

Synthesis of Gold, Silver and Core-Shell nanoparticles in Fed - Batch and Continuous methods

*An internship report submitted for
Summer Fellowship Programme – July 2019 (Department of Chemical Engineering)
Indian Institute of Science
Bengaluru, India*



Under the guidance of
Dr. S. Venugopal
Associate Professor
Department of Chemical Engineering
Indian Institute of Science
Bangalore - 560012

Submitted by
Koushik Sampath
IIIrd Year B. Tech
Department of Chemical Engineering
National Institute of Technology Tiruchirappalli

ACKNOWLEDGEMENT

Prima facie, I would like to express my sincere gratitude to my guide Dr. S. Venugopal for being a pillar of support and guidance throughout the internship period and giving me the opportunity to utilize the equipment and facilities in the lab. His lines “you are a researcher, not a technician” will always be in my mind for as long as I pursue research. He has helped me broaden my vision in the field of research and taught me how to introspect and reason the smallest of details in the experiments that I had carried out.

I am grateful to my mentor Mr. Sushant Kumar, a research scholar at the Department of Chemical Engineering, IISc Bangalore for his constant support and help. An alumnus of NIT Trichy, he was more like a dear senior throughout the course of the internship period than a mentor helping me in my personal commitments as well other than the project work.

I would also like to thank the other scholars of Venugopal Lab: Nikita, Madhavan, Khantesh, Abhishek, Dhishesh and Pritam for providing a fun atmosphere to work in the lab. From lab cleaning sessions to watching world cup matches, you have been a part of this memorable 2 months at IISc.

I also would like to thank the other summer interns Prahlad, Tharun, Varshan, Hariharan, Vasu, Vaishnavee, Bhavya and Rakshith who have provided a pleasant and comfortable atmosphere and have constantly provided support in the course of these 2 months.

I place on record, my sincerest thanks to the Girija ma’am and CEA committee for letting us witness various flavours of research that takes place in the department through the in-house symposium and a break from work by organizing the CEA Nite.

I would also like to thank Dr. Bhushan J. Toley for giving me permission to use the equipment in his laboratory and the members of his lab Navjot, Shruti and Dharithri who have supported me throughout the project.

I also wish to express my gratitude to one and all who have lent their hand directly or indirectly in this venture.

Above all, I would like to thank my faculty back in NIT Trichy for their constant support and guidance and my parents whose moral support and guidance has been an integral role in my life.

KOUSHIK SAMPATH

ABSTRACT

Metal nanoparticles and nano particle-based architectures have a wide range of applications such as fuel cells, electronics, sensors, drug delivery, medical analysis and so on. Considering the ever-growing demand of this industry, there is a need of size specific production of nano particles and different production methodologies which are more energy efficient and environment friendly. With all the different types of production methodologies for nanoparticles, bottom-up approach is considered the most economical methods to produce nanoparticles.

In this internship report, the bottom-up method discussed and utilized is “Chemical reduction method” where the metal salts are reduced using Tannic Acid. Tannic Acid can reduce metal salts at room temperature itself and is also a very good stabilising agent. Tannic acid at basic pH's breaks into gallic acid and glucose. Gallic acid is a reducing agent and glucose is a stabilizing agent. As opposed to this method is the reduction by Sodium Citrate method, but this requires the citrate solution to be heated up to 80 degrees Celsius. Tannic Acid reduction is better than Citrate reduction because the reaction happens at room temperature and Tannic Acid is a green compound (obtained from plant matter).

This report covers production of gold, silver and core-shell nanoparticles (gold core – silver shell and vice-versa) through tannic acid reduction method by both semi-batch and continuous processes. The metallic salt solutions are the fed reactants and tannic acid is the batch reactant. A basic pH of tannic acid is required for a more active and stable complex. pH of tannic acid is adjusted using a solution of potassium carbonate.

Fed- Batch methodology is carried out as per previous literatures which show that dropwise addition of the metal salt has lesser poly-dispersed particles as compared to dumping of the reactants and other methods of addition of reactant. Experiments are conducted with variation in concentrations and volumes of tannic acid and metal salts in order to optimize the conditions for production in batch production of nanoparticles and simulate similar conditions in continuous production of these particles.

Lower concentrations of tannic acid prove to give out better results in terms of production of core shell particles and gives lesser interferences in characterization procedures such as UV-vis spectroscopy.

In terms of producing core shell nanoparticles, other than the usual method of adding the shell solution to a pool of the core nanoparticle solution, an additional

methodology was also followed. Once the core particles were synthesized, the solution was centrifuged to remove tannic acid, dispersed in a solution of the shell salt solution of required concentration and this new solution was fed into a pool of tannic acid. This methodology proved to be better than the latter as the basic pH of tannic acid had a variation in reactivity and properties with variation in time.

For the synthesis of nanoparticles in continuous fashion, currently there are no specific methods followed for its production. Researchers use a wide range of setups from small plug flow reactors to micro channels. But all of these methods gave a small throughput of the metal nanoparticles and proved to be highly polydispersed. To counter act both problems and having a simple setup as a major priority, production of these nanoparticles was carried out in a simple overflow CSTR setup. Due to time constraints, advanced characterization of these particles was not possible, but if these fulfil the requirements, this method proves to be very economical and has a very high throughput compared to the other methods used for continuous synthesis.

CONTENTS

1	Introduction.....	6
1.1	Synthesis.....	7
1.2	Wet Chemical Method.....	8
1.2.1	Turkevich Method.....	8
1.2.2	Tannic Acid reduction Method.....	9
1.3	Tannic Acid behaviour.....	10
1.3.1	Effect of pH on Tannic acid behaviour.....	11
1.4	LaMer Model.....	11
1.5	Types of Nucleation.....	12
1.5.1	Homogeneous Nucleation.....	12
1.5.2	Heterogeneous Nucleation.....	13
1.6	Batch Process.....	13
1.7	Continuous Process.....	14
1.8	Colloidal Stability.....	14
1.8.1	Electrostatic Stability.....	15
1.8.1.1	Electric double layer.....	15
1.8.1.2	DLVO Theory.....	15
1.8.2	Polymeric Stabilization of Colloids.....	17
1.9	Core – Shell Nanoparticles.....	18
2	Experimentation and practical work.....	20
2.1	Fed – Batch Process.....	21
2.1.1	Experimental Setup.....	21
2.1.2	Synthesis of Gold Nanoparticles (GNP or AuNP).....	21
2.1.3	Seeded growth of Gold nanoparticles.....	23
2.1.4	Synthesis of Silver Nanoparticles (SNP or AgNP).....	24
2.1.5	Seeded growth of Silver nanoparticles.....	25
2.1.6	Core – Shell Nanoparticles (Au core Ag shell).....	26
2.1.7	Core – Shell Nanoparticles (Ag core Au shell).....	36
2.1.8	Tannic Acid behaviour.....	43
2.2	Continuous Process.....	44
2.2.1	Experimental Setup.....	45
2.2.2	Synthesis of Gold Nanoparticles (GNP or AuNP).....	46
2.2.3	Synthesis of Silver Nanoparticles (SNP or AgNP).....	47
2.2.4	Core – Shell Nanoparticles (Ag core Au shell).....	49
3	Conclusion.....	51
4	Scope for future work.....	51
5	Acknowledgements.....	52

1. INTRODUCTION

Nanoparticles are particles between 1 and 100 nanometres (nm) in size with a surrounding interfacial layer. The interfacial layer is an integral part of nanoscale matter, fundamentally affecting all its properties. The interfacial layer typically consists of ions, inorganic and organic molecules. Organic molecules coating inorganic nanoparticles are known as stabilizers, capping and surface ligands, or passivating agents. In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties. Particles are further classified according to diameter.

Nanoparticles are of great scientific interest as they are, in effect, a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of the surface in relation to the percentage of the volume of a material becomes significant. For bulk materials larger than one micrometre (or micron), the percentage of the surface is insignificant in relation to the volume in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. For example, gold nanoparticles appear deep-red to black in solution. Nanoparticles of yellow gold and grey silicon are red in color. Gold nanoparticles melt at much lower temperatures ($\sim 300^\circ\text{C}$ for 2.5 nm size) than the gold slabs (1064°C); Absorption of solar radiation is much higher in materials composed of nanoparticles than it is in thin films of continuous sheets of material.

In both solar PV and solar thermal applications, controlling the size, shape, and material of the particles, it is possible to control solar absorption. Recently, the core (metal)-shell (dielectric) nanoparticle has demonstrated a zero backward scattering with enhanced forward scattering on Si substrate when surface plasmon is located in front of a solar cell. The core-shell nanoparticles can support simultaneously both electric and magnetic resonances, demonstrating entirely new properties when compared with bare metallic nanoparticles if the resonances are properly engineered. Other size-dependent property changes include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials.

What would appear ironic is that the changes in physical properties are not always desirable. Ferromagnetic materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage. Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid.

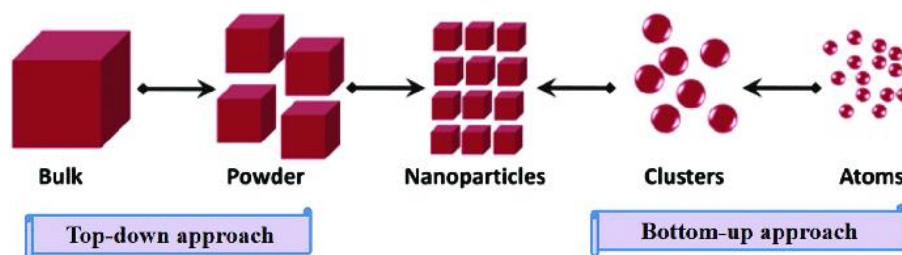
Technologists thus find tremendous potential of nanomaterials from consumer goods to space applications. In a span of few years there have emerged several manufacturers selling products like cosmetics, clothes, TVs, computers, medicines, toys, sports goods, automobile etc. which use some nanomaterial or the other. It is an interesting question as to, starting with a few atoms, how the bulk materials reach their structure and related properties.

Do they undergo any structural changes or even their smallest unit cell is like that in bulk material? This question has been addressed by many. There are reasons to believe that the small clusters or nanoparticles are not just the fragments of bulk materials. There can be entirely different structures as well as bonds and bond strengths in clusters which can even differ from nanomaterials. It has been well established now that all the materials, may be metals, semiconductors or insulator clusters or nanomaterials, have size dependent physicochemical properties. In most of the cases a cluster size is below 1 nm and that of nanoparticles is in the 1–100 nm range. Interestingly at such a small size even the shape of the material and interactions between clusters or nanomaterials decide the properties of the material. This opens a huge possibility of tailor making the materials, which have different properties just due to their size, shape and/or assembly.

1.1 SYNTHESIS

Synthesis of nano particles can be broadly classified into two types.

- a) Top – Down approach
- b) Bottom – Up approach



(Figure from researchgate.in)

Top Down Approach:

Top-down routes are included in the typical solid –state processing of the materials. This route is based with the bulk material and makes it smaller, thus breaking up larger particles using physical processes like crushing, milling or grinding. Usually this route is not suitable for preparing uniformly shaped materials, and it is very difficult to realize very small particles even with high energy consumption. The biggest problem with top-down approach is the imperfection of the surface structure. Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials. It is well known that the conventional top-down technique can cause significant crystallographic damage to the processed patterns.

Bottom Up Approach:

Bottom –up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. This route is more often used for preparing most of the nano-scale materials with the ability to generate a uniform size, shape and distribution. It effectively covers chemical synthesis and precisely controlled the reaction to inhibit further particle growth. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials.

Synthesis of nanoparticles to have a better control over particles size distribution, morphology, purity, quantity and quality, by employing environment friendly economical processes has always been a challenge for the researchers. The choice of synthesis technique can be a key factor in determining the effectiveness of the photovoltaic as studies. There are many methods of synthesizing titanium dioxide, such as hydrothermal, combustion synthesis, gas-phase methods, microwave synthesis and sol-gel processing.

1.2 WET CHEMICAL METHOD

Wet chemical method was the methodology used in all the experiments mentioned in this internship report. Wet chemical method is a type of Bottom up approach and is one of the most economical methods of producing nano particles of the sub-10 nanometres range. There are various methods which are classified collectively as different types of wet chemical methods, out of which two methods are the most commonly used protocols.

1.2.1 Turkevich Method

Turkevich method is commonly used for synthesis of metallic nanoparticles specifically gold and silver nanoparticles using Sodium Citrate as the reducing agent.

It produces modestly monodisperse spherical gold nanoparticles of around 10–20 nm in diameter. Larger particles can be produced, but at the cost of monodispersity and shape. In this method, hot chloroauric acid is treated with sodium citrate solution, producing colloidal gold. The Turkevich reaction proceeds via formation of transient gold nanowires. These gold nanowires are responsible for the dark appearance of the reaction solution before it turns ruby-red.

This method involves addition of the reducing agent to a pool of the metallic salt solution of required concentration which reduces the metallic cations to metal atoms and then leads to nucleation and growth of nanoparticles.

Multiple researchers have studied its mechanisms and with multiple tests on this method, it was found that reversing the process helps in the production of nanoparticles of sizes lesser than 10nm (adding the metallic salt solution to a pool of the reducing agent).

Turkevich method compared to Tannic acid reduction method has a setback, sodium citrate is an inorganic chemical and is only a stabilizing agent at room temperature and can acquire reducing capabilities only at escalated temperatures (around 80-90 degrees Celsius).

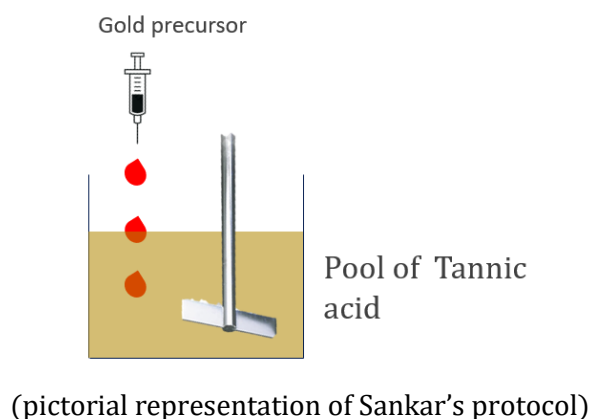
Hence to tackle all the setbacks posed by this method, another methodology / protocol was utilized in the experiments.

1.2.2 Tannic Acid reduction method

Tannic acid is a plant extract-based polyphenol consisting of five gallic acid chains mounted on a glucose molecule. Tannic acid synthesis is a green synthesis or protocol owing to the sources of the acid. Tannic acid synthesis is a replication of the “reverse Turkevich method” and can produce nanoparticles of the sub-10nm range.

Tannic acid is both a reducing agent and a stabilizing agent at room temperatures. At basic pH, tannic acid gets hydrolysed into its individual components gallic acid and glucose where gallic acid is a reducing agent and glucose is a stabilizing agent.

A protocol followed by a previous research scholar, **Sankar Kalidas**, was used as the basic framework of the experimentation procedures.

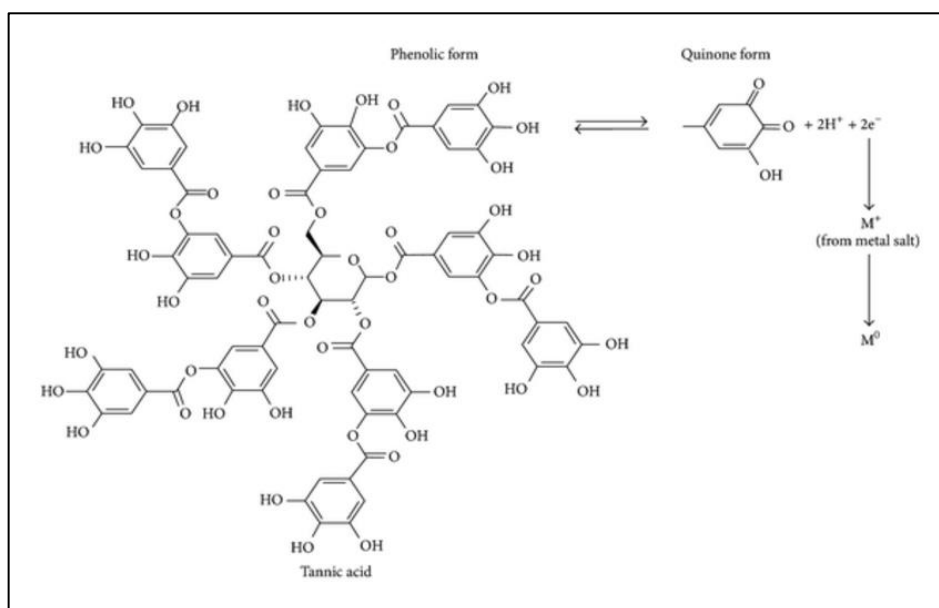


The protocol was found out to be the best method to synthesize nanoparticles of the desired range. It involved a dropwise addition of the metallic salts to a pool of tannic acid. Dropwise addition provided the best results: less polydispersity amongst other addition methods like dumping.

