Dendritic Ag Nanostructures: Synthesis, Characterization and Application

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Dendritic Ag Nanostructures: Synthesis, Characterization and Application

A thesis submitted for partial fulfilment of the requirement for the degree of

B.Tech-M.Tech Dual Degree in Chemical Engineering

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SUPERVISOR'S CERTIFICATE

This is to certify that this thesis entitled **"Dendritic Ag Nanostructures: Synthesis, Characterization and Application"**, submitted by **Prem Depan Nayak** (711CH1018) in partial fulfilment of the requirements for the award of the degree of B.Tech-M.Tech dual degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my guidance. To the best of my knowledge the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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Declaration of Originality

I, Prem Depan Nayak, Roll Number 711CH1018 hereby declare that this thesis entitled "Dendritic Ag Nanostructures: Synthesis, Characterization and Application" represents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela, is explicitly acknowledged in the thesis. Works of other authors cited in this thesis have been duly acknowledged under the section "References". I have also submitted my original work records to the scrutiny committee for evaluation of my thesis.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present thesis.

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Abstract

Silver has been at the forefront of material research and applications for many generations now. Decades long research to understand materials at macro, micro and nano level has brought us a huge knowledge about how size of materials affect their properties. Noble metals like Ag, Au and Pt have been historically classified as precious metals and were mostly used for jewellery, coinage etc. Later as we discovered their electrical and thermal properties, they started to be used as electrical contacts and other thermal and electrical conducting materials. Only recently we have been able to use them as nanoparticles in various ways.

The present work focuses on synthesizing Silver nanoparticles using novel methodologies and non-energy intensive methods. This method employs a hybrid method using both seed and light mediated synthesis methods to grow interesting dendritic silver nanostructures. These nanostructures are believed to be growing over the PVP we have used in these experiments.

Scientific community also defines these kind of nanostrucutres are plasmonic antennae since these structures can be used to concentrate the effect of light i.e. Surface plamon resonance at many specific locations of the structures. This enables these structures to be used for various plasmonic purposes including plasmon sensing and Surface Enhanced Raman and fluorescence sensing.

Keywords: Silver Nanoparticle, Plasmonic Nanoparticle, Heating, Sensing, Mercury, SERS

1. Introduction

1.1 Nanoparticles

Nano materials are broadly classified as materials having particles in the size range of less than 100 nm and this enables these particles so show new properties and improve many of its properties like the physio-chemical and biological ones. It has very recently evolved to become a very promising research field. Nanoparticles are not new and existed way before we knew or researched about them. It is the evolving technology in terms of material science, optics and overall understanding of nature that we have pushed boundaries and have known about this amazing new field. It has opened many new doors to understand particles, materials and matter at its very basic level. The origin of nanoparticles can be traced be traced back to 3 sources (a) cosmogenic, (b) geogenic and (c) biogenic, but nanoparticles produced by man unintentionally has been (a) by burning wood and oil etc. or (b) rarely noticed in craft items like coloured glass and ceramics and cosmetics.

Table 1: The history of inventions[1]

Discovery type	Name	Age	Start date
Industrial	Tools	Stone	2,200,000 BC
Industrial	Metallurgy	Bronze	3500BC
Industrial	Steam power	Industrial	1764
Automation	Mass production	Consumer	1906
Automation	Computing	Information	1946
Health	Genetic Engineering	Genetic	1953
Industrial	Nanotechnology	Nano age	1991
Automation	Molecular assemblers	Assembler age	2020
Health, industrial, automation	Life assemblers	Life age	2050

Synthesis of nanoparticles using artificial techniques has recently gained lots of momentum due to its ease in synthesizing the exact kind of nanoparticles for specific use in experiments as well as product development. Numerous methods and tools have been developed over the years to synthesize such particles but none of these have been accepted to be an ideal tool for developing nanoparticles. The decision mostly depends on the type of usage that can be done using these nanoparticles.

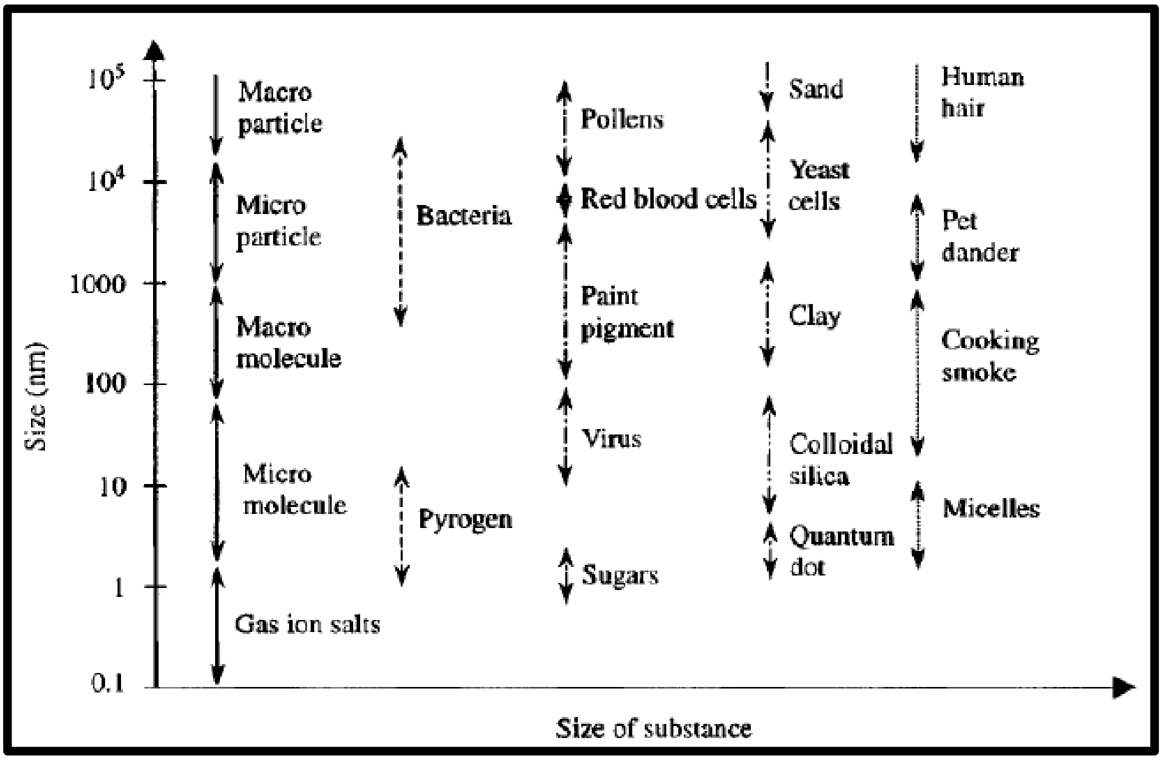

Figure 1: Chart representing examples of nanostructures or nanomaterials with their typical ranges of dimension [2]

Imperceptible to the normal eye, these materials suspended in a liquid disperse light without reflecting it, possess certain characteristic colour depending on the shape, size and surroundings. Characterization of nanomaterials is important because it helps in determining the structure, morphology, particle size, porosity, zeta potential, optical characteristics, etc., and enables us to determine the suitable nanoparticles for various applications.

1.2 Synthesis Techniques

Despite the numerous approaches for the development and synthesis of nanoparticles, the synthesis of nanoparticles can be broadly classified into two categories-

(a) Top Down Approach:

Nanomaterials are created in this technique by breaking down the bulk material. It is traditional method of synthesis or fabrication method in which particles are broken into very small pieces to reach into nano-scale by means of externally-controlled tools used to cut, mill and shape materials into the desired order and shapes, which usually involves application of severe plastic deformations. However, the biggest problem associated with this method is an imperfection of the surface structure. The common techniques involved in the top-down approach are lithographic techniques, attrition, high energy ball milling, mechano-chemical processing, etc. There is no significant difference in physical properties of materials irrespective of the synthesis routes adopted. This process is slow and is usually not recommended for large scale productions. Starting with initial larger structures, another widely used method for this approach is photolithography[3].

(b) Bottom-up approach:

Nanomaterials are created in this technique by the method of build-up from the bottom. It utilises the physical forces operating at nano-scale are used to combine basic units into larger stable structures. Nanoparticles are built up in this approach atom by atom or molecule by molecule. There is a spontaneous arrangement of particles into stable structures and aggregates. The defects obtained by bottom-up method are less. The synthesized materials have a homogeneous chemical composition. They also seem to have better short and long range ordering. Some examples of bottom-up approach are colloidal dispersion, chemical precipitation or co-precipitation, hydrothermal, solvothermal synthesis, forced hydrolysis, supercritical hydrothermal processing or supercritical fluid processing, sol-gel synthesis, microwave heating synthesis, etc. The fabrication techniques are also comparatively cheaper than the top down approach.

1.3 Organization of thesis

This contains five chapters. The chapters and their contents are as given below

Chapter 1: This is an introductory chapter giving brief introduction about Nanotechnology and its optical properties. It also talks about some of it applications.

Chapter 2: This chapter reviews the previously available literature on surface plasmon resonance and related applications. It discusses the history of its discovery and further goes on to mention milestones in theoretical development. Later discussions about its applications in various fields have been touched upon.

Chapter 3 and 4: These chapter deal with the inspiration behind the work and a summary of the work that was undertaken.

Chapter 5: In this chapter we discuss about all the experimental work and setup employed to reach our results.

Chapter 6: This is probably the most important chapter where we analyse our results to reach important conclusions.

Chapter 7: This is concluding chapter of this thesis which also include scope for the future work.

2. Literature Review

Control of the shape and size of the nanostructure is the single most important aspect of synthesizing nanoparticles because it is this that gives the unique properties to these. And makes themselves further useful for any time of applications.

