Effect of Ligands In Silver Nanoparticles Synthesis

A PROJECT REPORT

BY

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DEDICATED TO THE MEMORY

OF

MY MOTHER

ACKNOWLEDGEMENTS

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......Kingsuk Das.

"There is *Plenty* of Room at the Bottom"

-Richard P. Feynman at 1959 APS Meeting

CONTENTS

Chapter 1

Abstract

Ag nanoparticles can be syhthesised in aqueous medium at room temperature. For this purpose soluble inorganic salt of Ag is taken. In the method adopted by us Tannic Acid is used as reducing agent and potassium carbonate is added to maintain the pH of the reaction mixture in the alkaline range. On the other hand using stabilizing agent such as PVP the size of nano particles formed can be controlled. In these way many people has used different organic stabilizer and complexes , so that the size of Ag nanoparticles can be engineered.

Chapter 2

General Introduction

2.1 "NANO"

,"Nano" is actually a prefix that comes from the Greek word for dwarf. It simply means one billionth. So, one nanometer (1 nm) is one billionth of a meter.

This is how nano is represented mathematically. Ten to the negative 9th equals one billionth or 1/1,000,000,000.There are three important "nano" terms to consider when we are trying to understand the increasing news coverage and scientific developments in the field of nanotechnology. These terms are: Nanoscale, Nanoscience and Nanotechnology.

2.2 Nanotechnology

"Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications." –US le.Nnoparticles are defined as particles of less than 100nm in diameter that exhibit new or enhanced size – dependent properties compared to larger particles of the same material. Such changes arise due to three main reasons: i) an increase in the surface to volume ratio. i i)a change in the morphology of the crystal and/or iii) quantum confinement effects.

Nanoscience and nanotechnology are two word that have created a lot of   excitement in the research community in the recent past. Nanoscience is the study of fundamental principles of molecules and structures with at least of one dimension between 1 to 100nm, while nanotechnology is the application of these structures into useful nano scale devices.Its potential application lies in various fields like catalysis, biomedical engineering, electronics, energy conservations, photonics, sensors etc. The impact of on society and our lives of the continuous down scaling of microelectronic system is profound, and continues to open up novel frontiers and possibilities. The excitement generated by nanoscience and technology is a result of these efforts and our desire to explore arenas which have till now been left unexplored. The physical properties of solid materials at the nanoscale are much different as compared to their bulk properties. These include lowering of melting point, single electron charging, novel magnetic

and optical properties. The oldest example of an application of these properties are stained glass windows found in medieval and Victorian churches and glazes found on ancient properties. The beautiful colour they exhibit is due to the presence of nanoscale metal particles,which show a wide range of colours depending on their shape and size. In 1959, in a now famous speech, given to the American Physical Society, Richard Fenyman discussed how to manipulate and control matter on a molecular scalein order to achieve electronic and mechanical systems with atomic sized components.In recent times, with the advancement in technology, new methods for synthesizing and new tools for characterizing nanoparticles are under development. The synthetic route involves gaseous phase aerosol technique and solution phase techniques. The characterization method includes D.L.S, T.E.M, A.F.M, U.V spectrophotometry.

Silver as a nanoparticle has some potent use compared to as metallic silver. Although,the use of metallic silver has been discussed later but uses of silver nanoparticles find application in .fields of medicine, electronics, optics etc. It is essential to obtain perfect nanocrystallinity for physics modeling as well as device optimization.

2.3. Metal nanoparticles

Metal nanoparticles, i.e. particles in the approximate size range $1 - 100nm$ are used in a variety of applications, the most important of which is catalysis. Industrial processes such as petroleum reforming depend on catalytic metal nanoparticles, as do the catalytic converters used to clean up motor vehicle exhausts. Metal nanoparticles are also used in a range of other applications, including the labeling of biological samples and hydrogen storage. One of the challenges in this field is to make the particles as small as possible, with as narrow as possible a range of diameters. Dynamic light scattering (DLS) is an essential tool for this research to identify the size range of nanoparticles formed. .

The extremely small size of silver nanoparticles means they exhibit enhanced or different properties when compared with the bulk material. The extremely small size of nanoparticles results in the particles having a large surface area . In the case of silver nanoparticles this allows them to easily interact with other particles and increases their antibacterial efficiency. This effect can be so great that one gram

of silver nanoparticles is all that is required to give antibacterial properties to hundred of square metres of substrate material .

All bacteria use an enzyme as a form of 'chemical lung' in order to metabolise oxygen. Silver ions cripple the enzyme and stop the take up of oxygen. This effectively suffocates any bacteria, killing it within 6 minutes and leaving surrounding tissue or material unaffected. Viruses grow by taking over another living cell and reprogramming the nucleus to replicate the virus rather than the healthy cell. As part of this process, the cell reverts to a more primitive form that relies upon a primitive form of oxygen metabolizing enzyme as a chemical lung. Again the silver ions stop oxygen being brought into the virus-producing cell and it dies by suffocation. A fungus is composed of a series of single cells. Each cell survives by means of a 'chemical lung' much like that seen in bacteria. Just like bacteria, the presence of silver ions disables the chemical lung and the fungus dies. Antibiotic drugs can be used to kill the therapies. Silver nanoparticles kill all types of fungal infections, bacteria and viruses, including antibiotic resistant strains. No drug based antibiotic is effective on all types of bacteria. Additionally, research to date has shown that bacteria have been unable to develop any immunity to silver. Elemental silver occurs naturally. It is considered non-toxic, non-allergic, is not cumulative and is not known to harm either wildlife or the environment .pathogens attacked by silver nanoparticles but bacteria and viruses are becoming increasingly resistant to drug .
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2.4. Uses of silver

Silver metal in its pure state has a brilliant white metallic luster. It is a little harder than gold and is very ductile and malleable. It is classified with the precious metals. Silver is stable in pure air and water, but tarnishes when exposed to ozone, hydrogen sulphide, or air containing sulphur because of the formation of a silver sulphide.

The most important silver inorganic compound is, undoubtfully, the nitrate, because it is used in almost all the processes of production other compounds. Silver nitrate has a wide application in painting, xerography, chemical electroplating, in components for electric batteries and in Medicine as catalyst. Silver chloride is another important compound, due to its ductility

and malleability. The organic compounds of the element are used in the coating of several metals and in dynamite or other explosive bars.