1.3 TANNIC ACID BEHAVIOUR

Tannic acid is a specific form of tannin, a type of polyphenol. Its weak acidity is due to the numerous phenol groups in the structure. The chemical formula for commercial tannic acid is often given as $C_{76}H_{52}O_{46}$. Tannic acid has the ability to donate 20 electrons off a single molecule when in the aqueous phase. Generally, the process of tannic acid reduction leads to a fast reaction and smaller size of the nano particles formed owing to a lesser amount of nucleation which happens in the reaction phase.

It consists of a central core of glucose that is linked by ester bonds to polygalloyl ester chains. Tannic acid has 25 phenolic hydroxyl ($-OH$) groups in its structure; but, only ten pairs of 'ortho' dihydroxyphenyl groups can take part in redox reactions to form quinones and donate electrons, because of the chelating action of adjacent hydroxyl groups and constraints on carbon valency.



(Structure and oxidation of Tannic Acid)

The image shows the oxidation reaction of ortho dihydroxy phenolic form to quinones by donating two electrons. Hence, each tannic acid molecule can donate twenty electrons.

Tannic acid has a pKa value between seven and eight, depending on its extent of dissociation, and is known to partially hydrolyze under mild acidic/basic conditions into glucose and gallic acid units. Gallic acid at alkaline pH reduces silver nitrate into silver nanoparticles rapidly at room temperature, but the particles form aggregates

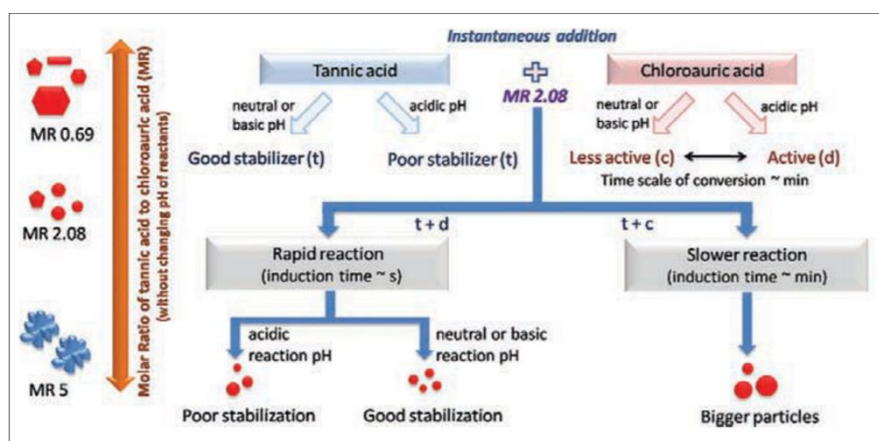
in solution as gallic acid is a poor stabilizing agent. Glucose is a weak reducing agent at room temperature, but it is an excellent stabilizing agent at alkaline pH. These findings suggest that tannic acid could be an ideal reducing and stabilizing agent under alkaline conditions at room temperature.

1.3.1 Effect of pH on Tannic Acid behaviour

The desired tannic acid properties can only be observed when present in a basic pH state. pH of the reactants plays a major role in the stability of the particles and their respective shape.

If the medium is acidic in nature, there exists a prominent role of oxidative etching which causes irregularities on the particle surface. Hence, basic nature of the reducing agent is recommended for enhanced stability and smooth particles surfaces. An example of GNP production with tannic acid is shown in the picture.

pH of tannic acid in the experiments is adjusted by adding 1 w/v of Potassium Carbonate, owing to its weak basic nature and at the same time being able to produce two KOH molecules in its aqueous phase.

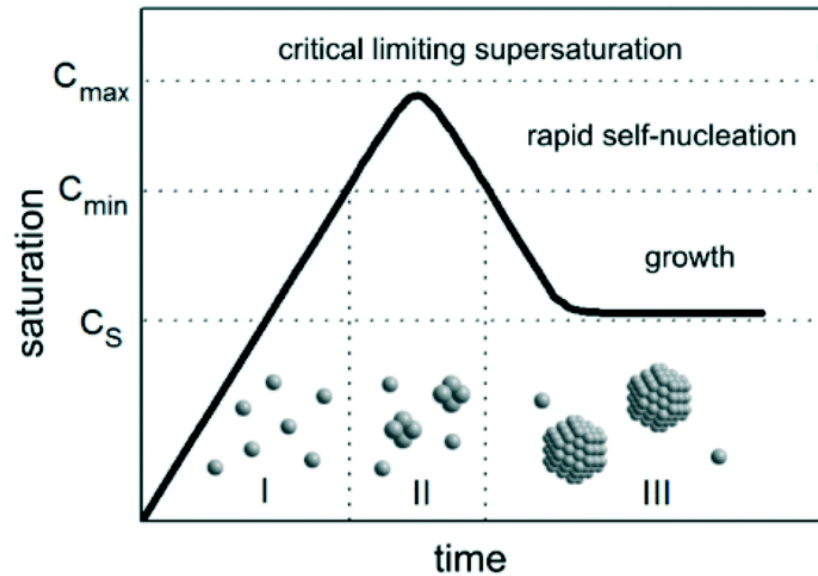


(schematic diagram of pH effect)

It is observed that neutral pH of tannic acid is a good stabilizer because of its ability to release glucose. More stability and more active the metal salts are, faster the reaction and smaller and more uniform the particles form. If the products are acidic in nature, there are changes or variations in the morphologies of the particles and is caused by the action of oxidative etching. The presence of acidic components cause this effect.

1.4 LaMer Model

On one side, it is understood about the methodologies on how to produce the required nanoparticles. It is essential to know how these nanoparticles are actually formed. LaMer model is the most widely accepted model to describe the formation of these nanoparticles through the wet chemical method. The LaMer model can be represented in the form of a graph (as shown below) of concentration vs time and can be divided into three specific zones:



(graphical representation of LaMer model)

Zone 1 : Generation stage. This is the stage where the metallic cations are reduced, and atoms are formed. This is also the beginning of the nucleation stage where stable nuclei begin to form.

Zone 2 : Nucleation stage. This is the zone where stable nuclei are constantly formed from the atoms. In this stage, the concentration of these nuclei reaches a maximum and then begin to decrease marking the beginning of the growth phase. This is the critical limiting supersaturation. In the portion above the C_{min} , nucleation and growth happen simultaneously. This means that theoretically, because these two states co-exist at the same time, it is not possible to produce mono-dispersed particles unless these two stages happen separately.

Zone 3 : Growth stage. This is the final stage in the formation of nanoparticles. The stable nuclei which formed in the previous stage experience a state of growth where in the atoms which are formed attach on to the nuclei forming bigger particles. The growth stage has a fixed concentration of nuclei indicating that any new addition of atoms only affects the size of these nuclei and no new stable complexes are formed.

1.5 Types of Nucleation

1.5.1 Homogeneous Nucleation

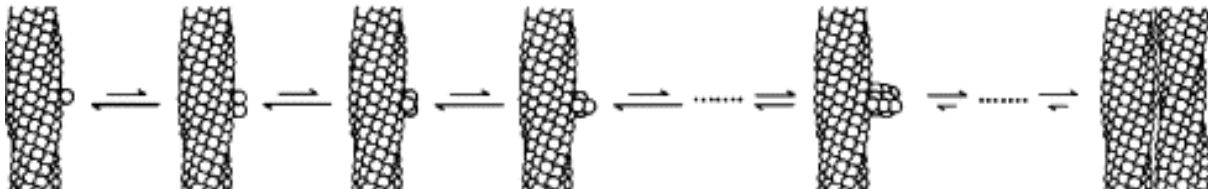
Homogeneous nucleation is the condition where the atoms form clusters or start nucleation with other atoms of the same nature.



(pictorial representation of homogeneous nucleation)

1.5.2 Heterogeneous Nucleation

Heterogeneous nucleation as opposed to homogeneous is the condition where atoms begin to nucleate on particles which behave as foreign particles to the reaction system. In the dropwise addition protocol that is followed in the experiments, a condition of heterogeneous nucleation is observed as once the first few drops are added, nuclei are formed and atoms which are formed in the reaction attach on to these nuclei and not other atoms.



(pictorial representation of heterogeneous nucleation)

1.6 Batch Process

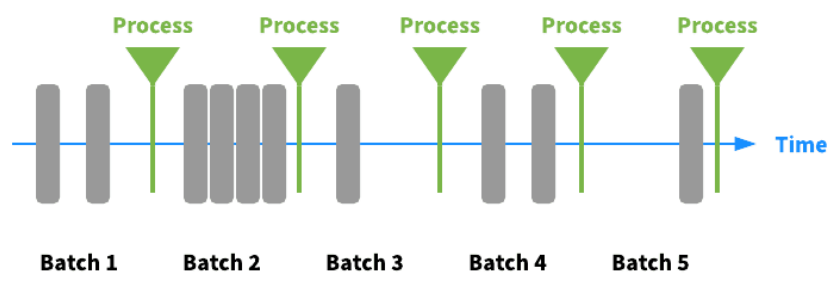
Batch processing is the concept of performing of an industrial process on materials in batches of a limited quantity. Fed – batch is a modification of the batch process where in one or more of the reactants is fed continuously while the others are already present in the reaction pool.

Advantages :

- Manufacturing in small batches aids with quality control.
- Flexibility in production of different product variations
- Ideal for trial runs and reduces the inventory
- Lowers the capital costs and risks involved

Disadvantages :

- Reconfiguration of the system for variations in products results in downtime and wastage of resources.
- Requirement of labour to shift the items manually from stage to stage
- Halt in production when there is a change of machinery
- Higher storage costs.



(pictorial representation of batch processing)

1.7 Continuous Process

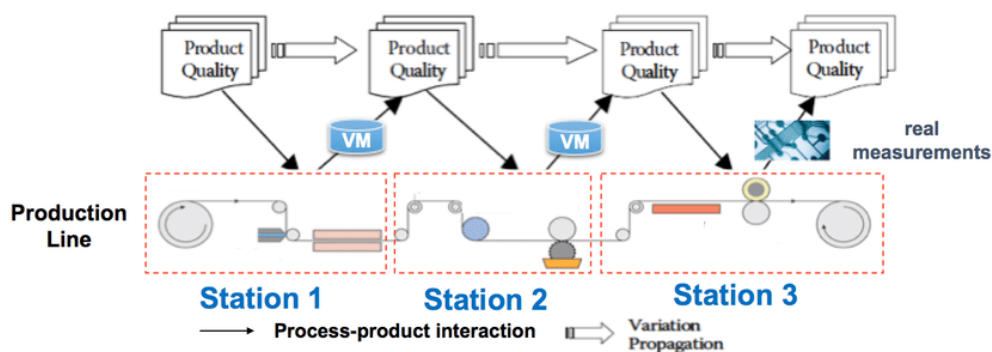
Continuous processing is a flow production method used to manufacture, produce, or process materials without interruption. Continuous production is called a continuous process or a continuous flow process because the materials, either dry bulk or fluids that are being processed are continuously in motion, undergoing chemical reactions or subject to mechanical or heat treatment.

Advantages :

- Quality of output is kept uniform
- Handling of materials is reduced due to the set pattern of production
- Repetitive nature of the processes makes production control easier
- Cost per unit is reduced due to the spreading of fixed costs of equipment over a large volume of output.

Disadvantages :

- Very rigid. Faults in one operation leads to a disruption of the entire process
- Constant checks must be performed to check for blockages in the lines
- More capital is required to install the production lines
- Low flexibility in product variation
- Profitable only if the demand is high and there is a requirement of mass production



(pictorial representation of continuous processing)

1.8 Colloidal stability

Based on different reaction systems and their outputs, stable complexes are formed by virtue of the reactants and their behaviour. Colloidal particles collide with each other due to the Brownian motion, convection, gravity and other forces. Collisions may result in coagulation of the particles and destabilization of the colloid. If a colloidal particle is brought to a short distance to another particle, they are attracted to each other by the van der Waals force. If there is no counteracting force, the particles will aggregate, and the colloidal system will be

destabilized. Colloidal stability is achieved due to repulsion forces balancing the attraction forces in the way similar to the stable mechanic equilibrium (if a body is disturbed it tends to return to its former position).

1.8.1 Electrostatic Stability

Electrostatic stabilization of Colloids is the mechanism in which the attraction van der Waals forces are counterbalanced by the repulsive Coulomb forces acting between the negatively charged colloidal particles.

1.8.1.1 Electric double layer

Electric Double Layer is the phenomenon playing a fundamental role in the mechanism of the electrostatic stabilization of colloids. Colloidal particles gain negative electric charge when negatively charged ions of the dispersion medium are adsorbed on the particles surface. A negatively charged particle attracts the positive counterions surrounding the particle. Electric Double Layer is the layer surrounding a particle of the dispersed phase and including the ions adsorbed on the particle surface and a film of the counter charged dispersion medium. The Electric Double Layer is electrically neutral.

An Electric Double Layer consists of three parts:

- **Surface charge** - charged ions (commonly negative) adsorbed on the particle surface.
- **Stern layer** - counterions (charged opposite to the surface charge) attracted to the particle surface and closely attached to it by the electrostatic force.
- **Diffuse layer** - a film of the dispersion medium (solvent) adjacent to the particle. Diffuse layer contains free ions with a higher concentration of the counterions. The ions of the diffuse layer are affected by the electrostatic force of the charged particle.

The electrical potential within the Electric Double Layer has the maximum value on the particle surface (Stern layer). The potential drops with the increase of distance from the surface and reaches 0 at the boundary of the Electric Double Layer.

When a colloidal particle moves in the dispersion medium, a layer of the surrounding liquid remains attached to the particle. The boundary of this layer is called slipping plane (shear plane). The value of the electric potential at the slipping plane is called Zeta potential, which is very important parameter in the theory of interaction of colloidal particles.

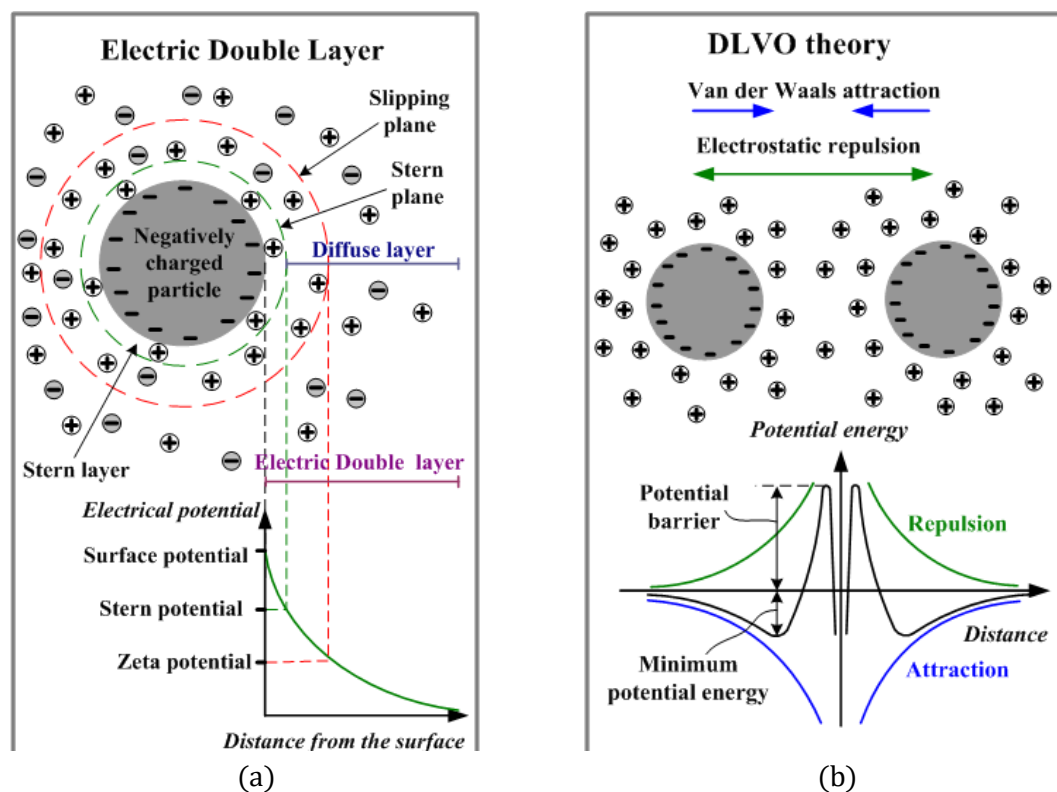
1.8.1.2 DLVO Theory

DLVO theory is a theory developed in 1940s to explain the stability of colloidal systems. Assumptions of DLVO theory:

- Dispersion is dilute
- Only two forces act on the dispersed particles: van der Waals force and electrostatic force
- The electric charge and other properties are uniformly distributed over the solid surface
- The distribution of the ions is determined by the electrostatic force, Brownian motion and entropic dispersion.

DLVO theory provides good explanation of the interaction between two approaching particles. The theory states that the colloidal stability is determined by the potential energy of the particles (V_T) summarizing two parts: potential energy of the attractive interaction due to van der Waals force V_A and potential energy of the repulsive electrostatic interaction V_R .

