

**SHAPE CONTROLLED SYNTHESIS OF GOLD NANOPARTICLES BY
TWEAKING OF PVP AND THEIR DYE DEGRADATION CAPABILITY**

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE AWARD OF THE DEGREE

**MASTERS OF SCIENCE
IN
PHYSICS**

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SACHIN



SHUBHAM PAL

ABSTRACT

Significant progress has already been made in developing synthetic methods for synthesizing nanoparticles of various sizes and morphologies over the last few decades, and a considerable number of recent studies have been devoted to the characterization and applications of metal nanoparticles. This research has looked into the synthesis of gold nanoparticles using the polymer poly(N-vinyl-2-pyrrolidone) (PVP). PVP's ability to reduce and capping nanoparticles determines their ultimate form after wet chemical synthesis. The conjugation behaviour of polymer PVP with solvent molecules and halide ions can change its ambient nature. Different shaped gold nanospheres, nanotriangles, and nano stars were synthesized by tweaking the reduction of gold precursor (Hydro-Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)) by PVP. The synthesized nanoparticles were characterized using UV–Vis absorption spectra, Transmission Electron Microscopy (TEM), and X-ray diffraction studies. Peaks in absorption spectra originating from localized surface plasmon resonance (LSPR) were well correlated with electron microscope images and reaction kinetics. Diffraction peaks obtained in XRD studies confirm the crystallization of nanoparticles in the fcc structure, while other structural parameters calculated reveal the differential shape growth.

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III. LIST OF SYMBOLS & ABBREVIATION

Symbol/Index	Meaning/Abbreviation
AU	Gold
NPs	Nanoparticles
GNPs	Gold Nanoparticles
PVP	Poly(N-vinyl-2-pyrrolidone)
DMF	Dimethyl Formamide
TEM	Transmission Electron Microscopy
SPR	Surface Plasmon Resonance
LSPR	Localized Surface plasmon Resonance
XRD	X-Ray Diffraction
UV	Ultraviolet
$HAuCl_4$	Hydro chloroauric acid
<i>CTAB</i>	Cetyl-trimethylammonium bromide
$LiAlH_4$	Lithium aluminium hydride
$NaBH_4$	Sodium borohydride
SDS	Sodium ethylene glycol
NaOH	Sodium hydroxide
NaBr	Sodium bromide
λ	Wavelength
D	Crystallite size
2θ	Peak position
β	Full width Half Maxima
ε	Micro strain

Chapter 1

Introduction

The physical, chemical, optical, and electrical properties of nanomaterials are influenced by their size, shape, and surface morphology. Because of its distinct and tunable Surface Plasmon resonance (SPR) and different applications such as sensing (such as SERS and SEIRA), catalysis/ dye degradation, medicinal science, and others, gold nanoparticles play a critical role in today's research. According to a large body of evidence, the morphology of gold nanocrystals determines its localised surface plasmon resonance (LSPR) position, spectrum area, and mode strength [1].

Nanoparticles are the most advanced nanomaterials, despite taking the greatest time to produce. Because of their unique properties, nanoparticles and nanotechnology are widely used and serve an essential role in a variety of disciplines, including health, biology, physics, chemistry, and sensing. Noble-metal nanoparticles (Cu, Hg, Ag, Pt, and Au) have attracted a lot of attention from scientists in comparison to other metal nanoparticles. The most stable of them are nano-spheres, nano-rods, and nano-tubes, as well as nano-branches, nano-flowers, nano-shells, nano-wires, and nano-cages (figure 1). They also feature a number of optical properties that can be changed.

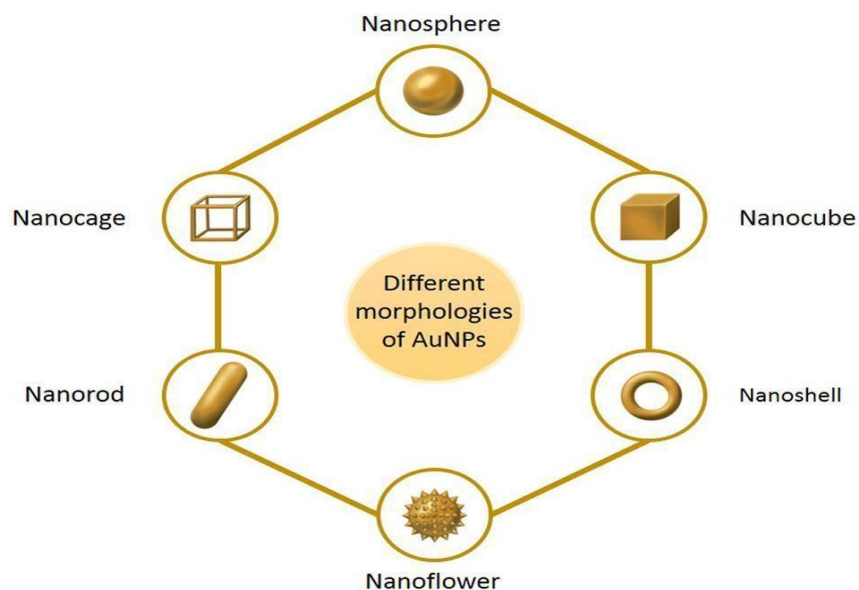


Fig.1 The main morphologies of AuNPs

The synthesis of gold nanoparticles with controlled morphology, such as spheres, rods, prisms, triangles, cubes, and nanorods, is encouraged by their size/shape unique optical properties, which have many predicted future applications in catalyst, nanoscience, optical devices, photon transport, and surface-enhanced Raman scattering [2,3]. To obtain crystallographic facet control, every physical or chemical technique for manufacturing nanostructures requires precision tuning of nucleation and growth processes [4, 5]. The wet chemical approach is employed to synthesise gold nanoparticles in this research because it allows for excellent control over nucleation/growth at the atomic level. As a result, wet chemically produced shape-controlled gold nanoparticles have well-defined surfaces and morphologies. The shape controlled synthesis of nanoparticles is generally achieved by using several capping agents. The capping chemicals can adsorb on certain crystal facets, restricting growth lacks/proceeds in specific crystal faces and therefore determining the size/shape of the resultant nanoparticles [6].

Due to its unique reduction and stability characteristics, the flexible polymer PVP was used in the synthesis of gold nanoparticles in this work, and a variety of odd shapes were generated by modifying various reaction conditions. XRD studies are extremely effective for assessing the crystallinity of gold nanoparticles since they demonstrate that the nanoparticles are naturally crystalline. Crystallite sizes calculated by the Debye-scherrer formula are congruent with TEM micrographs. Metal nanoparticles' photo-catalytic activity has recently received a lot of interest since, in the case of metal catalysts, it exhibits the properties of destroying organic molecules when exposed to solar light. This approach is less costly than prior techniques and has no negative side effects. Dye and other pollutant photo-catalysis is an excellent wastewater treatment technology [7]. The catalytic activity of Au-NPs was determined in this study by the degradation of Crystal Violet dye with NaBH₄.

1.1 Overview of the Thesis

To present the information, research methods, and findings in a systematic manner, our work has been divided into chapters and parts. The first chapters describe the fundamentals and analytical segments of our work. The findings and discussions will be discussed later. A closing chapter outlines the work and leaves room for change and potential reach.

The first chapter provided the reader with a general overview of the field of Nanoparticles, as well as a discussion of the importance of properties of nanoparticles in advancing science and technology and also in the field of medical sciences.

The Literature Review is introduced in Chapter 2. In order to provide a fundamental grasp of Surface Plasmon Resonance (SPR), LaMer's Mechanism is investigated. The diverse materials and fabrication procedures used to synthesize Gold Nanoparticles (GNPs) are discussed, as well as the applications.

The experimental work, material synthesis, and characterization are discussed in Chapter 3.

Chapter 4, discussed about the final synthesized gold nanoparticles that are proposed, its morphology, calculated parameters and also contains the complete analysis of the size/shape evolution of synthesized nanoparticles and their dye degradation capability.

References are included so that the reader can look at relevant and well-known works linked to this work.

Chapter 2

2.1 Surface Plasmon Resonance

The most striking phenomenon encountered in these nanostructures are the electromagnetic resonances due to collective oscillations of the surface electrons, termed as '*plasmons*' or to be precise '*surface plasmons*'. When frequency of this plasmonic oscillation matches with frequency of incident electromagnetic wave then resonance takes place and this resonance is called Localized surface plasmon resonance.