The most important alloy of this element is silver-copper, traditionally used in producing coins. Nowadays this alloy was replaced by a cheaper alloy, copper-nickel. There are other silver alloys used in producing radiators for the automobile industry, and in producing musical instruments.

The chemical industry uses metallic silver as catalyst of several oxidation reactions such as those of ethanol and other alcohols. The oil industry also uses silver nitrate as catalyst. For many years, the mirrors were made by deposition of a small silver coat on a glass surface. Nowadays aluminum is used for this purpose.

Silver as sterling silver is used mostly as a precious metal and as alloys for jewelry, silverware, coinage, in electrical contacts in electronics and radio equipment for more corrosion resistance and conductivity. Silver is used in the making of solder and brazing alloys and electrical contacts of high capacity silver-zinc and silver-cadmium batteries. Silver halogenated compounds are of the utmost importance in photography (where approximately 30% of the U.S. Industrialconsumptiongoesintothisapplication).

Silver's catalytic properties make it ideal for use as a catalyst in oxidation reactions, in organic and inorganic synthesis, e.g. in converting alcohols into aldehydes and acids or ethylene oxide.

Silver's sterilizing, antisepticising effects are commonly known: preparations have antibacterial, anastaltic and catheresis properties which are connected to their ability to disturb germs' enzyme systems and to precipitate proteins Apart from the uses of Ag mentioned above, the metal in the size range of nanoparticles exnibit certain enhanced physical and chemical properties.

2.5 Project Description

The objective of this project is to synthesise silver nanoparticles in solution phase . In solution phase synthesis , a metal precursor in solution is subjected to an appropriate chemical reaction so as to yield metal nanoparticles under suitable conditions essential for nucleation and growth. These synthesis techniques are relatively easy to use and do not require sophisticated phase synthesis.

The reduction of metal salt in solution is the most widely accepted method for generation of colloidal suspension of the metals . In aqueous system, the reducing agent must me added, but in non-aqueous systems, the solvent itself can act as reducing agent

My work includes some to use some basic sophisticated equipment and study the Ag nanoparticles formed and also to study.

ii) Role of precursor ligand in Ag nanoparticle synthesis

ii) Synthesis of Ag nanoparrticles

iii) Characterising the silver nanoparticles formed using D.L.S and U.V vis.

iii) Comparing the nanoparticles formed from the two different salts.

The report is arranged in four chapters, including the literature survey of silver nanoparticles synthesis using solvents ,at alkalinepH and different reducing agents used for the purpose. In the report there is also discussion regarding the PVP stabilized synthesis of silver nanoparticles and studying the variation in size.

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Chapter 3

Characterization techniques

The general characterization techniques used to analyze nanoparticles are Dynamic Light Scattering (DLS), Atomic force Microscopes (AFM), and Transmission electron microscope (TEM) and UV-Vis spectroscopy. DLS is used to analyze the size of nanoparticles where monochromatic light is passed through the laser beam and gets scattered depending on Brownian motion. In the present chapter we will be discussing the characterization of DLS and UV-Vis spectroscopy only.

3.1. Dynamic light scattering

It is also called as photon correlation spectroscopy or quasi elastic light scattering. Its objective is to measure size of the particles in sub micron range.

3.1.1. Principles:

A monochromatatic laser beam such as laser is focused onto a sample containing particles that are in Brownian motion. Because of this Brownian motion of the particles, the interference pattern formed at the detector and the scattering intensity measured by the detector changes with time. Since the incoming light is a laser, which has high intensity and optical stability, the fluctuations in the intensity of the scattered light can be measured. The translational diffusion co-efficient of the particle is measured based on the auto correlation function, which represents the correlation between the two scattered light signals different in time domain.

Using this translational diffusion co-efficient, hydrodynamic dynamic diameter of the particle will be measured from Stokes Einstien equation,
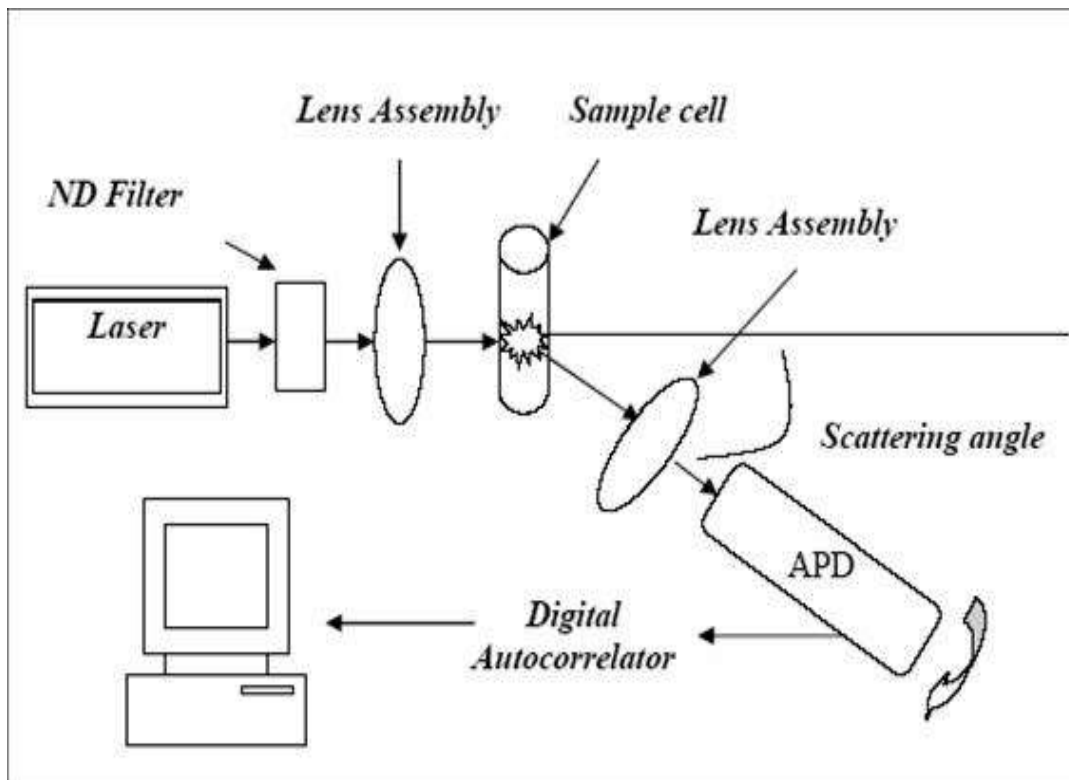
$$D_t = K_B T / 3\Pi \eta d_H$$

where

K_B = Boltzmanns constant

η = Viscosity of sample at temperature T

D_t = Diffusion coefficient

d_H = hydrodynamic diameter

Figure 3.1: Block diagram of Dynamic Light Scattering

3.1.2 Experimental set up of DLS:

DLS comprises of four sections namely source, sample cell assembly, detector optics and digital correlator.