Intensive research has been done in the field of metallic nanostructures over past several decades now due to their prospective application in magnetic, optical, electronic and optoelectronic devices. Moreover it has been found that these nanostructures have the potential to show performances at par or superior to their bulk counterparts[4].

Silver is a very unique material in so many senses because of its use since ancient times for different purposes. Some synthesis techniques of Ag date back centuries ago. Moreover Ag being the best conductor (both electrical and thermal) among metals, has been the default material for extremely conductive electrical contacts as well as for additives in conducting adhesives. But not to forget Ag despite its high electrical and thermal conductivity, has been used the most for its interesting optical activity. Photography films which are composed for Silver halides embedded in gelatine matrices[5].

Only recently Ag nanoparticles have been used for light amplification from 10-100 times, which has resulted in surface-enhanced Raman scattering and the enhancement factors are also very large in the order 10^6-10^8. Lots of groups in the scientific community have reached single molecule detection using SERS[5].

Surface Plasmon resonance and fluorescence features of gold and silver nanoparticles of different shapes greatly vary according to their shapes and morphology. Small changes in aspect ratios of noble metal Nano rods can affect these properties greatly[4]. For SERS number of spectral ranges and effective ones are greatly influenced by the shape and morphology shown by Gold and Silver nanostructures[4].

The origin of such a special optical behaviour is due to quantum confinement and the interaction of photons with the confined conduction electrons on the metal nanoparticles[6] .

Given that Ag is being used for plethora of purposes in its miniaturised form, better control over its structures which in turn influences its properties gives huge economic benefits. And since it's an established fact that taking particles to nanometer range has profound impact on its material, optical, magnetic, chemical, electrical and mechanical properties[5].

Analogous to the way sophisticated tools have been developed to give shape to macroscopic materials, we need to develop such tools to control the shape of nanomaterial.

In spite its dire need and importance we did not have this kind of technology to control the shape of the colloidal particles until recently.

Previously existing gas methods to produce or synthesize well defined shaped nanoparticles were able to do so only in small quantities but solution phase methods have opened up gates to huge number of methods to produce nanoparticles of well-defined shape in bulk quantities.

Only recently a lot of chemical methods have been developed for making metal and semiconductor nanobelts, nanowires and nanodots[7].

Sunlight has by far the highest theoretical potential of the earth's compared to other renewable energy sources. More energy from the sun falls on the earth in one hour than is used by everyone in the world in one year. Harnessing solar energy has recently gained attention in the field of nanotechnology. Researchers have made successful attempts in developing nanoparticles using metals such as gold and copper as well as carbon nanoparticles which can absorb sunlight and result in formation of steam (without the need of any external heating sources), followed by heating of the water. Synthesis of nanoparticles can also be made for this purpose which seems to have the optical property of absorbance in the NIR region.

2.1 Plasmonics

Plasmonics is associated with the localization, guiding, and manipulation of electromagnetic waves beyond the diffraction limit with tits limits down to the nanometer scale. A metal is the main component of Plasmonics because those are the only materials that support surface plasmon polariton modes. These modes are the electromagnetic waves which are resonating with the free electron density of the metal. Even though one kind find a rich variety of plasmonic nanostructures, but they can be classified into two kinds according to the type of plasmon polariton modes they allow on their surfaces: localized surface plasmons (LSPs) and propagating surface plasmons (PSPs)[8]. LSPs are generated when the time varying electric field associated with the light exerts a force on the free electron cloud of the metal surface and forces them to oscillate collectively at a resonant frequency w.r.t the light. As mentioned at a certain frequency of the exciton it will resonate with the light and the signal will become intense and strong as is the case with any kind of constructive resonance to produce what is known as a Localized surface plasmon mode[9]. This phenomenon has been illustrated in Figure 2.

A uniform electric field is experienced by structures that support LSPRs when they are exposed to light because of their small dimensions less than or comparable to the wavelength of light. PSPs in contrast have at least one dimension that is greater than or equal to the exciting wavelength. And as expected here the field is not uniform like the LSPs and so other non-uniform effects must be consider that affect the polariton modes. Nanowires can be taken as an example for such structures and it is seen that surface plasmons propagate back and forth from one end to other on those structures. Such a phenomenon can be described as a resonating Fabry-Perot resonator[10]. Another important factor would be the reflection from the ends of structure that could change the phase and resonant length. It has been seen that propagation lengths in nanowires vary in micrometres and high degree of control on PSPs can be achieved by varying geometrical parameters of structures[11].

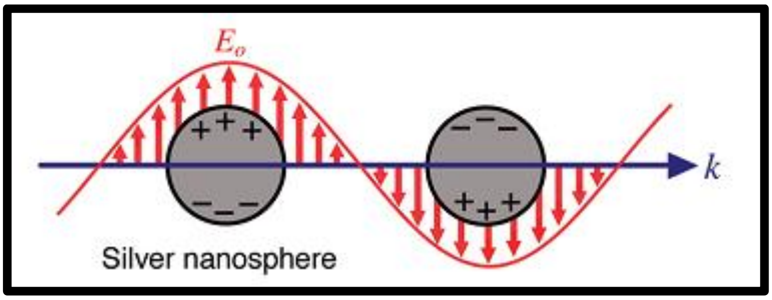

Figure 2: Schematic surface plasmon resonance process on Metal nanoparticles surface.

2.2 Silver nanoparticles properties

The most important plasmonic materials known to mankind is probably silver as it offers a lot more advantages over the other plasmon active materials in UV-Visible-Near infrared region like Au. Cu, Li and Al. Most important requirement of Plasmonics is that the materials should be able to support surface plasmons at the desired wavelength strongly and Silver is an excellent materials that can support SPs from 300 to 1200 nm. The dielectric function ε which consist of a real part (ε_r) and an imaginary part (ε_i) determines the capability of a nanoparticle to support surface plasmons on it. Both the real and imaginary parts vary according to many factors like surrounding medium and excitation wavelength (λ). This makes the dielectric function a hybrid function which reflects the materials interaction both with electrons and light. Mie suggested a simple theory to predict and understand LSPR by giving an expression to calculate the extinction cross section of a metal nanosphere[10,12].

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m{}^{3/2}}{\lambda} \left[\frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i{}^2} \right] \quad (1)$$

Where C_{ext} is the extinction cross section, R is the radius, and ε_m is the relative dielectric constant of the medium surrounding the nanosphere. The above equation clearly shows how the dielectric properties (εr and εi) strongly influence the interaction of light with nanoparticles. From an engineering point of view although other factors like environment and other parameters (light source etc.) are important but they are often fixed and what matters the most are the material properties[13]. The denominator of the bracketed expression is what one can play with because it is composed of the dielectric constant. If the denominator approaches zero then the C_{ext} large enough to for optical absorption and scattering to support surface plasmons for practical amounts of time. And this condition is known as the resonance condition. And as seen from the equation for this to be possible εr must be close to $-2\varepsilon m$. And according to standard values this is not possible for non-metals and standard dielectrics whose ε_r values between 1 and 50[14]. To support strong resonance condition it is necessary that εi should be close to zero as indicated by equation 1. It has been observed that never can a sufficiently strong PSP or LSP be formed without ε_r being negative. And a larger value of ε_i means a weaker or lossier plasmon. The quality factor (Q) describes the surface Plasmon strength or damping.

$$Q = \frac{w(d\varepsilon_r/dw)}{2(\varepsilon_i)^2} \quad (2)$$

Practically it has been seen that metals normally have material properties that may outweigh the differences created by the plasmonic ones. E.g. Lithium should be an equally good material as a plasmonic material as Gold, Silver or Copper but the metal is so reactive and unstable that never is it considered for plasmonic applications. Silver has been used historically because of its black colour when it forms large aggregates in many ways. Some of these uses are in photography and staining of biological tissues. As is widely known, Silver has the best thermal and electrical conductivity which makes it an ideal component for electrical joints as connections and as thermal fluids. Interestingly it is a common misconception that the black layer formed on Silver is an oxide whereas it is the formation of sulphide due to the trace amounts of hydrogen sulphide present in air this oxide layer is formed with regular exposure to air and is mostly transparent to visible light. The layer thickness can become about 60 Å in thickness in a day, month or a years time according to the amount of hydrogen sulphide in air.

2.3 Surface Plasmon Resonance

Surface plasmon resonance is otherwise defined as an oscillation due to resonance with incident light by oscillating electrons at an interface between a negative and positive permittivity of material. The resonance condition is established when the frequency of incident photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. SPR in subwavelength scale nanostructures can be polaritonic or plasmonic in nature[15].

From being an esoteric physical phenomenon Surface Plasmon Resonance (SPR) has become an inevitable name in the field of characterisations of interfaces be it in physical, chemical or biological applications. More recent has been the development of specialized metallic nanostructures for performing certain optical fuctions[16].

Surface plasmon polaritons can be explained using various proposed models such as the quantum theory or the Drude's model. But the simplest way is to describe the system as a homogenous continuum. This continuum is described by a dielectric functions. It is a complex function of relative permittivity between external medium and the surface. Now for the surface plasmons to exist on this interface the real part of the function must be negative and its magnitude must be greater than the dielectric. And this condition described allows plasmons to exist in the infrared-visible wavelength part for air/metal and water/metal boundaries(where the real dielectric constant of a metal is negative and that of air or water is positive)[17,18].

The surface plasmon polaritons mentioned earlier are electromagnetic waves travelling parallel to the metal/dielectric interface. And as expected since these waves or on the boundary, they are bound to be affected by any change in the boundary conditions like metal or external medium (air/water etc). They may change even due to adsorption of molecules on the boundary.