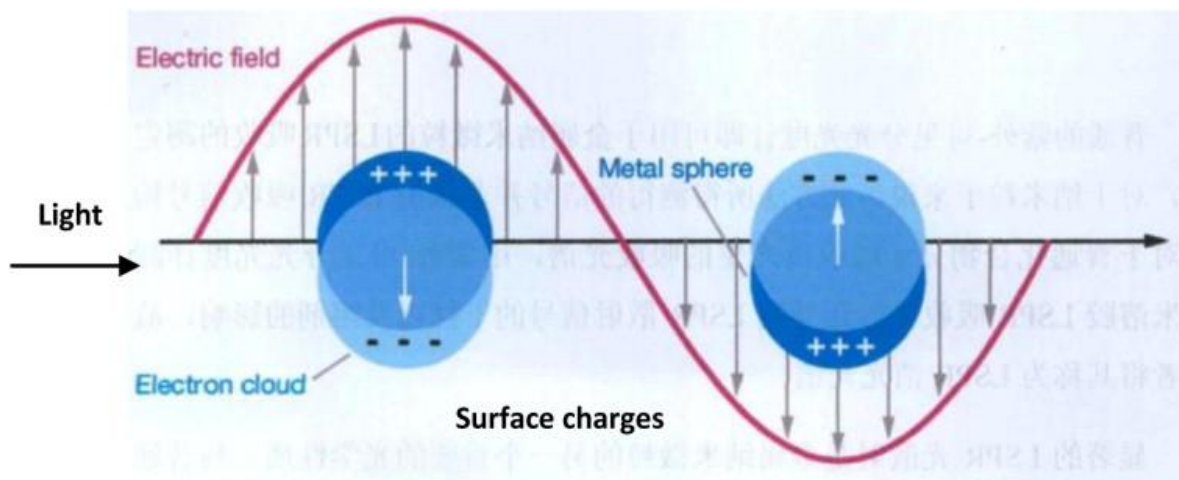


Fig.2 Surface Plasmon Resonance

Because the wave is generated at the conductor's interface with the external medium (such as air, water, or vacuum), any change inside that boundary, such as molecule deposition on the conducting surface, causes the oscillations to become exceedingly sensitive. Localised surface plasmon resonances (LSPRs) are light-excited collective electron charge oscillations in metallic nanoparticles. At the resonance wavelength, they exhibit a greater near-field amplitude. The LSPR's spatial resolution (subwavelength) is fully limited by the size of the nanoparticles, indicating localization. LSPRs improve amplitude-dependent phenomena like the magneto-optical effect by increasing field amplitude.

2.2 LaMer's Mechanism

Nanoparticles synthesis is typically described using the LaMer mechanism. In two phases, a process that mimics the LaMer's mechanism can be explained. The monomer is produced and accumulates in solution, causing it to become supersaturated, but no particles are present. The mechanism continues to grow nanoparticles without any extra nucleation in stage III. After the precursor is depleted, the Ostwald ripening process, in which bigger particles develop at the expense of smaller particles, lowers the overall surface energy of the system.

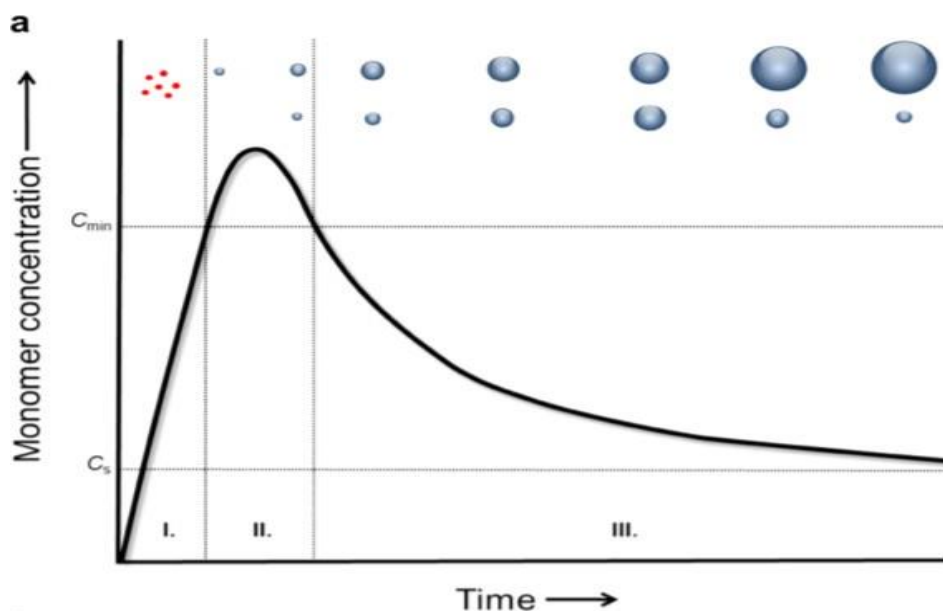


Fig 3 LaMer's mechanism

2.3 Influence of ligand on shape and size

The capping substance has a considerable influence on the form and size of the resultant nanoparticles during the development stage. As a result, ligands/surfactants play a crucial role in nano-particle control by permitting the stable formation of a wide range of thermodynamically unfavourable anisotropic nano-particles. In the absence of a counteracting force, the van der Waals force pulls colloidal metallic nanoparticles to one another. As a result, one of the most difficult challenges in managing nanoparticle form is overcoming this attractive pull.

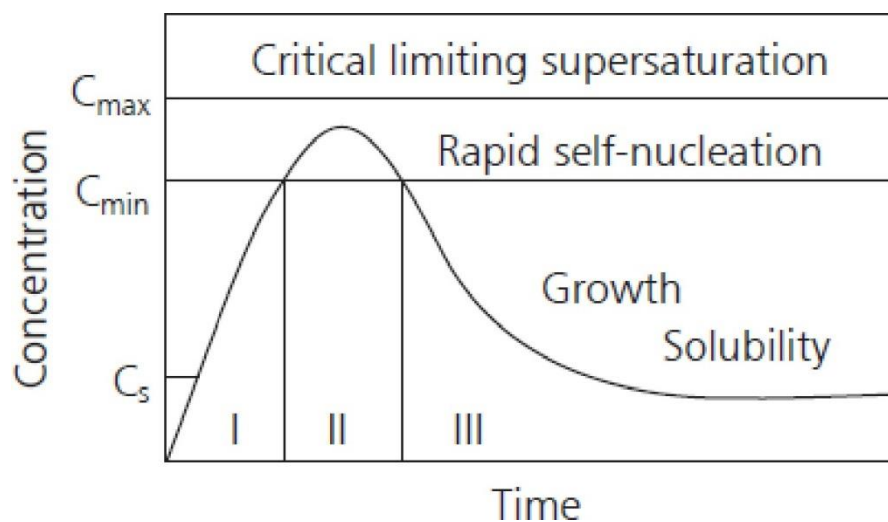


Fig 4 nucleation and Growth mechanism

Through electrostatic and/or steric stabilisation, a variety of capping agents can be utilised to balance these attraction forces. The type of capping agent used is influenced by the metal, predicted shape, and intended use of the nanoparticles.

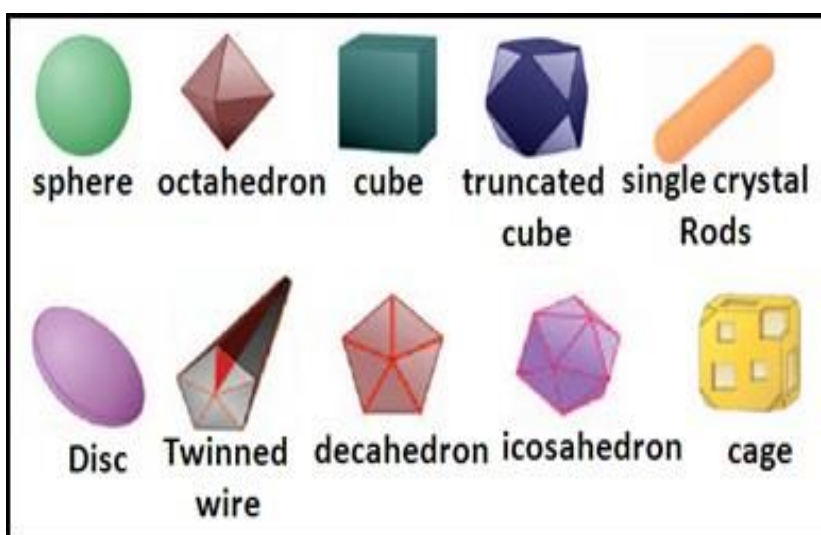


Fig.5 Different shape of nanoparticles by the effect of ligand

2.4 Synthesis of Nanoparticles

Two approaches for synthesizing distinct Au-NPs are the "bottom up" methodology and the "top down" method. Processes including "nano-sphere lithography, chemical, photochemical, electrochemical, templating, sono-chemical, and thermal reduction" are part of the bottom-up approach. The purpose of this approach is to assemble atoms (produced during ion reduction) into suitable nanostructures.