Source:

This section comprises of a laser (source) and an assembly which focuses the beam to the sample cell assembly. Here, He-Ne laser operated at 632.8nm. A neutral density (ND) filter with an optical density of 3 is used for varying the power of the beam. Steering lens assembly is used for focusing the beam to the sample cell.

Sample cell assembly:

Samples are transferred in to the sample cell and kept inside the assembly. The sample cell is surrounded by index matching liquid, decahydronapthalene (decalin) to reduce the stray light. The index matching liquid is kept inside the vat, cylindrical vessel.

Detector optics:

The front portion of the detector optic assembly consists of an eye piece which focuses light onto a slit. Behind the slit, a two position mirror is located. When the mirror adjustment is rotated counter clockwise, light can be seen on the eye piece else it passes through the variable pinhole and then through a filter into the photomultiplier tube. The pinhole wheel is used to change the aperture size. The filter wheel is used to allow the beam of desired wavelength. The filtered beam tehen passes through an Avalanche photodiode (APD) which detects the temporal fluctuations of the scattered light intensity from the sample. These fluctuations are fed to the correlator. The detector assembly is usually placed at an angle of 90%, where the effects of flare, dust and misalignment are insignificant.

Digital correlator:

BI-9001AT correlator is used. It has an adjustable delay range capable of producing continuous correlation function starting from 100ns. The mean particle size and polydispersity is

estimated by the method of cumulants, software packages like non- negatively constrained least squares (NNLS) and CONTIN.

3.1.3. Sample preparation

In DLS, the intensity varies as D^6. So, the intensity of scattering due to a micron size particle will be huge when compared with the sub micron size particle. Care has to be taken in the following steps to prevent scattering due to dust particles.

It involves 3 steps:-

1. Preparing the sample(chemicals, glass wares, water used)
2. Sample cell cleaning
3. Filtration of index matching liquid

During preparation of the sample, all glass wares must be cleaned with Aquaregia, deionised water. Dust must be avoided from all perspective. The index matching liquid can be filtered with the help of an externally connected filtration system.

Figure 3.2: Photograph of DLS setup

3.1.4. Precautions to be taken during measurement

The fluctuations in the average count rate (ACR) must be minimized. Intermediate jumps in the ACR represent the presence of dirt in the sample or decalin. With dilution of the sample with solvent, ACR should decrease. Increase of ACR with dilution indicates multiple scattering. Then, the temporal fluctuations of the intensity are not random. To make the motion random, sample must be free of multiple scattering which can be avoided by sample dilution. Too much dilution can make ACR very low. Recommended value of ACR is 10kcps to 200kcps. This can be obtained by adjusting either ND filter or pinhole wheel or filter wheel. A plot of ACR with time should not have any slope. Slope indicates the presence of
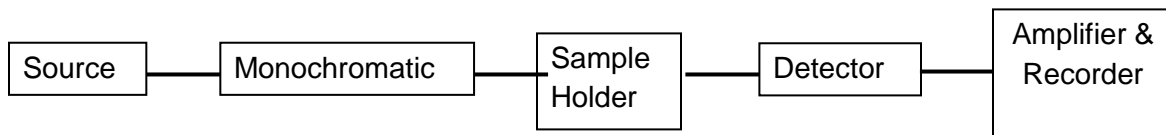
interparticle aggregation. This can be avoided by increasing either the concentration or increasing the measurement time.

In the correlator window baseline difference is reported. Baseline difference refers to the difference the measured baseline and the calculated baseline. Calculated baseline depends on the Seigart relationship while the measured baseline depends on the sample. The baseline difference must be positive and less than 1%. Negative baseline difference can be avoided by increasing the sample measurement time. High baseline difference indicates the presence of bigger size particles probably dirt. This can be avoided only by removing dirt from the scattered volume.

Hydrodynamic diameter is based on Stokes-Einstein equation which depends on the properties like temperature, viscosity of the sample. Hence, these properties can affect the result but their affect is not as significant as dirt .

3.2 UV-Visible spectrophotometer

In order to obtain an absorption spectrum, it is necessary to measure the absorbance of a substance at a known series of wavelengths. The instruments that are used to study the absorption or emission of electromagnetic radiation as a function of wavelength are called spectrometers or spectrophotometers. More or less similar optical principles are employed in these instruments. There are, however, some important differences in the specific components used in the regions of spectrum.

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┌─────────┐   ┌───────────────┐   ┌──────────┐   ┌──────────┐   ┌──────────────┐
│ Source  │───│ Monochromatic │───│  Sample  │───│ Detector │───│ Amplifier &  │
│         │   │               │   │  Holder  │   │          │   │  Recorder    │
└─────────┘   └───────────────┘   └──────────┘   └──────────┘   └──────────────┘
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Figure 3.3: of UV visible spectrum Scheme

3.2.1. Radiant Energy Sources:

Materials which can be excited to high energy states by a high voltage electric discharge or by electrical heating serve as excellent radiant energy sources. Most commonly used sources of ultraviolet radiation are the hydrogen lamp and the deuterium lamp. Both the systems consist of a pair of electrodes in a glass tube provided with a quartz window.

The most commonly used source of visible radiation is tungsten filament. It is inexpensive emits continuous radiation in the region between 350 and 2500nm.

