

Solvent Complexation Triggered Synthesis of Gold Nanoparticles

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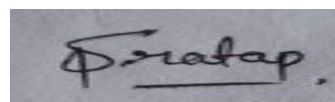
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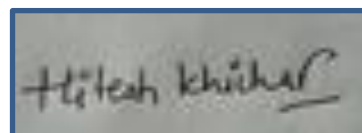
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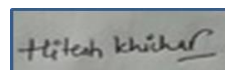
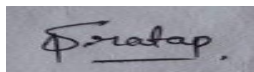
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ABSTRACT

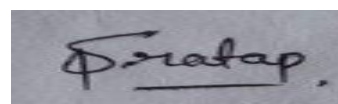
The novel room temperature wet chemical synthesis method for the reduction of hydrochloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) leading to the formation of distinct anisotropic size/shaped gold nanoparticles is largely dictated by conformational changes in the solvent complexation of Dimethylformamide (DMF) in aqueous as well as alcoholic solvents. A strong surface plasmon resonance (SPR) band in visible region, that is induced when the oscillation frequency of free electrons of the gold nanoparticles resonates with the frequency of incident light, indicates the formation of gold nanoparticles. The complexation of DMF with protic solvents like water and alcohols at different pH alters the reducing as well as capping capabilities of complex for hydro-chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$). Variation of optical properties of thus synthesized gold nanoparticles was quantitatively studied with UV-Vis absorption spectroscopy along with formation mechanism elucidated with FTIR measurements.

ACKNOWLEDGEMENT

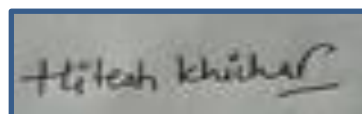
Firstly, and importantly, we would like to thank our supervisor **Dr. Renuka Bokolia** for allowing and giving us the golden opportunity to work in her lab. Without her mentoring and unconditional support, this work would not have been possible. We would like to thank her for her valuable time, feedback and suggestions. We would like to extend our deepest gratitude to **Dr. Manoj Verma**, Assistant Professor, Hindu college, University of Delhi, for helping us through thick and thin while performing experiments, for beginners like us which was not easy, also for his invaluable discussions on several topics that provided a good understanding of the topics. Their approach to scientific inquiry kept the joy of research alive during this thesis. We also extend our thanks to all the faculty members, CMRL Lab, M.Sc.(Physics) scholars and members of the Department of Applied Physics, Delhi Technological University for their suggestions and valued support. Lastly, we would also like to thank our parents for their enduring support and for believing in us always.

Place: Delhi

Date: 30 May 2023



Surya Pratap Singh



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LIST OF SYMBOLS AND ABBREVIATIONS

1	DMF	N,N-dimethylformamide
2.	HAuCl ₄	Hydro-chloroauric acid
3	NaOH	Sodium hydroxide
4	CH ₃ OH	Methyl alcohol
5	DI	Deionized water
6	AuNPs	Gold Nanoparticles
7	LSPR	Localized Surface Plasmon Resonance

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

The science of nanotechnology, which integrates elements of chemistry, physics, biology, environmental science, medicine, and agriculture, has the potential to address a wide range of issues, including drug delivery, solar energy conversion, wastewater treatment, and cancer treatment[1]. Researchers have been working on establishing consistent and effective techniques for producing nanoparticles with a size range of 1 to 100 nm as a result of the significant achievements in nanotechnology in recent years[2][3]. The interest in nanomaterials has grown as a result of their differences from their bulk equivalents in terms of optical, electrical, physiochemical, and magnetic properties. Metallic, polymeric, carbon-based, semiconductor quantum dot, and magnetic nanoparticles are some of the major groups of nanostructures with biological significance[4].

The surge of interest in metal nanoparticles having many branches, such as nanostars, is mostly due to their potential applications in plasmonics and sensing systems. The controllable optical properties of metallic nanoparticles, resulting from their size and shape variations, have garnered considerable attention in diverse fields of research. These areas encompass nanoelectronics, catalyst development, optical filters, photon transport, as well as applications like surface-enhanced Raman or fluorescence[5]. This has led to an upsurge in research focused on synthesizing nanogold and nanosilver with precise geometries, including cubes, spheres, rods, polyhedra, belts, nanokites, nanorice, and platelets[6].

The idea that light waves could not interact with anything smaller than their own wavelength was disproved for more than a century by the discovery that light interacts with nanostructures. Since extending optoelectronics into the nanoscale zone is difficult

due to the long wavelength of light. The transformation of light into plasmons offers a potential solution. They can transmit electronic signals and have wavelengths that are significantly shorter than those of light[7]. Plasmonics, or the study of surface plasmons (the collective excitation of free electrons on metal surfaces), is a subfield of nanophotonics.

In recent times, there has been a surge in interest regarding a new category of materials known as nanomaterials. This term refers to substances that possess at least one three-dimensional dimension at the nanoscale range, which typically spans from 0.1 to 100 nanometers.

Nanoparticles are a type of nanomaterial that has undergone extensive development over the years and currently represents one of the most advanced technologies in the field. Their widespread usage and significant contributions can be observed across various disciplines, such as health, biology, physics, chemistry, and sensing. This is primarily due to their unique properties, which make them highly valuable in these fields[8]. Noble metal nanoparticles (Cu, Hg, Ag, Pt, and Au) have drawn more study interest than other types of metal nanoparticles. The most stable of these are gold nanoparticles, which can now be made in a variety of sizes and forms, such as nanospheres, nanorods, and nanotubes, as well as nanobranches, nanoflowers, nanoshells, nanowires, and nanocages. Additionally, they have adjustable optical quality with a variety of features[9].