It is essential that there are free electrons present at the interface of materials for generation of surface plasmons (SPs) – and it is intuitive that one of the material should be a metal which has enough free electrons. And this conclusion can be arrived at mathematically by analysing the Maxwell's equations especially the Meta 1-dielectric interface ones. Once this analysis is done the picture is very clear on surface plasmons. It is evident that these surface plasmons are propagating waves composed of electrons and are active at the interface of the metal and the dielectric. In an alternate view they can be seen as electromagnetic waves that are strongly bound to this surface. And it is also seen that intensity of the plasmons can be greatly enhanced at this interface which is why this tool is used for plethora of interface studies[16].

2.4 Materials Showing Surface Plasmon Resonance

Noble and magnetic metallic NPs are among the most popular types of materials that are used for these kind of applications. These noble metal nanoparticles as is widely known are corrosion resistant and are robust materials under humid and mild acidic or basic conditions. Moreover, there main use as nanoparticles lies in their amazing and unique optoelectronic properties. If we look at the history of metal NPs in terms of its synthesis and understanding we would find that Michael Faraday in 1857[19], i.e. more than a century ago had already observed the optical properties shown by colloidal suspensions of metals by light absorption and scattering. 1908 was the year when Mie gave another in-depth concept to understand these interactions by proposing equations for spherical nanoparticles. He introduced the world to the concept of surface plasmon resonance and its physics dictated by electromagnetic waves interacting with free electrons on metal surfaces[12]. Subsequently there has been huge progress in understanding this phenomenon. And such understanding has led us to apply these materials in places we had never imagined before.

It will be highly useful to the scientific community if we could fine tune the plasmonic resonances of these nanoparticles. Many groups including the group of Naomi J. Halas were one of the first groups to synthesize nanoparticles with high plasmon tunability. The core-shell nanoparticles designed by them had a dialectic core surrounded by a metal shell. They further went on to vary the thickness of the metal shell to fine tune to plasmon resonance of the particles. It was found that varying the thickness could give a very efficient way to synthesize nanoparticles with exact plasmon resonances. The method is also capable of generating these NPs in very large quantitites[20,21,22].

These kind of tuneable nanoparticles can be used for various purposes such as SERS, colorimetric sensing, localized heating and many other purposes. Here they can be tuned for specific use or for working under a specific light source say sunlight or a more wavelength specific laser. In an application done by the Halas group, they tuned the nanoparticles absorption spectrum to the emission spectrum of sunlight. When exposed to sunlight in aqueous solution it was found that steam is produced in a manner of non-classical boiling where the individual steam bubbles are at high temperatures but the bulk water was not boiling[23].

2.3.1 Localized Surface Plasmon Resonance

Localized surface plasmons are charge density oscillations confined to metallic nanoparticles (Sometimes referred to as metallic clusters).

2.4 Synthesis Methods for Ag nanoparticles

Stabilising agent to prevent coagulation. Sodium borohydride, alcohols and sodium citrate are few of the reducing agents used with polymers and surfactants been used as the stabilizers. Directional growth of particles is also dictated by these stabilisers in many cases.

In 1982 Lee and Meisel were the first to report this easy method to synthesize Ag colloids by reducing AgNO3 using citrate which did not require extensive laboratory skills. In the typical process Silver nitrate solution and sodium citrate are mixed in specific concentrations and are brought to boiling for about 1 hour. Here citrate acts both as the reducing agent and the stabilising agent for the colloid. Today, the primary use of the citrate synthesis is in the light mediated synthesis. The mechanism of citrate reaction has eluded scientists for years due to unavailability of a detailed mechanistic study.

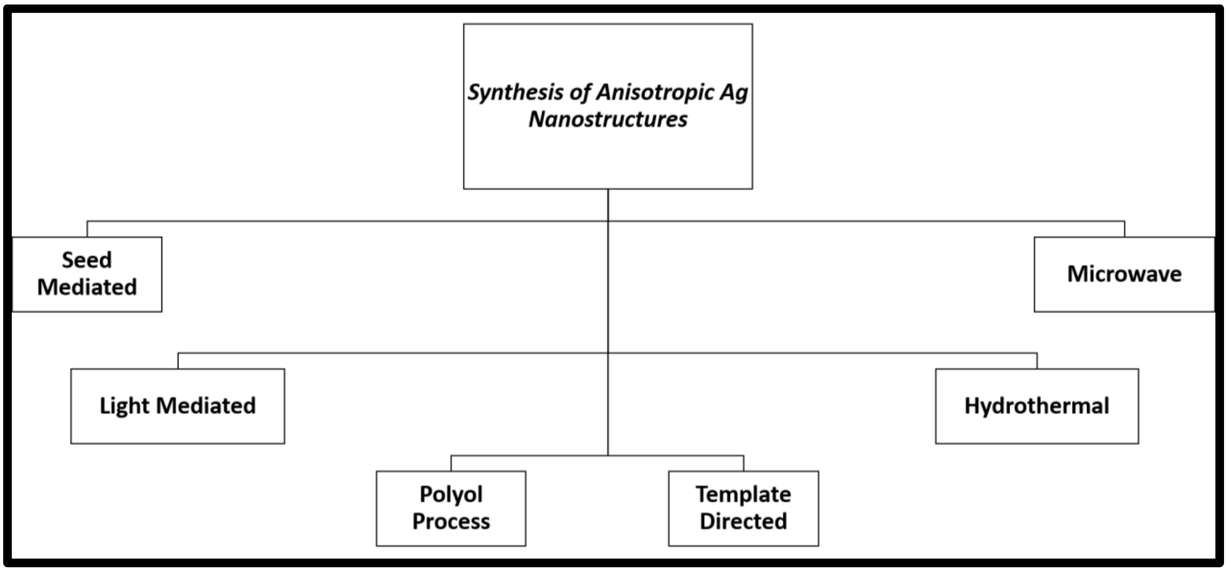

Figure 3: Schematic of synthesis methods

A relatively new method called the "Polyol process" has given a very robust and versatile to synthesize nanoparticles of wide variety of shapes and sizes. This method can achieve high degree of control over the size and shape of final products by controlling both nucleation and growth steps by varying reaction conditions such as temperature, reagent concentration and presence of trace ions. This method has been used to synthesize silver and gold cubes, right by pyramids and pentagonal wires.

Polyol process has been described in detailed in many reviews and mechanistic studies. But to give a basic overview, this process is a very highly temperature dependent with degree of sensitivity up to 5 degree Celsius. Typically the capping agent and the Ag precursor is injected into pre-heated ethylene glycol solution which leads to formation of silver ions and subsequently there is nucleation and growth. [10]

Stable Ag nanoparticles with different absorbance peaks were synthesized using a combined seed and light mediated method. Market grade LEDs were used as the light source for forming these particles in both steps. The process is highly dependent upon (LED colour, PVP, Citrate)

2.5 Applications

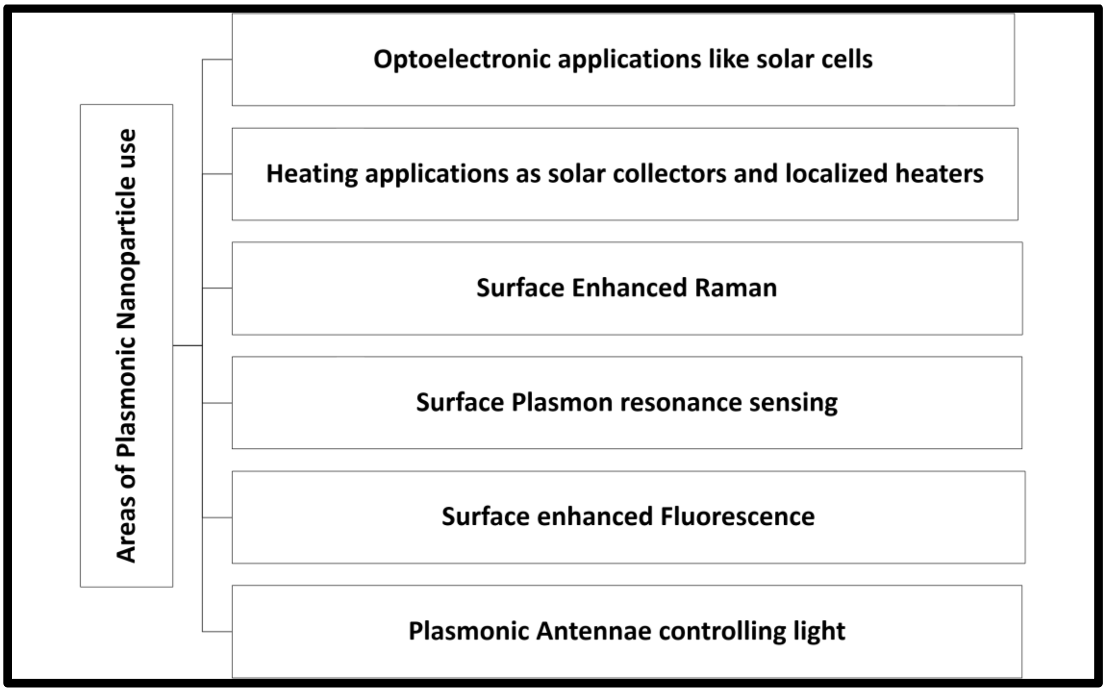

Figure 4: Schematic on applications of Plasmonic Nanoparticles

Plasmonics encompasses a fundamental light matter interaction; consequently, there are many scientific fields that stand to benefit from it. Already, many applications of Plasmonics have emerged in past decades like SERS, near-field optical microscopy, and LSPR-based sensing. Despite this wide range of research activities, current applications of plasmonic nanostructures can generally be categorized into three thrusts: (i) LSPR sensing and detection, (ii) concentration of light to enhance or manipulate the optical response of nearby molecules, and (iii) manipulation of light with plasmonic circuitry. The first thrust area takes advantage of the sensitivity of a nanostructure's LSPR properties toward its surroundings. The second exploits the intense E-fields and highly directional nature of LSPRs supported by nanostructures (in this context, they are often called nanoantennas) to enhance molecular scattering or emission cross sections and, in some cases, control the directionality of light propagation[24]. Finally, the third thrust encompasses the guiding and manipulation of PSP modes in one-dimensional nanostructures.