3.2.2. Wavelength Selectors

Filters operate by absorbing light in all other regions except one which they reflect. Gelatin filters are made up of a layer of gelatin, colored with organic dyes and sealed between glass plates. Most modern filter instruments, however, use tinted- glass filter. Filters resolve polychromatic light into a relatively wide bandwidth of about 49nm and are used only in colorimeters. One of the disadvantages of glass filters is their low transmittance (5-20%).

3.2.3. Sample containers

Samples to be studied in the ultraviolet or visible region are usually gases or solutions. Mostly, the spectrophotometer studies are made in solutions. The solutions are dispensed in cells known as cuvettes. Cuvettes meant for the visible region are made up of quartz. Since glass absorbs in the ultraviolet region, quartz or fused silica cells are used in this region. Standard pathlengths of these cuvettes is usually 1 cm. The surfaces of the cuvettes must be kept scrupulously clean; fingerprint smudges and traces of previous samples may cause serious errors in quantitative measurements. Rinsing with water should normally clean quartz cuvettes. If however, the dirt is abnormally tenacious, sulfonic detergents or nitric acid may be used. The use of rectangular cuvettes in spectrophotometers effectively curtails the chances of dirt being transferred during handling. The two sides of such cells through which the light passes are precision ground and polished to be optically flat. The other two sides are rough ground glass and the cell may be handled by these sides.

3.2.4. Detector devices

These near infrared detectors are usually photoconductive cells which detect infra red radiation in the range 0.8-3.0μ. The sensing element is a semiconductor (germanium lead sulphide, or lead telluride). Upon illumination with radiation of appropriate wavelength, the electrons of the semiconductor are raised to conduction bands. This causes a drop in electrical resistance. Consequently, if a small voltage is applied, a large increase in current can be noted. The resistance of the system is such that the current may be amplified and finally indicated on a meter is recorded [4].

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Chapter 4

4.1. LITERATURE REVIEW

Metal nanoparticles can be produced by different methods. Many of the methods reported for the preparation of the nanoparticles are applicable to many metals across the periodic table. The material of current interest is silver. Silver nanoparticles of desired size and monodispersity can be prepared by different protocols in literature .

Silver nanoparticles exhibit unusual optical, electronic and chemical properties, depending on their size and shape thus opening many possibilities technological applications They are produced by various methods including the chemical reduction of silver ion with or without stabilizing agents , laser ablation , sonochemical , electrochemical and reverse micelles . We get spherical, octahedral, tetrahedral, hexagonal, cubic, wire, coaxial. Cable, triangular prism, disc, triangular mark, belt, shell shapes have been manufactured.

Some advancement in strategies for synthesizing metal nanoparticles have enabled control of size, composition and shape. To ensure essential perfect nanocrystallinity for physics modeling is a potentially more significant issue, but substantial technological challenges arises.
. Some work on crystallinity of monodispersive silver nanoparticle has been reported.The report gives the pathway to control crystallinity of Ag nanoparticles by judicious choice of functional group.

Several methods have been reported for the preparation of organic inorganic hybrid materials. Most of the methods that can be used to incorporate metals into polymeric matrices include some form of chemical reactions such as sputtering, plasma deposition, and layer- by layer deposition. Most of these methods add cost, multi-step synthesis along with complexity to the processes for fabrication of metal doped materials. Hence, the preparation of nanoparticles without using eternal reagents in a single step (in situ) by excluding extra purification processes or transfer protocols will have advantages over the present methods. Also, silver nanoparticles

have known to exhibit antibacterial properties and this antibacterial activity mediated by silver nanoparticles have been investigated by many researchers. As the size of silver particles decrease to nanoscale regime their

4.2 ROLE OF PRECURSOR LIGAND

4.2.1Generation of MT and SC Ag NPs

Yun Tang And Min Ouyang used air stable silver phosphine complexes (PPh3)3Ag-R, where R represents –NO3 and –Cl group respectively. And amine molecules serving as both reducing and nanoparticle capping agent.. Silver nanoparticles with 10.5±0.4nm size were observed in TEM image., which are obtained from the precursor. The difference in two images is due to the clear inhomogeneous features developed in 100% of the nanopariclces.. Here we observe that thermodynamically stable disordered multiply twinned (MT) structures. On the otherhand due to different atomic energy sites on the crystallographic facets, the chemicakl activity of these multiply twinned is different with respect to their single crystalline counterpart.

Synthetic procedure:

In the synthesis method they have used ($PPh_3)_3$Ag-R precursor.

It is dissolved in anhydrous o-dichlorobenzene under He atmosphere , and after the clear solution is heated to desired temperature to it certatn amount of oleylamine was added followed by vigorous stirring. Here oleyl amine serves as both reducing agent and capping ligand. Of the Ag nanoparticles. The formation of nanoparticles in the solution can be accounted from the slow colour change of the solution. The nanoparticles can be precipitated out by adding methanol after the reaction is stoopped and the solution is cooled to room temperature.

Synthesis of (PPh$_3$)$_3$Ag-R; R= -NO, -Cl

Here 17mg AgNO$_3$ was dissolved in 2ml anhydrous acetonitrile and the resulting solution was added to the solution of 78.7mg of triphenylphosphine in 8ml acetonitrile. On agitation the crystal starts precipitating. It is recovered in the form of white powder by washing with acetonitrile .

Synthesis of different size MT and SC Ag nanoparticles:

Yun Tang and Min Ouyang has outlined a procedure in which they have varied the solvent concentration , reducing agent concentration, temperature and reaction time. Too fulfill their aim they have used the triphenyl complex of Ag atom havinG chloride and nitrate group respectively as precursor ligand. Table 1 and 2 highlights their approach and figure 1.1 and 1.2 shows the TEM images.