Among the numerous synthetic techniques that have been discovered, only a limited set enables researchers to precisely control the size and morphology of nanoparticles. Noteworthy methods include the polyol process, which relies on reducing inorganic salts using ethylene glycol; seeded-growth methods, where nanoparticles grow on smaller seed particles; and DMF reductions, which utilize N,N-dimethylformamide (DMF) as both a solvent and reducing agent[10].

This article aims to provide a comprehensive overview of the utilization of DMF in the synthesis of metal nanoparticles, particularly gold (Au) nanoparticles, with specific morphological features and distinctive characteristics. Hence, adopting DMF as a reducing agent, we cover the major developments in the wet chemical synthesis of metal nanoparticles[11]. Analyzing briefly how variation of size and shape might alter the optical response of metal nanoparticles.

1.2 Why Gold Nanoparticles?

Plasmonic metal nanoparticles, such as gold, silver, and platinum, exhibit excellent light absorption and scattering properties. The optical response of metallic nanoparticles can be controlled and manipulated across the ultraviolet, visible, and near-infrared regions of the electromagnetic spectrum[3][12]. This is achieved by modifying factors such as nanoparticle size, shape, and composition. For instance, spherical gold nanoparticles in solution appear ruby red as they strongly scatter and absorb light in the green region of the spectrum. In solution, silver nanoparticles exhibit a yellow color attributed to plasmon resonance in the blue region of the spectrum, while red and green light remain unaffected[13]. Through manipulation of the absorption and scattering properties, it becomes possible to finely adjust the color of nanoparticle dispersions and films.

Therefore, following are the reasons for studying the Plasmonic Gold Nanoparticles-

- Highly efficient at absorbing and scattering light.
- The optical response of metallic nanoparticles can be adjusted across a broad spectrum, ranging from ultraviolet (UV) to near-infrared (near-IR) regions.
- Color of nanoparticle dispersions and films can also be tuned.
- Plasmonic metal nanoparticles have a wide range of applications, including but not limited to:

Molecular detection

Solar energy materials

Cancer detection and treatment

Nano imaging

Surface-enhanced applications

Photothermal therapy

1.3 Localized Surface Plasmon Resonance (LSPR)

When specific wavelengths of light interact with metallic nanoparticles, they can induce collective oscillations of the conduction electrons[14]. This phenomenon, referred to as surface plasmon resonance (SPR), occurs at the interface between materials with negative and positive permittivity.

When frequency of this plasmonic oscillations matches with frequency of incident electromagnetic wave then resonance takes place and this resonance is called Localized Surface Plasmon Resonance (LSPR)[15][16].

Exciting surface plasmon resonances leads to a substantial increase in the absorption and scattering intensities of metallic nanoparticles compared to particles of the same size that lack plasmonic properties. In fact, these enhancements can reach up to 40 times higher values[17]. This phenomenon has been extensively observed and studied in the field of plasmonics and is of great interest for various applications, including sensing, imaging, and optoelectronics.

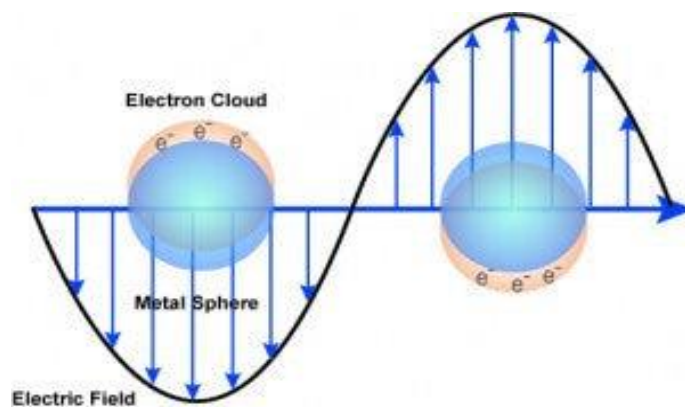


Figure 1.1 Schematic illustration of localized surface plasmon resonance

1.4 LAMER THEORY

Lamer theory effectively describes the kinetic formation of particles, where the diffusion of elements (such as particles, ions, etc.) plays a crucial role in their control and development.

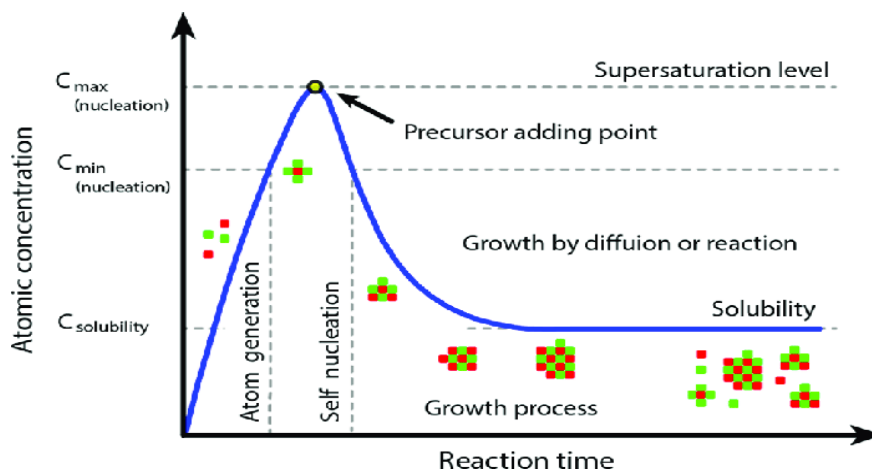


Figure 1.2 Schematic illustration of Lamer Theory

A process that follows the Lamer mechanism can be explained in two steps-

- The monomer is generated and accumulates in solution, causing it to become supersaturated, but there are no particles present;
- In stage III, the process continues to grow nanoparticles without additional nucleation.