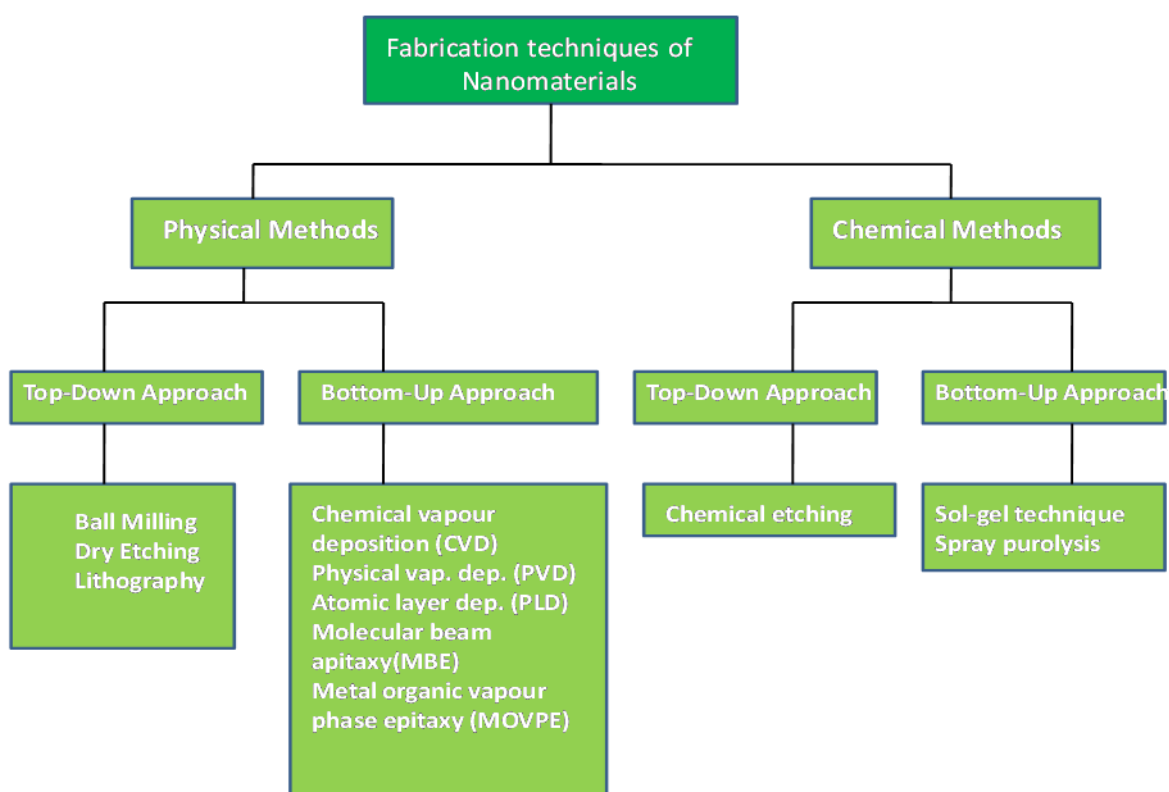


Fig.6 Synthesis of nanoparticles

2.5 Top - Down Approach

The top-down method is a subtractive method that begins with cutting raw material and culminates with self-assembled nano-scale objects. Micro-patterning and photo-lithography are the most common procedures. They used conventional and soft lithographical methods to demonstrate micro-patterning of a single layer of nanoparticles and micelles. The method was called -contact (micro-contact) de-printing, and it allowed researchers to swiftly and cheaply synthesise nanoparticles on a variety of surfaces. This category includes physical processes such as pyrolysis, lithography, thermo-lysis, and radiation-induced procedures. Another major method for making noble metal nanoparticles is pyro-lysis. Pyro-lysis comprises four major stages, as indicated in (fig.7), ranging from the creation of drops from a precursor solution to the synthesis of solid particles. To summarise, when it comes to managing the surface and structure of Au-NPs, which has a significant influence on their physical and chemical characteristics, the top-down technique has significant limitations. The size distribution is uncontrollable, and maintaining high-pressure and high-temperature conditions during these synthetic processes is energy intensive. As a result, meeting product requirements is both costly and time-consuming.

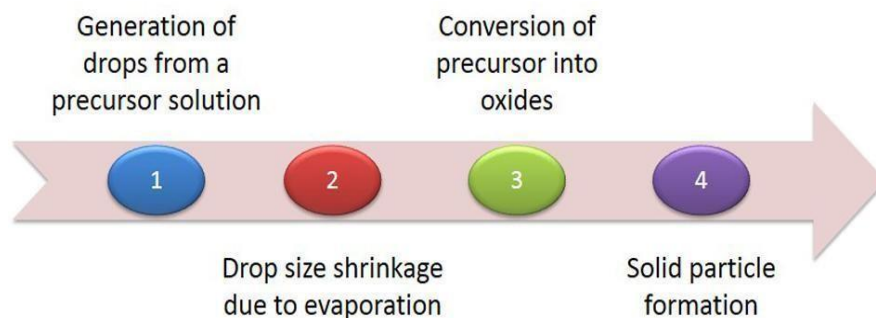


Fig.7 The four major steps of pyro-lysis

2.6 Bottom – Up Approach

Because AuNPs are such a common substance, they are likely to have a wide range of applications. However, with existing synthesis procedures, their yield is unacceptably low. In order to achieve technological scale manufacturing, the focus of research has switched to inventing more convenient and adaptable techniques to boost their preparation efficiency. The bottom–up approach has gained popularity in recent years.

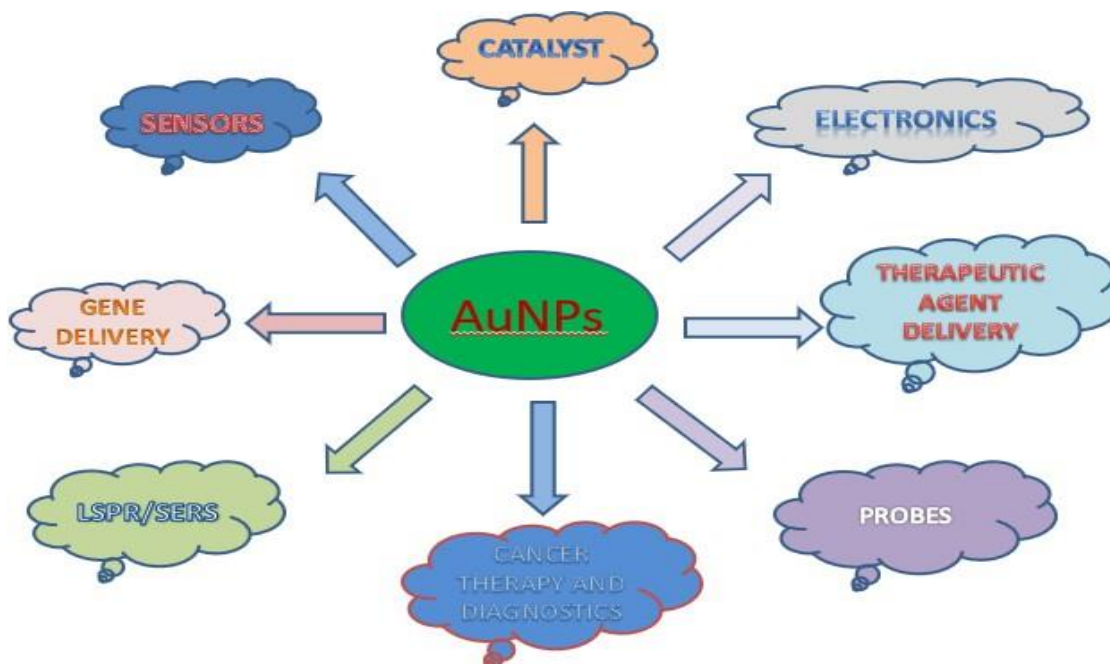
Bottom–up synthesis may be classified into three categories:

- physical methods such as laser ablation, sputter de-position, ion im-plantation, -ir-radiation, optical lithography, micro-wave (MW), ultra-sonic (US), and ultra-violet (UV) ir-radiation
- Chemical reduction of metal ions in solutions by adding chemical agents and stabilizers like Na-OH, Na-BH₄, C-TAB, Li-AlH₄, SDS, EG, and sodium citrate
- extracts from diverse plants are examples of biological techniques (leaves, stem, flower, fruits, peel, bark, and root).

2.7 Application of Gold Nanoparticles

Gold nanoparticles are versatile materials that can be employed for a variety of purposes. Researchers coated gold particles with DNA and put them into plants or cells. Ascertain that some genetic material enters and alters the cells.

Therapeutic Agent Delivery - The surface of gold nanoparticles can be coated with therapeutic chemicals. Due to their enormous surface area-to-volume ratio, gold nanoparticles can be coated



with hundreds of molecules (including therapeutics, targeting agents, and anti-fouling polymers).

Fig.8 Application of AuNPs

Sensor: These particles can be found in a variety of sensors.

Probes - When viewed under dark-field microscopy, gold nanoparticles scatter light and produce a variety of intriguing hues. The distributed colours of gold nanoparticles are currently being used in biological imaging applications. Furthermore, gold nanoparticles can be employed as transmission electron microscopy probes due to their density.

Cancer therapy and Diagnostics– Au nanoparticles are also used to discover biomarkers and detect heart problems, cancers, and infectious pathogens. They're also widely used in lateral flow immunoassays, such as the home pregnancy test.