TABLE

1

Size (nm)	8.8 ± 0.3	13.9 ± 0.5
Precursor *1* (mmol)	0.05	0.19
o-dicholorbenzene (ml) (240664, Sigma-Aldrich)	17.0	19.0
Oleyamine (mmol) (129540010, Acros)	7.2	3.6
Temperature (°C)	174.0	150.0
Reaction time (mins)	30	120
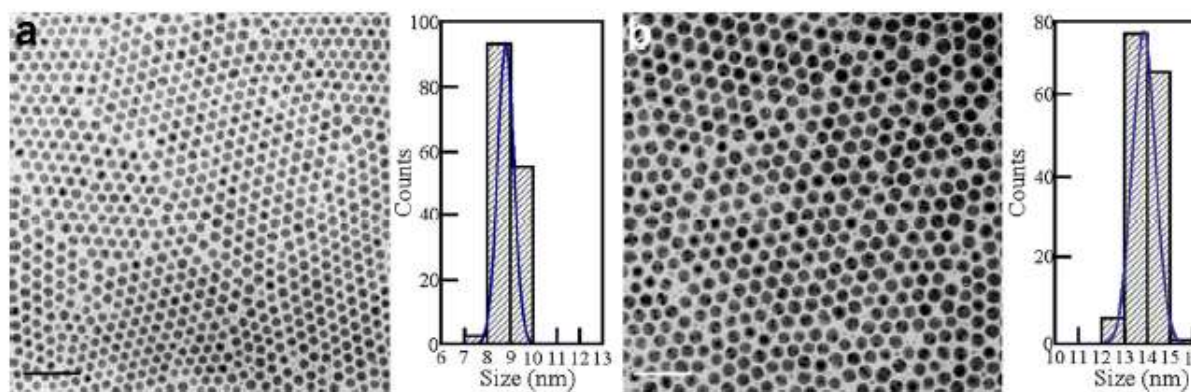
Figure 4.1: large scale TEM image left and histogram right, a NPs size is 8.8 ± 0.3nm; b NPs size is 13.9 ± 0.5nm.

TABLE 2

| Size (nm)	14.0 ± 0.6	20.0 ± 0.9
Precursor *2* (mmol)	0.19	0.19
o-dicholorbenzene (ml)	19.0	19.0
Oleyamine (mmol)	3.6	3.6
Temperature (°C)	140.0	150.0
Reaction time (mins)	120	240
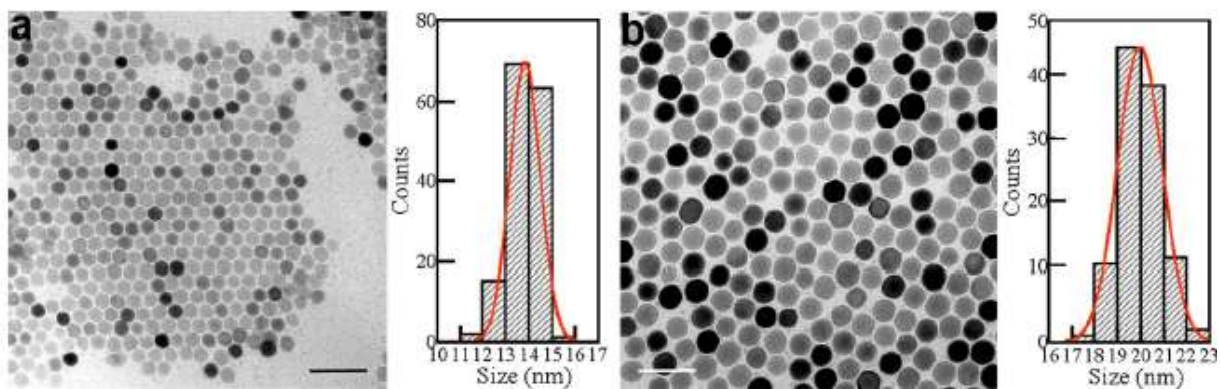
Figure 4.2; large scale TEM image left and histogram right; a NPs size is 14.0±0.6, b NPs size is 20.0±5

4.2.2 FORMATION OF NANOCUBES.

A basket of chemical methods have been developed for the synthesis of Ag nanostructures that have well controlled shapes including triangular plates , cubes, belts, wires ,

rods etc. Sang Hyuk Im , Yun Tack Lee and their group have used hydrochloric acid for the generation of Ag nanocubes.

The pathway they followed is the polyol synthesis of Ag atoms obtained by reducing AgNO3 with ethylene glycol through reaction shown below.

$$2\,HOCH_2CH_2OH \rightarrow 2\,CH_3CHO + 2\,H_2O$$

$$2\,Ag^+ + 2\,CH_3CHO \rightarrow CH_3CHO-OHCCH_3 + 2\,Ag + 2\,H^+$$
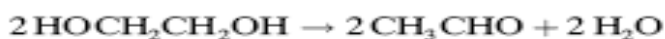
MECHANISM OF Ag NANOCUBE FORMATION