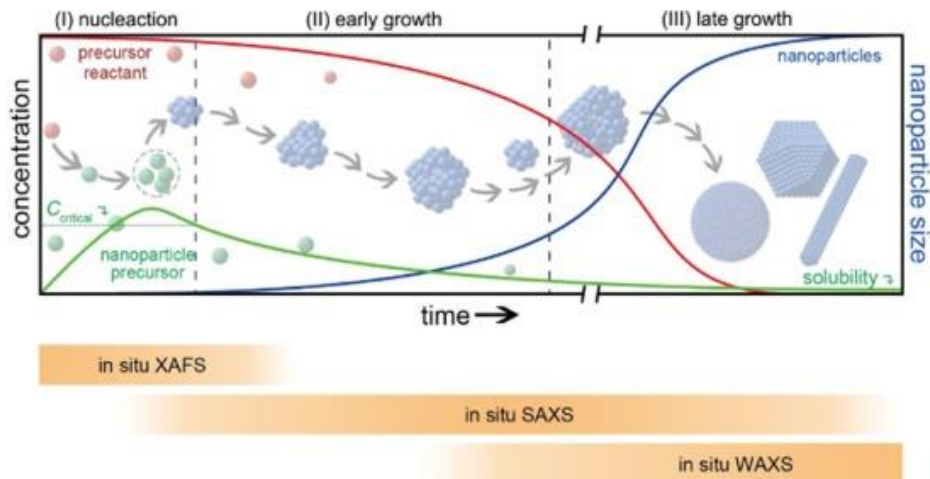


Figure 1.3 Schematic explanation of (i) nucleation, (ii) early growth & (iii) late growth

1.5 Top Down & Bottom Up Approach

The "bottom up" approach and the "top down" method are two ideas that can be used to produce distinct Gold Nanoparticles[18][19]. Processes including "nanosphere lithography, chemical, photochemical, electrochemical, templating, sono chemical, and thermal reduction" are included in the bottom-up approach[24].

To achieve the desired nanostructure, specific top-down techniques like photolithography and electron beam lithography are employed, which involve selectively removing material from the bulk material[20][21]. These techniques rely on precise patterning and etching methods to carve out the desired nanostructures on the surface of the material. By strategically removing excess material, the desired pattern and structure can be achieved[22].

Each process has its own set of drawbacks, such as poor mono dispersity in the case of bottom-up methods and significant material waste in the case of top-down methods, despite the fact that all of them can generate Gold Nanoparticles of the right shape and size[23][29].

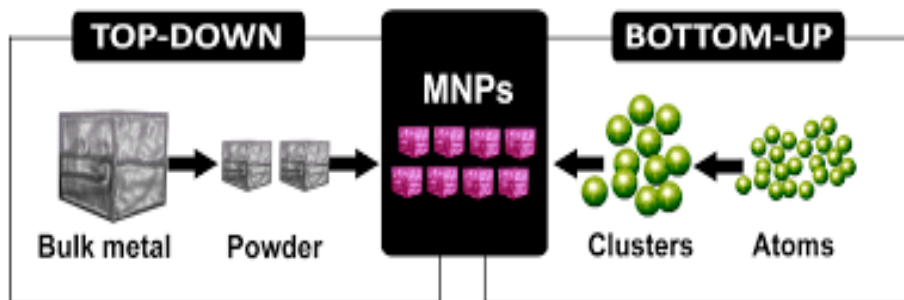


Figure 1.4 Schematic illustration of top down & bottom up approach

1.6 Literature Review

1.6.1 *Abhitosh Kedia and Pandian Senthil Kumar, "Solvent-Adaptable Poly(vinylpyrrolidone) Binding Induced Anisotropic Shape Control of Gold Nanostructures", The Journal of Physical Chemistry C 2012, 116, 23721–23728 , 10.1021/jp306952d*

- Hydro-chlorauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) reduction results in the creation of gold nanoparticles with a variety of anisotropic sizes and shapes.
- Different solvents used during synthesis of gold nanoparticles can lead to different shapes because of the different conformations of reducing and capping agent.
- Differential morphology of synthesized nanoparticles lead to variation in absorption spectra of nanoparticles.

Summary of this work is that solvent used in the synthesis of metal nanoparticles greatly contribute to the final size/shape of nanoparticle obtained.

