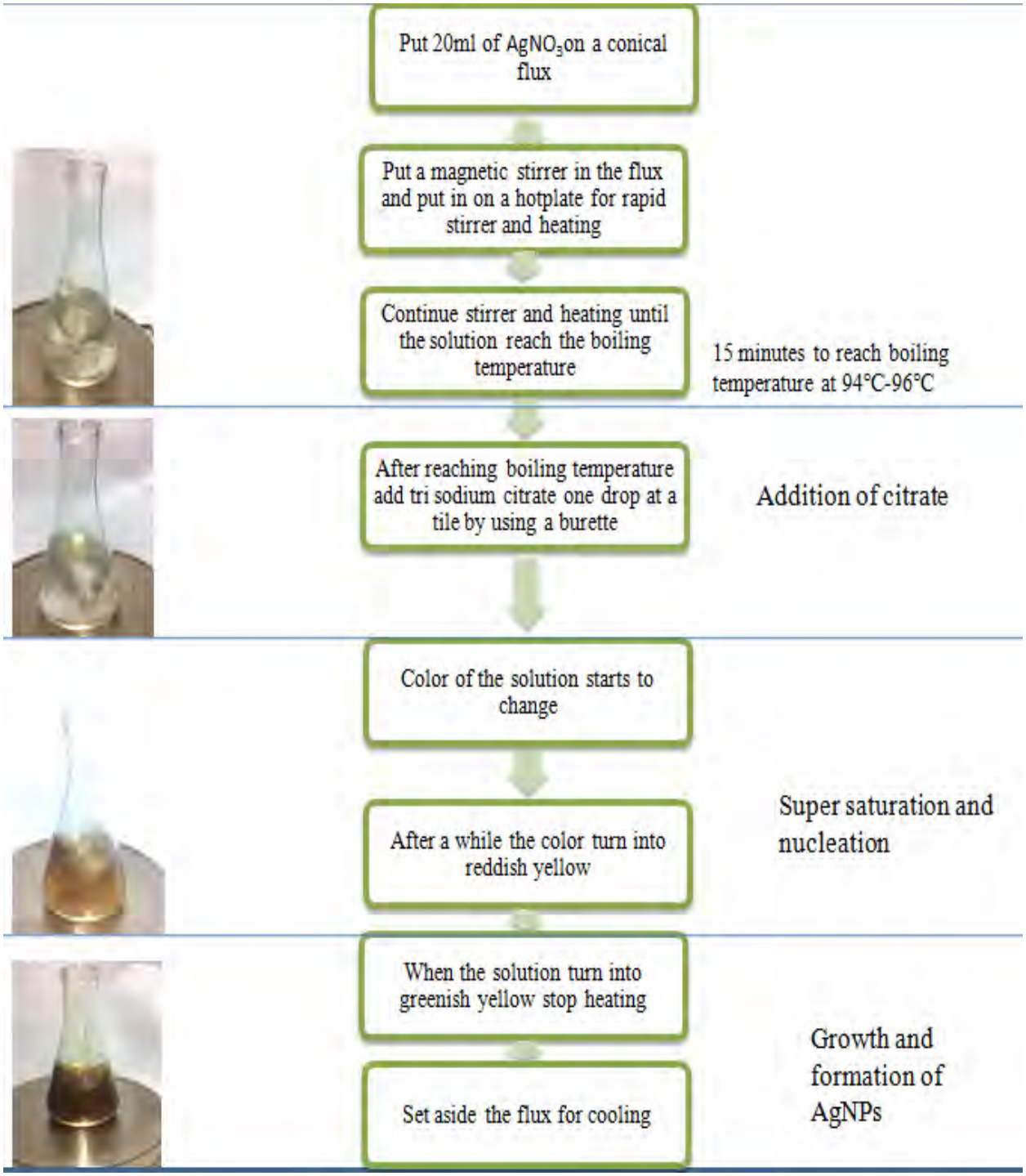


Figure 6: Flowchart of synthesis process

4.3 Observation and test

Figure 7: different phase of reaction

From these pictures we can see the different phase of synthesis. From left the first picture shows the solution of $AgNO_3$ which is on the hot plate and rapid stirrer is on. The color of the solution is transparent. The second picture is taken after the addition of trisodium citrate dehydrate approximately one drop per second. After the addition of citrate solution the color of the mixture starts to change. After 2 to 3 second the color of the solution changes into light yellowish. The light yellow color changed into reddish yellow after a few second. In the third picture we can see the changed color. The change of color continuous and after a few minutes the color changed into greenish yellow as the fourth picture is shown. The heating is stopped after this stage and set aside to cool down the solution. The whole process takes 20-30 minutes.

4.3.1 Laser Test

As nanoparticles have scattering and reflective properties passing a laser through the solution is a good way to confirm the existence of nanoparticle in a solution. In this approach we put the solution in a beaker and point a laser to it. If the laser path is visible through the solution then AgNPs is there. The laser path is visible due to scattering. We clearly saw the laser path on our solution. It confirms the presence of AgNPs. We also pass the laser through water and in water the laser path was not visible.