On adding AgNO3 and PVP to the hot solution of ethylene glycol, both twinned and single crystals seeds of Ag are formed through homogeneous nucleation. Due to relatively lower surface energies the twinned particles have the most abundant As the concentration of Ag atoms increases in the solution increases , with advancement of time it reaches the supersaturation value . On supersaturating they will start to nucleate and grow. In the mean time , nitric acid generated activates a backward reaction that dissolves solid AgNO3. So by adding HCl, reaction(3) could be driven further to right owing to the formation of more HNO3 from HCl and AgNO3.Due to presence ofrelatively lower surface energies the twinned particles have the most abundant morphology. These initially formed nanoparticles are dissolved owing to the relatively high concentration of HNO3 present in the early stages of reaction. As the time elapses, in the early stages , in the reaction medium, HNO3 is gradually consumed and second round of nucleation starts. When the nanoparticles grow in dimension they will be locked into either a single crystalline or twinned morphology.moreover the overall surface energy of twinned particles is lower , this happens at the expense of significant lattice distortion andsurface defects. So twinned particles are expected to a show stronger susceptibility towards etching. These seeds could continue to grow as they are stable in the environment because no lattice distortion required to form a single crystal . So by selective etching of twinned seeds by HNO3 , single crystal nanocubes result. Figure 3.3 and 3.4 shows the TEM image and UV vis spectra obtained by San Hyuk Im and Yun Tack Lee.
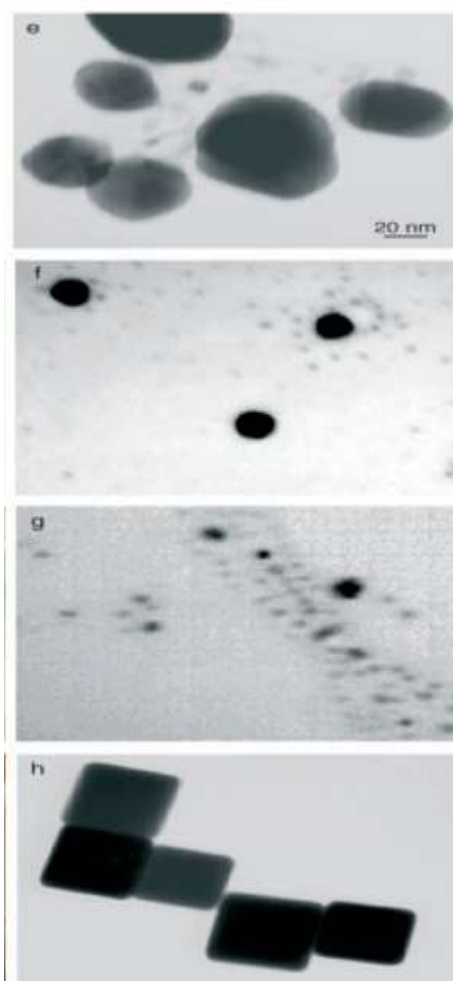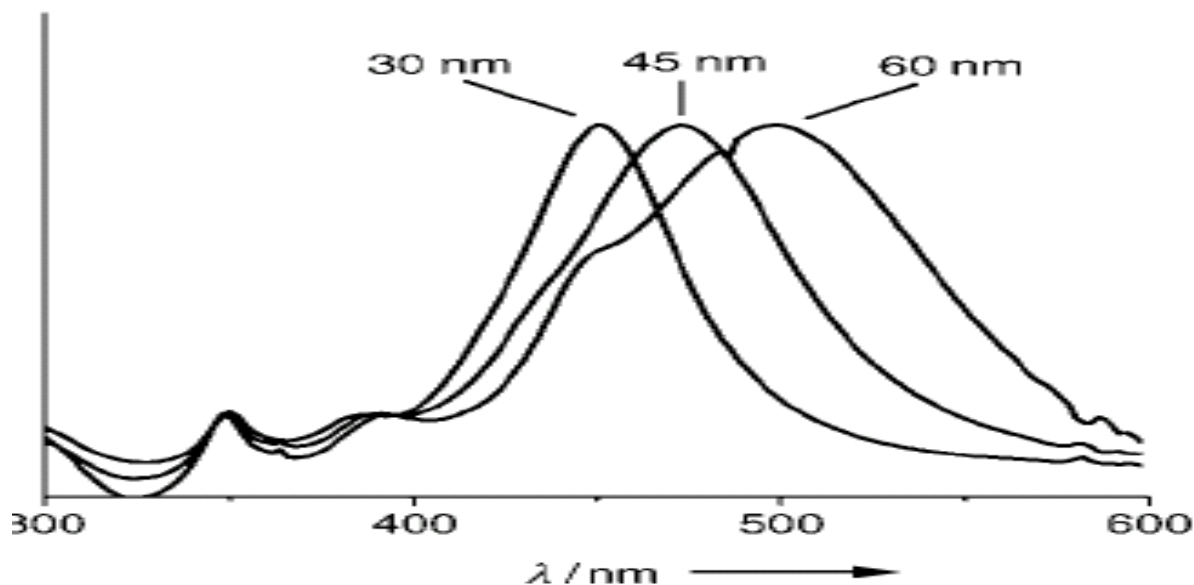
$$4\,HNO_3 + 3\,Ag \rightarrow 3\,AgNO_3 + NO + 2\,H_2O \qquad (3)$$
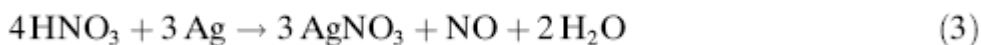
Figure 4.3 (e)-(f) TEM image of Ag NPs at t = 4,46 and 103 min and 15h. (e) size is 20nm (f) size is 20nm;5nm (g) size is 6nm (h) Ag nanocube with edge 30nm.

Figure 4.4 UV vis absorption spectra of aq. Solution that contains Ag nanocubes with different edge length.

4.3 SYNTHESIS OF Ag NANOPARTICLES

To synthesize metal nanoparticles it is crucial to understand the mechanism leading to the formation of the nanoparticles. An ideal synthesis produce monodispersive particle with uniform shape. We use solution chemistry as synthetic route because particle size and shape can be controlled efficiently by choosing the reaction temperature , order of addition of reagent and the ratio of protective agent.

Here are some of the methods.

- **CITRATE REDUCTION METHOD.**

Maribell D Guzman and Jean Dille used AgNO$_3$ solution (from 1.mM to6.0Mm) and 8%(w/w) sodium dodecyl sulphate(sds) as metal salt precursor and stabilizer respectively. Citrate of sodium solution (1.0Mm to 2.0Mm) were used as reducing agent At room temperature it can be used as stabilizing agent. The transparent colourless solution converted to the characteristic pale yellow and pale red colour, when citrate of sodium was used as stabilizing agent. The occurrence of colour indicated formation of Ag nanoparticles. Ag nanoparticles were purified by

centrifugation.TEM image showsparticles range in the size 8 to 50nm with mean diameter of 24nm. Figure 3.5 is the TEM image of the Ag nanoparticles obtained by Guzman and Dille.
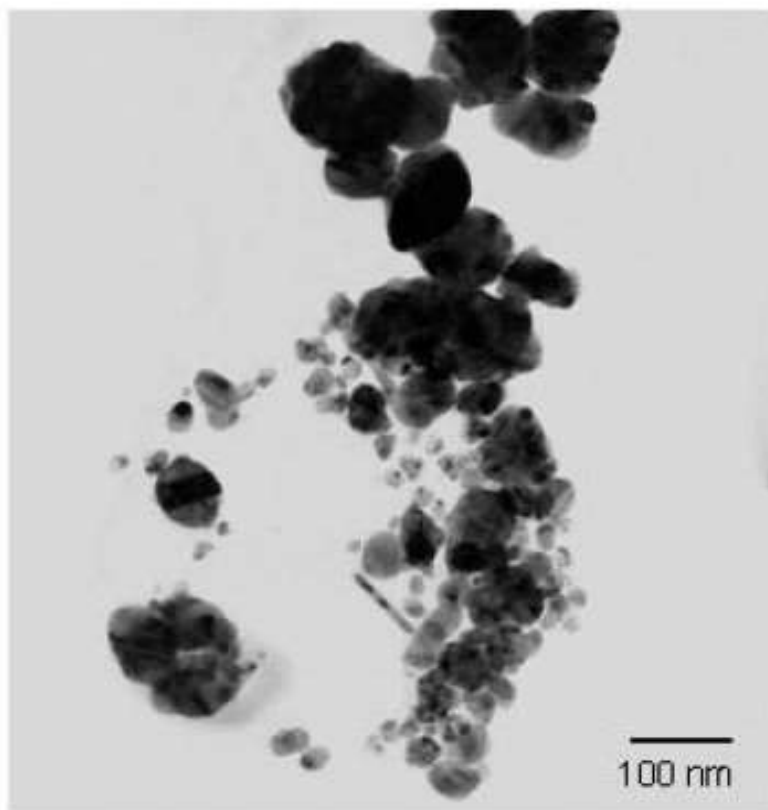