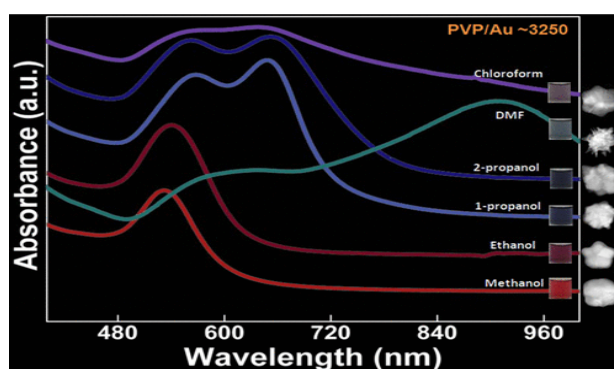


Figure 1.5 UV-Vis plot for different solvents

1.6.2 M. Sajitha, A. Vindhyasarumi, A. Gopi and K. Yoosaf, "Shape controlled synthesis of multi-branched gold nanocrystals through a facile one-pot bifunctional biomolecular approach", *The Royal Society of Chemistry Adv.*, 2015, 5, 98318–98324, 10.1039/c5ra19098c

- When L-DOPA at different pH is used to reduce HAuCl_4 , assembly of nanoparticles can be obtained.
- In the case of metals, isotropic spherical nanoparticles typically display a single plasmon resonance peak centered around 520 nm. However, anisotropic nanostructures like nanorods and nanostars exhibit multiple absorption maxima that correspond to different plasmon oscillation modes. These anisotropic structures give rise to diverse plasmonic properties due to their asymmetric shape, resulting in the presence of multiple resonant modes with distinct absorption peaks.
- Moreover 1-D or 2-D assemblies of isotropic nanoparticles can also give multi-peak spectra because of possible oscillations of electron cloud over the assembly.

Summary of this work is that tuning of optical properties of nanoparticles can be achieved effectively by in-situ assembly formation of nanoparticles.

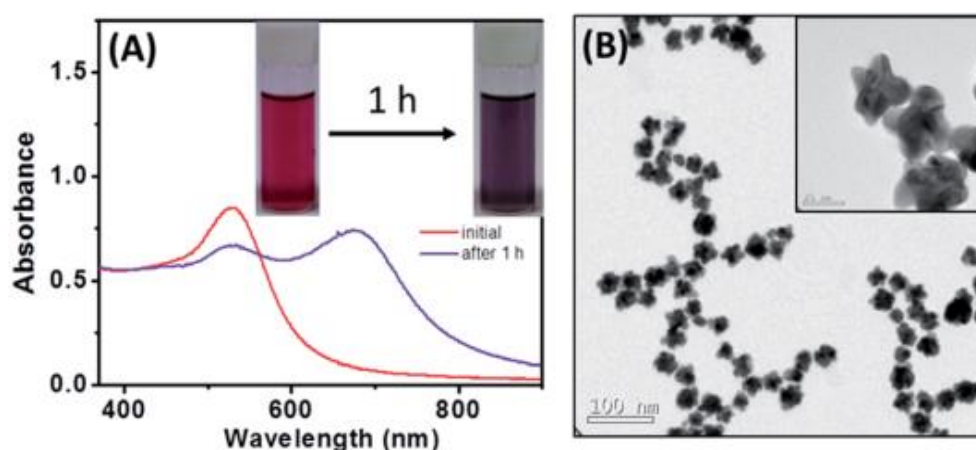


Figure 1.6 (A) Absorption spectra in the initial stages, the color of the solution appears red, while after one hour, it changes to violet. (B) corresponding TEM images

1.6.3 Isabel Pastoriza-Santos, Luis M. Liz-Marzán, “*N,N*-Dimethylformamide as a Reaction Medium for Metal Nanoparticle Synthesis”, *Advanced Function Materials*, 2009, 19(5), 679-688.

- *N,N*-dimethylformamide (DMF) is used as a solvent and for the reduction of metal salts, primarily Au and Ag.
- In addition to describing DMF’s capacity to decrease metal salts, this study also examines how various parameters affect particle shape.
- The modification of the optical response in colloids with variable size and shape metal nanoparticles based on DMF is briefly described.

Summary of this work is that Aprotic solvent DMF can be effectively used as a reducing agent for Hydro-chloroauric acid to synthesize gold nanoparticles and Conformation of DMF molecule in reaction medium is deciding factor in shape/size evaluation.

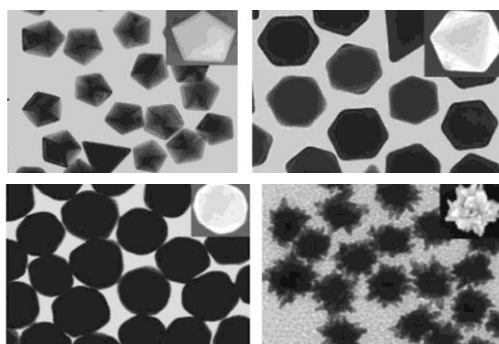


Figure 1.7 TEM images of different anisotropic shaped gold nanoparticles

1.7 Motivation of Current Research Work

- Based on our literature review, we have learnt that various applications of metal nanoparticles are highly dependent on optical properties exhibited by the nano-colloid.
- Tuning of optical properties of nanoparticles can be done not only by manipulating morphology of nanoparticles but can also be achieved by assembly formation of metal nanoparticles.
- DMF solvent at Kinetically favourable points can be used effectively as reducing agents for metal salts.
- Complexation of DMF with protic solvents like water & alcohols at different pH can alter reducing as well as capping capabilities of complex which effectively determines the morphology hence optical properties of gold nanoparticles.

CHAPTER 2

MATERIALS AND METHODOLOGY

2.1 Chemicals Used

Untreated samples of $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ (tetrachloroauric (III) acid), sodium hydroxide (NaOH), and methyl alcohol (CH_3OH) were used in their original states without any alterations. Deionized water (DI) was employed as a solvent for the experimental procedure.