Figure 8: Laser Test on AgNPs solution

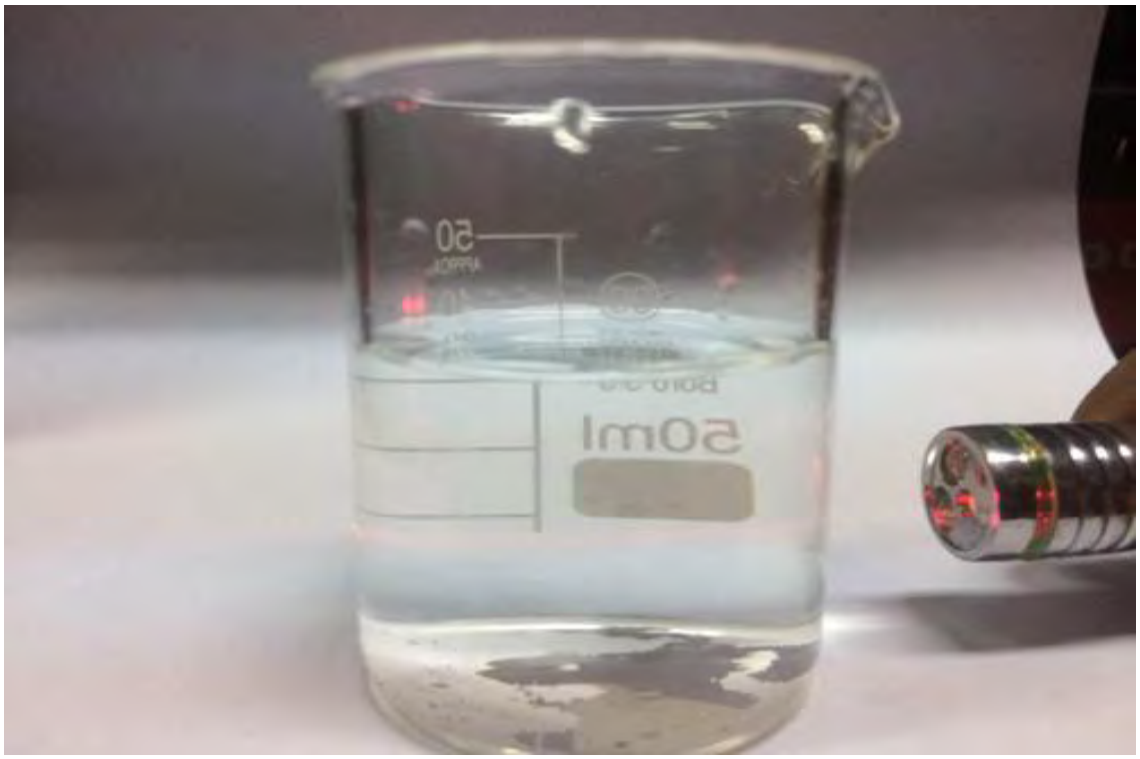


Figure 9: Laser test on water

4.3.2 Tyndall Effect

Tyndall effect is an effect of light scattering in colloidal. It is named after John Tyndall a 19th century's physicist. This effect is also known as Willis-Tyndall scattering. The Tyndall effect is an easy way of determining whether a mixture is colloidal or not. When light passed through a normal solution, the light passes cleanly through the solution, however when light is passed through a colloidal solution, the substance in the solution scatters the light and make it visible.

For tyndall effect shorter wavelength light is reflected and longer wavelength light is transmitted. As different size nanoparticle absorb different wavelength light we can see different wavelength light scatter through our solution [10].

Figure 10: Tyndall effect

From these pictures we can see the effect of tyndall effect. As we shine white light on these solutions we can see the red and yellow color due to scattering. The wavelength of red and yellow is in between 550nm to 650nm.

4.3.3 Salt test

To see the result of salt test we add 0.5 g of NaCl or simply table salt was dissolved in 10 ml of water to make the salt solution. Then we add a few drop of that solution to our silver nanopartilce solution. The color of the solution instantly changed to then it become transparent. We observe that there is formation of sediment after adding the salt. As the silver is positive cl^- ion react with positive silver ion and create agcl. Then sediment os this formed.

Figure 11: before and after adding salt on AgNPs

As we can see from the picture the color of our solution was orangish. After adding salt the color changed blackish and sediment is formed.

Chapter 5

Experiment with changed parameter

5.1 Introduction

Chemical reduction or citrate reduction method is used to create spherical shaped nanoparticle of different size. The size of the AgNPs can be changed by manipulating different parameter and concentration of citrate. By changing the concentration of $AgNO_3$ and citrate we can get different types of result.

5.2 Changeable parameter

There are two ways we can change the parameter of our synthesis system. As for the basic synthesis we used 20ml of 1mM $AgNO_3$ solution and 2ml of 1% tri sodium citrate dehydrate. We then changed the parameter in two ways and observe the effects of these changes. At first we change the citrate percentage and keep the 1mM $AgNO_3$ constant. Then we keep the citrate constant and changed the $AgNO_3$ concentration.

5.2.1 Change of citrate concentration

In this experiment we only changed the citrate concentration and other parameters were kept as it was. We used 1mM $AgNO_3$ and changed the citrate. 1%, 2%, 3%, 4%, 5%, 7%, 10% were used to conduct this experiment.

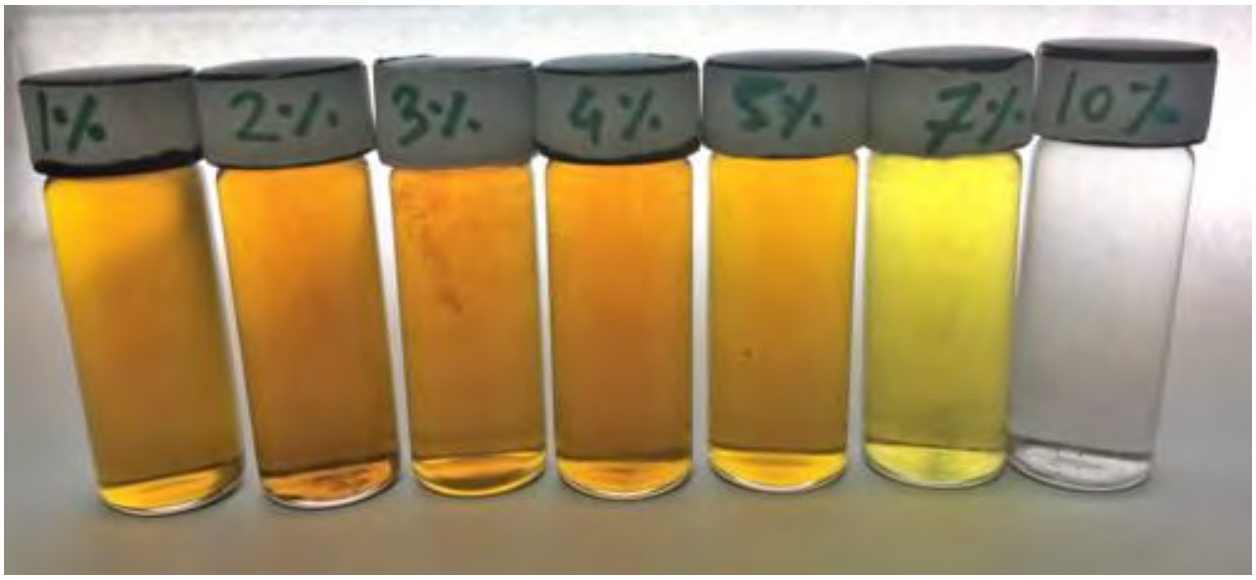


Figure 12: AgNPs made by different % of citrate

As we can see in the picture the color is changing. From left we can see the orangeish color which is changed to greenish yellow at 7%. 10% solution is transparent as sediment is formed.

Silver solution (mM)	Citrate (%)	Amount of silver solution(ml)	Amount of citrate (ml)	Color of AgNPs	Sediment
1	1	20	2	Orange	No
1	2	20	2	Orange	No
1	3	20	2	Deep orange	No
1	4	20	2	Deep orange	No
1	5	20	2	yellowish	No
1	7	20	2	Greenish yellow	No
1	10	20	2	transparent	Yes

Table 2: change of citrate concentration

5.2.2 Change of silver solution concentration

In this experiment we kept tri sodium citrate 3% solution constant and changed $AgNO_3$ concentration. We use 0.5mM,1mM,2mM,3mM,4mM,5mM,10mM,20mM and observe he change in color.