The graphs describing the potential energy of the interaction between two particles are presented in the figure above. The minimum of the potential energy determines the distance between two particles corresponding to their stable equilibrium. The two particles form a loose aggregate, which can be easily re-dispersed. The strong aggregate may be formed at a shorter distance corresponding to the primary minimum of the potential energy (not shown in the picture). In order to approach to the distance of the primary minimum the particle should overcome the potential barrier.



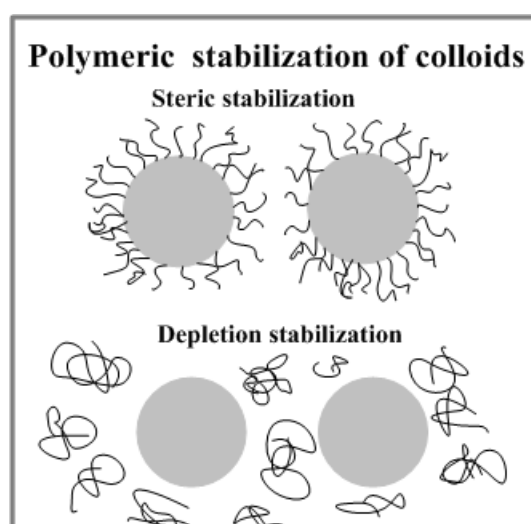
[Figures a and b representing Electric double layer and DLVO theory, Dr. Dmitri Kopeliovich]

1.8.2 Polymeric stabilization of colloids

Polymeric stabilization of Colloids involves polymeric molecules added to the dispersion medium in order to prevent the aggregation of the colloidal particles. The polymeric molecules create a repulsive force counterbalancing the attractive van der Waals force acting on a particle approaching another particle.

There are two types of polymeric stabilization:

- **Steric stabilization of colloids** is achieved by polymer molecules attached to the particle surface and forming a coating, which creates a repulsive force and separates the particle from another particle.
- **Depletion stabilization of colloids** involves unanchored (free) polymeric molecules creating repulsive forces between the approaching particles.



[Figure representing Polymeric stabilization of colloids, Dr. Dmitri Kopeliovich]

Stability of the particles can be disturbed or disrupted by addition of chemicals based on the system and type of stability. The experiments stated in this report show the case of electrostatic stability and the system can be destabilized by disruption of the charge layers through addition of bases or acids.

Acids because of their extreme ionic strength cause the particles to crash or agglomerate and cannot be dispersed back to its original state, whereas for the same situation to occur with addition of bases, a large amount of basic matter must be added. Usually addition of bases causes a temporary disruption of the ionic layers around the particles causing a condition known as flocculation. The particles can be dispersed back to its original state by using methods such as sonication.

An example of crashing or agglomeration is shown in the picture below, the system is a silver nanoparticle (SNP) system in which approximately 4ml of concentrated hydrochloric acid was added.



(SNP system)

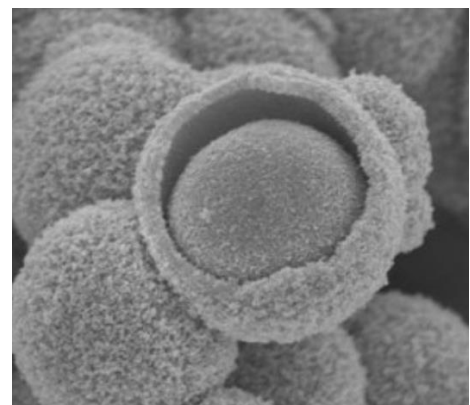
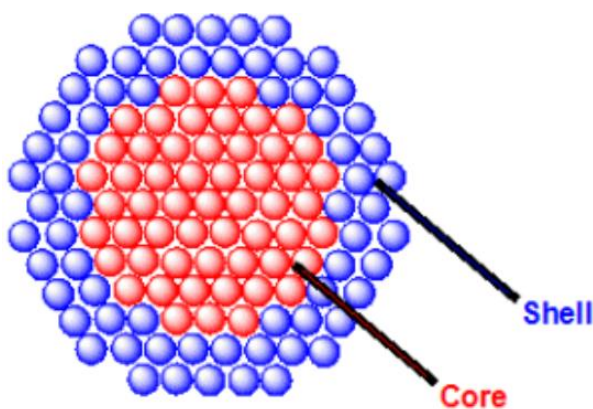


(Crashed system)

1.9 Core – Shell Nanoparticles

The materials at nano dimension have significant importance in altering the chemical, optical, electrical behaviours associated with them. Initially nanoparticles were thought to have much better properties than the bulk materials. Later, further research found that heterogeneous, composite or sandwiched colloidal nanoparticles had better efficiency than their corresponding single particles. In some cases, they develop new properties which are not shown in either of its individual particles. These particles are termed as “core-shell nanoparticles”.

They are used in a wide range of applications such as biomedical and pharmaceutical applications, catalysis, electronics, enhancement of photoluminescence, creating photonic crystals, etc. Their properties are not only dependant on their size but also linked with their shape. Properties such as blocking temperature, magnetic saturation and permanent magnetization are dependent on particle size but the coercivity of the particles is dependent on the particle shape because of surface anisotropy effect.



(core shell nanoparticles, pictorial and SEM images)

2. Experimentation and Practical work

The experimentation part is distributed amongst two parts based on the two different methodologies followed: Fed – Batch and continuous process.

Once synthesized, the samples were further characterized using UV-Vis spectroscopy and a few samples were also analysed further using TEM (transmission electron microscopy). SEM is not used in these experiments because most of the products obtained are below 10nm in size and SEM is not very sensitive in this size range.

Chemicals utilised for experiments:

- 1) Tannic Acid (reducing and stabilising agent) | Molecular mass: 1701.19 g/mol
- 2) Chloroauric Acid (trihydrate) (gold salt) (HAuCl_4) | Molecular mass: 393.833 g/mol
- 3) Silver Nitrate (silver salt) (AgNO_3) | Molecular Mass: 169.87 g/mol
- 4) Potassium Carbonate (to adjust the pH) | Molecular Mass: 138.205 g/mol (used as 1 w/v and 10w/v aqueous solutions)

The pH of Tannic acid is adjusted as per the experiment. Usually in the synthesis of gold nanoparticles or a gold shell, the pH of tannic acid is maintained at 10 and in the case of silver, the pH is maintained at 8. This is because chloroauric acid is an acidic salt and silver nitrate is a basic salt. If silver is synthesized with tannic acid pH being 10, there is a high chance of the double layer boundary getting disrupted due to the presence of ionic compounds in the reaction system, causing flocculation.

The equipment used for UV-vis spectroscopy was Multiskan Sky 1530-00560, which uses a 96 well plate to hold the samples and with a sensitivity of 4nm.

2.1 Fed – Batch Process

2.1.1 Experimental setup



(pictorial representation of Fed – Batch setup)

The setup consists of the following components:

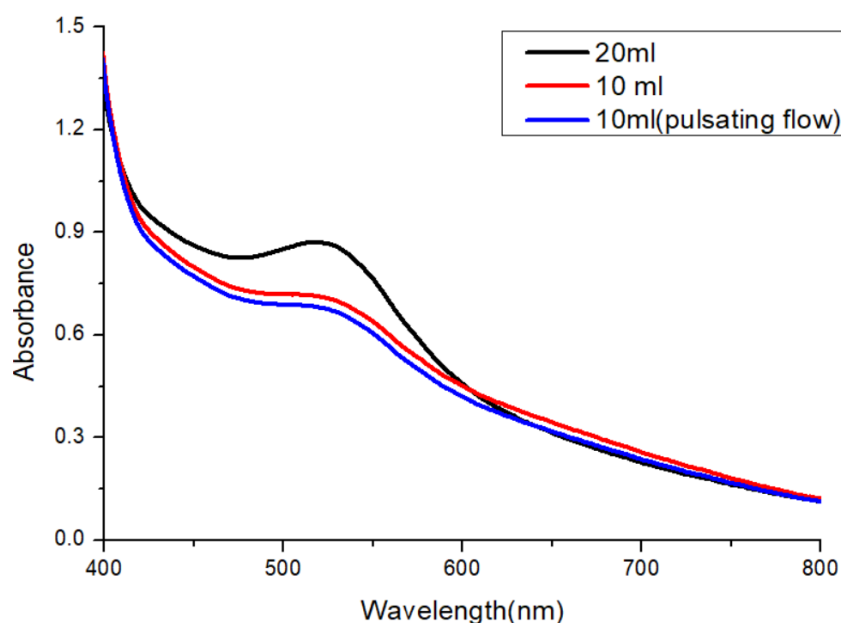
- Ruston turbine with speed controller
- Stand with a screw jack
- Syringe pump
- Disposable syringes
- Teflon baffles and impeller
- Silicon tubes
- Beakers
- Burette Stand
- Stopwatch
- Microtips (200 μ l)
- Blade
- Necessary chemicals

2.1.2 Synthesis of Gold Nanoparticles (GNP or AuNP)

Initial experimentation was conducted as per Sankar's protocol and checked for reproducibility. As basics, gold nanoparticles were synthesized using chloroauric acid and tannic acid. GNP gives an absorbance peak at around 510 to 520nm.

- Tannic acid solution is prepared of the concentration 0.89mM and the pH is adjusted to 10 using 1w/v of potassium carbonate solution.
- Chloroauric acid solution is prepared of the concentration 0.64mM.
- All solutions are prepared using DI water.
- 15ml of tannic acid is taken as the batch reactant in the beaker and chloroauric acid solution is added to the pool through the syringe at 1ml/min.

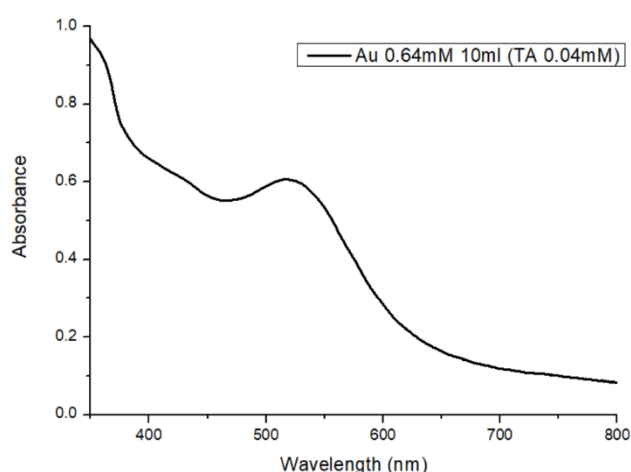
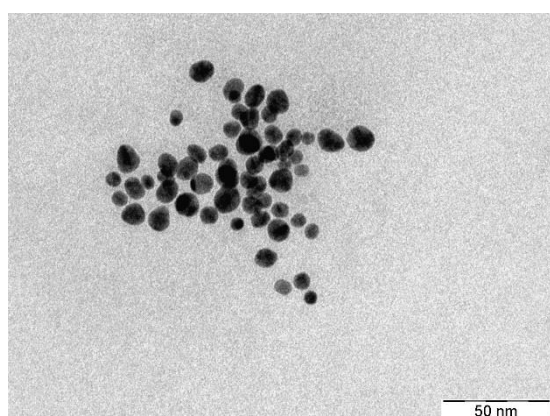
Impeller Rotation – 1000 rpm Chloroauric Acid : 0.64 mM Tannic Acid : 0.89 mM					
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25					
Sample	Input mode	V of Tannic Acid (ml)	V of Chloroauric Acid (ml)	pH of final solution	Amount of gold in the solution (mg)
1	Pulsating	15	10	8	1.2608
2	Dropwise	15	10	7 - 8	1.2608
3	Dropwise	15	20.5	7	2.5847



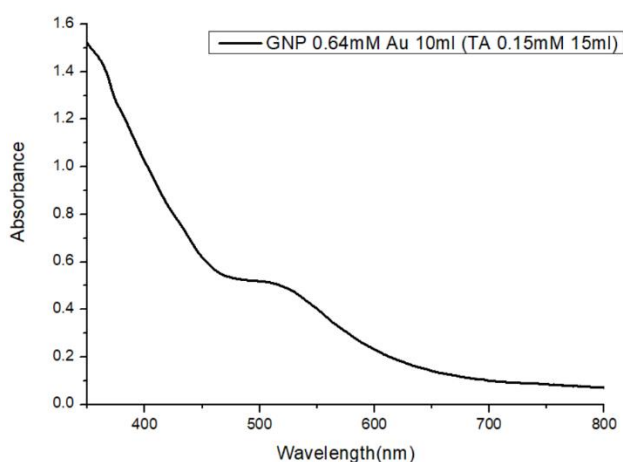
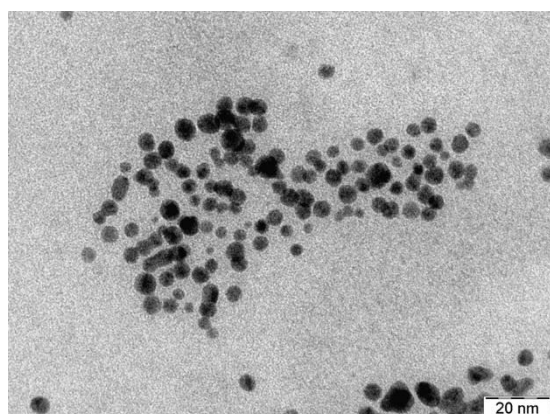
The experiment showed reproducing results as that of Sankar's thesis. But the higher concentration of Tannic Acid proved to be a hassle when it was used to synthesize core-shell nanoparticles. Hence lower concentrations of Tannic Acid were used for the same process and apart from UV-vis spectroscopy, TEM was also performed on these samples to check for their size.

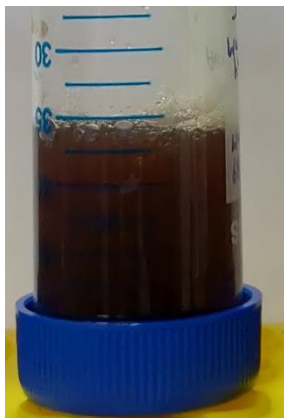
Gold is in its +3 state in chloroauric acid. It requires 3 electrons to reduce to Au^0 . Tannic Acid can donate 20 electrons off each molecule. Ideally for 0.64mM of gold salt solution, the minimum required concentration of tannic acid must be around 0.096mM. The first trial was performed with tannic acid's concentration at 0.04mM which is lesser than the minimum required concentration. The second trial was performed at 0.15mM concentration of tannic acid.

Tannic Acid : 0.04mM, Average size : 5.1 ± 1.9 nm



Tannic Acid : 0.15mM, Average size : 4.5 ± 0.9 nm





(GNP samples, 0.64mM Au salt, 0.89mM Tannic Acid)

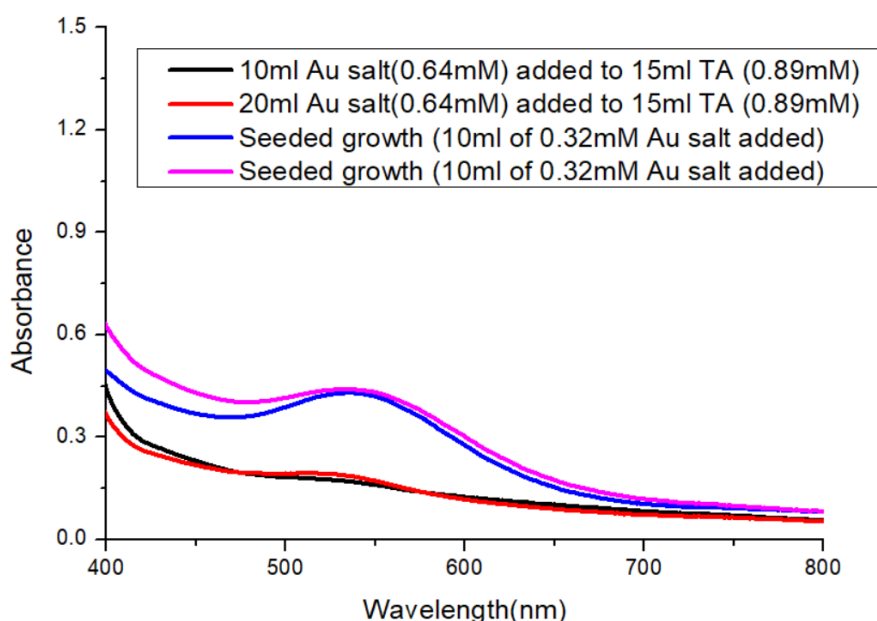
As per the picture, it is observed that the particles of the given size range form a wine-red coloured colloidal suspension.

2.1.3 Seeded growth of gold nanoparticles

The gold nanoparticles synthesized in the previous experiments were tested for seeded growth. In this case, the gold nanoparticles are the seeds and additional gold salt solution is added to the previous product mixture to test for growth on these seeds. The seed solution is prepared by taking 2.5ml of the previous GNP solution and diluting it to 15ml using DI water.

Chloroauric acid solution of 0.32mM concentration is taken as the growth solution. Growth solution is added dropwise whereas the seed solution is the batch reactant.