3. Motivation

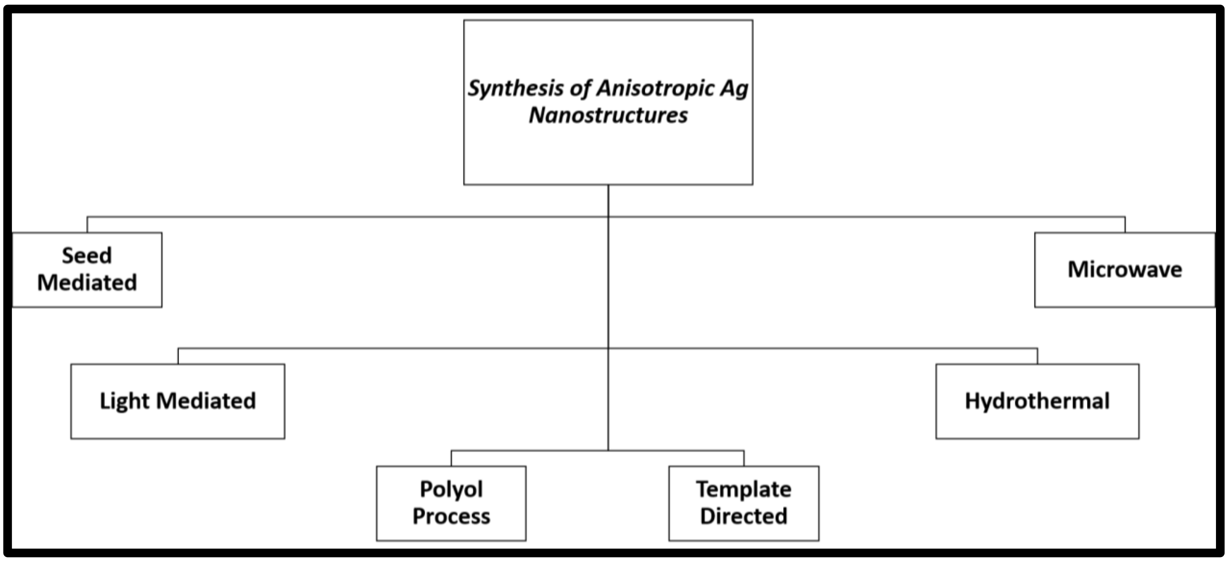

Figure 5: Schematic of types of method to prepare Ag nanostructures using wet synthesis methods.

There are a plethora of methods of available at the moment for synthesizing these nanoparticles. The level of tunability that is needed and which can be achieved by a certain method determines the type of synthesis pathway one may need to use. For our purposes of achieving highly tunable NPs seed mediated, light mediated, polyol and template directed methods are equally comparable to each other. The problem with template directed and polyol process is the level of purity that is needed. Slight contamination in the polyol process can lead to failed experiments or unwanted products[5].

It has been found that nobody has attempted to synthesize Ag nanoparticles by combined method. So we got inspired to work on a simple method of synthesizing Ag nanoparticles using an easy light and seed mediated combined method to synthesize Ag nanoparticles[24–28]. Moreover our inquisitiveness and despair use this hybrid method to prepare these NPs.

4. Objectives

The objectives of this project are:

- Designing a novel method for synthesizing Ag NPs with highly tunable plasmonic properties.
- Incorporating both seed and light mediated methods to introduce a hybrid method for synthesis of Ag nanoparticles.
- Making this method very economic and the setup very user friendly.
- To use this method for plasmon sensing applications of a dangerous inorganic industrial pollutant- Mercury.
- Designing methods for detecting other single molecules using Surface enhanced Raman Spectroscopy.

5. Experimental Procedure

The simple process of preparing Ag colloids using Silver Nitrate as a precursor, Tri sodium citrate as a capping agent and Sodium borohydride involves mixing each of these in proper stoichiometric ratios and stirring it well continuously at room temperature.

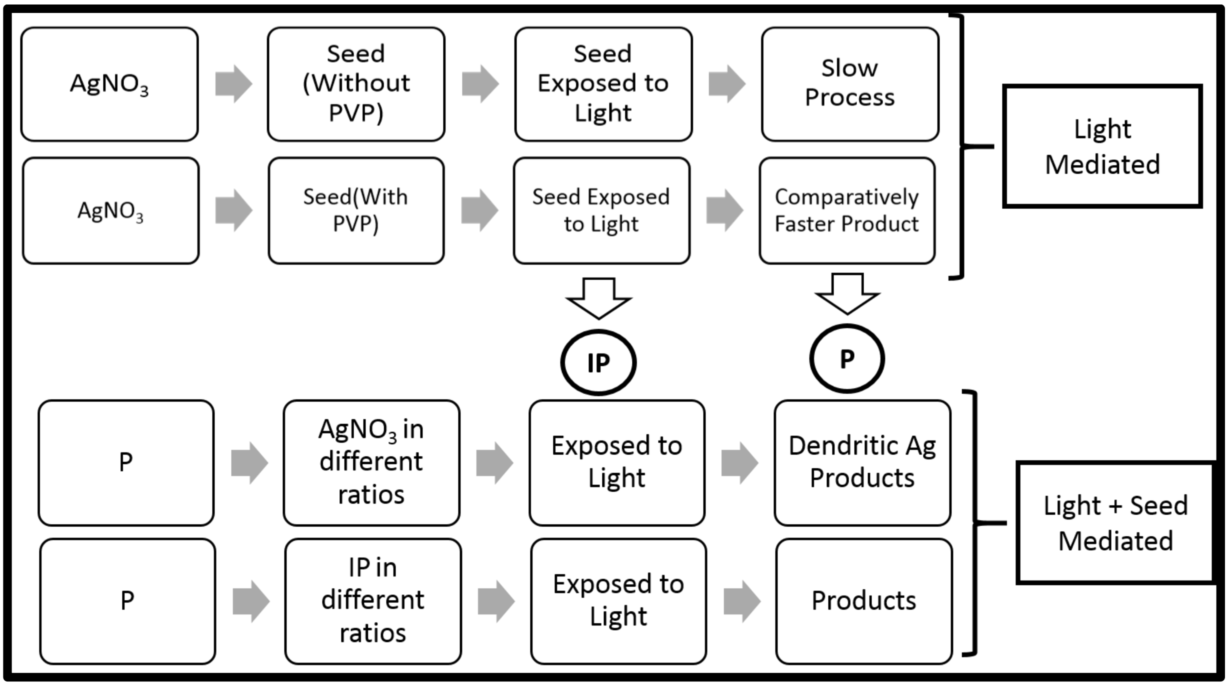

Figure 6: Overall schematics of synthesis

5.1 Materials

Silver Nitrate ($AgNO_3$) and Tri Sodium Citrate were purchased from Merck and Sodium Borohydride ($NaBH_4$) was purchased from Sigma Aldrich. PVP (Mol Wt. 360000g/mol) was purchased from Sigma Aldrich. All reagents were of analytical grade.

5.2 Synthesis

5.2.1 Silver Nanoseeds (Without PVP)

Synthesis of Silver Nanoseeds was done using the ion reduction method where Silver Nitrate was mixed with Tri Sodium citrate (Capping cum slow reducing agent) and stirred well. Later required amount of freshly prepared Sodium Borohydride is added to the solution drop by drop until the solution turns yellow. The whole reaction is done in dark environment.

5.2.2 LED Modified Ag Nanoseeds (Without PVP)

Different samples of seed solution were kept inside an LED setup with four different kinds of LEDs (Red, Blue, Green and White) fitted. Solutions of different colours were formed in the process.

5.2.3 Silver Nanoseeds (With PVP)

Synthesis of these seeds was done using the ion reduction method where Silver Nitrate was mixed with Tri Sodium citrate (Capping cum slow reducing agent) and stirred well. PVP was added into the solution. Later required amount of freshly prepared Sodium Borohydride is added to the solution drop by drop until the solution turns yellow. The whole reaction is done in dark environment. Hereafter we refer to this product as **IP**.

5.2.4 LED modified Ag nanoseeds (With PVP)

The above seed solution was exposed to green LED for 6-8 Hours and a blue colour solution is formed. We refer the product formed as **P** from this point onwards.