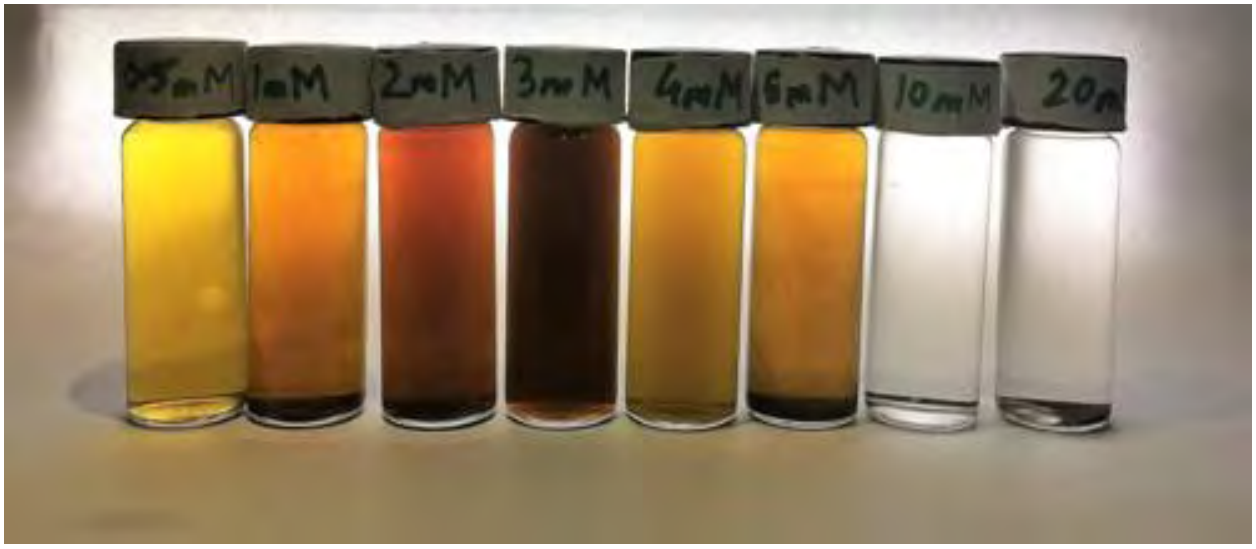


Figure 13: AgNPs made by different silver solution

As we can see in this picture different concentration of silver solution reacted with 3% citrate and gives us different colors. 10mM and 20mM is transparent as sediment is formed.

Silver solution (mM)	Citrate (%)	Amount of Silver solution (ml)	Amount of citrate (ml)	Color of AgNPs	Sediment
0.5	3	20	2	Yellow	No
1	3	20	2	Orange	No
2	3	20	2	Red	No
3	3	20	2	Green	No
4	3	20	2	Light orange	No
5	3	20	2	Yellowish	No
10	3	20	2	Transparent	Yes
20	3	20	2	Transparent	Yes

Table 3: Change of Silver solution

Chapter 6

Characterization

6.1 Introduction

AgNPs can be characterized by different method. We will describe spectroscopy, scattering of light, polarization, SEM and TEM. From these method result can be varying for different size and shape of AgNPs.

6.2 Spectroscopy

Interaction between matter and electromagnetic radiation can be known by spectroscopy, which is occurred for transition of electron between different energy level. Electromagnetic radiations are called as photon. These package of energy oscillate electric and magnetic field perpendicular with each other. When light passes through the tri sodium citrate dehydrate of AgNPs, some outer band electron absorbs the light differently according to their wavelength and goes to the higher energy level. As it doesn't stay that level much time, it gets back the previous level and emits the light of same wavelength. We can find the intensity of absorbed radiation for different wavelength. By analyzing the wavelength vs absorption graph it is possible characterize the nanoparticles. Because of same absorbed and emitted wavelength, energy difference between two band gaps, where the electron jumps can be fund from the equation below:

$$\Delta E = h\frac{C}{\lambda}$$

Where,

ΔE is the difference of energy between two energy level

h is Planck constant (6.626×10^{-34} m^2 kg / s)

C is the light speed in vacuum

$\boldsymbol{\lambda}$ is the absorbed wavelength

6.3 UV-Vis Spectroscopy

Most of the nanoparticles like AuNPs or AgNPs are being excited at ultra-violate and visible region of light which has the wavelength between 190 to 1100 nm and the spectrum of this region is called UV-Vis spectrum. In this spectrum, ultraviolet and visible region of light send to pass through the sample of AgNPs by a source. Then it measured absorbance rate by a medium in different wavelengths from the spectrophotometer. How much the particle inside the solution exited gives the information about their size and shape. Peak of the graph goes higher wavelength region demonstrates bigger particle. Beer Lambert equation can figure out the way to find the absorbance as well as molar absorptivity.

$A = log10\frac{Io}{I} = \varepsilon lc$ [11]

Here,

A is absorbsion

Io is intensity of light coming in

I is intensity of light coming out

ε is molar absorptivity ($Lmol^{-1}cm^{-1}$)

l is the length of the solution passes by light (cm)

c is the concentration of the solution (mol L^{-1})

6.3.1 Instrumentation of UV-Vis spectrum

The things we need to measure the UV-Vis spectrum are:

Source

Monochromator

Sample compartment

Detector

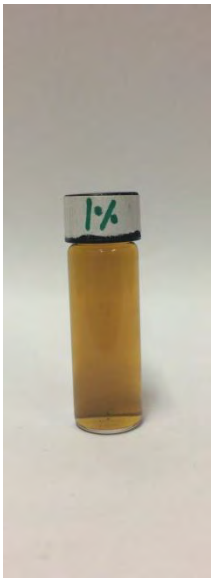
Recorder

At first source passes the white light to the monochromator. Monochromator has three parts. The entrance slit, dispersion device and exit slit. Interred light into the entrance slit pass through the dispersion device that differentiate the light according to their wavelength and select which wavelength can pass through the exit slit. It makes the light come into the solution kept in a cell to measure its absorbance. As its needed to measure absorbance in both ultraviolet and visible region, the cell should be transparent in all of these wavelength of light. Though normal glass is transparent in visible light, the molecules of glass interact with ultraviolet light. So it is not transparent for ultraviolet light. In this matter quartz or fused silica cuvette work well. It is rectangular in shape consist 1 cm width inside. At first cuvette filled with water and measured the its absorbance and list it, so that the absorption of cuvette can be illuminated from the data. Then it filled with required solution and take the measurement. The light passing out sample go inside the detector. It takes the intensity of light comes to it and from the known incident light it find the absorbance by using Beer Lambert equation. This process is continuing for a huge amount of wavelength between ultraviolet and visible range [12].