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.32 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Gold Salt (ml)	V of Seed soln. (ml)	V of Growth soln. (ml)	pH of final solution	Amount of gold in the solution (mg)
2	Dropwise	10	15	10	7	0.9456
3	Dropwise	20.5	15	10	7	0.9456



Comparing the peaks of the seed solution and the solution after seeded growth, there is a shift in the peak of about 10nm towards the increasing wavelengths, indicating that there is no or minimal secondary nucleation and there is prominent growth on these particles.

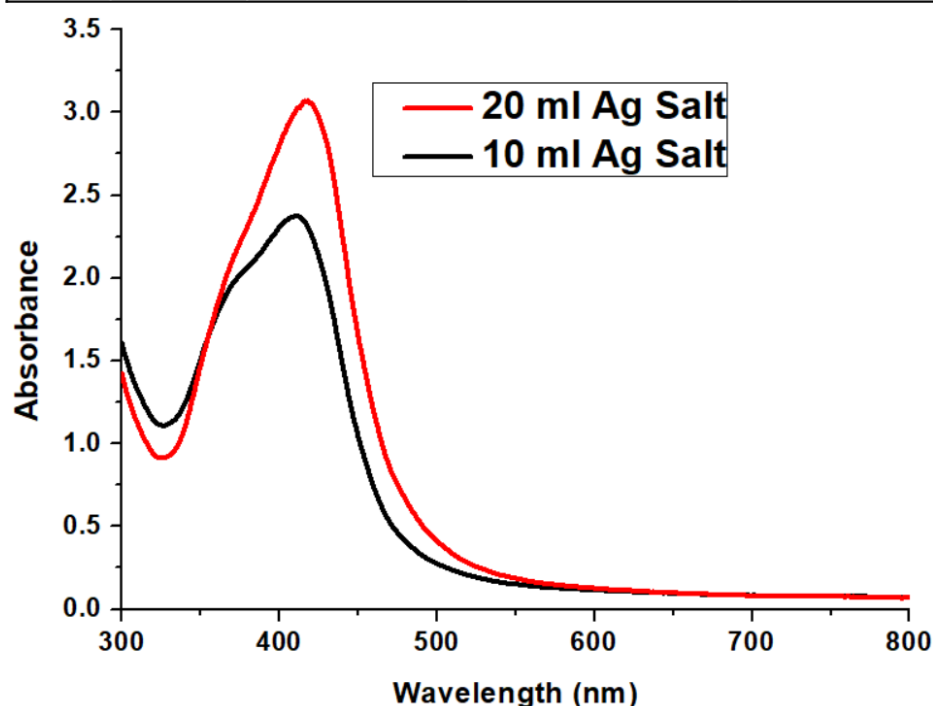
A lower concentration of the shell solution is taken to avoid secondary nucleation of gold nanoparticles during the reaction. Lesser the concentration, lesser the chances of secondary nucleation.

2.1.4 Synthesis of Silver nanoparticles (SNP or AgNP)

Silver nanoparticles were also synthesized as per Sankar's protocol. SNP gives a peak at around 410-415nm. Silver is present in its +1 state in silver nitrate and requires only 1 electron to reduce to Ag⁰ state. Unlike gold which used almost 10 times its minimum required concentration of tannic acid, in this experiment, the concentration of tannic acid is just above its minimum requirement.

- Tannic acid solution is prepared of the concentration 0.04mM and the pH is adjusted to 8 using 1w/v of potassium carbonate solution.
- Silver nitrate solution is prepared of the concentration 0.64mM.
- 15ml of tannic acid is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Silver Nitrate : 0.64 mM Tannic Acid : 0.04 mM				
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25				
Sample	Input mode	V of Tannic Acid (ml)	V of Silver Nitrate (ml)	pH of final solution
1	Dropwise	15	10	7
2	Dropwise	15	20	6 - 7





(SNP samples Ag salt 0.64mM, Tannic Acid 0.04mM)

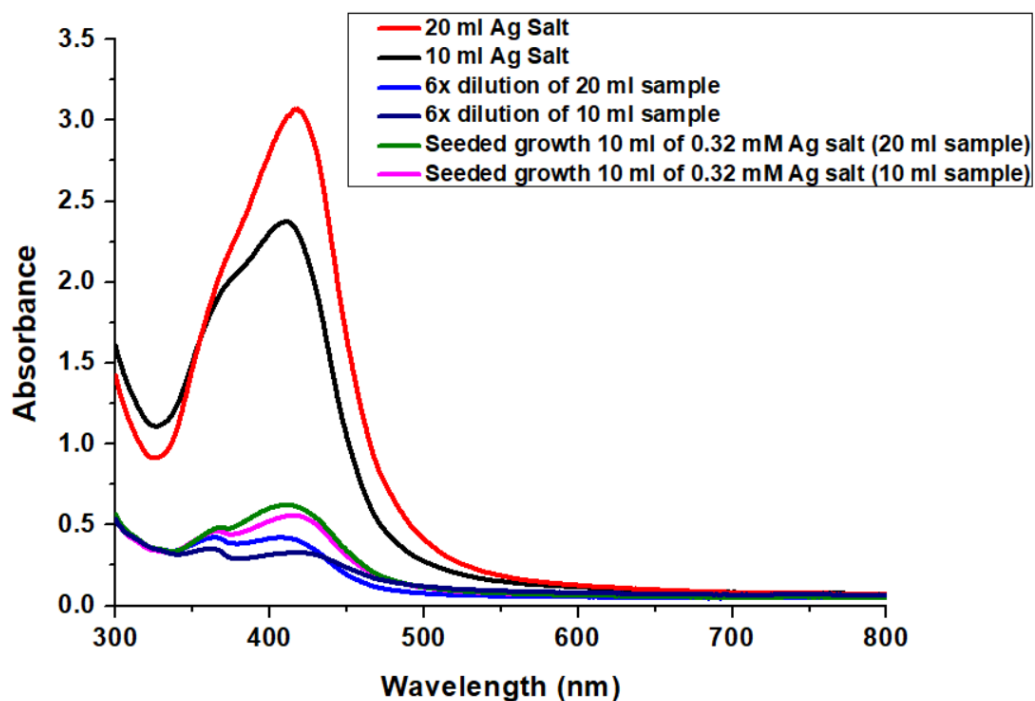
As per Sankar's protocol, reproducible results were obtained for the synthesis of silver nanoparticles. Silver nanoparticles of the given size form a dark yellowish colloidal solution.

2.1.5 Seeded growth of Silver Nanoparticles

Like that of gold nanoparticles, similar procedures were followed for the seeded growth of silver nanoparticles. The seed solution is prepared by taking 2.5ml of the previous SNP solution and diluting it to 15ml using DI water.

Silver nitrate solution of 0.32mM concentration is taken as the growth solution. Growth solution is added dropwise whereas the seed solution is the batch reactant.

Impeller Rotation – 1000 rpm Silver Nitrate : 0.32 mM					
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25					
Sample	Input mode	V of Silver Salt (ml)	V of Seed soln. (ml)	V of Growth soln. (ml)	pH of final solution
1	Dropwise	10	15	10	7
2	Dropwise	20	15	10	7



Comparing the peaks of the seed solution and the solution after seeded growth, there is a slight shift in the peak towards the increasing wavelengths, indicating that there is no or minimal secondary nucleation and there is prominent growth on these particles. Again, a lower concentration of the shell solution is taken to avoid secondary nucleation of silver nanoparticles during the reaction.

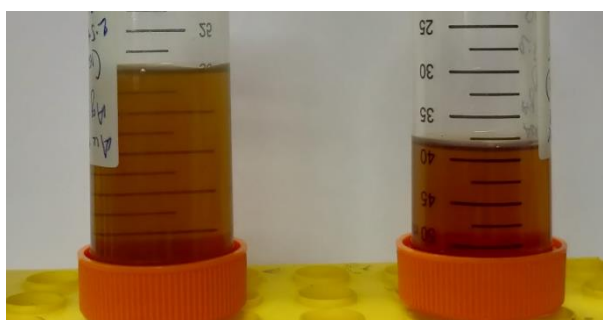
2.1.6 Core – Shell Nanoparticles (Au core Ag shell)

Synthesis of core-shell particles is a special case of seeded growth. Unlike seeded growth where the growth solution is the same salt solution itself, in core shell experiments, seed particles remain the core of the newly formed nanoparticles and the growth solution is the salt solution of the required shell.

Using the basics of Sankar's protocol which is dropwise addition of the salts solutions, various experiments were conducted with different concentrations and volumes to optimize this process.

4 different methodologies were followed in the synthesis of Au core and Ag shell particles.

- Dilution
- No dilution
- Centrifugation
- Combinations



(Au core Ag shell colloidal solution)

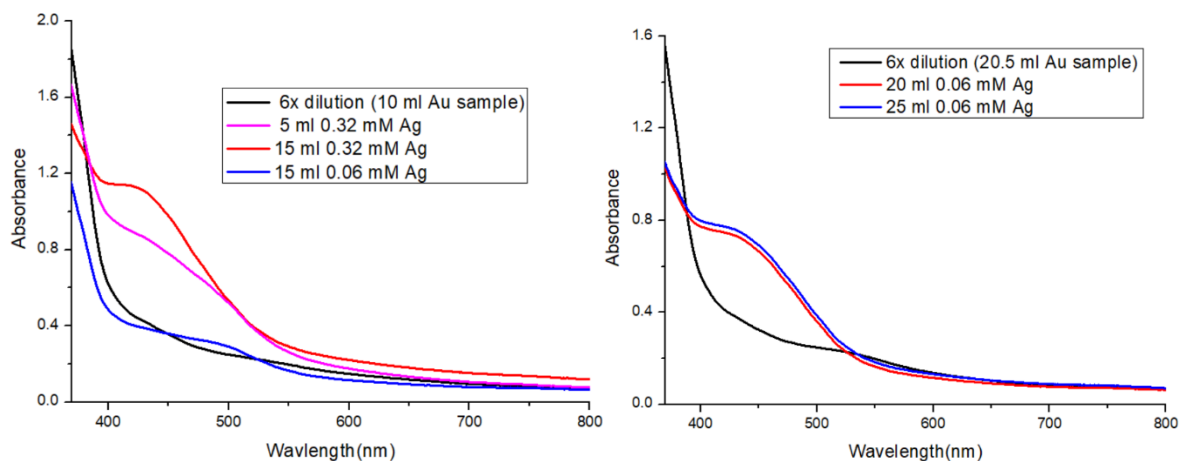
Ideally, if proper core shell nanoparticles are formed, the colour of the product colloidal solution is orangish-brown to yellow in colour.

Trial 1 (dilution)

- Gold nanoparticles synthesized earlier (TA 0.89mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (1 w/v of potassium carbonate)
- Silver nitrate solution is prepared of the concentration 0.06mM and 0.32mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.

For the first trial set of experiments, both 10ml and 20.5 ml samples of GNP were used to check for variations. A total of 5 different samples were prepared in this trial set.

Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM & 0.32 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.32	5	7
2	Dropwise	10	15	0.32	15	6 – 7
3	Dropwise	10	15	0.06	15	7
4	Dropwise	20.5	15	0.06	20	7
5	Dropwise	20.5	15	0.06	25	6 – 7



From the spectrum graphs it is observed that the seed solution which has an absorbance at around 520nm shifts to around 450nm indicating the formation of silver around the gold nanoparticles. Higher values of absorbance might be due to partial secondary nucleation because of higher volumes of the shell solution.

Though these graphs show the successful appearance of the silver peak and disappearance of the gold peak, there posed another setback to the experiment. It was unsure whether addition of the silver solution caused complete secondary nucleation. Though there was no peak at 510-520 nm, it was suspected that addition of the silver solution might have just diluted the gold particles to such an extent that the peak disappears.

In the subsequent experiments, the graphs were compared to the absorption of the seed solution diluted to the same volume as that of the core shell particles but with DI water.

Trial 2 (dilution)

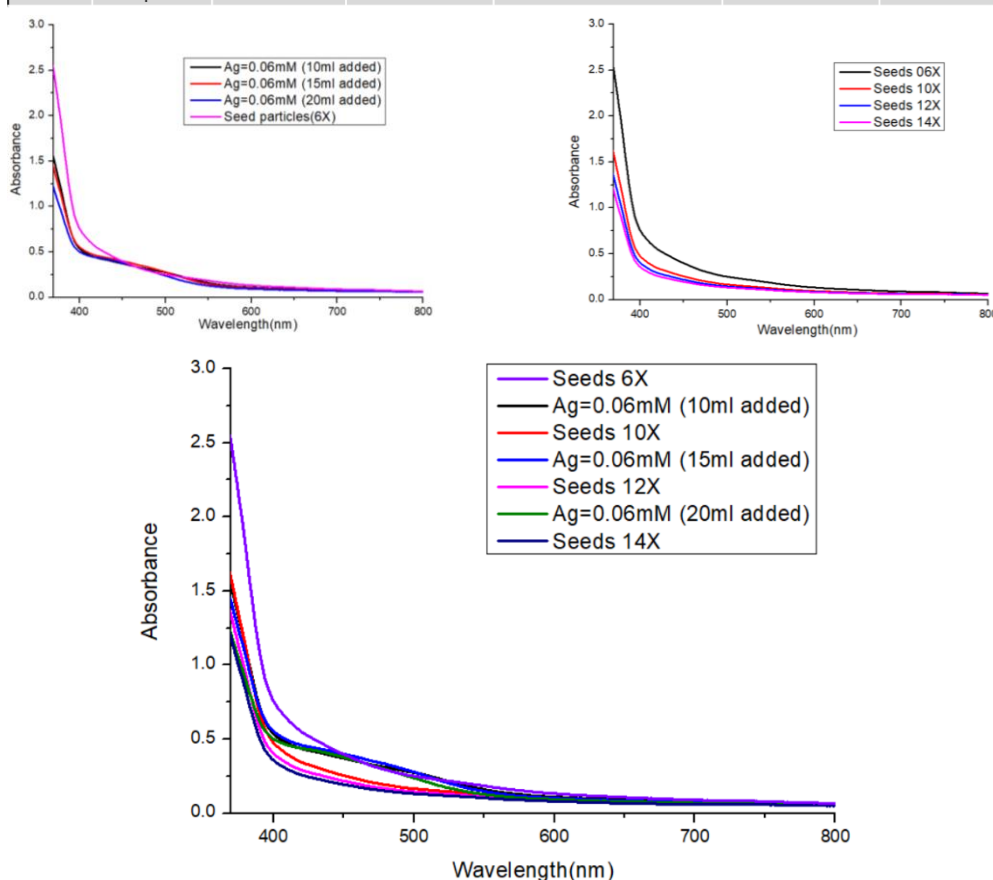
With the seed solution used up completely for seeded growth and the previous core shell experiments, GNP samples were prepared again with the same parameters but in this trial, the pH was adjusted with 10w/v of potassium carbonate.

This trial was performed to check for reproducibility of the 1st trial products. Though no variations were expected because of the change in concentration of potassium carbonate,

the spectrum post the experiment showed no signs of proper peaks in comparison to the previous trial.

- Gold nanoparticles were synthesized (TA 0.89mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (10 w/v of potassium carbonate)
- Silver nitrate solution is prepared of the concentration 0.06mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	10	7
2	Dropwise	10	15	0.06	15	7
3	Dropwise	10	15	0.06	20	7



Though the cause of this result being the change in concentration of potassium carbonate was not known yet, another trial was performed to re-check the results.

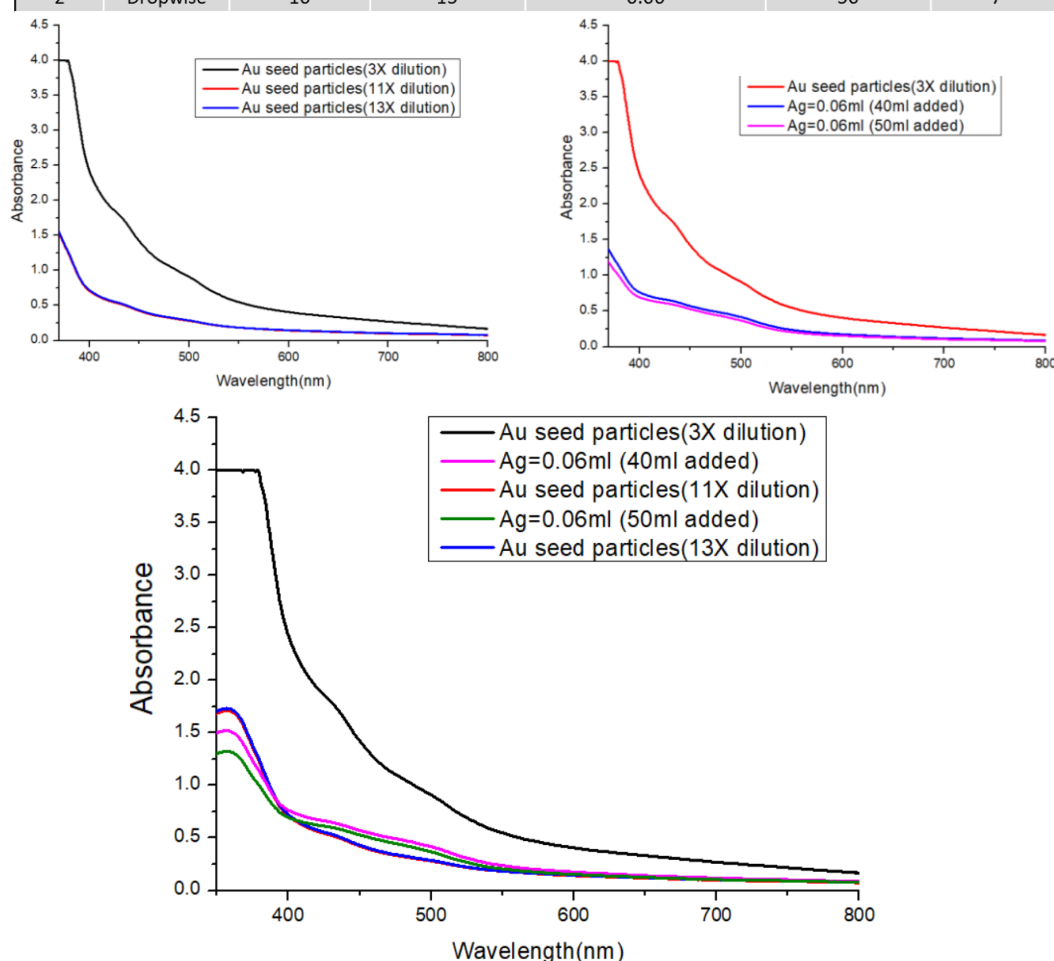
Trial 3 (dilution)

The third trial was almost similar to the second one. The modification made in this trial was the dilution of seed particles. Previous experiments had the dilution of seed or core

particles to be 6 times (2.5 ml to 15 ml). Keeping the final volume constant, the dilution factor was decreased to 3 times (5ml to 15 ml).