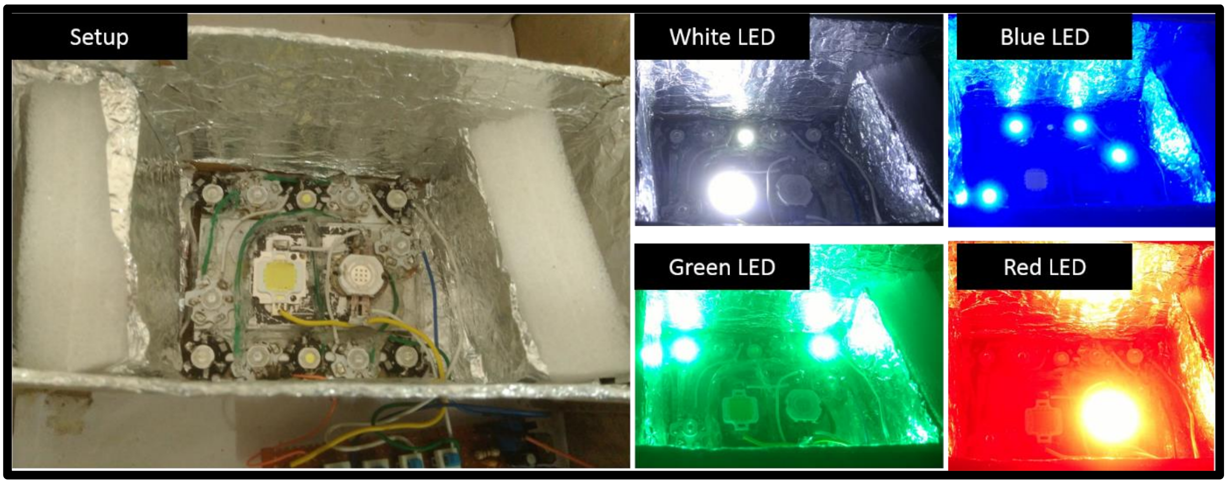

Figure 7: LED setup for light mediated synthesis

5.2.5 Hybrid Method for Ag Nanoparticle growth with Silver Nitrate Addition

Different calculated amounts of $AgNO_3$ was added to fixed amount of solution **P** and was exposed green LEDs for 3-4 hours and the solution turned into dark brown colour.

5.2.6 Hybrid Method for Ag Nanoparticle growth with Silver seed (with PVP IP) addition

Calculated amounts of **IP** was added to fixed amount of Solution P and was kept under LED light.

5.3 Applications

Solution P was diluted 5 times and different quantities of $HgCl_2$ solution were added to 5ml of the solution in 5 glass vials.

5.4 Characterization

Each of the samples after synthesis were analysed optically using UV-Vis-NIR spectrophotometry. Most of the samples were seen under SEM, FESEM and TEM. XRD analysis was done for these structures.

6. Results and Discussion

6.1 Optical Property Measurements

Optical properties of the synthesized particles were measured using Shimadzu UV-Vis-NIR Spectrophotometer. We can visibly see that the same silver nanoparticles show different types of colours.

6.1.1 Surface Plasmon Resonance

Figure 8: Synthesized seed particles

Figure 8 shows the yellow coloured initial seed. There is no visible difference as such to the naked eye for PVP incorporation. These seed particles need to be exposed to light as soon as they are synthesized.

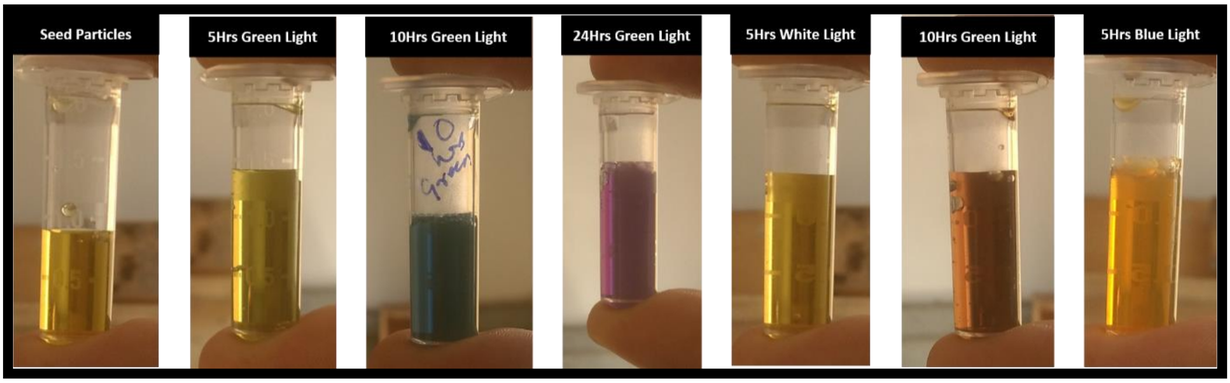

Figure 9: Silver seed (without PVP) exposed to LED lights of different types

Figure 9 shows the different coloured solutions that are formed on exposure to different types of LEDs. Here it can be observed that the wavelength to which the sample is exposed and the amount of time it exposed hugely contributes to the final appearance of the sample.

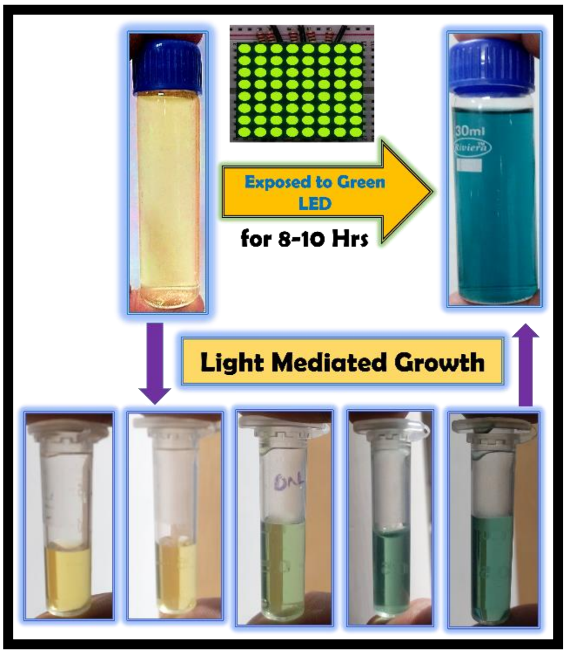

Figure 10: Process of conversion from seed (with PVP) to modified seed.

The seed solution was exposed to light and at every 60 minutes and 1 ml of solution was collected for analysis. Figure 3 shows the colour of the solution w.r.t time.

Figure 11: Shows the change in colour with the hybrid method applied.

Once the modified seed solution (**P**) is formed, calculated amounts of $AgNO_3$ is added to the solution and exposed to light again and the figure above shows the colour change.

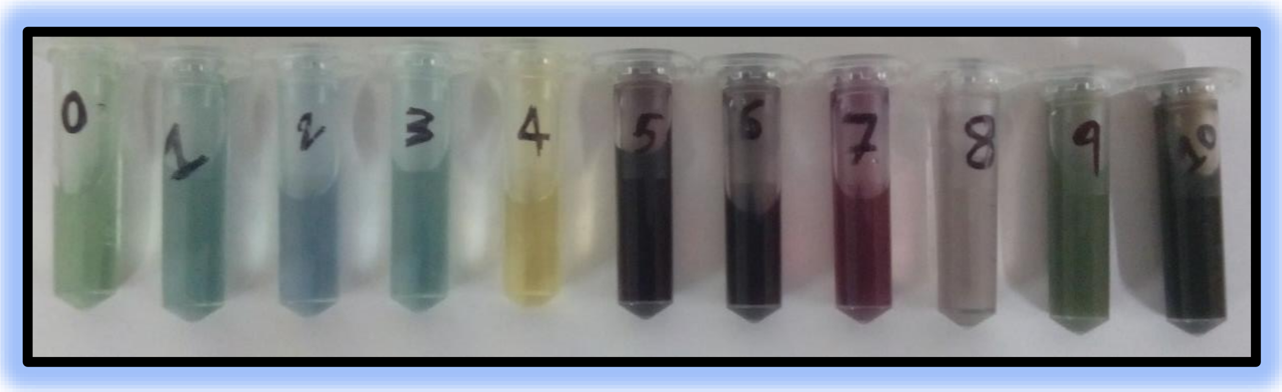

Figure 12: Shows the different kind of SPR activity that the hybrid method can achieve.

Above figure gives a clear demonstration about the versatility of this method to achieve tunability of SPR wavelength. These solutions are all kept in green LED after adding different amounts of Silver Nitrate and solution **IP.**

6.1.2 UV-Vis-NIR Spectrophotometry

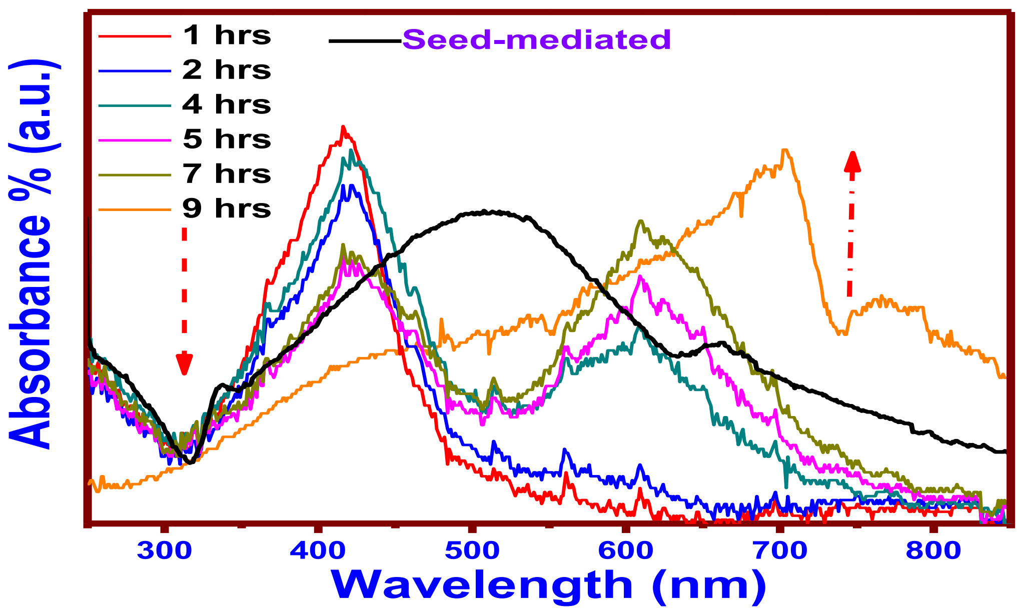

Figure 13: Graph of solution **IP** to **P** under green LED at certain intervals of time. Another black line shows the SPR for the final solution containing dendritic nanoparticles.