6.3.2 Findings from some UV-Vis spectroscopy

Silver has a tiny band gap, which causes the electron inside the outer band of silver can move freely. But when it has been created as nano sized particle, difference between valance band and conduction band increase a lot. As changing band gap makes the outer shell electron excited differently and that things changes the color of the nanoparticles too. By seeing UV-Vis spectroscopy we can get the particle size, impurities and shape of the particles [13]. The absorbance peak shifted rightward means the particle inside the solution are bigger and narrowed first peak is determination of spherical particles. Other things we can measure is impurities. Those things can be figure out by the amount of noise at the first peak. For AgNPs the particles aggrigates so fast, so the first peak of AgNPs becomes more gradually decrease and spreader with time. We have measure UV-Vis spectroscopy of 1mM 1%, 3%, 7% citrate and 3% citrate

with 2mM, 3mM 5mM, 10 mM and after plotting the data to the origin software we found these graphs [12].



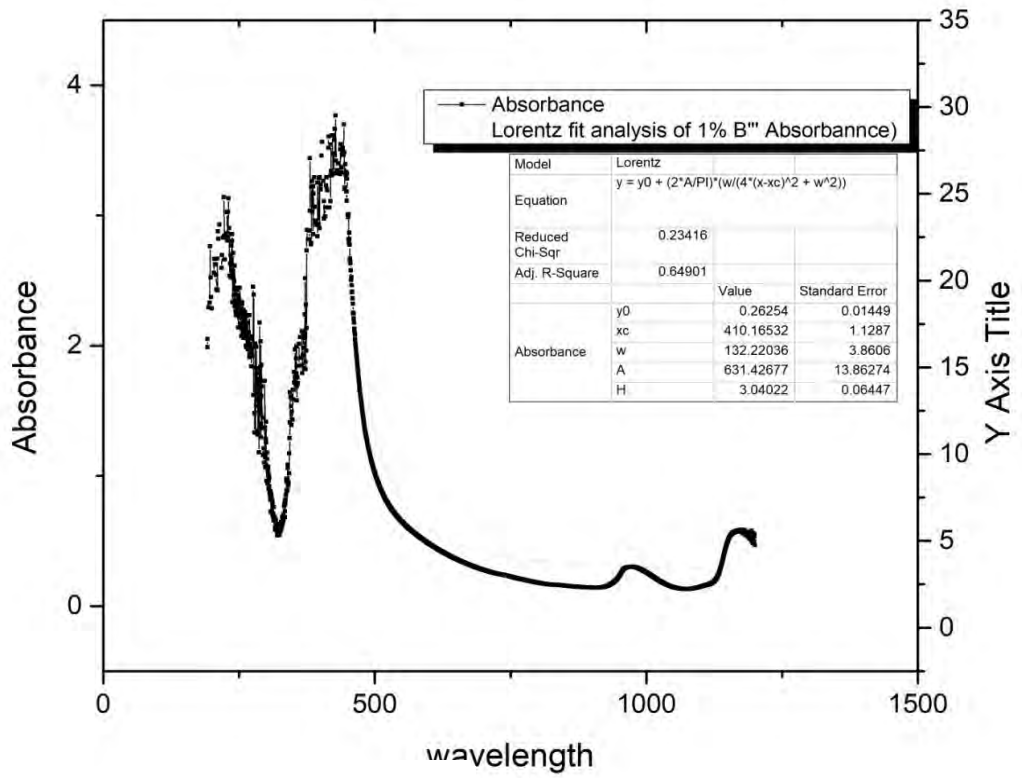


Figure 14: 1mM 1%

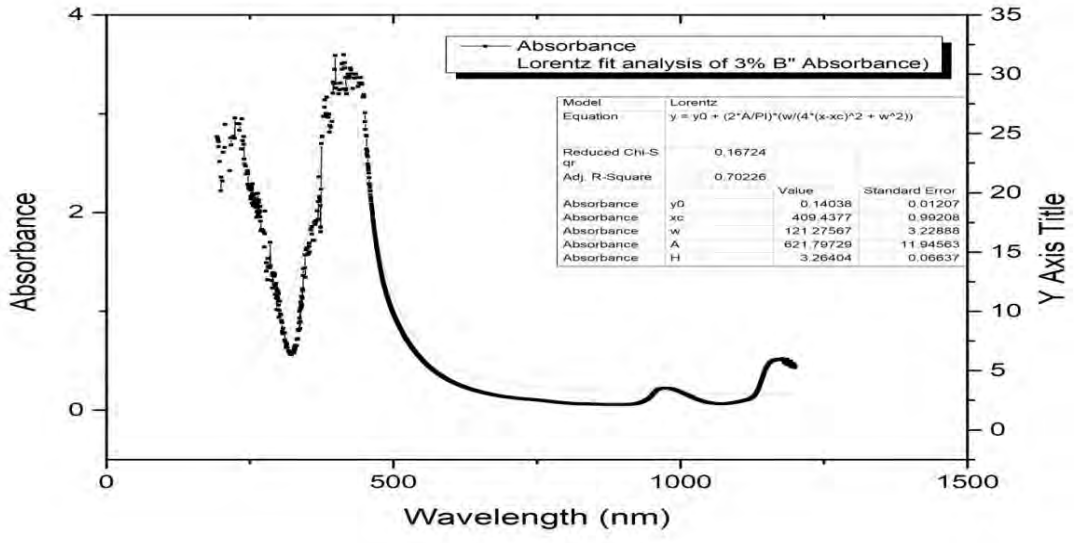


Figure 15: 1mM 3%

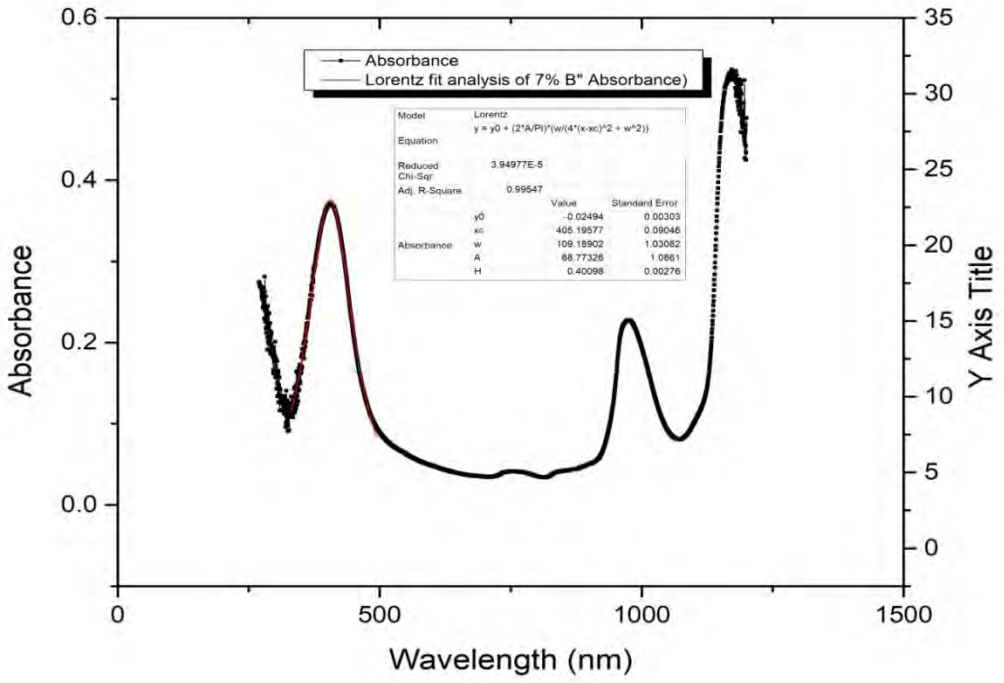


Figure 16: 1mM 7%

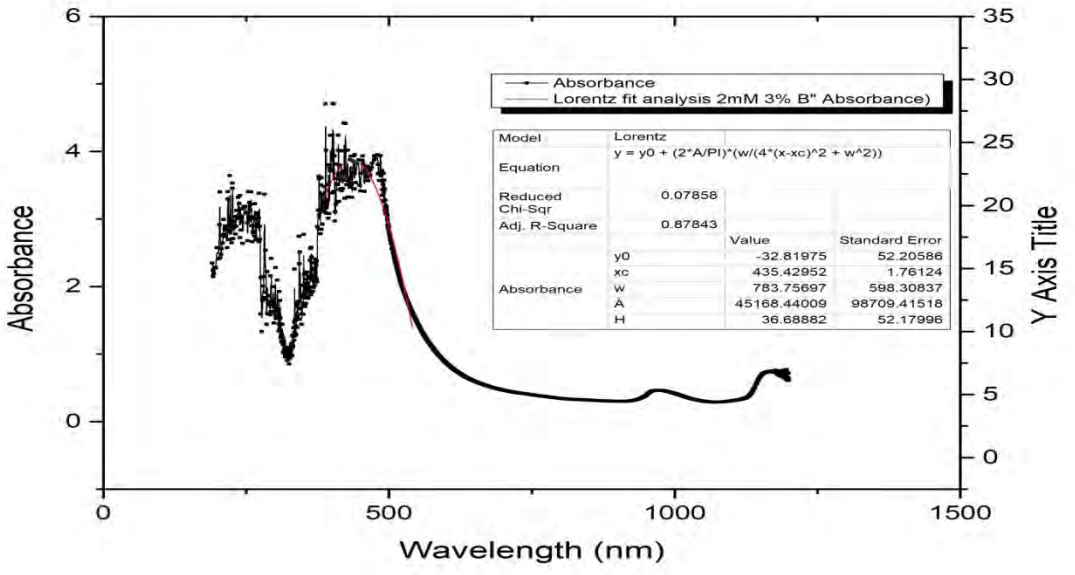


Figure 17: 3% 2mM

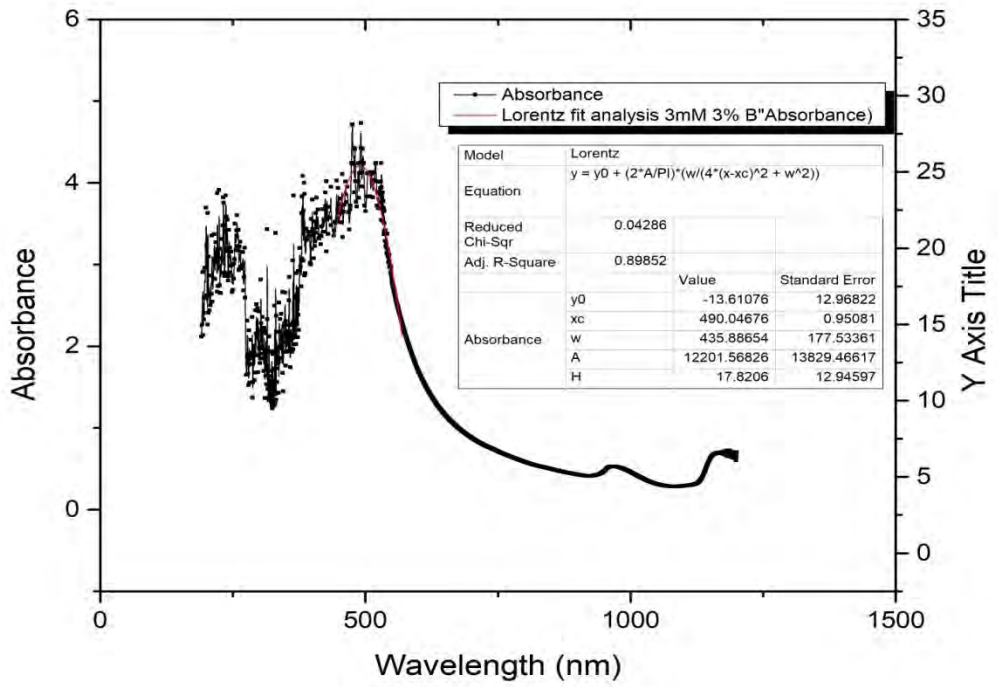


Figure 18: 3% 3mM

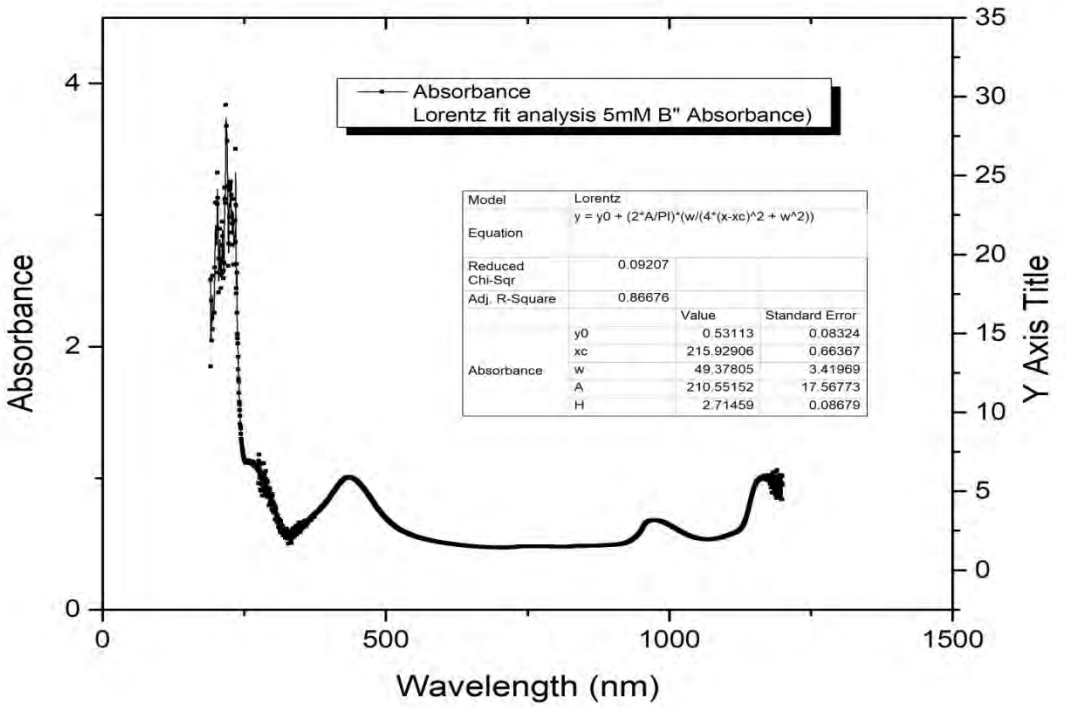
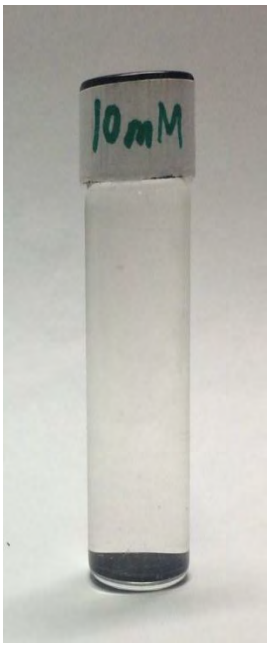


Figure 19: 3% 5mM



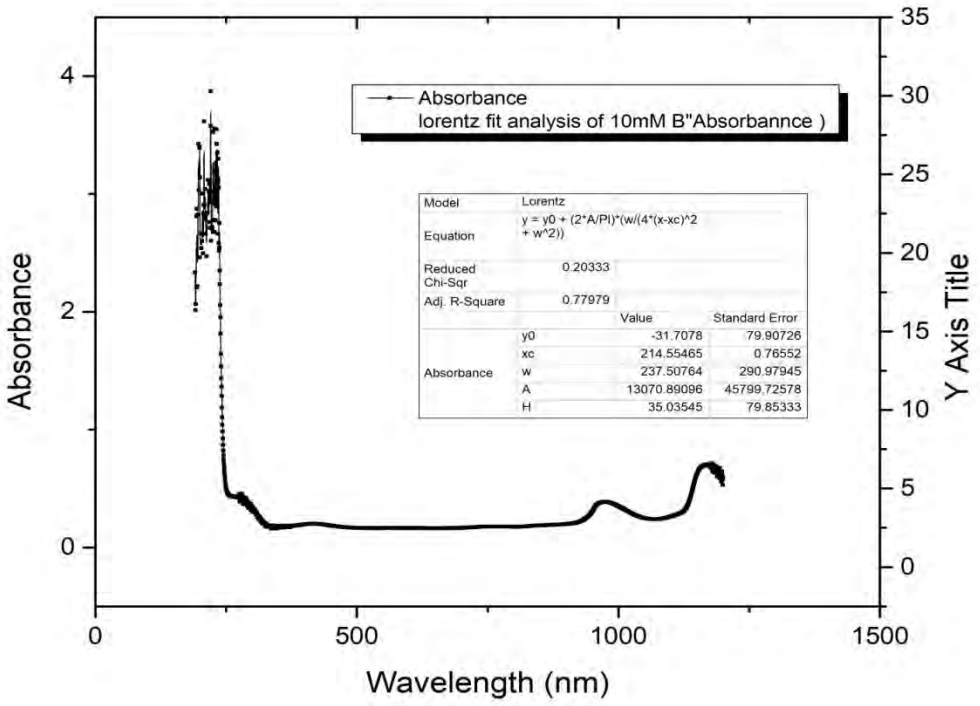


Figure 20: 3% 10mM

here it is shown that all of our nanoparticles have higher impurities and most of them are bigger in size. The reason behind that is late for the measurement. Though our assumed particles were not that much bigger in size, it has aggregate a lot for delayed of our UV-Vis measurement.

6.4 Resistance measurement

As the resistance of anything is directly proportional to the difference between valance band and conduction band, so if the band difference increases there should create some effect in resistance. We put the citrate solution of AgNPs in a beaker and took the measurement. For measuring these resistance, it was important tokeep the multimeter probe's distance same for all the measurement and also had to be ensure that probe's are not touching the glass.