Catalysis – In a variety of chemical processes, GNPs are utilised as catalysts. A gold nanoparticle surface can be employed for selective oxidation or, in some situations, to accelerate a process (nitrogen oxides). Fuel cells are being created with gold nanoparticles. These

developments might help the automobile and display industries.

Gene Delivery – Au-NPs have the potential to load nucleic acids in gene delivery via direct conjugation or adsorption via pre-grafted cationic polymeric stabilizers. Au-NPs can be functionalized with a variety of polymeric or biological ligands due to their unique chemical properties, resulting in stable and biologically beneficial multifunctional colloidal systems.

Chapter 3

3.1 Material synthesis

Aldrich chemicals provided the PVP, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, and Na-Br, which were utilized as received. Methanol and DMF from Merck were procured and used without further purification. 0.25 mM aqueous hydro-chloroauric acid ($\text{H-Au-Cl}_4 \cdot 3\text{H}_2\text{O}$) was mixed with 15 mL of 10 mM poly-vinyl-pyrrolidone (PVP average MW = 10,000) solution in methanol and stored at room temperature in a typical manufacture of gold spherical nanoparticles. The transformation of light yellow to ruby red fluid after 4 hours of reaction demonstrates the creation of gold spherical nanoparticles. Mixing a 0.25 mM aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with 15 mL of a 10 mM PVP solution in DMF yielded star-shaped nano-particles. The generation of gold star-shaped nanoparticles is shown by the shift of pale yellow to light blue solution within 12 hours of the reaction. Before adding 0.25 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to the PVP– methanol (10 mM) solution to make gold nanotriangles, 1.5 mM NaBr was added.

The formation of anisotropic nanoparticles was necessitated by slow reaction kinetics (about 60 hours) found in this example.

3.2 Characterization

The UV-3101PC UV–VIS–NIR spectrophotometer was used to detect optical absorption in the wavelength range of 200–1100 nm. The FEI-Tecnaï G2 system was used to obtain TEM images at a 300 kV accelerating voltage. A Bruker D-8 Advance X-ray diffractometer was used to collect XRD spectra. For a typical dye-degradation process, 600 μL of 1 mM stock Crystal violet solution was well mixed in 4 mL of triple-distilled water. 600 μL of ice cold NaBH_4 was added and stirred vigorously. Finally, different volumes of Au-NP solution (nano-spheres, nano-stars, and nano-triangles) were added to the reaction mixture at various periods, while the number of Au particles remained constant.

Chapter 4

Result and Discussion

The nucleation and growth phases of crystallization influence the form and size of nanoparticles. The polymer Poly-vinyl-pyrrolidone (PVP) is utilized as a reducing and capping agent in this work. Because the oxidation potential of the polymer PVP reduces dramatically when dissolved in different solvents, such as Methanol and DMF, distinct reduction rates of gold sol were identified in the Methanol and DMF cases. The differential adsorption of PVP onto the growing facets of nano-crystals affects the development rates along the same, resulting in differing morphologies in the PVP Methanol and PVP-DMF systems.

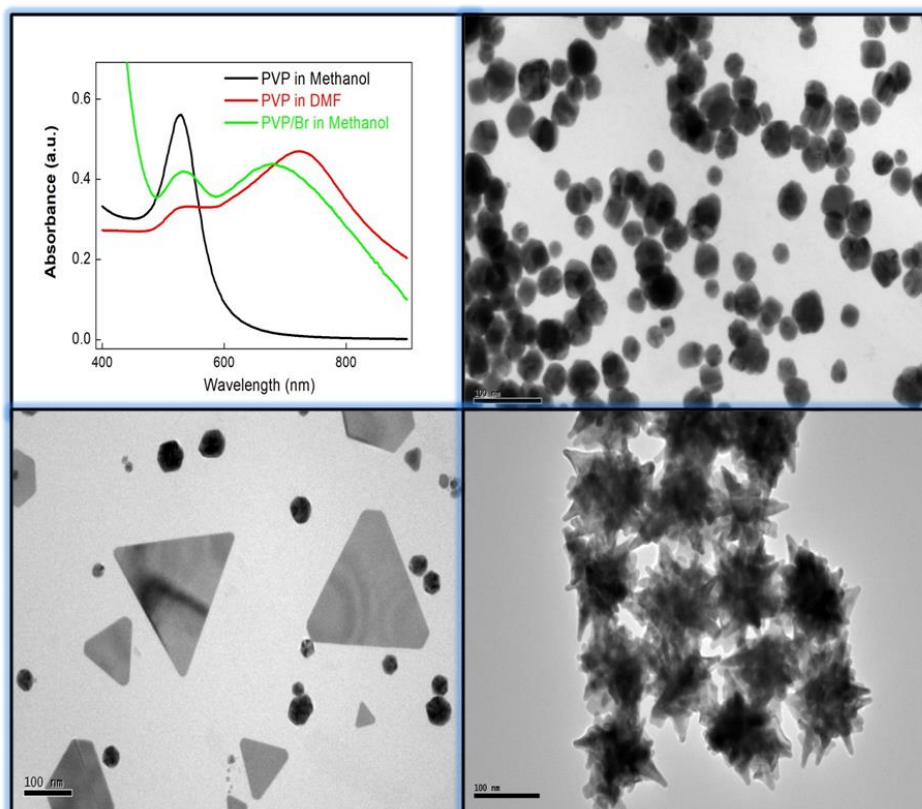


Fig 9. (a) UV – Visible absorption spectra of synthesized nanoparticles in this study. (b -d) TEM images (scale bar 100 nm) illustrating different shape evolution in different Approaches adopted in this study.

The reaction/reduction kinetics appeared to be fast when PVP was dissolved in Methanol, meaning that the synthesised nanoparticles formed/evolved in a spherical shape of roughly 30 nm, as confirmed by Absorption spectra and TEM images (Fig. 9(a) and (b)). The absorbance spectra of synthesised gold nanoparticles yield a single Plasmon resonance peak at roughly 530 nm because plasmonic oscillations on spherical shaped nanoparticles are isotropic (see Fig. 9a).

The reaction/reduction kinetics were significantly sluggish when PVP was dissolved in DMF, indicating the evolution of anisotropic structure, and further HRTEM investigations confirmed that star shaped nanoparticles were produced in this case (Fig. 9(a) and (d)). Transversal and longitudinal oscillation of surface plasmons onto an anisotropic shape in the absorption spectra of synthesized gold nanoparticles (which found to be star shape with size 90 nm as observed from TEM studies) can be attributed to dual Plasmon resonance peaks at around 530 nm and 750 nm.

To control the shape of the nanoparticles, we used the substantial tendency of halide ions to adsorb on metallic crystallographic facets during development. In general, halide ions can be chemisorbed on low-energy facets, which stimulate growth on high-energy facets, resulting in the evolution of nanoparticles with a variety of shapes [8, 9]. We have given different halide ions (particularly chloride, bromide, and iodide ions) prior to adding gold sol in the PVP-Methanol system, following these essential crystal formation requirements. There was a notable divergence in reaction kinetics for the bromide ion, indicating anisotropic shape growth in this case. Dual Plasmon resonance peaks at roughly 530 nm and 680 nm can be attributed to transversal and longitudinal oscillation of surface plasmons onto gold nanotriangles with size 140 nm in this example (confirmed from TEM studies) Figure 9.

4.1. Probing shape evolution through X-ray diffraction studies

X-ray diffractions of the resulting nanoparticles were analysed to delineate the differential crystal structure arising during the creation of distinct shaped nanoparticles. In the case of a face centred cubic structure of metallic gold, XRD investigations on all three samples exhibit diffraction peaks corresponding to (111), (200), (220), (311), and (222) facets, which match the JCPDS, file No. 04-0783. (see in Fig. 10).