figure 4.5 TEM image with Ag NPs of 100nm.s

- **REDUCTION IN ORGANIC MEDIUM.**

Grijalva used 29.4 Mm $AgNO_3$ and dissolved it in 0.05ml de-ionised water. Then, 30 ml acetone was added and resulting solution was mixed under magnetic agitation. After 30 min. of agitation 1.5g PVP dissolved in de-ionised water was added. The solution was kept for 24h and the UVvis result gave maximum absorption peak at 438nm, giving evidence regarding the presence of Ag nanoparticles.

- **TANNIC ACID METHOD.**

- Silver nanoparticles- 2 ml 6% $AgNO_3$ added to 100ml distilled water

- 24mg tannic acid added to mixture.

- Heat to 70-80°C

- 2.4ml 1% Na_2CO_3 – stir vigorously.

- Time for completion of reaction – 30 m

- Stoichiometric ratio is 0.4

- Silver nanoparticle size obtained is 14 nm (TEM).

References

1   Tailoring properties and functionalities of metal nanoparticles through crystallinity engineering ; Yun Tang and Min Ouyang

2   Large scale synthesis of nanocubes; Sang Hyuk and Yun Tack Lee.

3   Nickel, A.Caswell, Langmuir. 2000

4   K.P.Velikov, G.E.Zegres, Langmuir ,2003

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Chapter 5

RESULTS AND DISCUSSION

Our aim is to synthesize smaller nanoparticles at room temperature with reduced polydispersity. TANNIC ACID reduction of AgNO3 and AgCl was carried out at room temperature. On the basis of different parameters some results were obtained.

The parameters are:

1 EFFECT OF CHANGE IN pH using RHUSTON TURBINE
2 EFFECT OF ADDING PVP AS STABILISER.
3 EFFECT OF CHANGING THE SALT.

5.1 Effect of change pH using Rhuston Turbine.

The experiment was conducted at room temperature .The solutions used were 1%(w/v) AgNO3 in de-ionised water, Tannic Acid in de-ionised water and K2CO3 in de-ionised water.The bulk solution was 50ml obtained by adding 25ml solution of silver nitrate and 25ml solution containing potassium carbonate and tannic acid. The baffles were used for mixing, the rpm of turbine was varied from 50 to 250 rpm. The result is given in table1 and figure 4.1 shows the baffles.

Table1

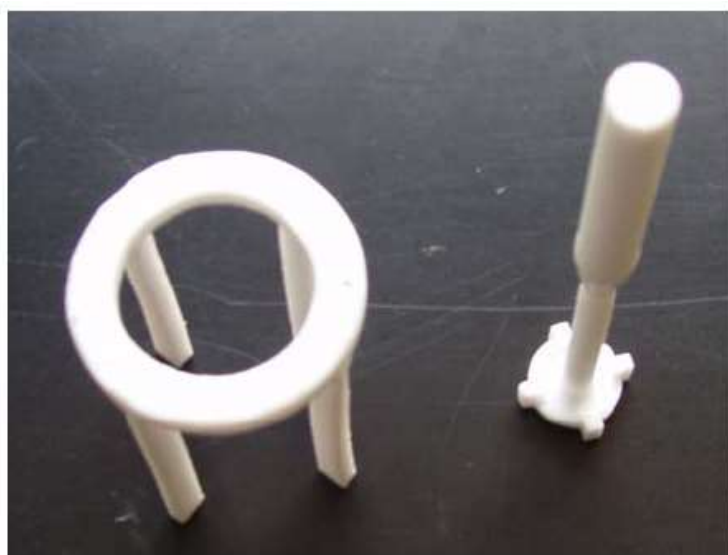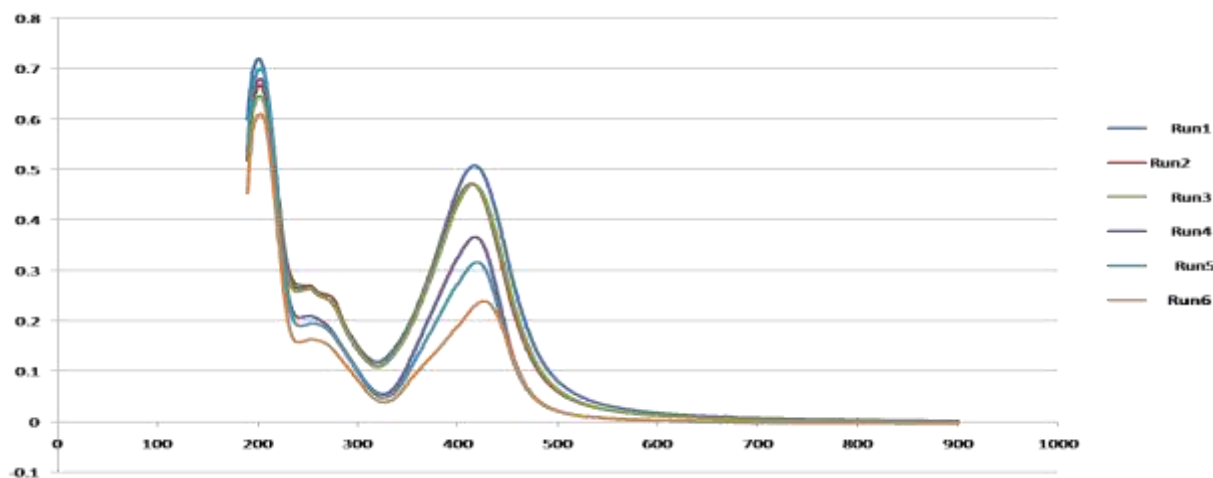| AgNO3 1% w/v (mM)	pH	TA 1% w/v (mM)	K2CO3 (mM)	DLS dia (nm)	Remarks
1.18	8	0.059	0.3	18.50(9.88-26.09)	Less than 50 rpm
1.18	8	0.059	0.32	19.90(16.45-22.69)	Less than 250 rpm
1.18	10	0.059	0.64	7.13(6.14-8.12)	Less than 50 rpm
1.18	10	0.059	0.64	7.31(6.45-8.12)	Less than 250 rpm