N,N-Dimethylformamide (DMF) is highly regarded for its significant synthetic utility, which stems from its wide array of advantageous properties. These properties encompass a wide temperature range for liquids, high stability against chemical and thermal influences, significant polarity, and a broad solubility range for both organic and inorganic compounds[30]. DMF finds extensive use in various synthetic processes owing to these desirable characteristics. This strong and versatile molecule has been employed as a solvent in a vast array of synthetic processes. As per the studies, DMF can work as a reducing agent to reduce gold ions under the right circumstances, even at room temperature[31].

2.2 Sample Preparations

A total of 3.3978 grams of HAuCl_4 was introduced into 100 mL of deionized water (DI water) to produce a stock solution with a concentration of 500 mM for tetrachloroauric acid. Similarly, 199.985 milligrams of NaOH was dissolved in 10 mL of DI water to create a stock solution with a concentration of 500 mM for sodium hydroxide (NaOH). For the solvent mixture, 1 mL of DI water was combined with 4 mL of N,N-Dimethylformamide (DMF) in small test tube glass bottles at room temperature. 0, 20, 100 & 200 microlitres of 500mM NaOH stock solution was taken using a micro pipette which is equivalent to 1, 2, 10, 20 mM NaOH solution respectively. They are labelled as 3A, 3B, 3C, 3D respectively. Furthermore, 0.015 mL

of 500 mM HAuCl_4 stock solution (i.e. equivalent to 0.3 mM HAuCl_4) was added to the solution. Nanoparticles Synthesis was visually confirmed by change in color of precursor solution with course of time. More homogeneous and symmetrical nanoparticles are formed as a result of the prolonged, continuous reduction of gold nanoparticles. For subsequent analysis, these samples were kept at room temperature. Figure 2.1 shows the prepared sample before colour shift.

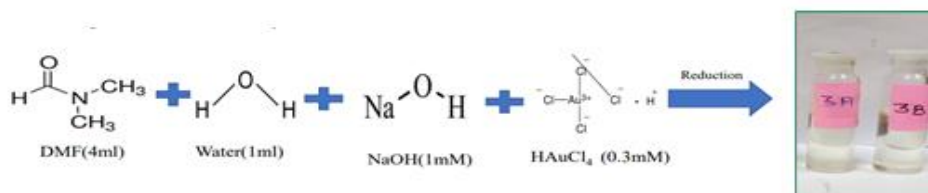


Figure 2.1 Schematic illustration of sample preparations

2.3 Synthesis of gold nanoparticles

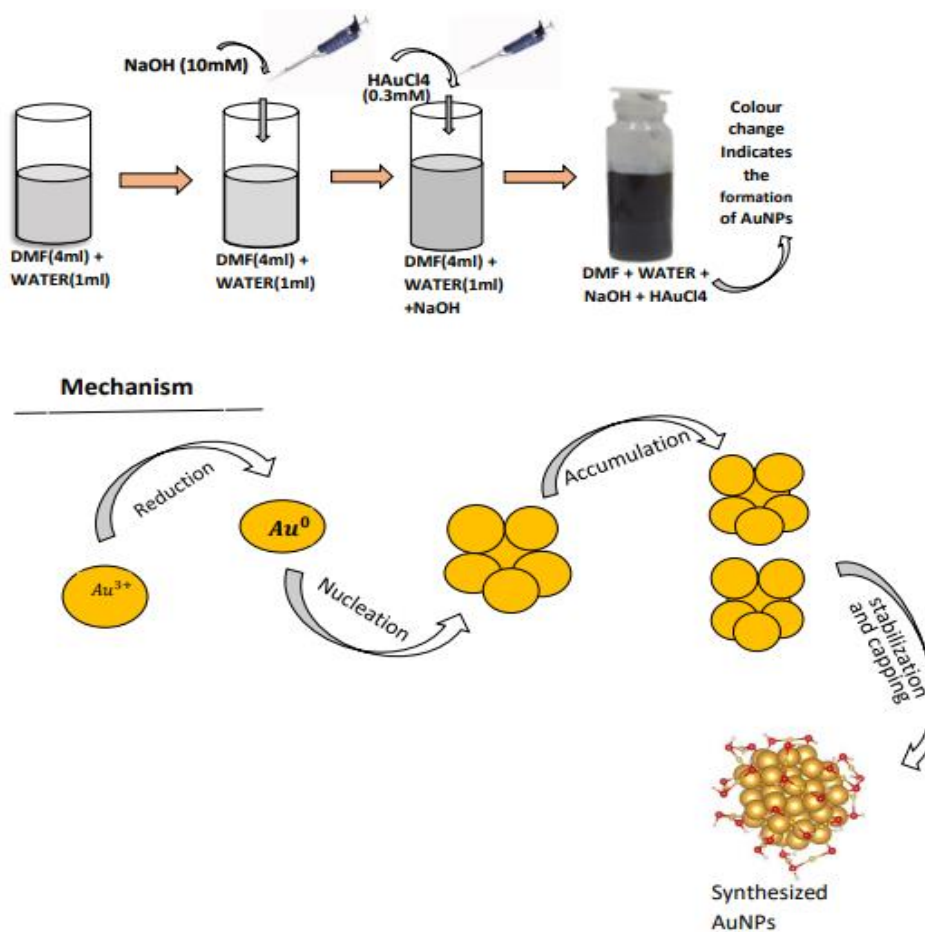


Figure 2.2 Schematic explanation of synthesis of gold nanoparticles

Trivalent Au^{3+} ions is reduced to zerovalent Au^0 atoms and coalesce of these zerovalent atoms leads to nanoparticle formation.