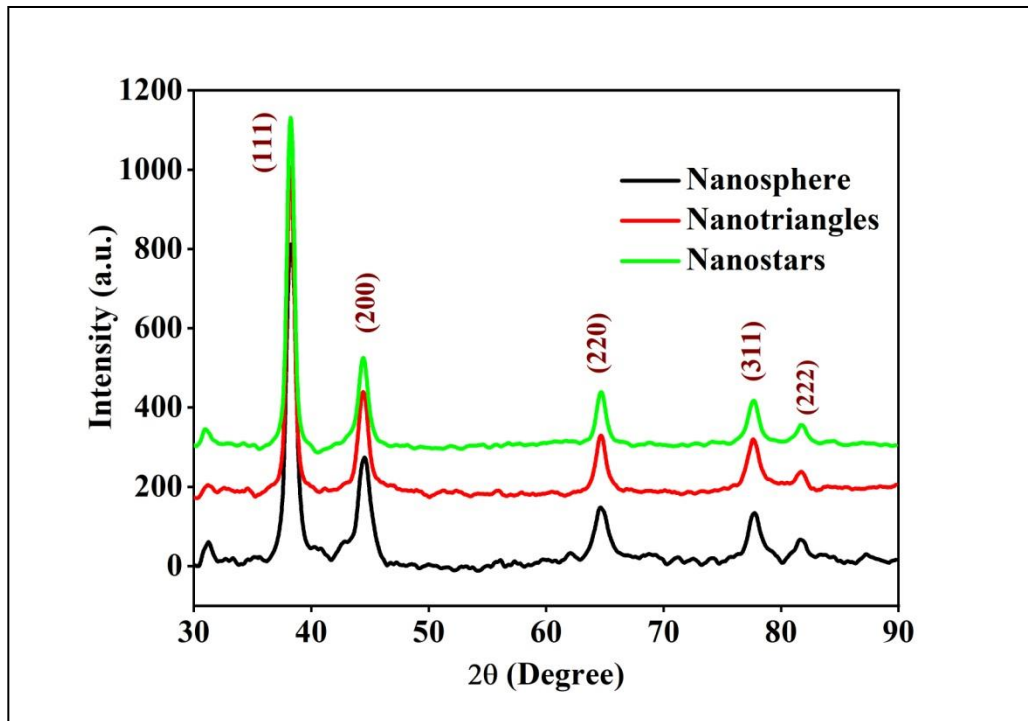


Fig 10. X-ray diffraction patterns of synthesized gold nanoparticles.

We investigated the various parameters using XRD data. Debye-equation Scherer's $D = 0.9\lambda/\beta\cos\Theta$ correlating to all peaks produces an average particle size of 07.18 nm in the case of nanospheres (see in Fig.11). D denotes crystalline size, k denotes wavelength, and β denotes Full Width at Half Maximum (FWHM). As the peaks value increases, the d -spacing values decrease. When there is a deviation from the ideal crystalline structure, XRD peak widening occurs. This broadening can be both instrumental and related to the composition of the sample.

	Sr. No.	Peak Position 2θ (degree)	Full Width Half Maxima (\AA)	Full Width Half Maxima (radians)	Crystallite Size D (nm)	d-spacing (\AA)	Micro-strain (ϵ)
Nanospheres	1	38.282	1.0026	0.01749	8.3476	2.3483	12.6043
	2	44.497	1.3681	0.02387	6.2440	2.0336	14.5929
	3	44.497	1.4897	0.02600	6.2828	1.4388	10.2608
	4	77.746	1.4391	0.02511	7.0569	1.2269	7.78974
	5	81.069	1.3008	0.02270	7.9977	1.1847	6.63737
Nanotriangles	1	38.232	0.7841	0.01368	10.6724	1.1858	12.6043
	2	44.425	1.1081	0.01934	7.7073	1.9744	14.5929
	3	64.666	1.0916	0.01905	8.5724	3.0149	10.2608
	4	77.611	1.1847	0.02067	8.5641	4.1572	7.78974
Nano stars	1	38.239	0.7470	0.01303	11.2016	2.3508	9.4031
	2	44.414	1.050	0.01832	8.1334	2.0372	11.2227
	3	64.677	1.0236	0.01789	9.1425	1.4394	7.0543
	4	77.631	1.2742	0.02223	7.9639	1.2284	6.91115
	5	81.710	1.3051	0.02277	8.0098	1.1770	6.58437

Fig 12. Various X-ray diffraction parameters of different shaped gold nanoparticles.

Microstrain is a dominant factor, defined as the root mean square of differences in lattice parameters across the sample (see Fig. 11). Crystallite size follows the same pattern as nanoparticle size acquired from TEM image in each of the examples, as shown in the XRD parameter table. The evolution of distinct shaped nanoparticles is readily explained by differential microstrain values on various planes.

4.2. Investigation of dye degradation capabilities of the prepared NPs

The Crystal-Violet CV dye (Tris(4-(dimethylamino)phenyl) methylum chloride) ($C_{25}H_{30}N_3Cl$) gives a blue-violet colour when dissolved in water [10]. CV (Tris(4-(dimethylamino)phenyl) methylum chloride) ($C_{25}H_{30}N_3Cl$) was dispersed in 8 mL double distilled water to make a 1 mM crystal violet solution. To decrease 10 mL of 1 mM dye solution, three different shaped nanoparticles were put to a reaction medium of $NaBH_4$ (2.5 mM). The concentration of gold nanoparticles in each case was kept constant at 0.05 mM by introducing different amounts of centrifuged samples to the system.

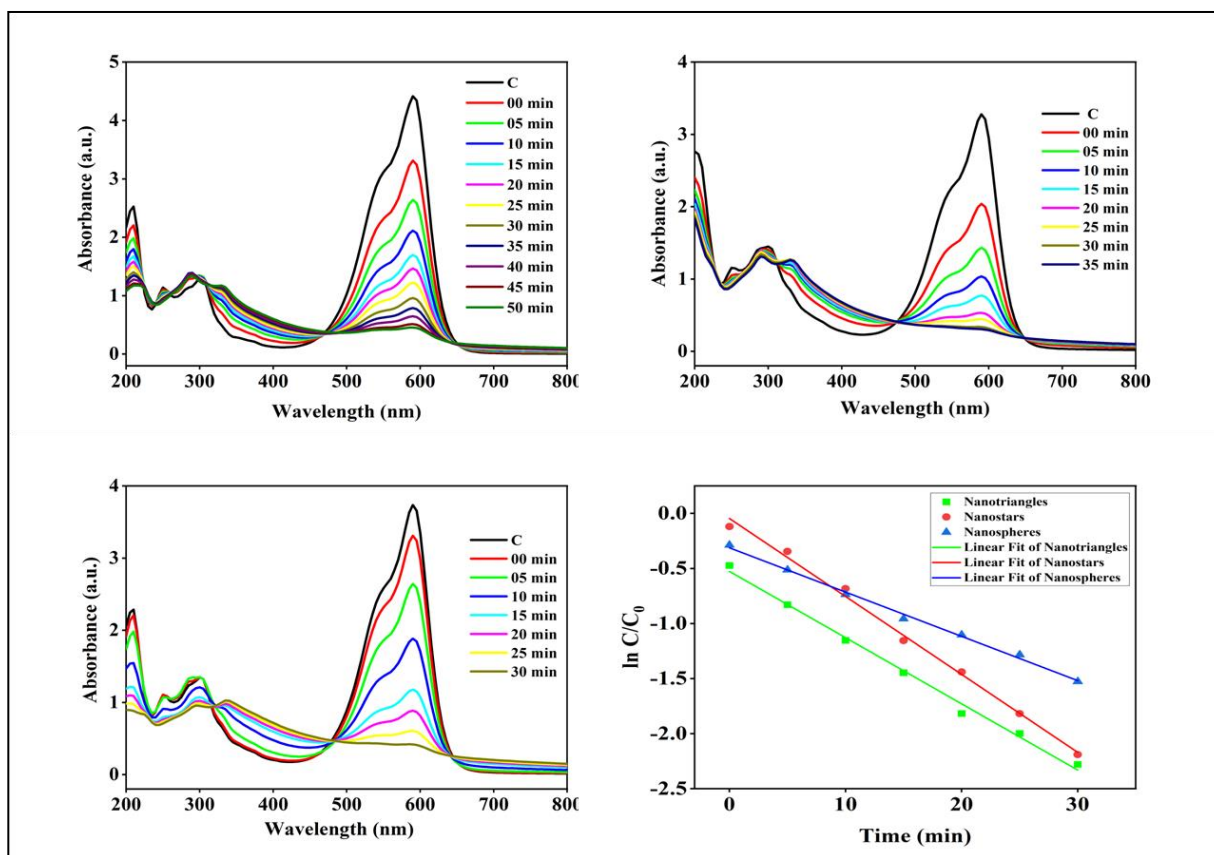


Fig. 12. (a-c) Absorption curves of CV degradation when adsorbed on different nanoparticles. (d) Rate constant curve for different nanoparticles.

The crystal violet dye shows a definite absorption at 590 nm (Fig. 12(a-c)), and when the visible light irradiation time increases to 50 minutes in the case of nano-spherical gold particles, the

intensity of the absorption maximum falls, indicating dye photodecomposition.

Crystal violet dye is totally eliminated by nano-triangle and nano-star gold particles in 30–35 minutes. The bright purple colour of the crystal violet solution fades as the irradiation period is extended, and it becomes nearly colourless. The rate constants for dye degradation were estimated by calculating the slope of first order degradation curves, and the rate constants for nanospheres, nanotriangles, and nanostars are $3.9 \times 10^{-2} \text{ min}^{-1}$, $5.5 \times 10^{-2} \text{ min}^{-1}$, and $7.0 \times 10^{-2} \text{ min}^{-1}$, respectively (Fig. 12d). Greater anisotropy in nanoparticle form appears to enhance/improve rate constant, which can be attributed to increased coordination of surface gold atoms to CV molecules.