figure5.1

Figure 5.2: UVspectra for AgNO$_3$

5.2 Effect of Adding PVP As Stabiliser

In the above experiment concentrations of the reagent where preserved and to it 1%(w/v) solution of PVP was added.

1. 0.25ml PVP: 7.14nm(6.86-7.43)

2. 0.50.75ml PVP: 10.65nm(10.09-11.06)

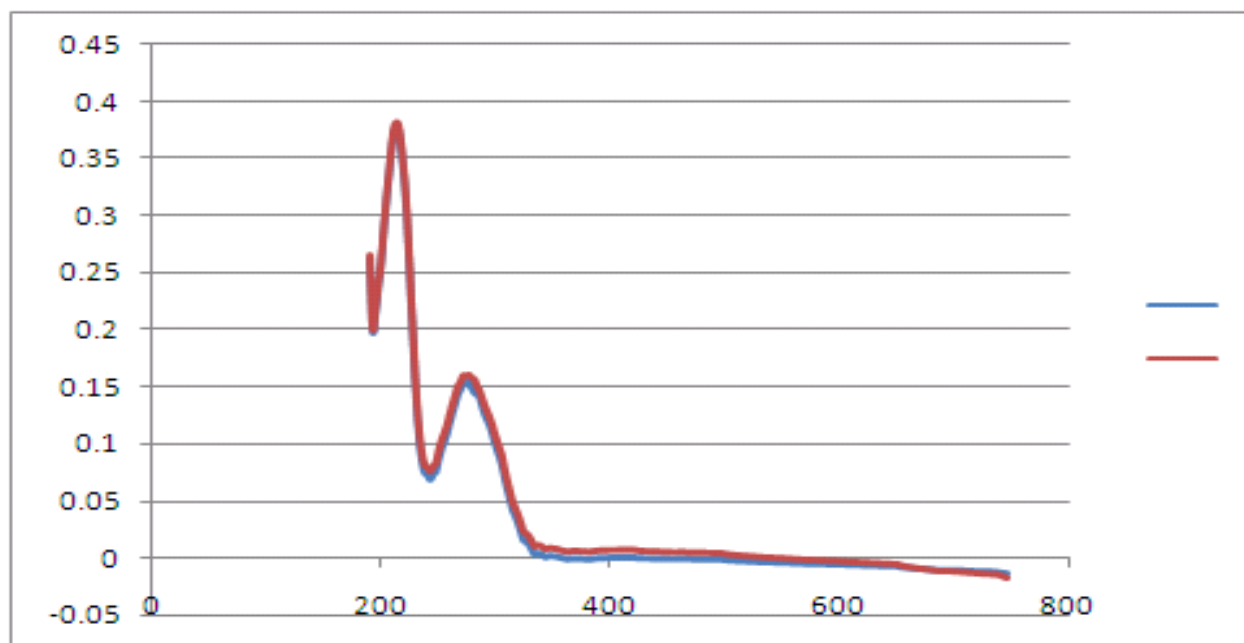3. 0.75ml PVP: 7.15nm(6.31-7.72)

4. 1ml PVP: 10.15(8.57-12.47)

5.3 Effect of Adding Salt

Bulk reaction mixture using AgCl, TA AND K$_2$C0$_3$using Rhuston turbine at an rpm of ~400 using1%(w/v) solution.

At SR1 was done at room temperature.

1. D.L.S DATA AT pH 8 : 77.36nm

2. D.L.S DATA AT pH10 : 25.42nm

The UV absorption spectra for above experiment is in figure 4.3

Figure 5.4: UV spectra for AgCl

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References

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Chapter 6

Conclusion

In the synthesis process of Ag nanoparticles, the result obtained using $AgNO_3$ was better as evident from the result obtained from DLS and UV absorption spectroscopy. On changing the precursor ligand that is using AgCl instead of $Ag\ NO_3$ gave inefficient output as obtained from DLS and UV spectrometer. This is because due to the low solubility of AgCl in water. So better solvent should be found in order to dissolve AgCl. On the other hand some people have worked with Ag complexes by changing the precursor ligand.Here AgCl has given better result as its solubility has been enhanced.By using these methods they have got interesting structures of Ag nanoparticles in the form of crystals.

APPENDICES

Appendix 1

1. Materials Required

In the experiment silver nitrate, tannic acid, potassium carbonate and aqua regia (1:6 HCl and HNO_3) was used . De-ionised water from millipore was used to prepare the aqueous solution.

2. Experimental procedure

- Glass wares were rinsed with Aqua Regia and washed thoroughly with tap water followed by de-ionised water.
- 1% (w/v) solution of silver nitrate and silver chloride was prepared by dissolving 0.025g of Ag salt in 2.5ml de-ionised water.
- In case of silver nitrate pH8 was obtained by adding 220 microlitres of 1%(w/v) solution of potassium carbonate in reaction mixture.Here pH10 was obtained by adding 800 microlitres of same potassium carbonate solution in the reaction mixture.
- During mixing the rpm of Rhuston turbine was maintained below 500
- The gloves should be used as safety measure.

Appendix2

Chemicals Supplier Information

- Silver nitrate (99.99%) from MERCK
- Silver Cloride (99.0%) from THOMAS BAKER
- Potassium Carbonate from MERCK
- Tannic Acid from MERCK