- Gold nanoparticles synthesized earlier (TA 0.89mM), 5 ml of that solution is taken and diluted up to 15 ml. (10w/v of potassium carbonate)
- Silver nitrate solution is prepared of the concentration 0.06mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	40	7
2	Dropwise	10	15	0.06	50	7



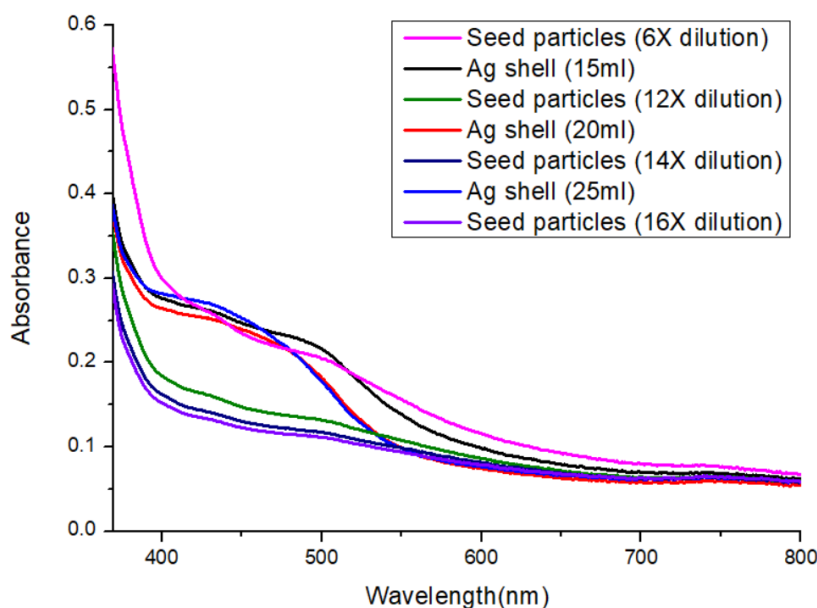
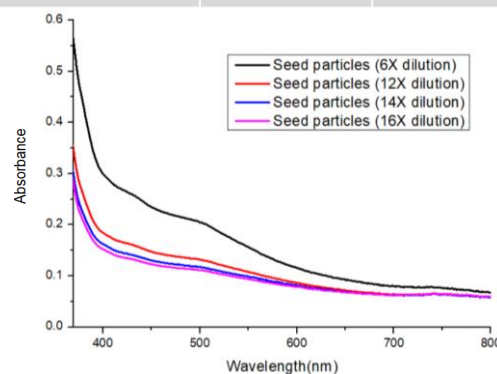
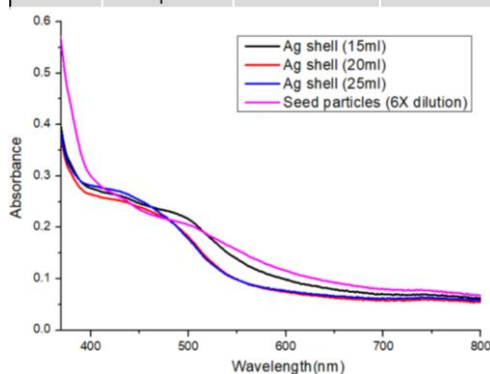
The spectrums again didn't show the trend as that of trial 1. It was then suggested that the higher concentration of potassium carbonate might have interfered in the reaction mixture. In the subsequent trials, the concentration of potassium carbonate was reduced back to 1w/v.

Trial 4 (dilution)

Modifications were made to the seed solution. New seeds were prepared with 1w/v of potassium carbonate to neglect the errors caused by it. In this trial, seeds were prepared with a higher concentration of tannic acid. As opposed to the 0.89mM which was utilised earlier to make GNP seeds, this trial had used the 0.15mM tannic acid concentration. 0.15mM is slightly more than the minimum concentration required as per the stoichiometric ratios of the reaction, this concentration was chosen to replicate the same molar ratios as that of the silver nanoparticles synthesis.

- Gold nanoparticles synthesized earlier (TA 0.15mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (1w/v of potassium carbonate)
- Silver nitrate solution is prepared of the concentration 0.06mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Silver Nitrate : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	15	7
2	Dropwise	10	15	0.06	20	7
3	Dropwise	10	15	0.06	25	7



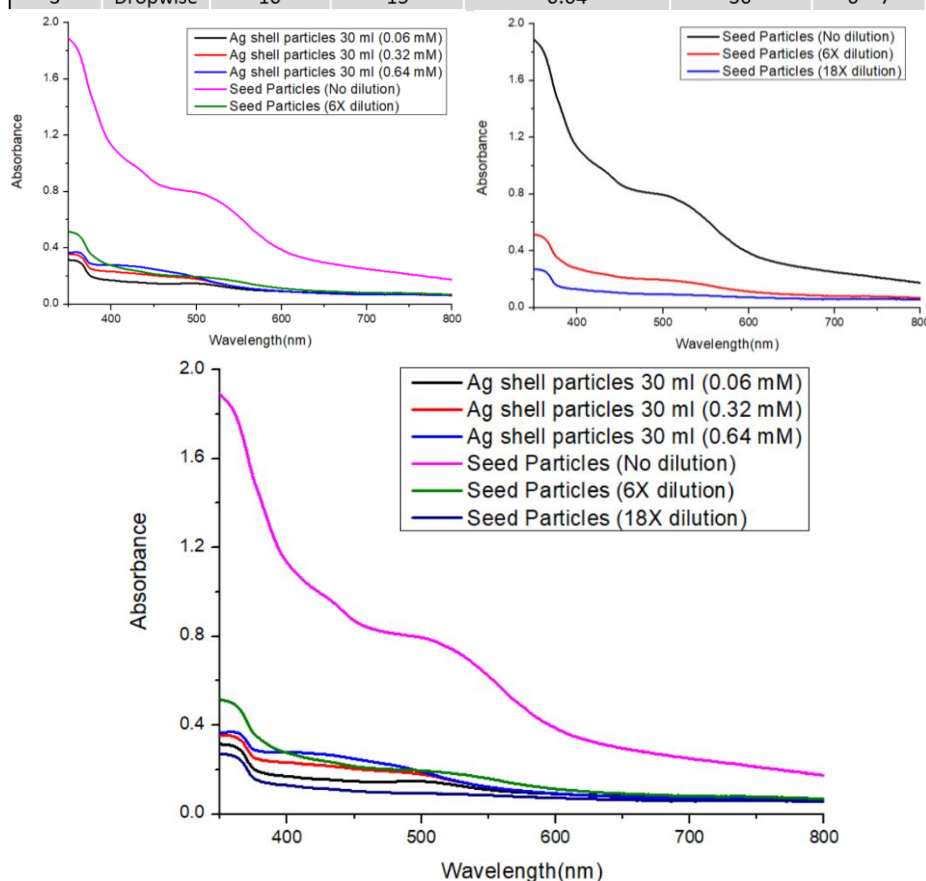
This trial had shown significant peaks as compared to the previous trials. This helped to conclude that higher concentrations of potassium carbonate tamper with the production of the particles. To check for reproducibility of these samples another trial was performed because of the modifications in tannic acid concentration.

Trial 5 (dilution)

This trial has a few modifications as compared to trial 4. Seeds were prepared again but with a small variation in the concentration of tannic acid from 0.15mM to 0.1mM. This trial also had the usage of multiple concentrations of shell solutions like that of trial 1.

- Gold nanoparticles were synthesized (TA 0.1mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (1w/v of potassium carbonate)
- Silver nitrate solution is prepared of the concentration 0.06mM, 0.32mM and 0.64mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Silver Nitrate Solution : 0.06 0.32 0.64 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Gold Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	30	7
2	Dropwise	10	15	0.32	30	7
3	Dropwise	10	15	0.64	30	6 – 7



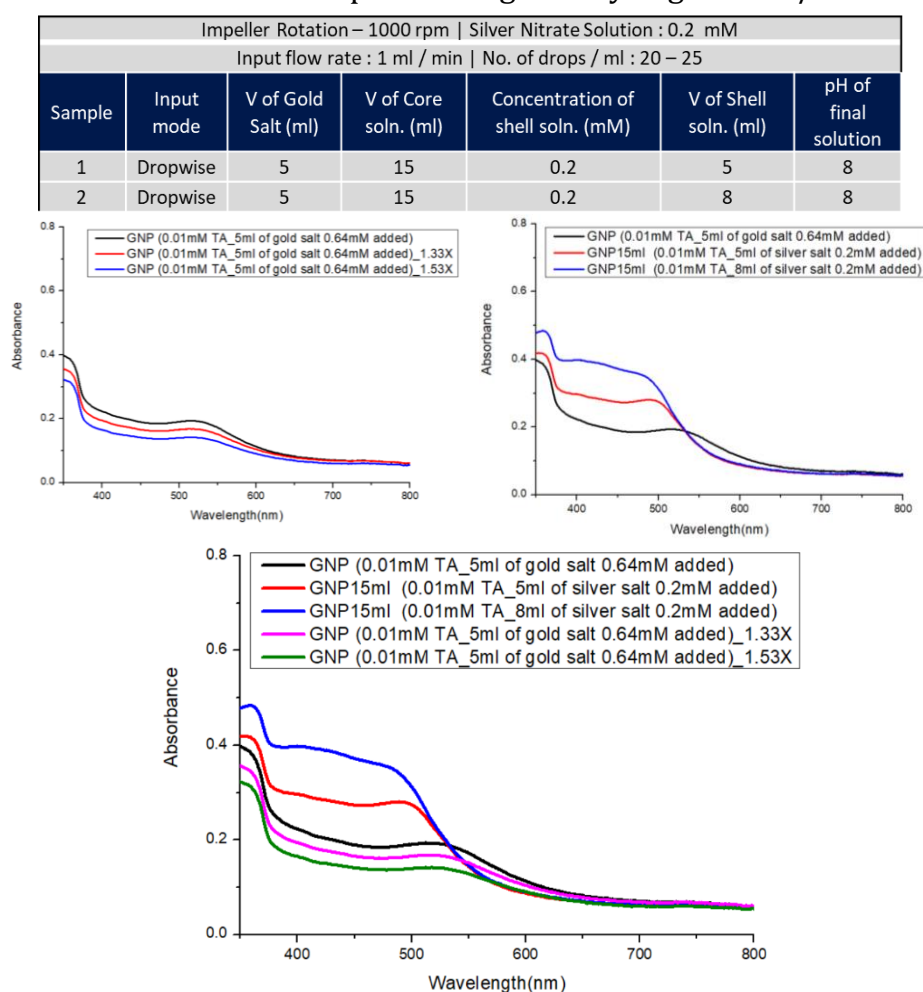
Analysing the spectrum data, we get a clear comparison of the variance with respect to different concentrations while having a constant volume. However, addition of 30 ml of the shell solution amounts to a large value of dilution of the products.

On comparing all the trials in the case of dilution methodology, it can be concluded that lower concentrations of tannic acid provide significantly good results with respect to UV-vis spectroscopy and the concentration of potassium carbonate must be low.

Trial 6 (no dilution)

Unlike the previous 5 trials, in the 'no dilution' methodology, the seed particles are not diluted, rather, just a portion of the seed solution is used directly for experimentation. In this trial, tannic acid of 0.01mM concentration is used, which is 9 times lesser than the minimum stoichiometric requirement.

- Gold nanoparticles were synthesized (TA 0.01mM), 5 ml of gold salt was added to 40 ml of tannic acid, 15 ml of the solution is taken for further experiments (1w/v of potassium carbonate)
- Silver nitrate solution is prepared of the concentration 0.2mM
- 15ml of the seed solution is taken as the batch reactant in the beaker and silver nitrate solution is added to the pool through the syringe at 1ml/min.



Due to the lesser concentration of tannic acid, there is lesser interference at 300 to 500 nm range giving us prominent peaks and curves. 5 ml of the shell solution shows a clear shift in peak whereas the 8 ml of shell solution shows an additional hump at 410 nm which indicates that there might be secondary nucleation.

Trial 7 (Centrifugation)

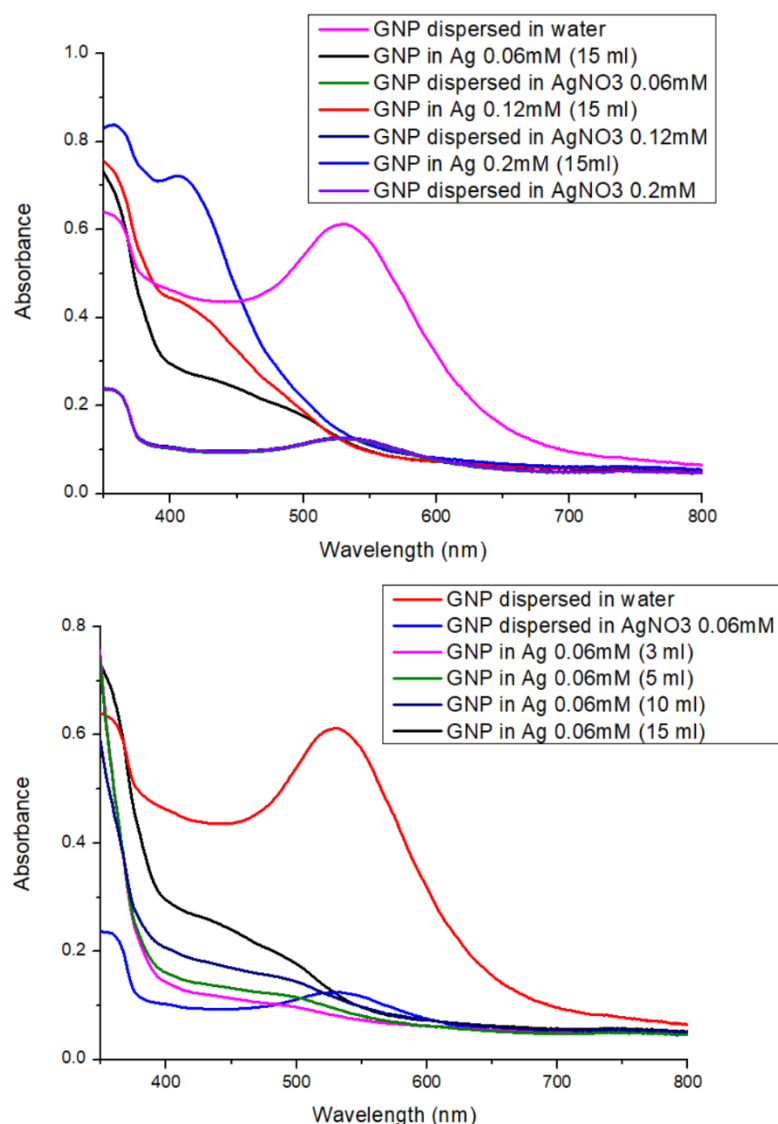
Tannic acid in higher concentrations has a high interference with the absorbance spectrums of the nanoparticles which are synthesized. To optimize the process even more by not only using a lesser concentration, the samples (1.5 ml per centrifuge tube) are centrifuged to remove any excess tannic acid present in the solution.

The pellet thus formed at the bottom of these centrifuge tubes is then dispersed in 1 ml of DI water. Each centrifuge tube is made up to 6 times its original volume as per the trials performed in the dilution experiment, 1.5 ml to 9 ml, but instead of DI water, the solutions are dispersed in the shell solution of required concentration. This solution of the shell salt and the core nanoparticles is added to a pool of tannic acid.