Chapter 5

CONCLUSION

In this paper, we employed only one polymer (PVP) in several conformations to create varied shaped nanoparticles (nanospheres, nanotriangles, nanostars). Because literature reveals numerous such comparisons of different shaped nanoparticles made either by distinct synthesis procedures or by different chemical agents, it was extremely conclusive to examine the discrete effect of nanoparticle form on its dye degradation capabilities. The well-crystalline character of produced nanoparticles was confirmed by XRD measurements, and many structural parameters influence the evolution of these variously shaped nanoparticles. The first order rate constants of CV dye degradation for various shaped nanoparticles were determined, and it was discovered that nanostars, which are very anisotropic in nature, performed the best photocatalytic degradation. Furthermore, we used a chemical synthesis method in this study, which is not very environmentally friendly, so in the future, we will try to use a green synthesis approach in shape controlled synthesis and then evaluate/establish the shape contribution of the nanoparticle on its various physio-chemical properties (and thus) and study other applications like SERS and SEIRA.

REFERENCES

- [1] A. Kedia, P.S. Kumar, Solvent-adaptable poly(vinylpyrrolidone) binding induced anisotropic shape control of gold nanostructures, *J. Phys. Chem. C* 116 (44) (2012) 23721–23728.
- [2] F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, Platonic gold nanocrystals, *Angew. Chem., Int. Ed.* 43 (2004) 3673–3677.
- [3] Y. Sun, Y. Xia, Shape-controlled synthesis of gold and silver nanoparticles, *Science* 298 (5601) (2002) 2176–2179.
- [4] T.K. Sau, C.J. Murphy, Room temperature, high-yield synthesis of multiple shapes of gold nanoparticles in aqueous solution, *J. Am. Chem. Soc.* 126 (2004) 8648–8649.
- [5] P.S. Kumar, I.P. Santos, R.-B. Gonzalez, F.J. Garcia de Abajo, L.M. Liz-Marzan, High-yield synthesis and optical response of gold nanostars, *Nanotechnology* 19 (2008) 015606–15611.
- [6] M. Sajitha, A. Vindhysarumi, A. Gopi, K. Yoosaf, Shape controlled synthesis of multi-branched gold nanocrystals through a facile one-pot bifunctional biomolecular approach, *RSC Adv.* 5 (119) (2015) 98318–98324.
- [7] T. Begum, P.K. Gogoi, U. Bora, Photocatalytic degradation of crystal violet dye on the surface of Au doped TiO₂ nanoparticles, *Indian J. Chem., Technol.*, January 2017 pp. 97–101.
- [8] J. Lee, B.o. Hua, S. Park, M. Ha, Y. Lee, Z. Fan, H. Ko, Tailoring surface plasmons of high-density gold nanostar assemblies on metal films for surface-enhanced Raman spectroscopy, *Nanoscale* 6 (1) (2014) 616–623.
- [9] J. Kumar, R. Thomas, R.S. Swathi, K.G. Thomas, Au nanorod quartets and Raman signal enhancement: towards the design of plasmonic platforms, *Nanoscale* 6 (2014) 10454–10459.
- [10] N.C. Joshi, P. Gururani, S.P. Gairala, Metal oxide nanoparticles and their nanocomposite-based materials as photocatalysts in the degradation of dyes, *POA J.* 12 (5) (2022) 6557–6579.



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Shape controlled synthesis of gold nanoparticles by *tweaking* of PVP and their dye degradation capability

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ABSTRACT

During the last few decades, significant work has already been done into creating synthetic methods for producing nanoparticles of diverse sizes and morphologies, and a large number of recent characteristics have been devoted to the characterisation and uses of metal nanoparticles. The synthesis of gold nanoparticles synthesized using the polymer poly(N-vinyl-2-pyrrolidone) (PVP) was studied in this research work. Reducing and capping abilities of PVP defines the final shape of nanoparticles obtained in wet chemical synthesis. Ambient nature of polymer PVP can be manipulated by its conjugation nature with solvent molecules and halide ions. Tweaking the reduction of gold precursor (Hydro-Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)) by PVP yielded different shaped gold nanospheres, nanotriangles and nanostars. UV-Vis absorption spectra, Transmission Electron Microscopy (TEM), and X-ray diffraction studies were used to characterize the synthesized nanoparticles. Localized surface plasmon resonance (LSPR) peaks originating in absorption spectra were well correlated with electron microscopy images as well as reaction kinetics. Diffraction peaks obtained in XRD studies demonstrate the crystallization of the nanoparticles in the fcc structure, and other structural parameters calculated reveal the differential shape evolution.

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1. Introduction

Nanomaterials' size, shape, and surface morphology affect their physical, chemical, optical, and electrical characteristics. Gold nanoparticles play a crucial role in today's research because of their distinctive and tunable Surface Plasmon resonance (SPR) and various applications including sensing (such as SERS and SEIRA), catalysis/ dye degradation, biomedical science etc. A lot of research suggests that morphology of gold nanocrystals dictates its localized surface plasmon resonance (LSPR) position, spectrum region as well as strength of modes [1].

Their size/shape unique optical properties, which have many predicted future applications in catalyst, nanoscience, optical devices, photon transport, and surface-enhanced Raman scattering, encourage the synthesis of gold nanoparticles with controlled morphology, such as spheres, rods, prisms, triangles, cubes, and nanorods [2,3]. Every physical or chemical strategy for producing

nanostructures involves fine tuning of nucleation and growth processes to achieve crystallographic facet control [4,5].

In this paper, the wet chemical method is used for synthesis of gold nanoparticles because of excellent control over nucleation/growth at atomic levels in this synthesis method. So, shape controlled gold nanoparticles synthesized by wet chemical synthesis have well-defined surfaces and morphologies. Generally the use of different capping agents enables the shape controlled synthesis of nanoparticles. The capping agents can adsorb on specific crystal facets, confining growth lacks/proceeds in specific crystal faces, thus specifying the resulting nanoparticle size/shape [6]. In this study, a versatile polymer Poly(N-vinyl-2-pyrrolidone) (PVP) was used in synthesis of gold nanoparticles and because of its distinctive ability of reduction as well as stabilization, different exotic shapes were achieved by tuning various reaction parameters. XRD studies are highly useful in assessing the crystallinity of gold nanoparticles since they reveal that the nanoparticles are well crystalline in nature. The Debye-scherrer formula yields crystallite sizes that are consistent with TEM micrographs. Photocatalytic activity of metal nanoparticles has lately attracted a lot of attention since, in the case of metal catalysts, it exhibits the characteristics of

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degrading organic molecules when exposed to solar light. This approach is less costly than existing processes and produces no hazardous byproducts. Dye and other pollutant photocatalysis is an effective wastewater treatment method [7]. The catalytic activity of AuNPs was demonstrated in this study by degrading Crystal Violet dye with NaBH_4 . The catalytic properties of nanoparticles of different sizes and shapes synthesized under the above mentioned physicochemical conditions were studied.

2. Materials and methods

Poly(N-vinyl-2-pyrrolidone) (PVP), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and NaBr were obtained from Aldrich chemicals and were used as received. Merck's solvent methanol and DMF were obtained and utilized without additional purification. Herein, 0.25 mM aqueous hydro chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was combined with 15 mL of 10 mM polyvinylpyrrolidone (PVP average MW = 10,000) solution in methanol and maintained at room temperature in a typical synthesis of gold spherical nanoparticles. The change of pale yellow solution to ruby red solution over 4 h of reaction demonstrates the synthesis of gold spherical nanoparticles.

Stirring a 0.25 mM aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with 15 mL of 10 mM poly-vinyl-pyrrolidone solution in DMF yielded star-shaped nanoparticles. The synthesis of gold star-shaped nanoparticles is also indicated by the changing of pale yellow solution to light blue solution within 12 h of reaction. Prior to adding 0.25 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 1.5 mM NaBr was added to the PVP-methanol (10 mM) solution for the synthesis of gold nanotriangles. In this instance, slow reaction kinetics (about 60 h) were found, which dictated the formation of anisotropic nanoparticles.

3. Characterization

The UV-3101PC UV-VIS-NIR spectrophotometer was used to analyze optical absorption in the wavelength range of 200–1100 nm. The 5-fold centrifuged samples were dried in ethanol at 6500 rpm on carbon Formvar coated copper grids (to reduce excess PVP), and TEM images were acquired using the FEI-Tecna G2 system at a 300 kV accelerating voltage. The crystal structure parameters were obtained using five-fold centrifuged nanoparticle samples dropped on a glass substrate and $\text{Cu-K}\alpha$ X-ray diffraction (XRD) spectra collected using a Bruker D-8 Advance X-ray diffractometer. For a typical dye degradation reaction, 600 μL of 1 mM stock Crystal violet solution was mixed well in 4 mL of triple distilled water. 600 μL of newly made ice cold NaBH_4 was added and well mixed. Finally, different volumes of Au NP solution (nanospheres, nanostars, and nanotriangles) were added to the reaction mixture independently, with the quantity of Au particles remaining relatively constant.