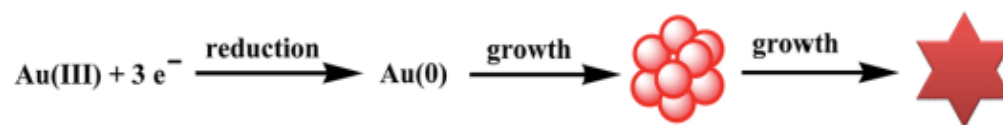


Figure 2.3 Schematic illustration of reduction of gold nanoparticles

CHAPTER 3

CHARACTERIZATION AND DISCUSSION

3.1 UV–Vis Absorption Spectra

The UV-visible spectrum displays surface plasmon resonance band of gold nanoparticles, which is influenced by various factors including their size, shape, refractive index, and interactions with the substrate. Through experimentation, it has been observed that the highest peak of plasmon resonance for gold nanoparticles can vary between 520 and 565 nm, depending on the average particle size.

Figure 3.1 shows the UV-Vis absorption spectra of samples 3A, 3B, 3C and 3D for different concentrations of NaOH i.e. 1mM, 2mM, 10mM and 20mM respectively with solvent complexation of DMF & Water (4mL+1mL).

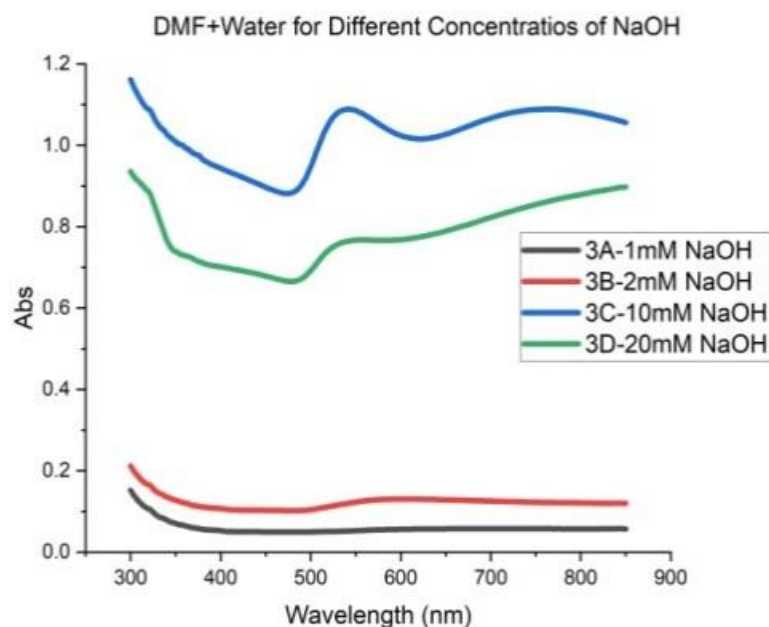


Figure 3.1 UV–Vis Absorption Spectra of samples 3A,3B,3C & 3D

After approximately 2 minutes, the solution exhibited a light blue color, indicating the formation of metal nanoparticles. Over the course of 1 hour, the color of the solution gradually transitioned to a dark blue hue.

The SPR band of colloid 3B, 3C & 3D occurs at 526, 534 & 545 nm respectively. The Surface Plasmon Resonance occurring in the plane is what causes this long-wavelength absorption, which exhibits a significant difference in the morphology of the AuNPs. In the case of 3C and 3D the existence of two well-defined surface plasmon bands at 540 nm and 750 nm signifies the formation of a nanoparticle assembly. These plasmon bands correspond to distinct modes of plasmon oscillations, namely the transverse and longitudinal modes, respectively. The transverse plasmon band at the lower wavelength (higher energy) is attributed to the metallic nanoparticle core, while the longitudinal band at the higher wavelength (lower energy) is induced by the surface tips or edges.

Furthermore, compared to other known anisotropic branched or multipod gold nanostructures, the (DMF + Water) solvent complexation results in a significantly higher number, sharpness, and length of the tip-like structures. This attribute amplifies and extends the longitudinal plasmon band into the near-infrared (IR) region.

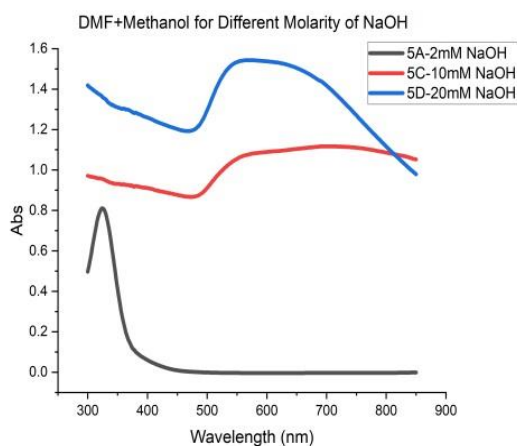


Figure 3.2 UV–Vis Absorption Spectra of samples 5A,5C & 5D

In case of DMF & Methanol complexation (Figure 3.2), the gap between transverse and longitudinal peaks is very less compared to that of Figure 3.1. Therefore the extent of assembly formation of nanoparticles is much less in case of DMF & Methanol complexation. Also the concentration of NaOH with DMF & Methanol is changing the final colloidal morphology as illustrated by the absorption spectra.