The above graph depicts the transformation of products takes place under green LED illumination. The original peak gets diminished and the new peak is formed as time passes.

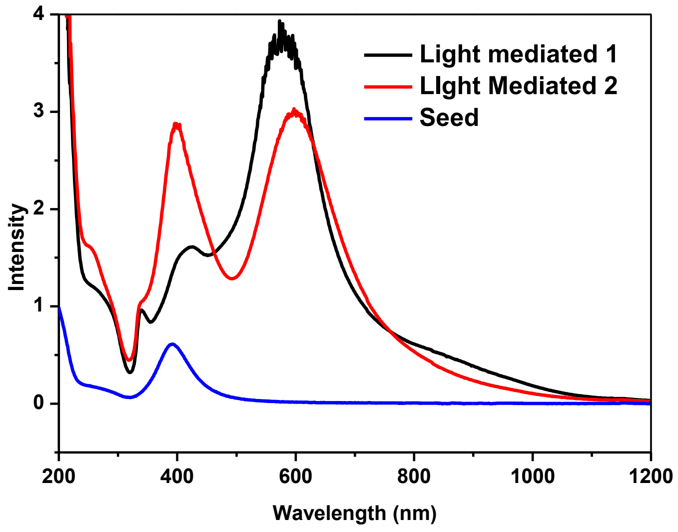

Figure 14 Initial change in optical seed under LED. This seed doesn't contain PVP activity of.

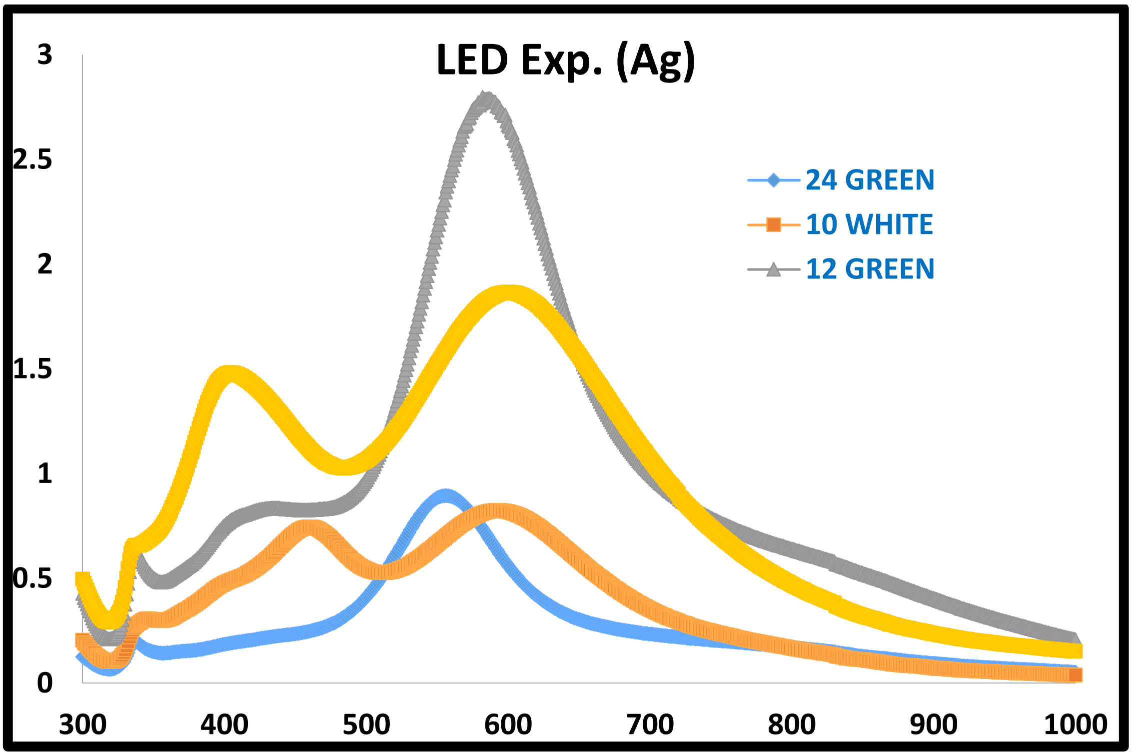

Figure 15: The UV-vis spectra shows another distribution under different color light as mention inset of figure.

6.2 Microscopy

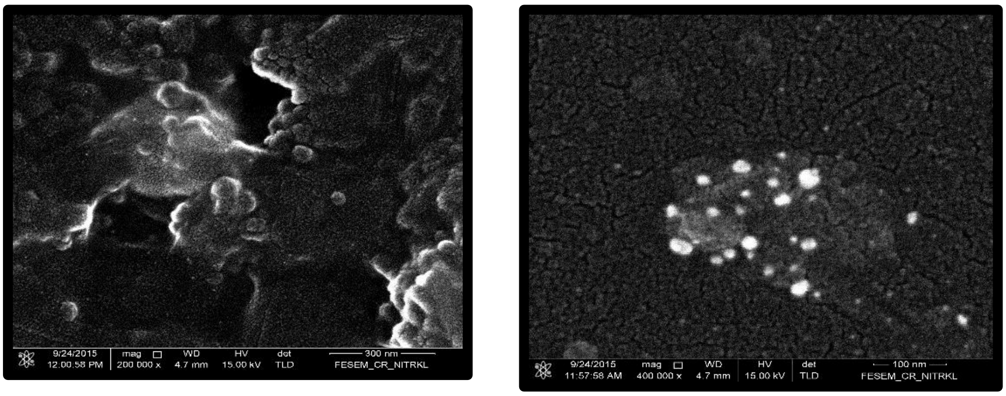

Figure 16: SEM microscopy of modified seed which were synthesized without the use of PVP.

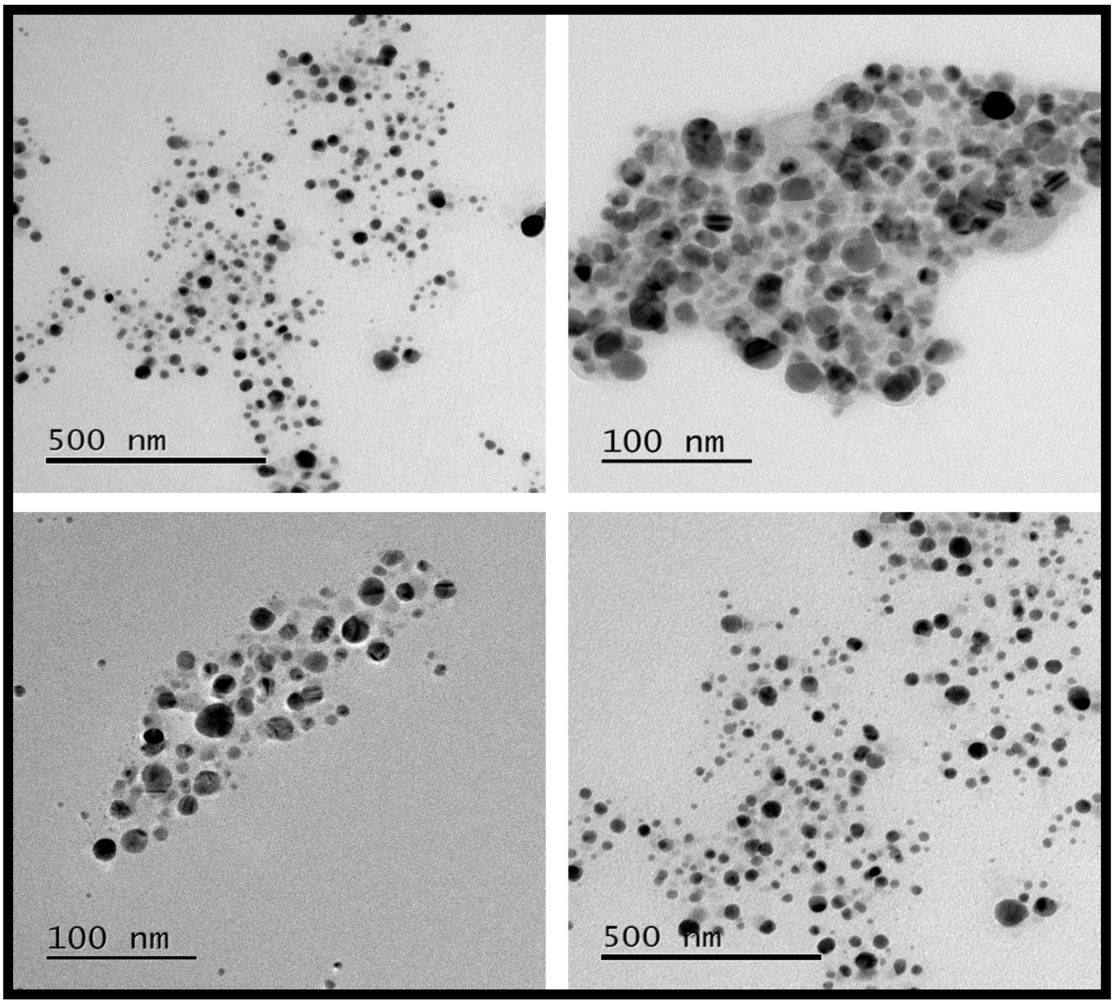

Figure 17: TEM images of solution P which are modified seeds in Green LED in presence of PVP.