4. Result and discussion

The nucleation and growth phases of crystallization are critical for nanoparticle shape and size. The polymer Poly(N-vinyl-2-pyrrolidone) (PVP) employed in this work functions as a reducing and capping agent. Because the oxidation potential of polymer PVP decreases dramatically when dissolved in different solvents such as Methanol and DMF, distinct reduction rates of gold sol were found in the cases of Methanol and DMF. Furthermore, because the conformation of PVP in these two distinct solvents is extremely different, the differential adsorption of PVP onto the

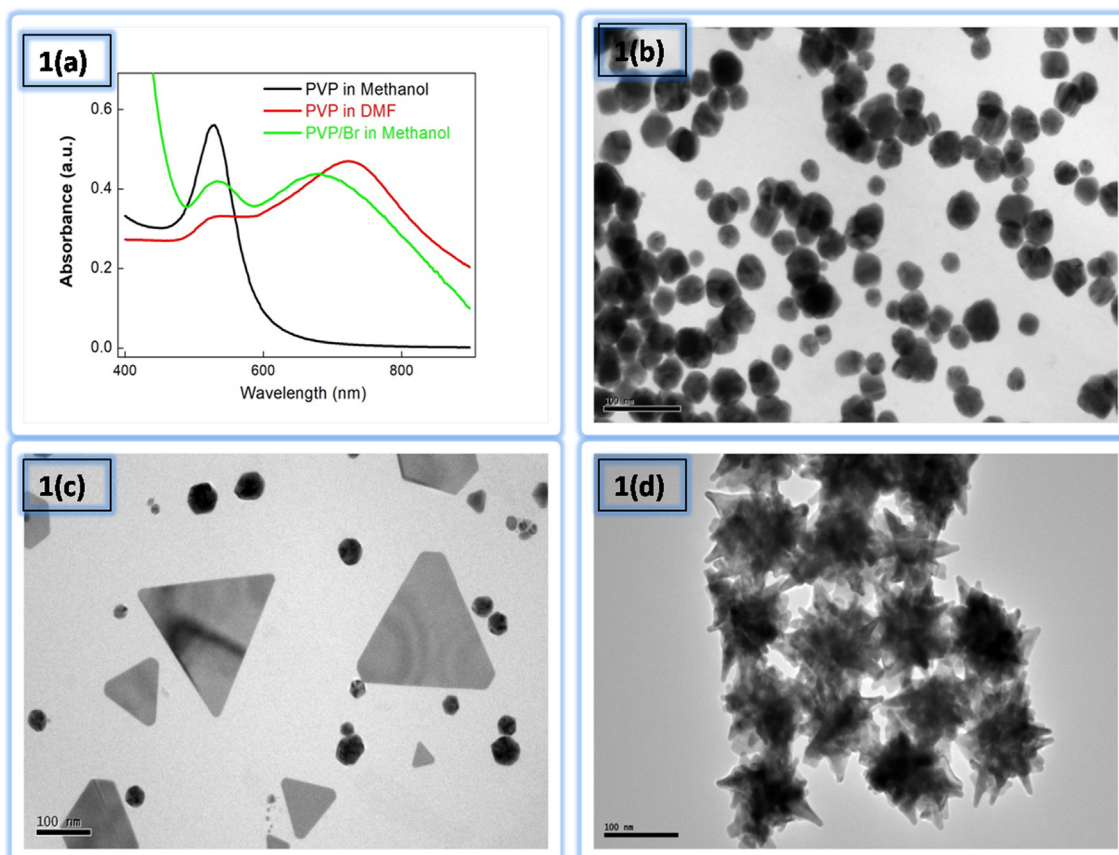


Fig. 1. (a) UV – Visible absorption spectra of synthesized nanoparticles in this study. (b –d) TEM images (scale bar 100 nm) illustrating different shape evolution in different approaches adopted in this study.

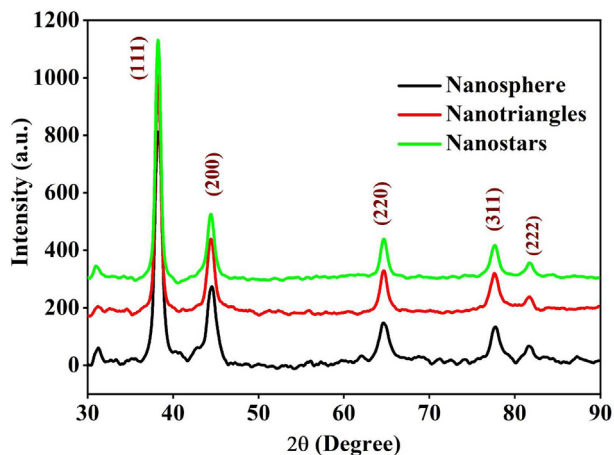


Fig. 2. X-ray diffraction patterns of synthesized gold nanoparticles.

developing facets of nanocrystals modifies the growth rates along the same, resulting in different morphologies in the PVP-Methanol and PVP-DMF systems.

When PVP was dissolved in Methanol, the reaction/reduction kinetics appeared to be quick, implying that the synthesized nanoparticles formed/evolved in a spherical shape of around 30 nm, as confirmed by Absorption spectra and TEM images (Fig. 1(a) and (b)). Because plasmonic oscillations on spherical shaped nanoparticles are isotropic, the absorption spectra of synthesized gold nanoparticles yield a single plasmon resonance peak at around 530 nm (see Fig. 1a).

When PVP was dissolved in DMF, the reaction/reduction kinetics were considerably sluggish, indicating the evolution of anisotropic structure, and later HRTEM analyses revealed that star-shaped nanoparticles were synthesized in this instance (Fig. 1(a) and (d)). Dual plasmon resonance peaks at around 530 nm and 750 nm can be attributed to transversal and longitudinal oscillation of surface plasmons onto an anisotropic shape in the absorption spectra of synthesized gold nanoparticles in this instance

	Sr. No.	Peak Position 2θ (degree)	Full Width Half Maxima (\AA)	Full Width Half Maxima (radians)	Crystallite Size D (nm)	d-spacing (\AA)	Micro-strain (ϵ)
Nanospheres	1	38.282	1.0026	0.01749	8.3476	2.3483	12.6043
	2	44.497	1.3681	0.02387	6.2440	2.0336	14.5929
	3	44.497	1.4897	0.02600	6.2828	1.4388	10.2608
	4	77.746	1.4391	0.02511	7.0569	1.2269	7.78974
	5	81.069	1.3008	0.02270	7.9977	1.1847	6.63737
Nanotriangles	1	38.232	0.7841	0.01368	10.6724	1.1858	12.6043
	2	44.425	1.1081	0.01934	7.7073	1.9744	14.5929
	3	64.666	1.0916	0.01905	8.5724	3.0149	10.2608
	4	77.611	1.1847	0.02067	8.5641	4.1572	7.78974
Nano stars	1	38.239	0.7470	0.01303	11.2016	2.3508	9.4031
	2	44.414	1.050	0.01832	8.1334	2.0372	11.2227
	3	64.677	1.0236	0.01789	9.1425	1.4394	7.0543
	4	77.631	1.2742	0.02223	7.9639	1.2284	6.91115
	5	81.710	1.3051	0.02277	8.0098	1.1770	6.58437

Fig. 3. Various X-ray diffraction parameters of different shaped gold nanoparticles.

(which found to be star shape having size 90 nm as observed from TEM studies).

We utilized the significant tendency of halide ions to adsorb on metallic crystallographic facets during growth to control the morphology of the nanoparticles. In general, halide ions can be chemisorbed on low-energy facets, stimulating growth on high-energy facets, resulting in nanoparticles with diverse shapes evolving [8,9]. In the instance of the PVP-Methanol system, we had supplied distinct halide ions (specifically chloride, bromide, and iodide ions) prior to adding gold sol, following these fundamental crystal growth regulations. In the case of the bromide ion, there was a noticeable difference in reaction kinetics, pointing to an anisotropic shape development in this instance. Absorption spectra in this case shows dual plasmon resonance peaks at around 530 nm and 680 nm which can be assigned to transversal and longitudinal oscillation of surface plasmons onto gold nanotriangles having size 140 nm (confirmed from TEM studies) Fig. 1.

4.1. Probing shape evolution through X-ray diffraction studies

To delineate the differential crystal structure evolving during formation of different shaped nanoparticles, X-ray diffractions of the obtained nanoparticles were studied. XRD studies on all three samples show diffraction peaks corresponding to $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, $\langle 311 \rangle$ and $\langle 222 \rangle$ facets in case of face centered cubic structure of metallic gold which match with the JCPDS, file No. 04-0783 (see in Fig. 2).

From XRD data, we studied the different parameters. In the case of nanospheres, Debye-Scherrer's equation $D = 0.9\lambda/\beta \cos \theta$ corresponding to all peaks yields an average particle size of 07.18 nm (see in Fig. 3). Here D represents the crystalline size, λ represent

wavelength and β represents Full Width at Half Maximum (FWHM). The values of d-spacing are decreasing as an increase in peaks $\langle hkl \rangle$ value. XRD peak broadening happens when there is a divergence from the ideal crystalline structure. This widening can be both instrumental and related to the sample's composition. Microstrain, which is expressed as the root mean square of variations in the lattice parameters throughout the sample, is a dominating factor (see Fig. 3).