Multiple speeds and time were tried on the core nanoparticles, for the chosen concentration of tannic acid, 0.04mM, 9000 rpm and 90 minutes gave optimal results. Lower speeds and time showed a high number of nanoparticles in the supernatant whereas higher speeds and time resulted in agglomeration of the particles.

- Gold nanoparticles were synthesized (TA 0.04mM), 10 ml of gold salt was added to 15 ml of tannic acid (1w/v of potassium carbonate).
- Silver nitrate solution is prepared of the concentration 0.3mM
- 1.5 ml of GNP samples are taken in centrifuge tubes and centrifuged for 90 mins at 9000 rpm
- The supernatant is removed, and the pellet is dispersed in 1 ml of DI water. Each centrifuge tube is made up to 9ml using the silver nitrate solution such that three solution are obtained of the concentration 0.06mM, 0.12mM and 0.2mM.
- This solution is added to a pool of tannic acid (15ml) of concentration 0.03 mM whose pH is adjusted to 8.

Impeller Rotation – 1000 rpm Silver Nitrate Solution : 0.06 mM					
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25					
Sample	Input mode	V of Gold Salt (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	0.06	3	8
2	Dropwise	10	0.06	5	7-8
3	Dropwise	10	0.06	10	7-8
4	Dropwise	10	0.06	15	7
5	Dropwise	10	0.12	15	7
6	Dropwise	10	0.2	15	7



Two sets of experiments were conducted. First, the volume of the gold nanoparticles in silver nitrate is fixed to 15ml and the concentration is varied. This experiment shows significant results for 0.06mM of silver nitrate whereas the other concentrations seem to show signs of secondary nucleation.

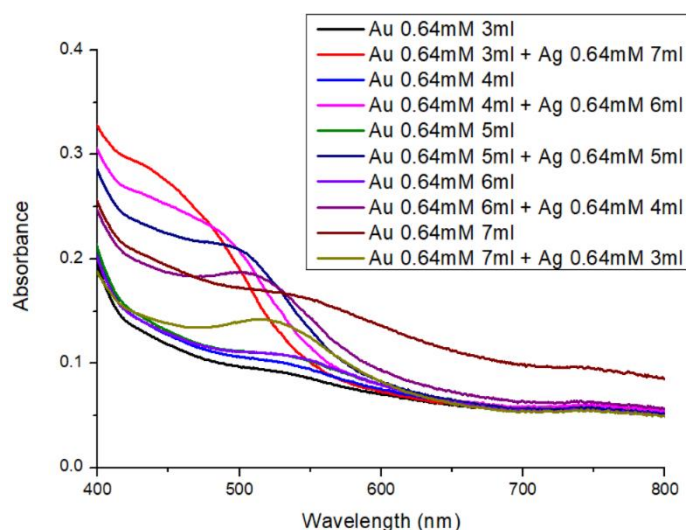
The second set of the experiments were carried forward by keeping the concentration fixed at 0.06mM and varying volumes. Of the 4 experiments which were conducted for the set concentration, 10ml of the solution proved to have the best results. A smooth shift in peak is observed with no significant change in the intensity of absorbance.

Trial 8 (Combinations)

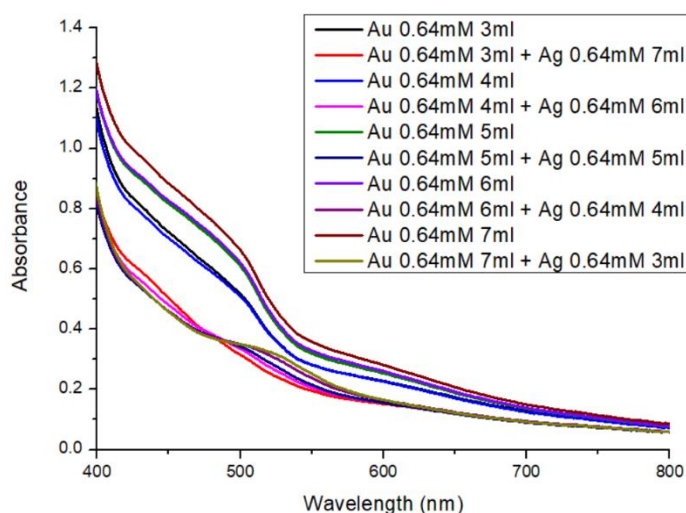
The last methodology in the Au core – Ag shell experimentation was the combination methodology. This method involved addition of different volumes of gold and solver salts of the same concentration fixed at 0.64mM to the same pool of tannic acid. Fixing the total volume of salt solution added to 10 ml, the experiment begins with addition

of 'X' ml of gold salt solution to form core nanoparticles and '10-X' ml of silver salt solution to form the shell. Volumes of gold salt added to the pool of tannic acid are 3, 4, 5, 6 and 7ml.

Two different concentrations of tannic acid, 0.15mM and 0.89mM, are used to check for the variation of production of these particles with the concentration of tannic acid.



(Tannic Acid : 0.15mM)



(Tannic Acid : 0.89mM)

It can be observed from the two spectrums that the shift in peaks is clearly observed in the case of 0.15mM concentration of tannic acid. Considering the option of synthesis of core-shell nanoparticles, these results help to conclude once more that lower concentration of tannic acid provide optimum results.

2.1.7 Core – Shell Nanoparticles (Ag core Au shell)

Silver core and gold shell have a slightly modified mechanism in which these nanoparticles are formed. With reference to their reduction potentials, silver has a reduction potential of 0.8V whereas in the case of gold, it is 1.52V.

As per the galvanic displacement table, elements with lower reduction potential can displace the metals from its salt solution having a reduction potential higher than the latter element. In this case, silver which is present in its metallic nanoparticle form can displace gold from its chloroauric acid solution owing to its lesser reduction potential.

This process also creates a form of an alloy with silver and gold. This fact could also be linked to the atomic and ionic radius of the elements. In fact, both Au and Ag have Cubic Centered Faced lattices.

For Au: ionic radius is 85 pm and atomic is 135 pm

For Ag: ionic radius is 115 pm and atomic is 160 pm

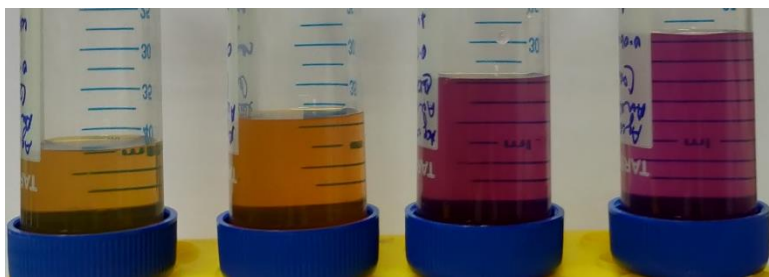
So the interdiffusion of Au^{3+} (85 pm) is easy into Ag lattice (160 pm) while the reverse is difficult or not possible ($135 > 115$). By increasing the temperature, there is an induction of lattice dilatation and the interdiffusion increases, creating a state of an alloy of gold and silver. But with operating conditions being room temperature, there is a higher chance of galvanic displacement being more prominent than alloy formation.

Theoretically, core shell nanoparticles with silver being the core and gold being the shell, with progression from the centre to the outer surface it can be observed that the core is made of silver, leading to a small interface of gold and silver alloy. With enough addition of gold salt to the reaction mixture, there is a growth of a pure gold shell above this interfacial layer.

Experimental procedures for silver core and gold shell is carried out only in two methodologies :

- Dilution
- No dilution

Centrifugation of silver nanoparticles does not produce significant results as most of the particles remain suspended in the supernatant. This could be because of the smaller size of silver nanoparticles. With respect to the combinations experiment, due to time constraints, the methodology could not be tested.



(silver core and gold shell with varying volumes of shell solution)

Trial 1 (dilution)

The first trial is similar to that of the first trial in the case of gold core and silver shell. The silver samples which were synthesized at 0.04mM concentration of tannic acid, 2.5 ml of this sample is taken and diluted up to 15 ml using DI water. The experiments are performed with the shell solution concentration fixed at 0.06mM.

- Silver nanoparticles synthesized earlier (TA 0.04mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (1w/v of potassium carbonate)
- Chloroauric acid solution is prepared of the concentration 0.06mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and chloroauric acid solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	10	6 - 7
2	Dropwise	10	15	0.06	15	6 - 7
3	Dropwise	10	15	0.06	20	6
4	Dropwise	10	15	0.06	25	6

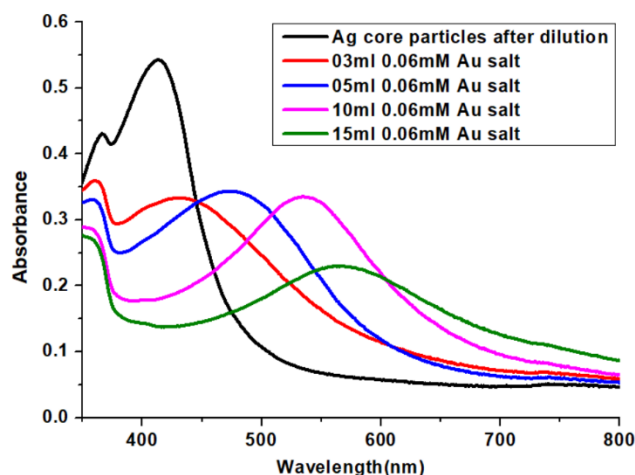
The first set of experiments in this trial were performed without change in pH. Since chloroauric acid is to be reduced, the desired pH of the reactant must be 10. The first set did not produce any significant results and the product solution was colourless to very light black.

The subsequent experiments were performed after the adjustment of pH.

The second set showed prominent results as compared to the first set and in a lower volume also. This set was performed at lower volumes owing to this change.

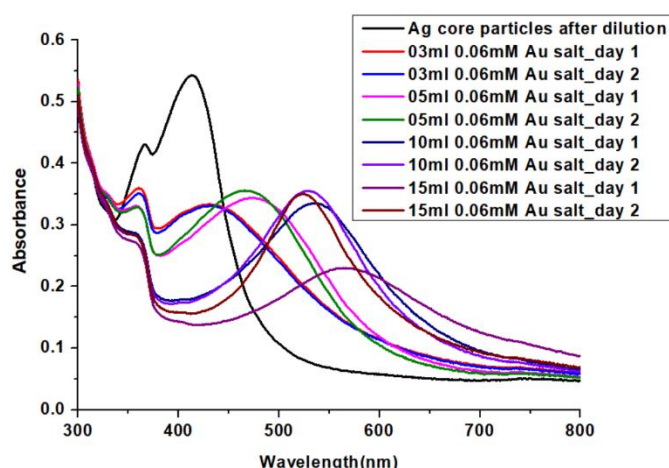
Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	3	7 - 8
2	Dropwise	10	15	0.06	5	7
3	Dropwise	10	15	0.06	10	7
4	Dropwise	10	15	0.06	15	7

3 ml showed slight orangish colour which led to darker orange at 5ml. This is the transitional state indicating that the particles are on the process of getting coated



The second set shows clear and significant peaks with their shifts indicating that the particles are increasing in size as they are getting coated and lesser or no secondary nucleation. To check for reproducibility of these experiments, they were repeated without any modification in the solutions or any other parameters.

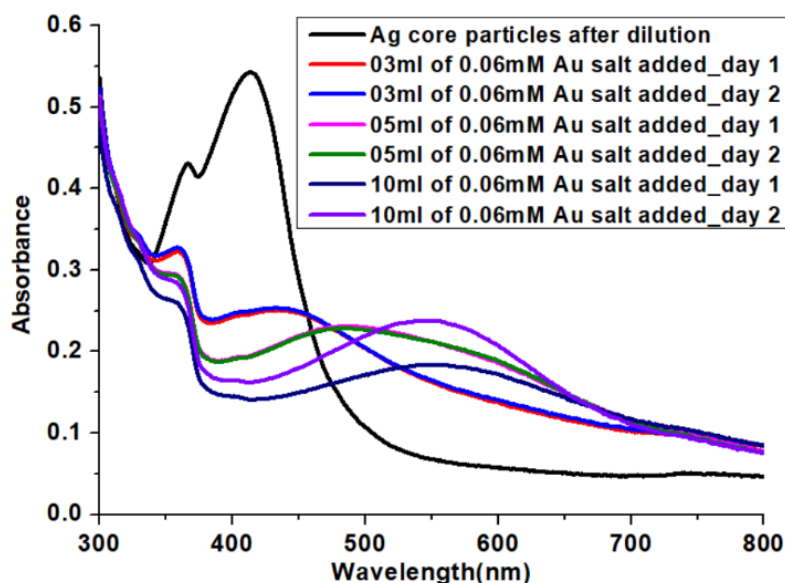
Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	20	15	0.06	3	7
2	Dropwise	20	15	0.06	5	7
3	Dropwise	20	15	0.06	10	7
4	Dropwise	20	15	0.06	15	6 – 7



A similar trend appeared indicating reproducible results. The solutions were tested a day later again because of a visible colour change and this showed slight deviations which meant that the solutions were still reacting.

Hence to confirm again for reproducibility, the experiments were repeated one more time. Since there was less amount of core solution remaining, the experiment was conducted only for three different sets of volumes of shell solutions 3, 5 and 10 ml.

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 - 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	20	15	0.06	3	7 - 8
2	Dropwise	20	15	0.06	5	7
3	Dropwise	20	15	0.06	10	7



This showed similar trends to that of the previous set of experiments and showed a visible shift again on day 2.

Experiments were continued with variations in solution concentrations and other parameters.

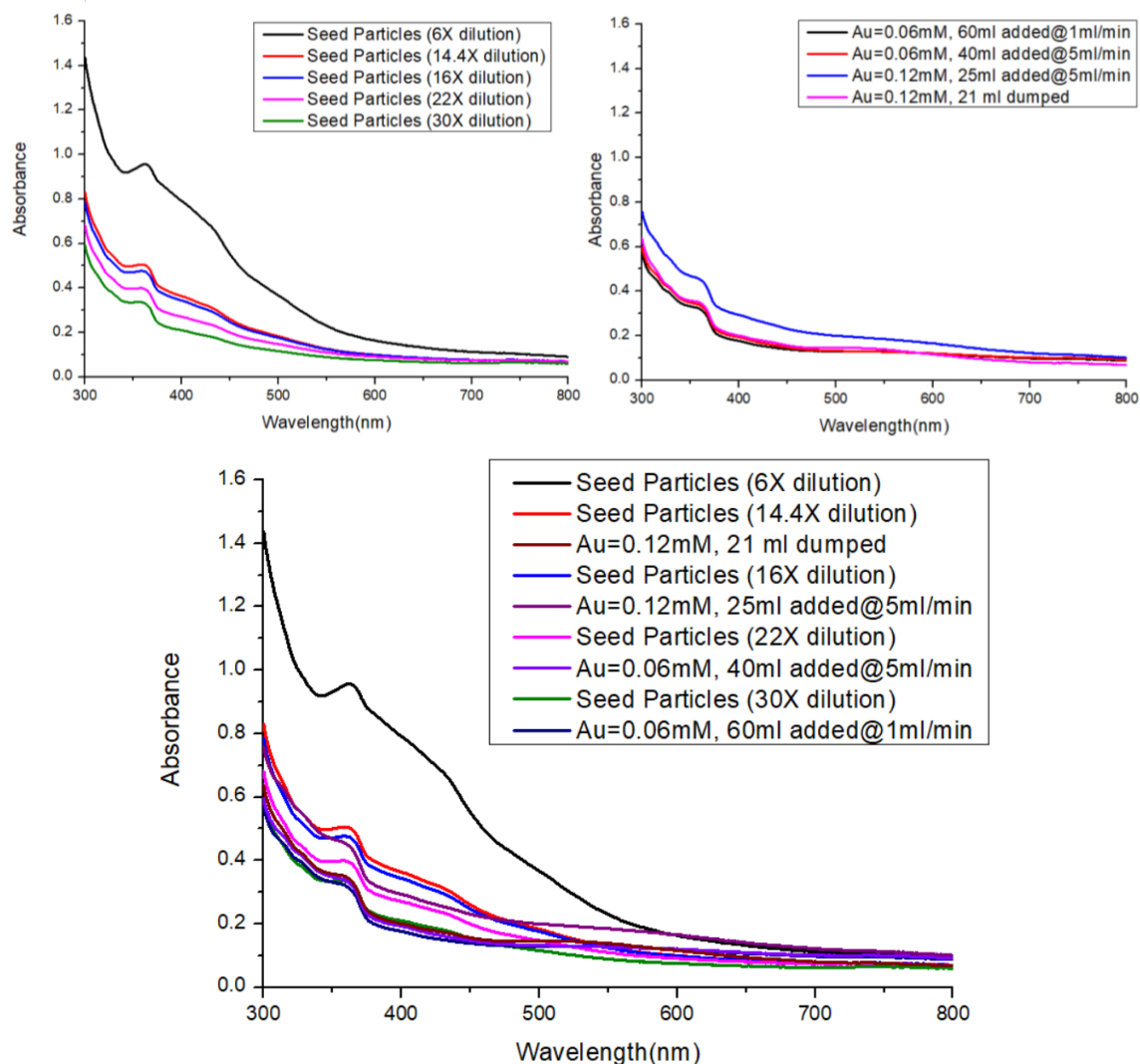
Trial 2 (dilution)

This trial was conducted with modifications in the core solution. Silver is synthesized with a higher concentration of tannic acid and with 10 w/v of potassium carbonate.