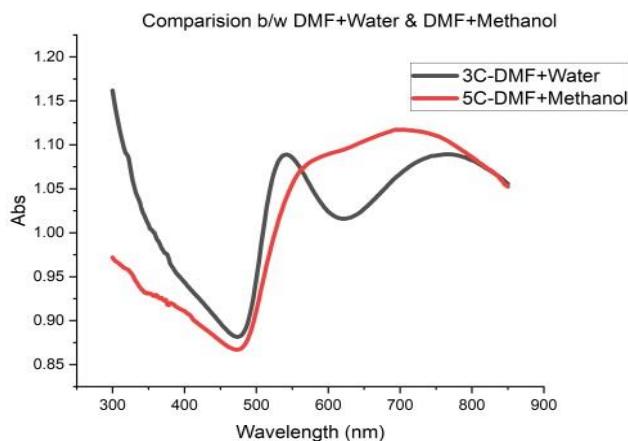


Figure 3.3 Comparison of UV–Vis Absorption Spectra of samples 3C & 5C

3.2 Effect of pH

The pH of a solution greatly affects the ability to control the size and shape of gold nanoparticles. Varying the concentration of NaOH in the solution alters its pH, resulting in a change in the absorption intensity of colloids. Specifically, increasing the concentration of NaOH (and subsequently raising the pH) leads to an increase in the absorption intensity of the colloidal solution. Figure 3.4 shows the change in absorption maxima with increase in NaOH concentration. The Absorption Maxima Peak shows Bathochromic Shift (Red Shift) for increase in concentration. NaOH dictates the complexation of DMF with other solvents hence it decides the final colloidal morphology (shape, size, assembly formation etc) of gold nanoparticles. These spectral changes could be attributed to the extent of assembly formation of metal nanostructures which can be detailed through further studies.

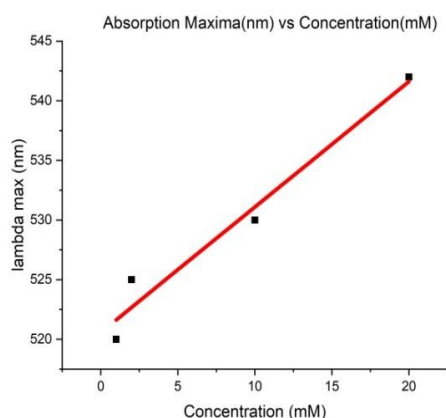


Figure 3.4 Plot of Absorption maxima vs concentration

3.3 FTIR Spectroscopy Analysis

The term "Fourier transform infrared" (FTIR) represents the commonly used technique in infrared spectroscopy. Infrared spectroscopy methods rely on the principle that certain infrared radiation is absorbed as it passes through a material. By analyzing the radiation that enters the sample, valuable information about the sample can be obtained. These spectroscopic measurements can be utilized to identify and distinguish between different molecules, as each molecule emits a unique spectrum based on its specific structure.

Covalent bonds present within molecules possess the ability to selectively absorb light at particular wavelengths, resulting in changes in the vibrational energy of the bond. The type of vibration, such as stretching or bending, induced by the interaction with infrared radiation depends on the nature of the atoms involved in the bond. Due to these variations, different molecules exhibit distinct transmittance patterns, as specific bonds and functional groups absorb particular frequencies. The representation of the spectrum involves plotting the wavenumber (cm^{-1}), which indicates the energy of molecular bond vibrations, on the X-axis, while the transmittance is plotted on the Y-axis. Analyzing the spectrum entails identifying the groups and bonds associated with each peak.

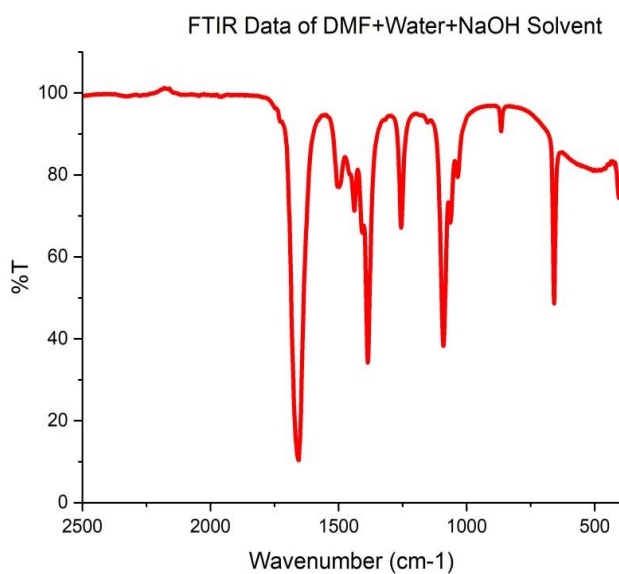


Figure 3.5 FTIR spectra of DMF+Water+NaOH solvent

Table 3.1 Table of observed peaks from the FTIR spectra

SR. NO.	OBSERVED PEAKS	PEAK ASSIGNMENT
1	1654	symmetric (c=o) stretch
2	1498	ring (C-N) stretch
3	1438	CH bending , C-N ring stretch
4	1408	CH bending , C-N ring stretch
5	1386	C-H bend + Ring (CH ₂) wag + C-N stretch
6	1255	CH ₂ twist + CN stretch
7	1091	CN stretch
8	1063	CN stretch
9	865	C-C ring
10	658	(N-C=O) bend

Table 3.1 presents the selective FTIR peaks observed for the (DMF+Water+NaOH) solvent, highlighting the remarkable complexing ability of DMF. In the case of DMF in Water, several notable changes are observed. The observed changes in the spectrum include a progressive rise in frequencies associated with C–N stretching and a notable decrease in the absorption frequency of C=O. These modifications, along with variations in other peaks mentioned in the table, can be attributed to dipole-dipole interactions and hydrogen bonding occurring between DMF and water. These interactions contribute to the strengthening of the C–N bond in DMF. Further investigations will be conducted to examine the complexation of DMF with water and alcohols under different pH conditions.