In each of the cases, as seen from the XRD parameter table, crystallite size follows the same pattern as of nanoparticle's size obtained from TEM image. Interestingly differential microstrain values on various planes clearly explains the evolution of different shaped nanoparticles.

4.2. Investigation of dye degradation capabilities of the prepared NPs

When (Tris(4-(dimethylamino)phenyl) methylum chloride) ($C_{25}H_{30}N_3Cl$) {Crystal-Violet CV} dye is dissolved in water, it produces a blue-violet color [10]. 1 mM crystal violet solution was prepared by dispersing CV (Tris(4-(dimethylamino)phenyl) methylum chloride) ($C_{25}H_{30}N_3Cl$) in 8 mL double distilled water. Three distinct shaped nanoparticles were added to a reaction medium of $NaBH_4$ (2.5 mM) to reduce 10 mL of 1 mM dye solution. By introducing varied quantities of centrifuged samples to the system, the concentration of gold nanoparticles in each case was kept constant at 0.05 mM.

The crystal violet dye has a significant distinctive absorption at 590 nm (Fig. 4(a-c)), and the intensity of the absorption maximum decreases as the visible light irradiation time grows to 50 min in the case of nano-spherical gold particles, showing dye photodecomposition. Similarly, nano-triangle and nano-star gold particles

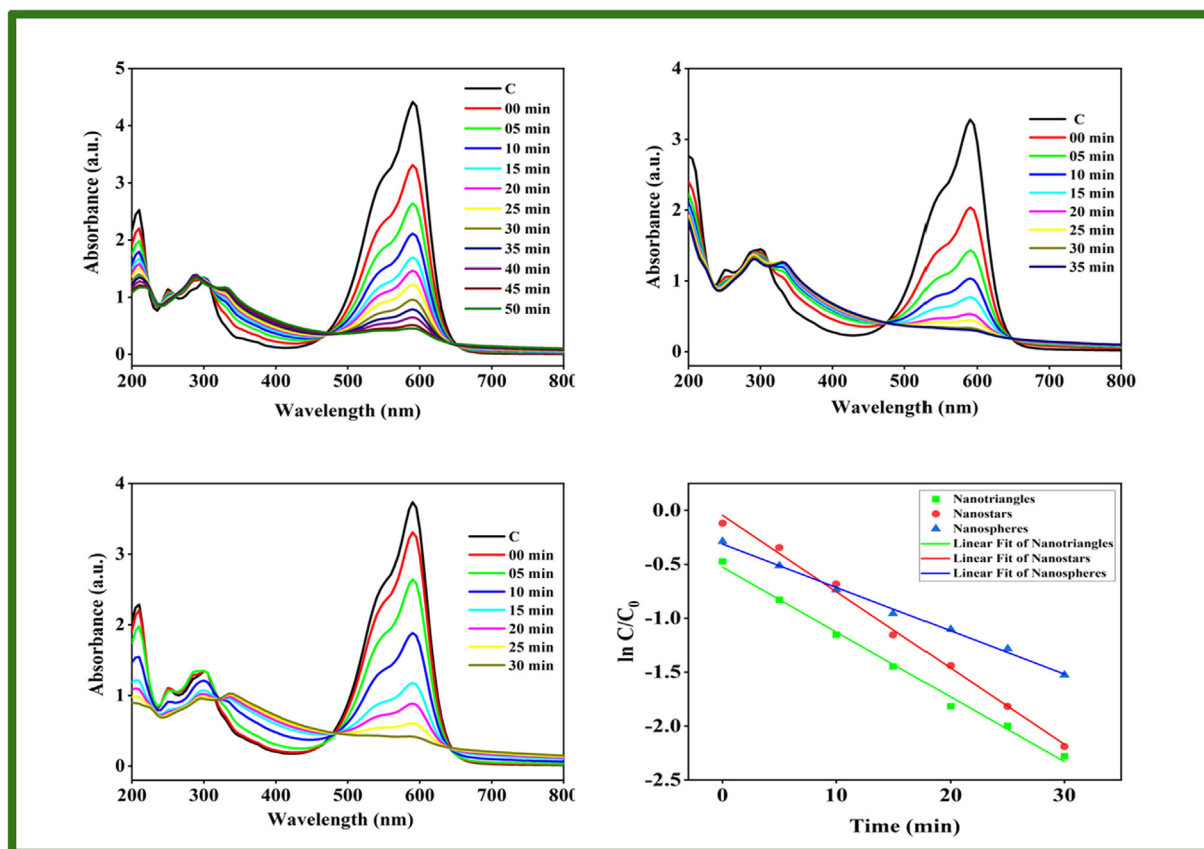


Fig. 4. (a-c) Absorption curves of CV degradation when adsorbed on different nanoparticles. (d) Rate constant curve for different nanoparticles.

completely eliminate crystal violet dye in 30–35 min. As the irradiation period is prolonged, the crystal violet solution's intense purple color diminishes and becomes practically colorless. The rate constants of dye degradation were calculated by finding the slope of first order degradation curves and respective rate constants are $3.9 \times 10^{-2} \text{ min}^{-1}$ for nanospheres, $5.5 \times 10^{-2} \text{ min}^{-1}$ for nanotriangles and $7.0 \times 10^{-2} \text{ min}^{-1}$ for nanostars (Fig. 4d). Rate constant seems to enhance/improve with increase in anisotropy in nanoparticle's shape which can be attributed to increased coordination of surface gold atoms to CV molecules.

5. Conclusion

In this report we have used only a single polymer (i.e PVP) in different conformations to synthesize distinct shaped nanoparticles (nanospheres, nanotriangles, nanostars). By doing so it was very conclusive to see the *discrete* effect of nanoparticle's shape on its dye degradation capabilities as literature shows many such comparisons of different shaped nanoparticles but synthesized either by different synthesis routes or by using different chemical agents. XRD studies revealed the well crystalline nature of synthesized nanoparticles and various structural parameters dictates the evolution of these different shaped nanoparticles. First order rate constants of CV dye degradation were obtained for different shaped nanoparticles and it was established that nanostars being highly anisotropic in nature performed best photocatalytic degradation. Moreover, in this study, we have used chemical synthesis method which is not so environment friendly so in future, we will try to use green synthesis approach in shape controlled synthesis and then evaluate/establish the nanoparticle's shape contribution on its various physio-chemical properties (and hence) and study other applications like SERS and SEIRA.

CRedit authorship contribution statement

Sachin: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft. **Shubham Pal:** Conceptualization, Methodology, Investigation, Data curation, Writing – original

draft. **Renuka Bokolia:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] A. Kedia, P.S. Kumar, Solvent-adaptable poly(vinylpyrrolidone) binding induced anisotropic shape control of gold nanostructures, *J. Phys. Chem. C* 116 (44) (2012) 23721–23728.
- [2] F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, Platonic gold nanocrystals, *Angew. Chem., Int. Ed.* 43 (2004) 3673–3677.
- [3] Y. Sun, Y. Xia, Shape-controlled synthesis of gold and silver nanoparticles, *Science* 298 (5601) (2002) 2176–2179.
- [4] T.K. Sau, C.J. Murphy, Room temperature, high-yield synthesis of multiple shapes of gold nanoparticles in aqueous solution, *J. Am. Chem. Soc.* 126 (2004) 8648–8649.
- [5] P.S. Kumar, I.P. Santos, R.-B. Gonzalez, F.J. Garcia de Abajo, L.M. Liz-Marzan, High-yield synthesis and optical response of gold nanostars, *Nanotechnology* 19 (2008) 015606–15611.
- [6] M. Sajitha, A. Vindhayarumi, A. Gopi, K. Yoosaf, Shape controlled synthesis of multi-branched gold nanocrystals through a facile one-pot bifunctional biomolecular approach, *RSC Adv.* 5 (119) (2015) 98318–98324.
- [7] T. Begum, P.K. Gogoi, U. Bora, Photocatalytic degradation of crystal violet dye on the surface of Au doped TiO₂ nanoparticles, *Indian J. Chem., Technol.*, January 2017 pp. 97–101.
- [8] J. Lee, B.o. Hua, S. Park, M. Ha, Y. Lee, Z. Fan, H. Ko, Tailoring surface plasmons of high-density gold nanostar assemblies on metal films for surface-enhanced Raman spectroscopy, *Nanoscale* 6 (1) (2014) 616–623.
- [9] J. Kumar, R. Thomas, R.S. Swathi, K.G. Thomas, Au nanorod quartets and Raman signal enhancement: towards the design of plasmonic platforms, *Nanoscale* 6 (2014) 10454–10459.
- [10] N.C. Joshi, P. Gururani, S.P. Gairala, Metal oxide nanoparticles and their nanocomposite-based materials as photocatalysts in the degradation of dyes, *POA J.* 12 (5) (2022) 6557–6579.