As opposed to the previous 0.04mM, it is increase to 0.3mM, a similar molar ratio as that of gold nanoparticles in the initial trials. This trial also uses two different concentrations of the shell solution.

- Silver nanoparticles were synthesized (TA 0.3mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (10 w/v of potassium carbonate)
- Chloroauric acid solution is prepared of the concentration 0.06mM and 0.12mm.
- 15ml of the seed solution is taken as the batch reactant in the beaker and chloroauric acid solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 0.12 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	60	6 – 7
2	Dropwise	10	15	0.06	40	6 – 7
3	Dropwise	10	15	0.12	25	7
4	Dumped	10	15	0.12	21	7



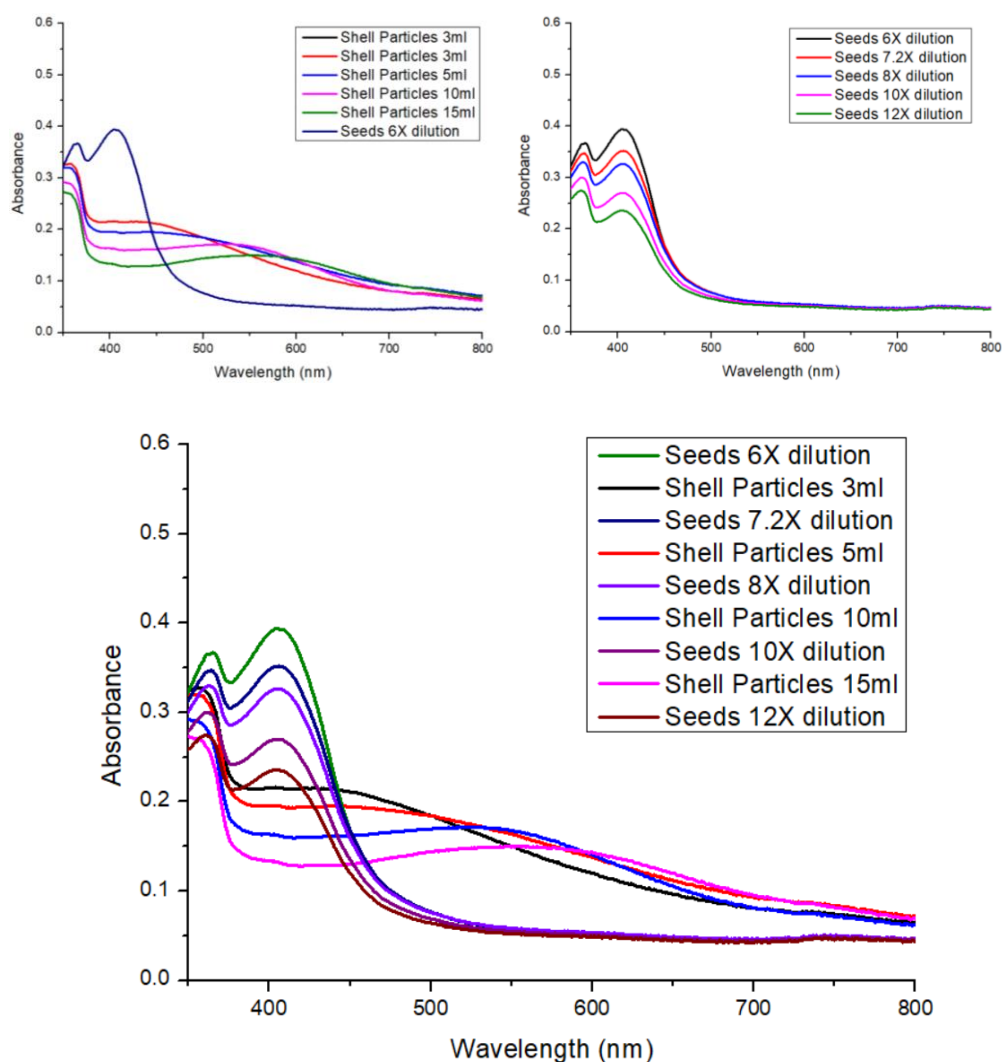
In accordance to the previous experiments, usage of 10w/v of potassium carbonate does not produce any prominent peak or hump. The next trial is performed with the same parameters as the first trial to check again for reproducibility.

Trial 3

This trial is an exact retry of the first trial which used 0.04mM of tannic acid for the core particles and 0.06mM for the shell solution.

- Silver nanoparticles synthesized earlier (TA 0.04mM), 2.5 ml of that solution is taken and diluted up to 15 ml. (1w/v of potassium carbonate)
- Chloroauric acid solution is prepared of the concentration 0.06mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and chloroauric acid solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	10	15	0.06	3	7-8
2	Dropwise	10	15	0.06	5	7-8
3	Dropwise	10	15	0.06	10	7
4	Dropwise	10	15	0.06	15	7



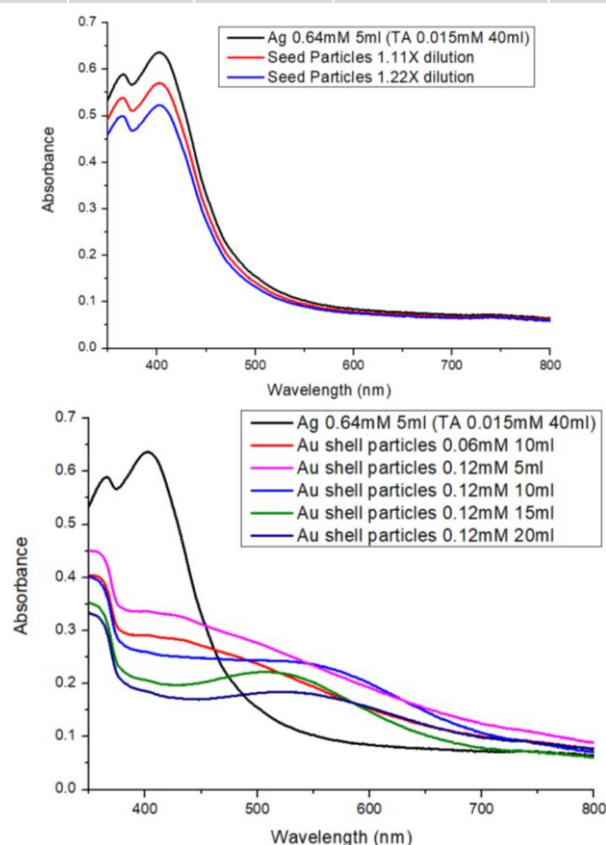
This trial produces results of a similar trend as that of the first trial. Though there are no prominent peaks like the previous one, the shift in absorbance is observed clearly in this experiment which reconfirms that the combinations used are reproducible.

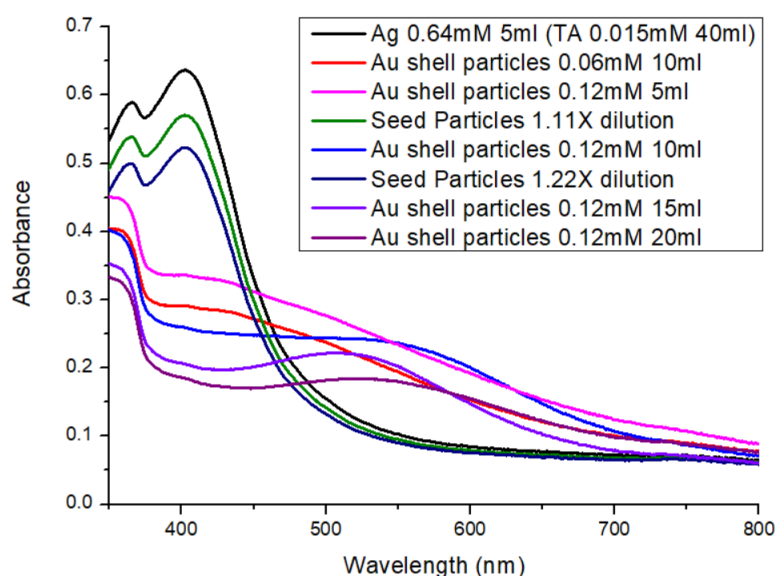
Trial 4 (No dilution)

Since the dilution experiments are optimized, the experiments were progressed to the next methodology of not diluting the core particles. This trial followed similar reaction parameters as that of the no dilution trial in gold core and silver shell experiments. The concentration of tannic acid used was much lower than the minimum requirement. Initially conducted for 0.06 and 0.12mM of the shell solution and fixing the volume added to 10 ml, the 0.12mM experiment gave a significant result and the experiment was proceeded with 0.12mM of chloroauric acid solution.

- Silver nanoparticles were synthesized (TA 0.015mM : 40ml) (silver salt 5ml), 15 ml of this solution is used as the core solution (1w/v of potassium carbonate)
- Chloroauric acid solution is prepared of the concentration 0.06mM and 0.12mM.
- 15ml of the seed solution is taken as the batch reactant in the beaker and chloroauric acid solution is added to the pool through the syringe at 1ml/min.

Impeller Rotation – 1000 rpm Chloroauric Acid : 0.06 mM & 0.12 mM						
Input flow rate : 1 ml / min No. of drops / ml : 20 – 25						
Sample	Input mode	V of Silver Salt (ml)	V of Core soln. (ml)	Concentration of shell soln. (mM)	V of Shell soln. (ml)	pH of final solution
1	Dropwise	5	15	0.06	10	7-8
2	Dropwise	5	15	0.12	5	7-8
3	Dropwise	5	15	0.12	10	7
4	Dropwise	5	15	0.12	15	7
5	Dropwise	5	15	0.12	20	7



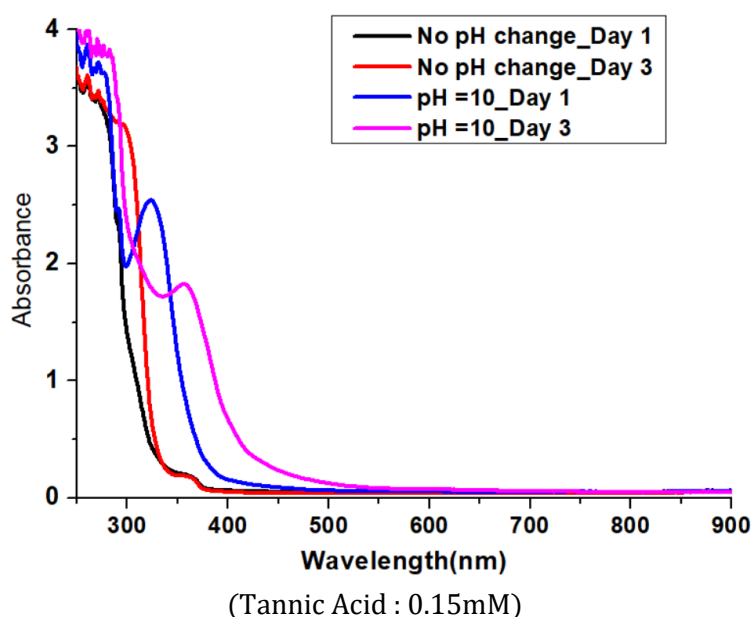


This trial also shows prominent and significant results as compared to the previous experiment. A clear shift in peaks is visible implying that the particles are getting coated.

2.1.8 Tannic acid behaviour

Theoretically, excess tannic acid should provide better results as it would ensure that there is no unreacted salt solution remaining in the reactor. But practically, higher concentrations of tannic acid prove to interfere with the UV-vis spectrums. Though additional characterizations would prove to support the theoretical statement, it is not possible to constantly analyse samples through methods like SEM and TEM because the process is highly time consuming and not economical.

One of the main reasons for this interference is the behaviour of tannic acid in basic pH.



Two samples of tannic acid were prepared of the concentration 0.15mM. One sample was adjusted to pH 10 using 1w/v of potassium carbonate solution while the other was not adjusted. Both samples were checked for their UV-vis spectrums on the day of preparation and two days later, the trend as shown in the graph was observed.

Basic pH of tannic acid splits the molecule into its individual components, gallic acid and glucose. The absorbance at 350 – 400nm is because of the benzoid bands present in the gallic acid molecule.

Higher concentrations of tannic acid during experimentation results in higher absorbance at these wavelengths which interfere with the experiments products' absorbance.

It is also observed that with time, there is a change in the activity of tannic acid. Hence it is essential that during experiments, tannic acid must be prepared freshly for every experiment. This must also be followed for the metallic salts as well, as they are sensitive to light and can be reduced to their corresponding metal atoms if exposed to light.

2.2 Continuous Process

With increase in demand for nanoparticles to a few kilos per person in the next 5-6 years, batch production of these particles cannot meet the extreme demand in the upcoming years.

Production of these particles as per the previous methodologies gives us a maximum of 1.3mg of gold and around 2.1 mg of silver per experiment. Whereas continuous synthesis can give upto a few grams per hour of experimentation depending on the methodology used.

Unlike batch processing, there is no specific method used for continuous production. From microchannels, jet streams, plug flow reactors, CSTRs and many more, there are a wide range of equipment to use for its production based on the requirement.

Of all the different equipment, CSTRs and jet streams provide particles which are the least polydispersed of the lot.

The setup used in the experiments is an overflow type continuous stirred tank reactor (CSTR) with a volume of 72 ml. The reactor is initially filled with tannic acid and then the experiment is started. In the case of core shell particles, the reactor is filled with the core solution before the inlet of the seed solution. Particles obtained till the reactor has obtained steady state are in a transitional state. For a well performing reactor, the steady state is expected to come at around 4 to 6 times of the residence time of the reactants.

2.2.1 Experimental Setup



The setup consists of the following components :

- Ruston turbine with speed controller
- Plastic stand
- Teflon reactor, baffles and impeller
- Peristaltic pumps
- Beakers
- Stopwatch
- Necessary chemicals
- Silicon tubes
- Microtips (200 μ l)
- Blade
- Scotch tape

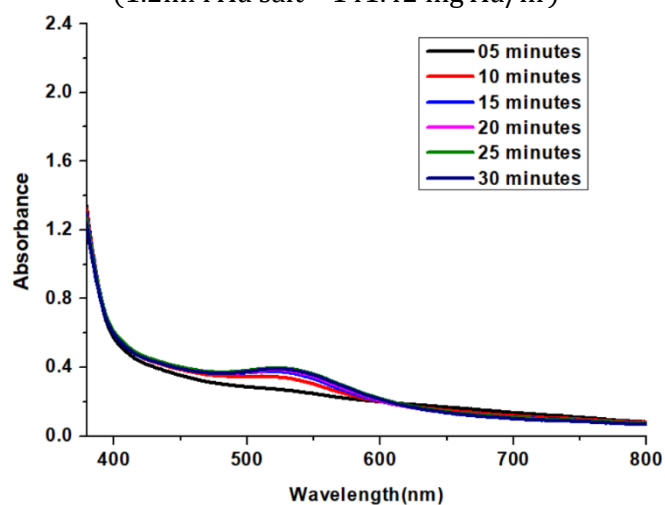
2.2.2 Synthesis of Gold Nanoparticles (GNP or AuNP)

Continuous synthesis allows for usage of the reactants in higher concentrations for higher throughput of the required nanoparticles. For the synthesis of gold, the concentration of tannic acid is taken to be 1.2mM which is in excess for the experiments. Concentration of the gold salt solution is taken as 1.2mM, 2.4mM and 3.6mM.

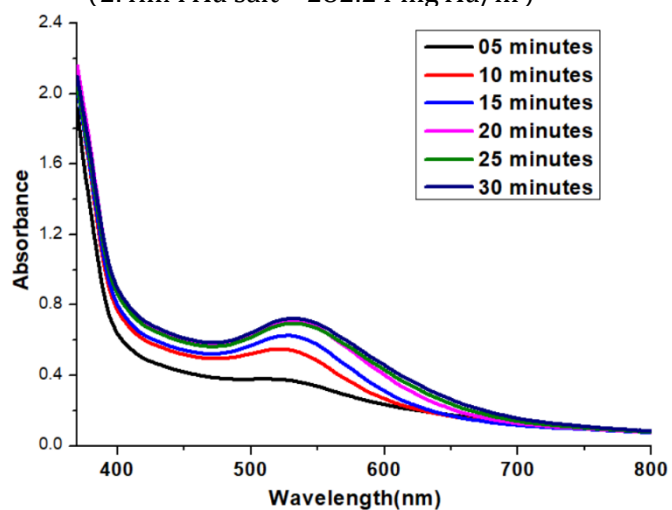
- Tannic acid solution is prepared of the concentration 1.2mM and pH is adjusted to 10 using 10w/v of potassium carbonate.
- Chloroauric acid solutions are prepared of the concentrations 1.2mM, 2.4mM and 3.6mM
- Tannic acid's flow rate is fixed at 6ml/min whereas that of chloroauric acid is fixed at 10ml/min.