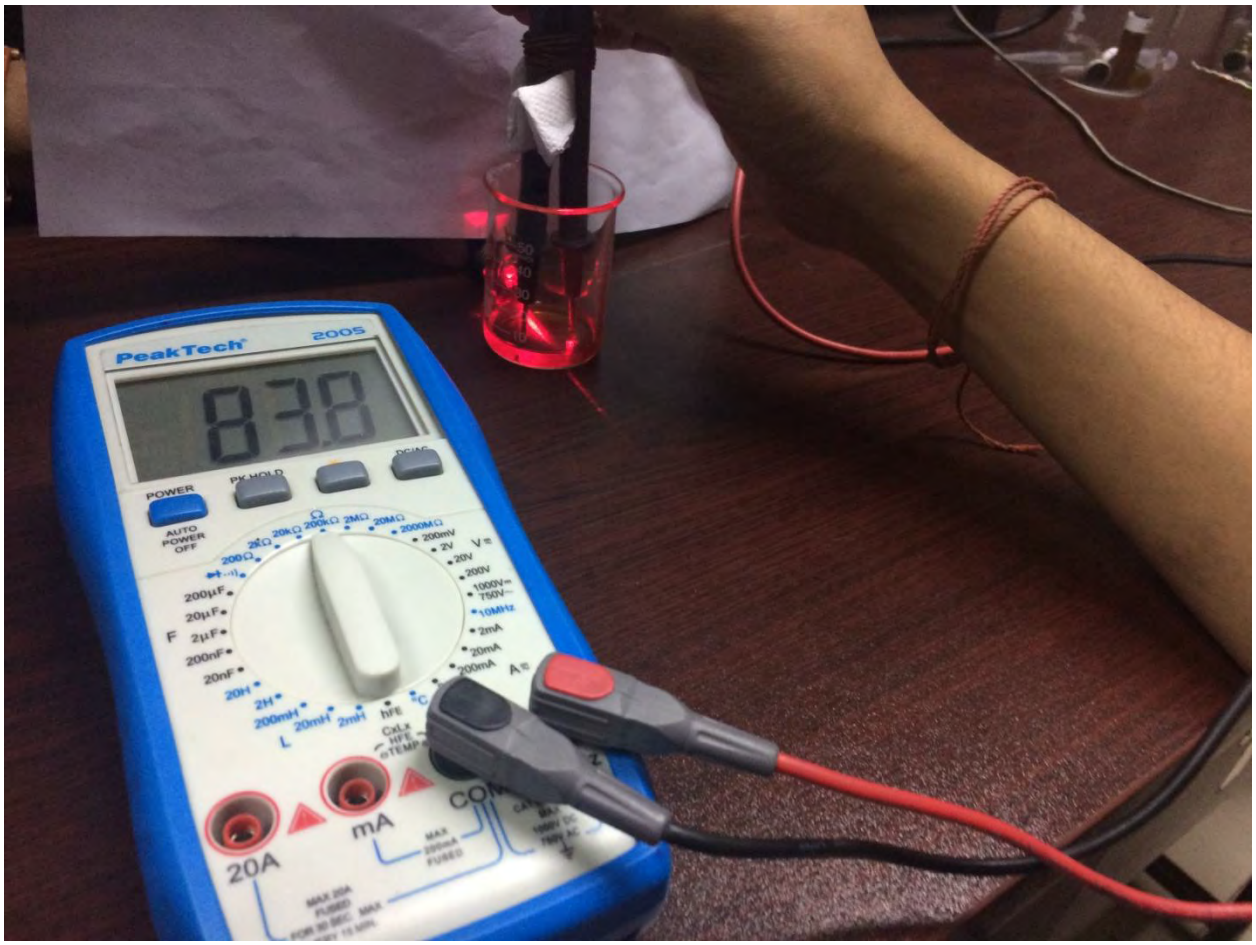


Figure 21: Measuring resistance of AgNPs

The data we found for different citrate is given below:

Keeping 3% citrate as same, increase the molarity of the solution-

1mM	2mM	3mM	4mM	5mM	10mM	20mM
36.833 kΩ	50.8 kΩ	119.33 kΩ	67.5 kΩ	79.16 kΩ	95.5 kΩ	191.83

Table 4: resistance of increased molarity

Keeping molarity as 1mM constant, increasing the percentage of citrate

1%	2%	3%	4%	5%	7%	10%
98 kΩ	143.57 kΩ	114 kΩ	140.167 kΩ	220.37 kΩ	196.67 kΩ	97.83 kΩ

Table 5: Resistance of increased citrate concentration

By using the origin software we plotted a molarity vs resistance graph and make it continuous.

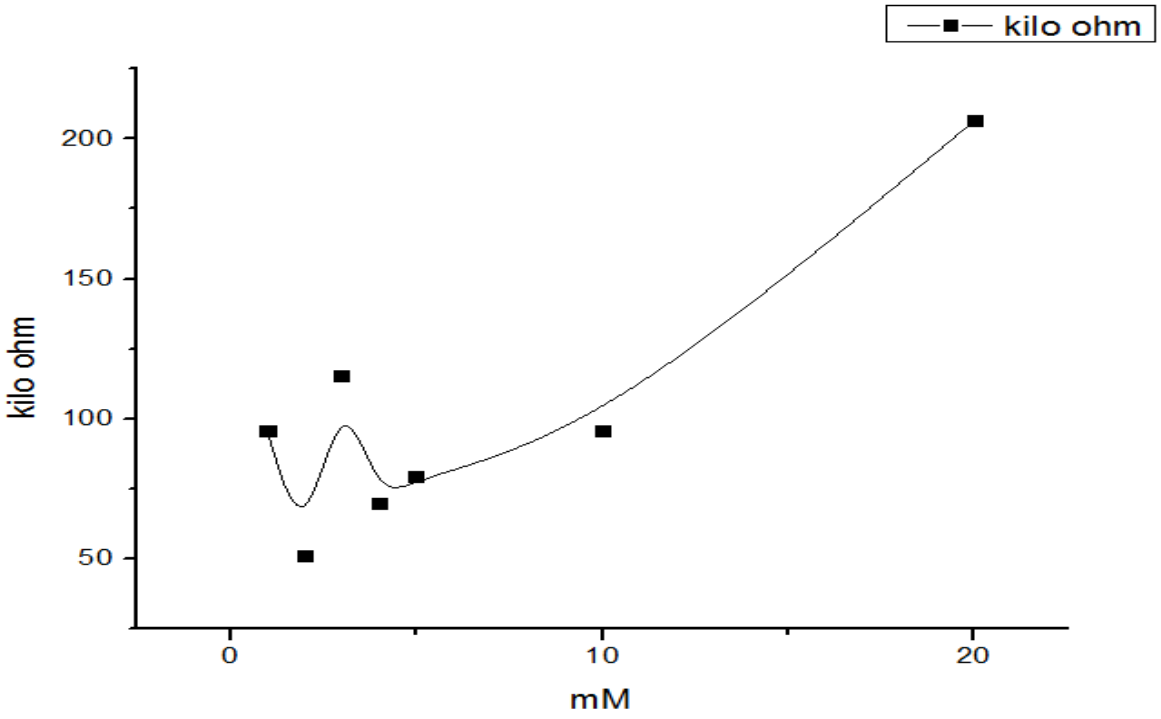


Figure 22: Resistance at 3% citrate constant

It shows clearly that increasing molarity can also increase the resistivity with a peak located near the 3mM.

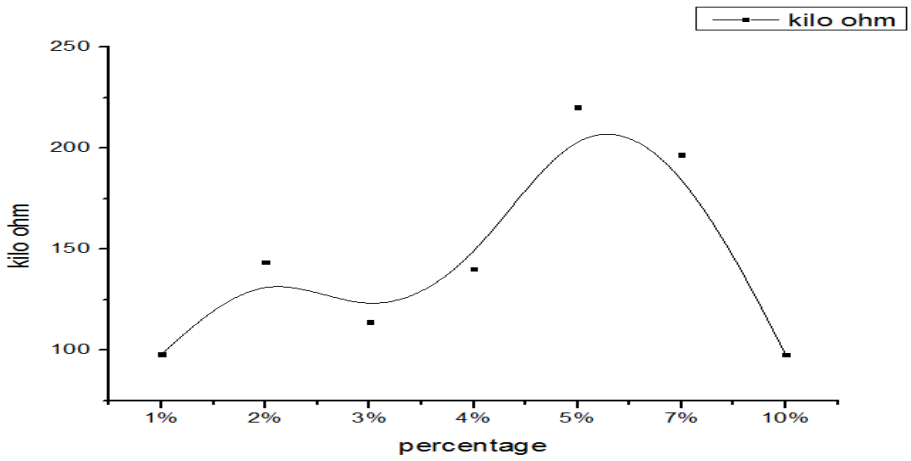


Figure 23: Resistance at 1mM silver solution constant

Here the light also increases gradually, but there are two peaks in the spectrum. One is located at 2% and another one is at 6% citrate.