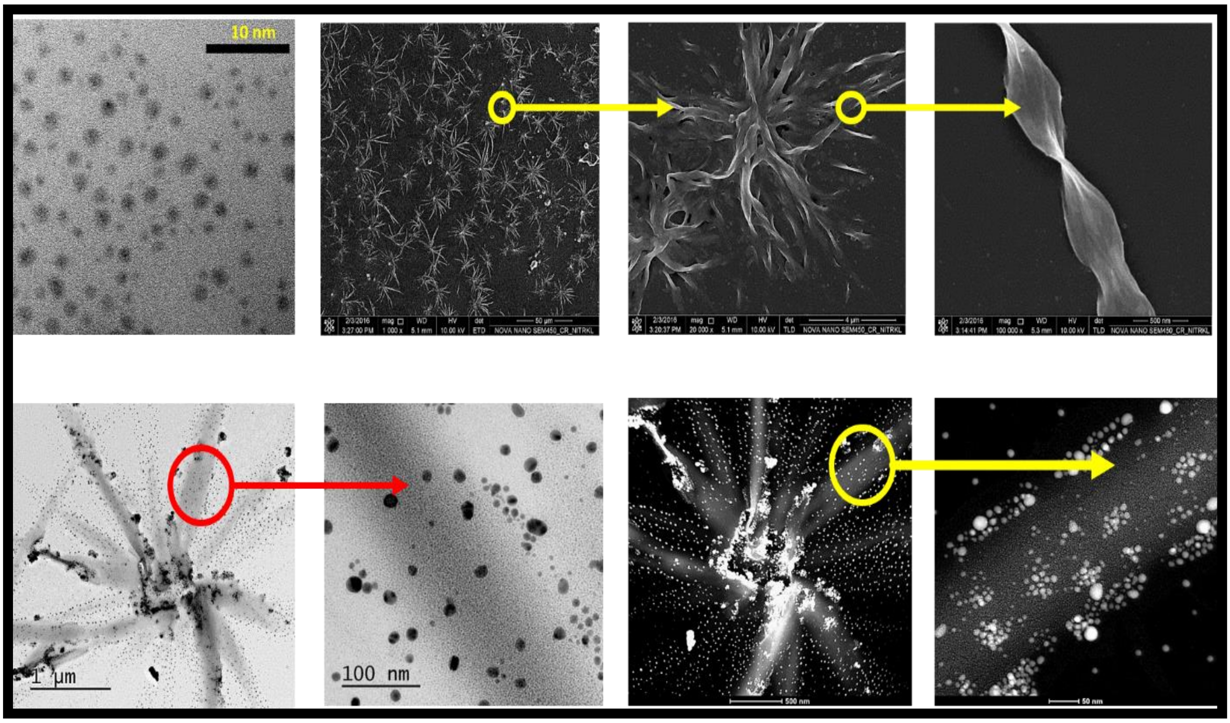

Figure 18: TEM and SEM images of dendritic Silver nanoparticles synthesized by hybrid method.

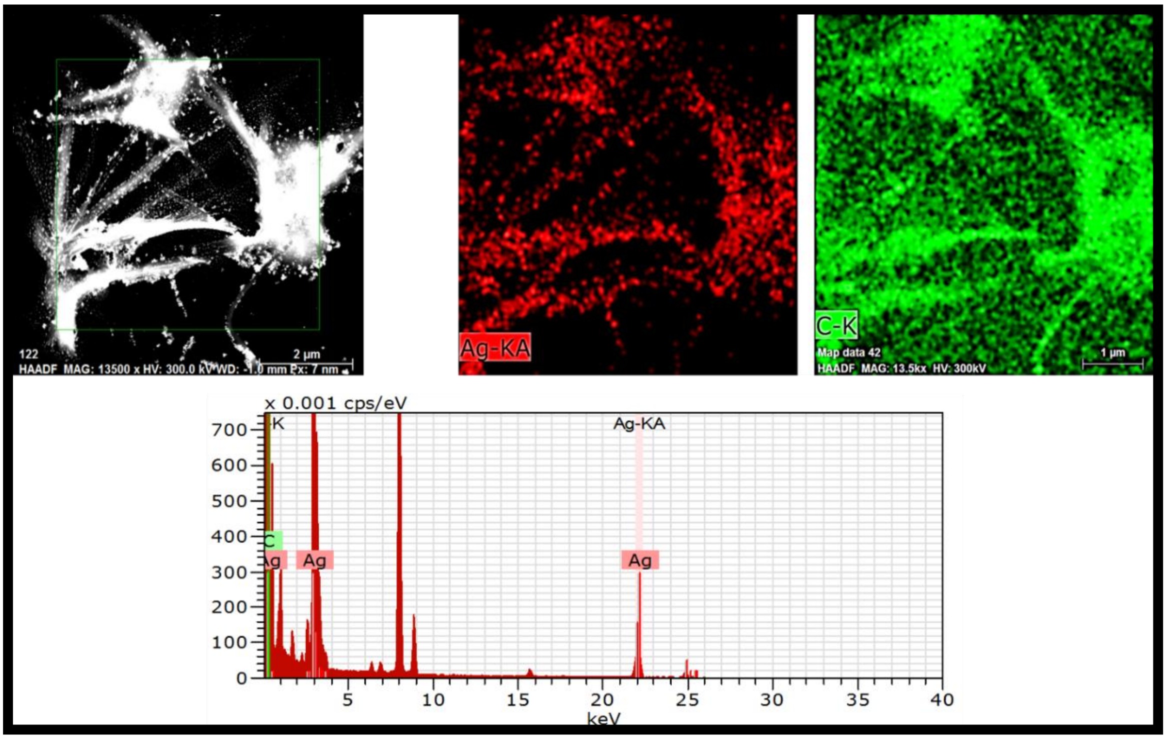

Figure 19: Energy dispersive spectrometry of dendritic Ag nanostructures.

The micrographs show clearly how the seed solution containing extremely small particles in the range of 4-5 nm grow to form small clusters as they are kept under illumination of LEDs.

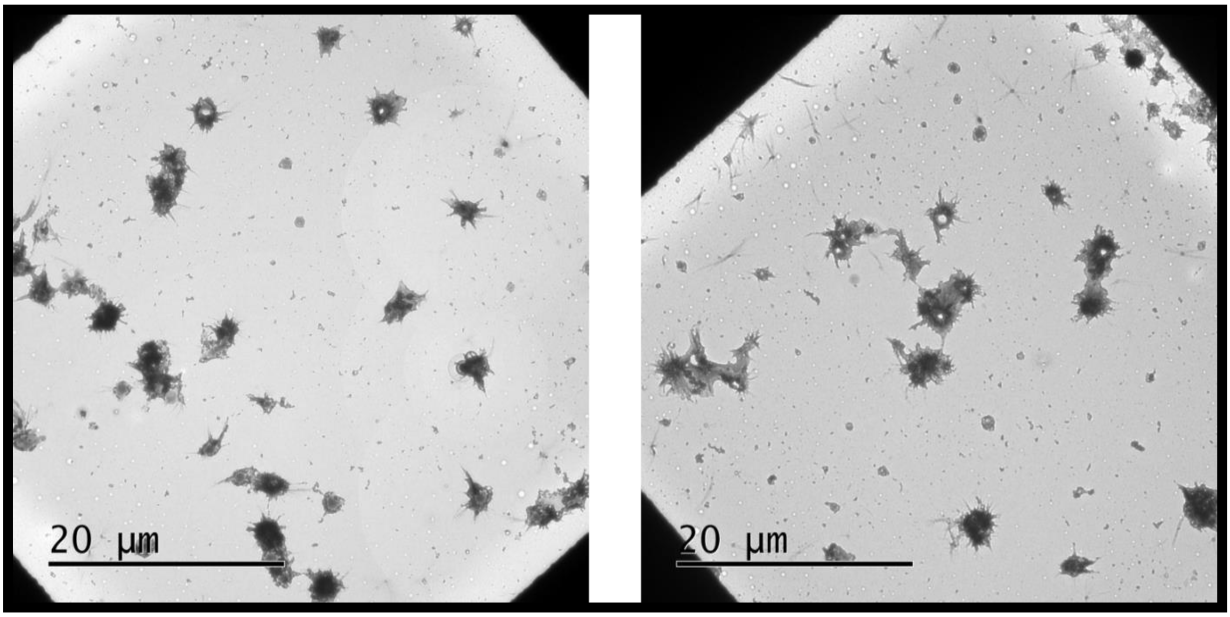

Figure 20: Distribution of Ag dendritic structures under TEM.