- The reactor is first filled with tannic acid and then supply of chloroauric acid is begun. Once steady state occurs, samples are collected every 5 minutes

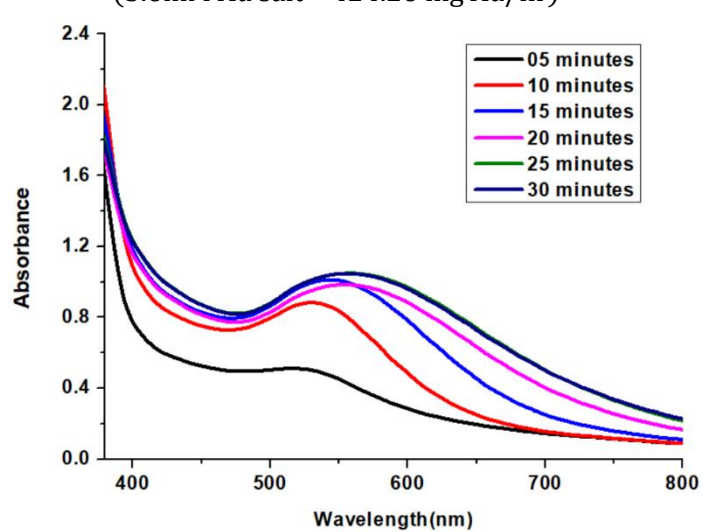
(1.2mM Au salt – 141.42 mg Au/hr)



(2.4mM Au salt – 282.24 mg Au/hr)



(3.6mM Au salt – 424.26 mg Au/hr)



The solutions are highly concentrated and hence exceeds the range of the testing instrument. The solutions are diluted 12 times for UV-vis characterisation.

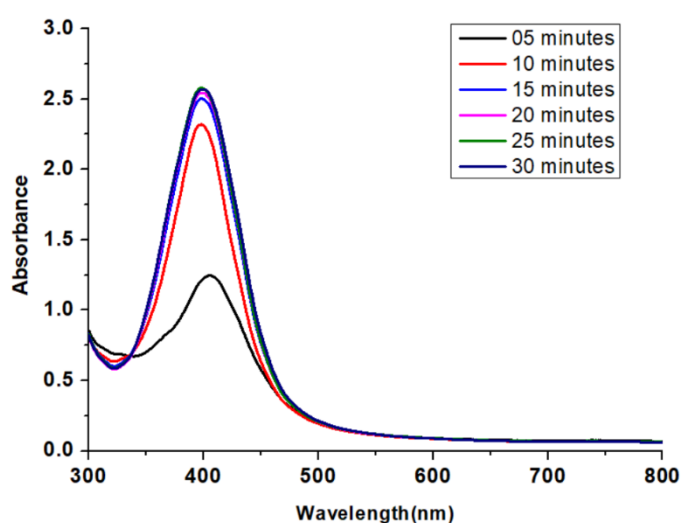
Observing all three spectrums, it is seen that lower concentrations of the gold salt result in a steady state at 15 minutes itself, whereas with increase in concentration, time taken to achieve steady state increases. Ideally by the 25-minute mark, the system attains a steady state output. As time progresses, a shift in peak is also observed indicating that seeded growth occurs in the system.

2.2.3 Synthesis of Silver Nanoparticles (SNP or AgNP)

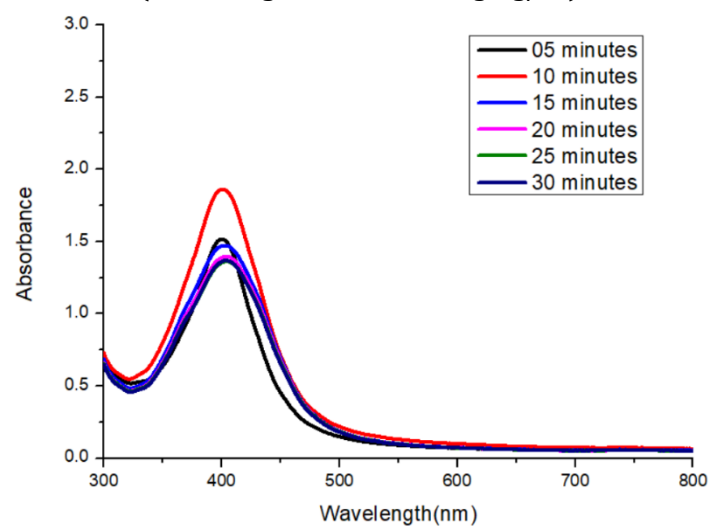
Similar set of experiments are conducted to produce silver nanoparticles. Owing to a higher availability of the silver nitrate salts, experiments were performed for five different concentrations from 1.2mM to 6mM at steps of 1.2mM. Tannic acids concentration was fixed to 0.03mM, which was lesser than the required concentration for the experiments.

- Tannic acid solution is prepared of the concentration 0.03mM and pH is adjusted to 8 using 10w/v of potassium carbonate.
- Silver Nitrate solutions are prepared of the concentrations 1.2mM, 2.4mM, 3.6mM, 4.8mM and 6mM
- Tannic acid's flow rate is fixed at 6ml/min whereas that of silver nitrate is fixed at 10ml/min.
- The reactor is first filled with tannic acid and then supply of silver nitrate is begun. Once steady state occurs, samples are collected every 5 minutes

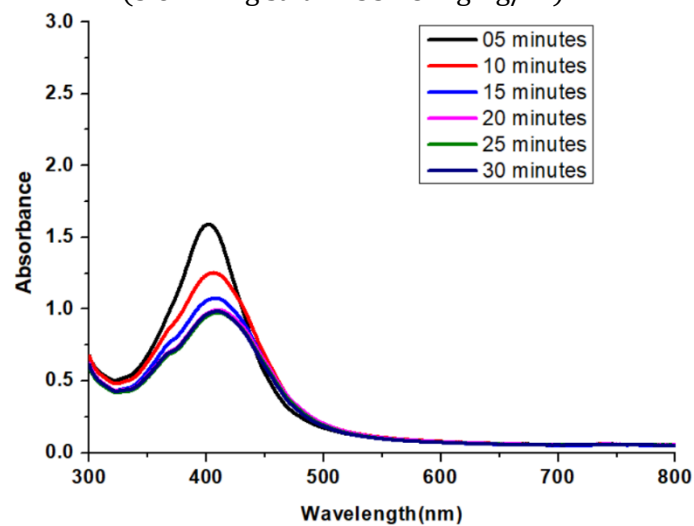
(1.2mM Ag salt – 77.76 mg Ag/hr)



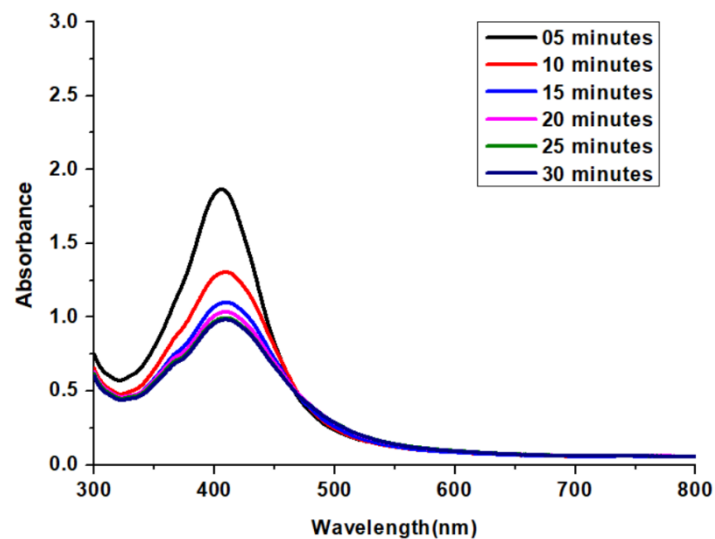
(2.4mM Ag salt – 155.52 mg Ag/hr)

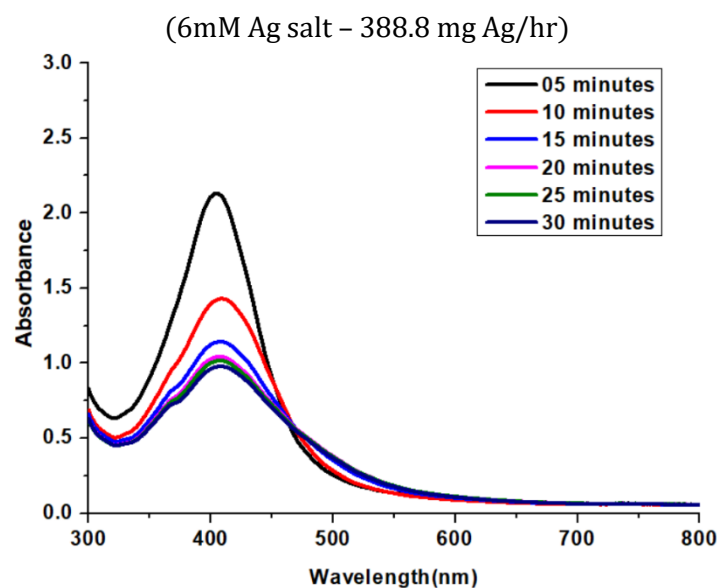


(3.6mM Ag salt – 233.28 mg Ag/hr)



(4.8mM Ag salt – 311.04 mg Ag/hr)





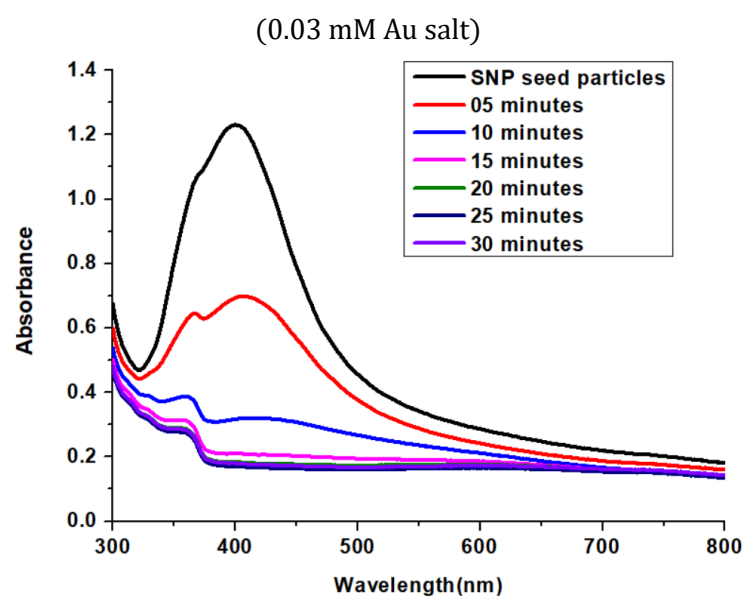
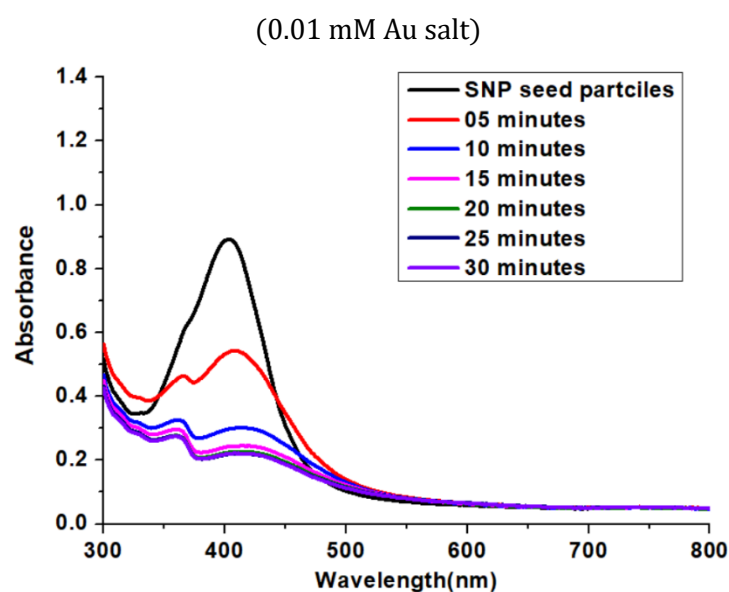
A similar trend is observed in the silver experiments as that of the gold experiments. Steady state is observed from 20 minutes in the lower concentrations and from 25 minutes in the higher concentrations. Since the samples are of higher concentrations, the samples are diluted 6 to 12 times before the UV-Vis spectroscopy is conducted.

2.2.4 Core – Shell Nanoparticles (Ag core – Au shell)

Steady state samples of the silver nanoparticles experiment are used for the core shell experiment. Like that of the batch experiments, the core solution is diluted to 6 times its original volume. Two experiments are conducted in this set.

- Silver nanoparticles synthesized at 1.2mM concentration is used. Samples at 25 minutes and 30 minutes are diluted and pH is adjusted to 10 using 10w/v of potassium carbonate.
- Chloroauric acid solutions are prepared of the concentrations 0.01mM and 0.03mM
- Seed solution's flow rate is fixed at 6ml/min whereas that of chloroauric acid is fixed at 10ml/min.
- The reactor is filled with the core solution and then the supply of chloroauric acid is begun. Once steady state occurs, samples are collected every 5 minutes

As a trial and due to time constraints, only two experiments could be performed. Lower concentrations were chosen to replicate the batch process. This was compensated by the higher flow rate for the shell solution with respect to the core solution.



Analysing the spectrum of the first experiment, there is a very small shift in the peaks but insignificant for any conclusion. The growth on the particles formed might have stopped with the alloy layer and hence there is no clear peak or hump at the 510-530 nm range.

With regards to the second spectrum, the disappearance of the peak at lower 400nm indicates the covering of silver core particles. A small hump is observed close to 600nm and absorbance at higher wavelengths show that the particles formed are not spherical in nature and have significant changes in its morphologies.

Experiments for Gold core and Silver shell nanoparticles could not be conducted due to time constraints.

3. Conclusion

Nanoparticles have a wide range of applications which play an integral role in the functioning of multiple devices and life saving mechanisms. Nanoparticles can be synthesized in multiple methods which are broadly classified into two types: Bottom up and top down approaches. All experimentation was done using the Wet chemical method or the Chemical reduction method which is type of synthesis method under the bottom up approach. This method is one the most economical methods of producing nanoparticles.

The experiments covered production of gold, silver and core shell (Au core Ag shell and vice versa) nanoparticles through fed-batch and continuous methods. Experimentation covered variations in reaction parameters such as concentration of the reactants. pH of the reactants if required to be changed were adjusted using potassium carbonate solution. Analysing the outputs of all the experiments conducted state that for production of core shell nanoparticles, a lower concentration of tannic acid is preferred. Another major conclusion was the concentration of potassium carbonate. Usage of 10w/v solution of potassium carbonate does not provide significant results when compared to the usage of 1w/v solution of potassium carbonate.

Continuous synthesis used a simple overflow CSTR as the reactor setup. This setup had the ability to provide high throughputs and with the given working conditions was able to provide steady state results in around 20 minutes of functioning which is 4.44 times its residence time. If further characterisations of the output nanoparticles prove to be favourable and in accordance to the required results, it is a step forward to meet the rising demand of nanoparticles with a very economical and efficient reaction system.

4. Scope for future work

New methods to produce these nanoparticles can be fabricated which are more economical and efficient than the current methods. Producing monodispersed particles is of utmost priority as a major chunk of the properties of these particles are dependant on its size.

A fixed methodology for Continuous synthesis of nanoparticles can be formulated which not only provide high throughputs but also are more economical and efficient. The current methods and new methods must be altered in such a way that the reaction by products are non-polluting and the entire process is greener.

5. Acknowledgements

1. Sankar Kalidas, Metal nanoparticle engineering: Development of a process 'toolkit' for synthesis and self – assembly into functional nanoscale architectures
2. Joerg Polte, Fundamental Growth Principles of Colloidal Metal Nanoparticles – a new Perspective
3. Sankar Kalidas, Iniyan Elango, Sanjeev Kumar, Venugopal Santhanam, A green protocol for room temperature synthesis of silver nanoparticles in seconds
4. Sankar Kalidas, Sanjeev Kumar, Venugopal Santhanam, Monodisperse sub-10nm gold nanoparticles by reversing the order of addition in Turkevich method – the role of chloroauric acid
5. Tufail Ahmad, Reviewing the Tannic Acid Mediated Synthesis of Metal Nanoparticles
6. Sankar Kalidas, Sanjeev Kumar, Venugopal Santhanam, Room-temperature synthesis of gold nanoparticles – Size-control by slow addition
7. Sanjeev Kumar Gupta, Lecture notes on Interfacial and Colloidal Phenomena
8. Jacob N. Israelachvili, a book on Intermolecular and Surface Forces.
9. Robert J. Hunter, a book on Foundations of Colloid Science
10. Warren C.W. Chan, a book on Bio-applications of Nanoparticles
11. Sulabha K. Kulkarni, Nanotechnology: Principles and Practices