6.5 Polarization

In previous section we saw that light can be scattered in the nanoparticle solution. In this time, we did same kind of experiment in different way. We used a polarizer and silver nanoparticles solution here. Firstly we pass a white light through the nanoparticle solution and took the picture of its black shadow at the white background. Secondly, we placed a polarizer which is vertically / horizontally polarized with land and took another photo without AGNPs citrate.These two picture we will use as the reference to detect the difference of next two picture. After that our third and fourth picture is mostly important picture, which was taken with a polarizer placing between the AgNPs citrate and light but in both the case, direction of polarizer was perpendicular to each other.

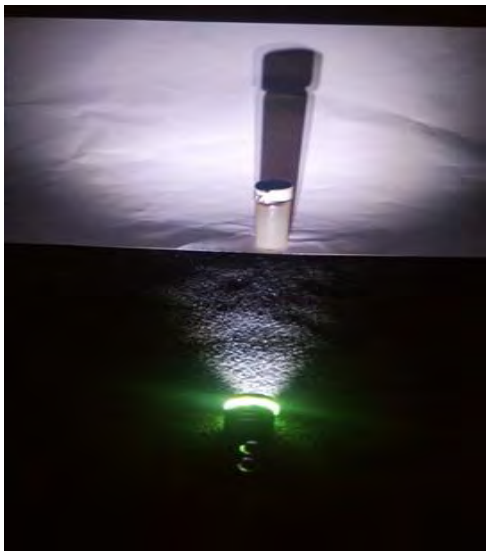


Figure 24: Shadow of AGNPs citrate without polarizer

Figure 25: Shadow of only polarizer

Figure 26: Polarizer placed vertically with AgNPs

Figure 27: Polarizer placed horizontally with AgNPs

From this experiment, it is clearly seeing that the above pictures with same column have the same kind of shadow. The reason is the scattered light in AgNPs solution is being polarized horizontally. That is why when the polarization slits inside the polarizer placed horizontally to the land, it can pass through the polarizer, but when it placed in vertically polarized slit the scattered light cannot pass through.

6.6 Other ways of characterization

Scanning Electron Microscopy (SEM)

Along with Transmission Electron Microscopy, Scanning Electron Microscopy is also considered as the standard for nanoparticle detection or characterization [14]. This method gives high resolution images of nanoparticles from which many important data like size, shape, size distribution, surface structure etc. can be determined. An SEM works in a similar way as the TEM, an electron gun transmits an electron beam which is focused on the specimen/sample with the help of condenser lenses which are basically electromagnets. The focused beam hits the specimen and gives off electrons of its own which are ultimately registered by a detector and gives a high resolution microscopic image. After the electron beam hits the specimen there are mainly two types of electrons which come off from the specimen. The initial electron beam is known as the primary electrons, secondary electrons are the electrons which are emitted by the specimen itself after it has absorbed the primary electron beam and the back scatter electrons are actually the same electrons from the electron gun which have been reflected off the surface of the specimen. There are two types of detectors which are positively charged for the two types of electrons. The back scatter electrons are useful for getting the surface features of the specimen which is one of the main reasons for using a scanning electron microscope [15].

Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What you can see with a light microscope is limited by the wavelength of light. TEMs use electrons as light source and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope.These high resolution images allows quantitative analysis of gold nanoparticle size distribution with the help of a software average diameter of goldnanoparticles can be measured [16].To sum up, although an expensive method TEM gives a very magnified high resolution image from which we can interpret the size(diameter) and exact shape of the nanoparticle.

Chapter 7

Conclusion

7.1 Summery

Synthesis and characterization of Silver nanoparticle is successfully done after twelve months of research. The key purpose of the thesis is to create Silver nanoparticle and observe the characteristic of nanoparticle. In our thesis we figure out that a slight change in parameter can change the size of silver nanoparticle in the solution. As silver nanoparticles have absorption and reflection properties and it depends on the size of the particle we can assume that we produced different size of silver nanoparticle is our thesis. We can safely assume that with the increase of concentration the size of the nanoparticle increases. We measure the resistance of silver nanoparticle and we find the output in kΩ range. So there is a scope to do future work with it.

7.2 Limitations and Challenges

Trough out the whole thesis time we faced some difficulties. Such as…

Availability of Characterization techniques

Some of the equipment and machine that we needed to characterize our AgNps were not available for us to work on. Transmission Electron microscope and the Scanning electron microscope could be used for our tests but Transmission Electron microscope is not available in our country. Due to the lack of this machine we could not measure the actual size of the nanoparticle. Scanning electron microscope is available for us to use. However, we were unable to use it for its high price range. One characterization technique that we succeeded in performing - The UV-VIS spectroscopy. But we faced some difficulties here as well. This machine is not available in our university. So we had to travel far to conduct this technique and it cost us time.

Not Long Lasting

The AgNPs solutions that we made were not long lasting. We could not preserve the solution for more then 4-5 days. The solution starts to lose color after 4days. This was happened due to aggregation.

Residues sticking to interior walls

We conduct our synthesis a numerous time. We made sure to clean the equipment that we used after every experiment. Generally washing the equipment with distilled water is enough but as we increased the % of citrate we saw residues on the wall of flux. These stains were really tough to get rid of as normal water or distilled water was not working on it. We had to clean the flux magnetic stirrer and other equipment with soap and then with distilled water. We had to make sure to get rid of residue of previous experiment before doing the next one.

Figure 28: residue on wall

7.3 Future Implementation and research of AgNPs

Nanoparticle research is developing rapidly. As nanoparticles have various properties it has a vast field of research and implementation. Silver nanoparticles have different properties such as nano-electronics, biomedicine, sensing, and catalysis and anti bacterial properties. In our country not much research is occurred about silver nanoparticle. Water purification by Inkjet fibrous membrane can be a handy application of Silver Nanoparticles in our country. Beside this, there are many scopes to improve electronics devices such as flexible, durable devices for upcoming generation. Furthermore, AgNPs can be used for industrial purposes to reduce toxic chemicals and microbial agents from environment. As there are more research are ongoing, there will be more application of Silver Nanoparticles on the field of Biomedicine, electronics and environment.

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