CHAPTER 4

RESULTS AND CONCLUSIONS

Highly efficient gold nanoparticles were successfully synthesized, and the formation of nanoparticles with course or time was confirmed with the help of absorption spectra. The broad nature of longitudinal peak established the assembly formation of nanoparticles. It's not the anisotropic shape which is evolving but it's the assembly formation which is creating this type of optical response.

In case of DMF & Water complexation the longitudinal peak was observed at 765nm but in case of DMF & Methanol complexation the longitudinal peak was blue shifting at 692nm so it establishes that the extent of assembly formation of gold nanoparticles is less in case of methanol.

NaOH dictates the complexation of DMF with other solvents. By increasing the concentration of NaOH , the complexation of DMF is changing and therefore the final colloidal morphology is changing.

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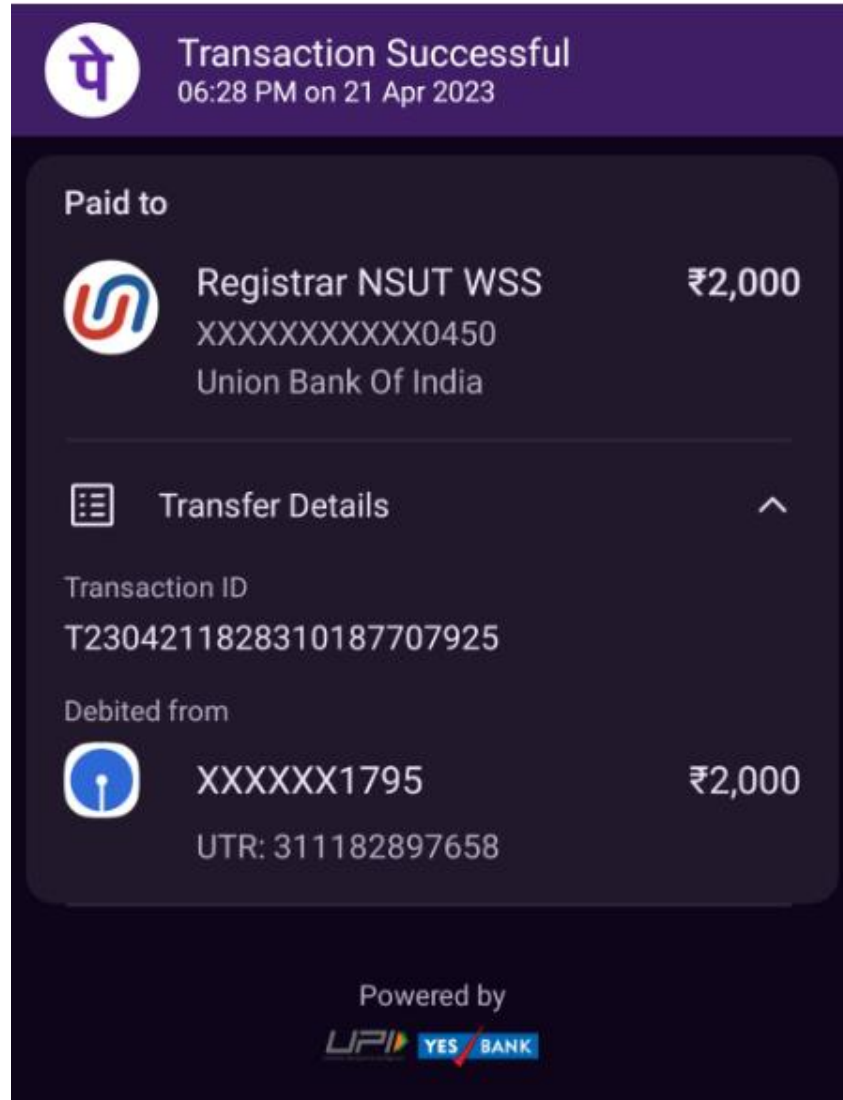
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CONFERENCE PAPER

Solvent Complexation Triggered Synthesis of Gold Nanoparticles

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ABSTRACT

The novel room temperature wet chemical synthesis method for the reduction of hydro-chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) leading to the formation of distinct anisotropic size/shaped gold nanoparticles is largely dictated by conformational changes in the solvent complexation of Dimethylformamide (DMF) in aqueous as well as alcoholic solvents. A strong surface plasmon resonance (SPR) band in visible region, that is induced when the oscillation frequency of free electrons of the gold nanoparticles resonates with the frequency of incident light, indicates the formation of gold nanoparticles. The complexation of DMF with protic solvents like water and alcohols at different pH alters the reducing as well as capping capabilities of complex for hydro-chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$). Variation of optical properties of thus synthesized gold nanoparticles was quantitatively studied with UV-Vis absorption spectroscopy along with formation mechanism elucidated with FTIR measurements.

Keywords: Gold nanoparticles; Surface Plasmon Resonance; Dimethylformamide; Solvent Complexation in Wet Chemical Synthesis