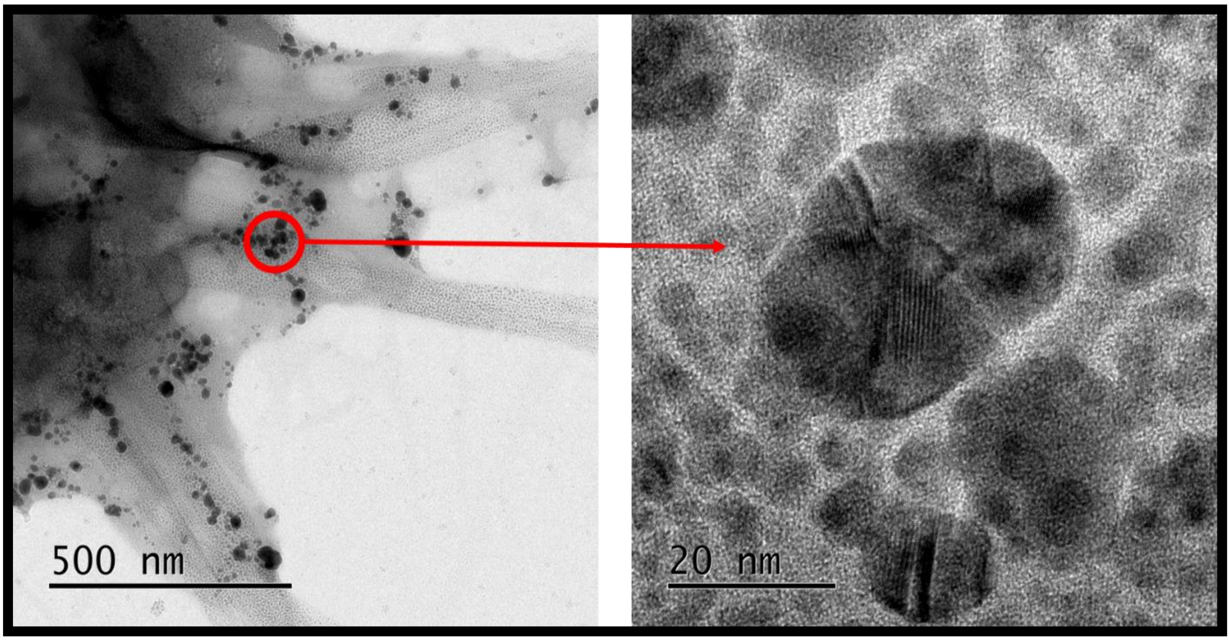

Figure 21: Fringe pattern analysis for Ag Nanoparticles inside these dendritic structures.

The dendritic structures formed after using the hybrid method are extensively studied under SEM, FESEM and TEM for detailed view and analysis of the structures. These structures are clearly formed from the modified seeds i.e. the blue solution. When these dendritic structures were seen in detail it was found that the structures were actually composed of Ag nanoparticles of different sizes i.e. a multi modal distribution. These structures were formed on a PVP template and this was verified by the EDS analysis.

6.3 XRD Analysis

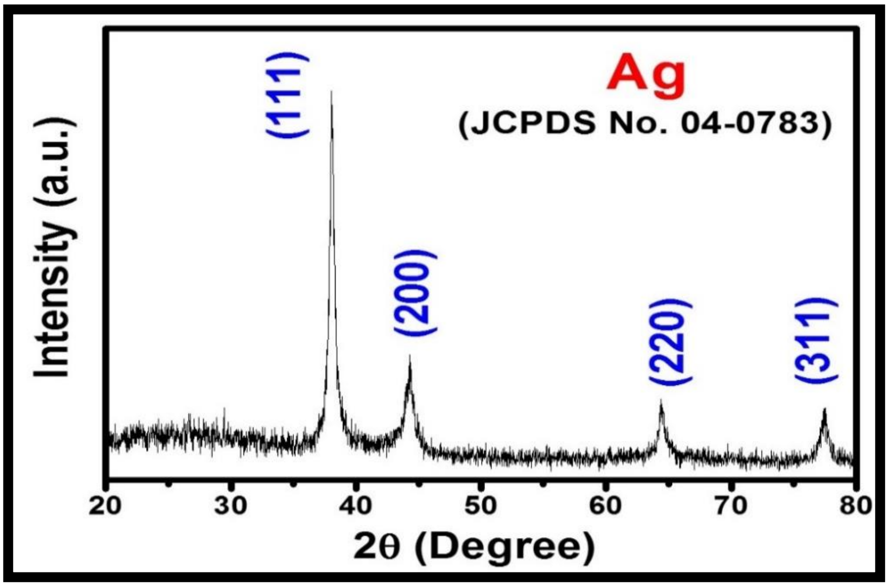

Figure 22: XRD of dendritic Ag nanostructures

XRD analysis was done at every step and was found that it is same for all kinds of structures which confirms no change in the crystal structure.

6.4 Sensing of Hg^{2+} ions

6.4.1 Visible Colorimetric Sensing

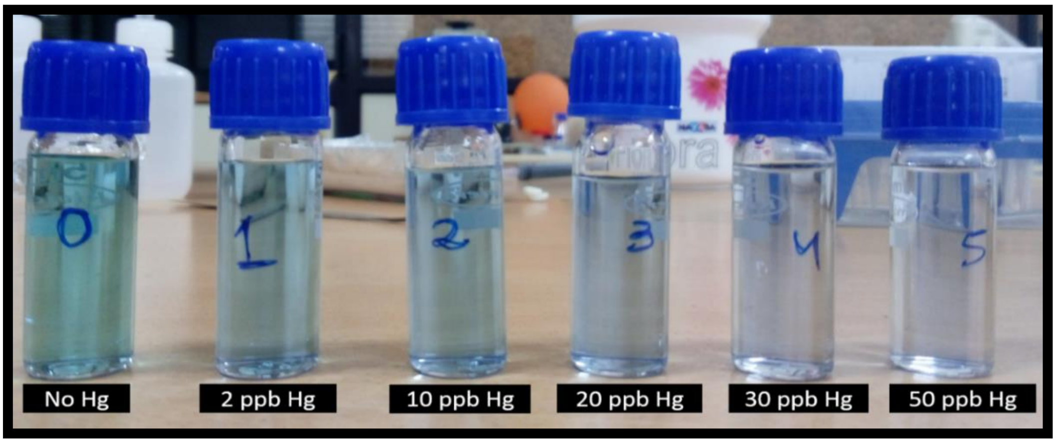

Figure 23: Visible colorimetric change for sensing of Hg^{2+} ions.

6.4.2 UV-Vis-NIR Spectrophotometry

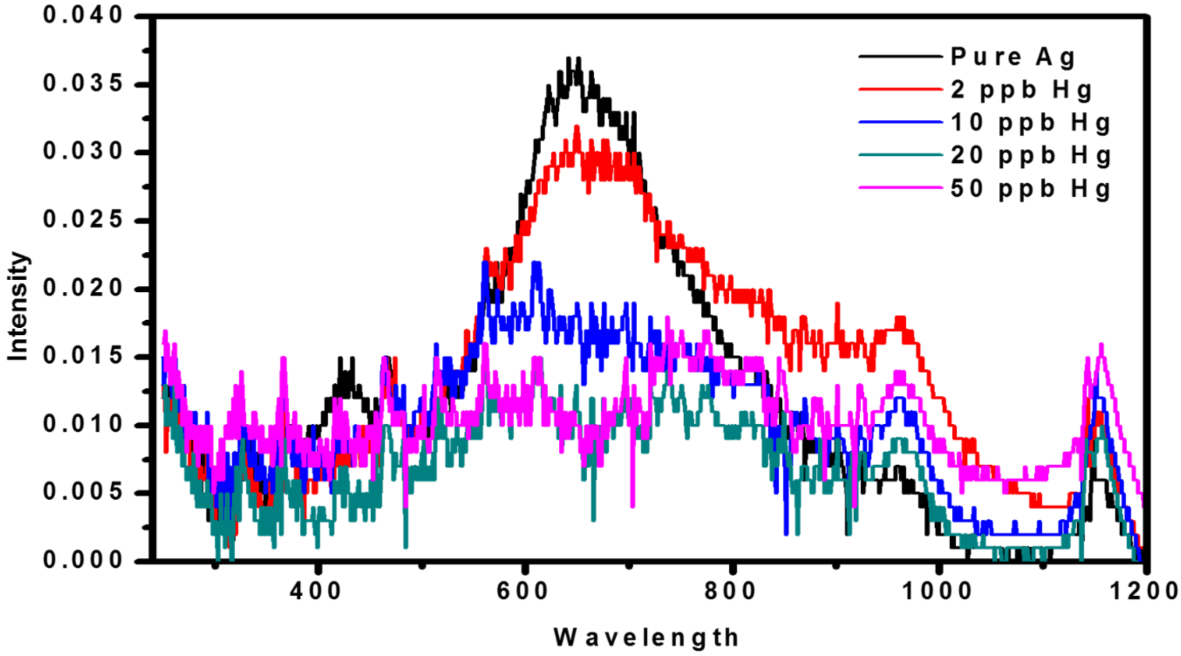

Figure 24: It show the easy colorimetric change in sensing of Mercury ions.

Sensing experiments show the high quality sensing of these nanoparticles which respond to concentrations as low as 2 ppb. Colorimetric sensing also shows good response visibly. UV graphs shows us the change in SPR as we keep adding Hg^{2+} ions.

7. Conclusion

The inspiration for this work started when we set about to develop nanoparticles with highly tunable plasmon resonances for purposes of localized heating and sensing. In this process we choose silver and also choose a very interesting method i.e. the light mediated one to finally get to our final product. Out of despair and inquisitiveness we followed a very less trodden path of using both methods of seed and light mediated synthesis to create a hybrid method.

In this process we have been able to produce particles of quite interesting shapes and properties. The dendritic silver nanoparticles are seen to be grown on a PVP template and are promising structures for plasmon enhancement applications.

To demonstrate the plasmonic activity and its power as a sensor we have sensed Hg^{2+} to levels as low as 2ppb which is the maximum level of allowed Mercury content in drinking water.

So to summarize we have been able to:

- Synthesize Ag particles of very novel nature.
- The synthesis method used is also very novel as it involves very widely popular method to synthesize nanoparticles of highly tunable plasmon resonances.
- The method is very low energy consuming and the setup can be prepared anywhere. The LEDs used are quite inexpensive and are of very low power rating.
- The method also requires very less time to prepare these nanoparticles
- To test the SPR action of the nanoparticles we did sensing of a major inorganic pollutant i.e. Hg.
- Hg ions were sensed in very small quantitates by these particles.

7.1 Future Work

The Silver nanoparticles synthesized could be used for Surface enhanced Raman Spectroscopy sensing and other light harvesting techniques. The mechanism of the formation of such particles could be explored much more detail.

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