A

Thesis

On

"Effect of Surfactants on Morphology of Gold Nanostructures Synthesized by Seedless Method"

Submitted in the fulfilment of the partial requirements for the award of degree of

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Submitted by

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A grateful heart is a beginning of greatness

I dedicate this thesis to my parents. I am really thankful for providing me the best education and inspiring me so that I can accomplish my dreams.

CERTIFICATE

This is to certify that this thesis entitled **"Effect of Surfactants on Morphology of Gold Nanostructures Synthesized by Seedless Method"** is submitted by **Ms. Diksha Malana** (Roll. No. 301504010) in the partial fulfilment of requirement for the award of degree of Master of Science in Physics from School of Physics and Materials Science, Thapar University, Patiala (Punjab), India. It is an exclusive record of candidate's own research under the supervision of **Dr. Bhupendra Kumar Chudasama.**. This Thesis in part or full has not been submitted in any other institute for award of such kind of degree.

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Diksha Malana

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Abstract

In this thesis, effect of surfactant on the morphology of gold nanostructures has been evaluated. Gold nanostructures are synthesized by single-step seedless approach. When CTAB is used as shape directing agent, nanoparticles grow in form of nanorods. When CTAB is replaced with pluronic F-127, gold forms star like nanostructure. Effects of pH on the surface resonance bands of gold nanorods and gold nanostars have also been evaluated. Gold nanorods show red shift with decrease in the pH of growth solution while gold nanostars display blue shift with decrease in the pH of the growth solution. Tunability viz-a-viz their plasmon resonance bands and their dimensions have been achieved in both type of nanostructures by means of concentration of surfactant, volume of reducing agent and pH of growth solution.

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Chapter 1 Introduction

1.1 Nanotechnology and Nanoscience

Nanotechnology refers to a developing field of science that includes synthesis and development of various nanomaterials. Ideal size range according to nanotechnology refers to one billionth of a meter. Therefore, it is a science that deals with matter at molecular and nanoscale level and is also the study of manipulating matter at the atomic and molecular scale [1]. There are four generations of nanotechnology as shown in *Table 1.1* [2]:

Table 1.1 *Generations of nanotechnology*

Year	**Generation**	**Examples**
~2000	Passive nanostructures	Aerosols and polymers
~2005	Active nanostructures	3D transistors, targeted drugs
~2010	Systems of nanosystems	Robotics, hierarchical architectures
~2015-2020	Molecular nanosystems	Atomic design, emerging functions

Nanotechnology is able to create new devices and materials with variety of applications in the field of biomaterials, energy production, medicine [3], electronics [4], etc. Nanotechnology can overcome many serious issues which mankind is facing since many decades. Examples of the current research topic in nanotechnology and their applications are shown in *Table 1.2*.

Table 1.2 *Current research topics in nanotechnology*

Material science	Powders, Coatings, Carbon nanomaterials, C-nanofabrics
Energy	Solar power and photovoltaic, LED white light, Hydrogen fuel cells
Medicine/Biotech	Genomics, C-Nanotubes
Electronics	Q-Dots, MRAM, NRAM
Devices	Lithography, AFM, MEMS

1.2 Nanoparticles

The word 'nano' derives from the Latin word 'nano', which means dwarf or extremely small. Particles whose sizes fall in the size range of 1-100 nm is generally called nanoparticle [1]. At this scale material shows different properties than their bulk counter parts. At nanoscale matter follows quantum mechanics rather than Newtonian physics [5].

Nanometer - One billionth (10^{-9}) of a meter

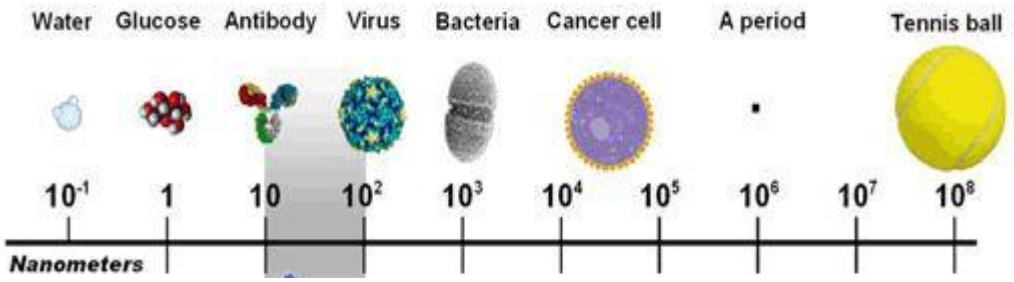


Figure 1.1 *Dimensions of different objects in the related length scale*

- 1 nm is only three to five atoms wide.
- ~40,000 times smaller than the width of an average human hair.
- 100 times smaller than DNA molecule.

- At nanoscale, physical, chemical and biological properties of materials differ from bulk matter.

Nanoparticles are a number of atoms or molecules bonded together and intermediate in size between individual atoms/molecules and bulk materials. Properties of nanoscale particles are neither like individual atoms nor like bulk material. Properties of bulk materials have been studied by scientists for many years but the materials which are ranging in size of 1-100 nm were not studied in past. It has been recently proved that properties of the materials are dependent on size and shape of the material [6]. When the size reduces to the nanoscale then the properties of materials start to differ from corresponding bulk material. Their properties differ even though they are made of same atoms. This is because nanoparticles have large surface area to volume ratio, which results in "surface" dependent properties of material. As size and shape of nanoparticles is completely different from bulk material so it influences the properties of the material [7].

1.2.1 Properties of nanoparticles [8]

Melting point- Nanoparticles have lower phase transition temperature or melting point and reduced lattice constant due to its high surface-to-volume ratio.
Mechanical properties- Nanoparticles have higher mechanical strength than the bulk material due to fewer of defects present at nanoscale in the materials.
Optical properties- Their optical property is different from the bulk crystals. In case of semiconductor nanoparticles, optical absorption peak shifts to shorter wavelength because of increase in the band gap. Color of nanoparticles also changes as a function of particle size.
Electrical conductivity- With reduced size, electrical conductivity decreases because of the surface scattering increases at this dimension.
Magnetic properties- At nanoscale, ferromagnetic behavior changes and show superparamagnetism.

1.2.2 Applications of nanoparticles [9]

Optical functions- Cluster of different sizes have different absorption spectra and hence different color. Nanoparticles which are smaller than the wavelength of light are used to make high penetration conducting materials.
Catalyst function- Due to high surface-to-volume ratio they have better catalytic efficiency.
Thermal function- Melting points of nanoparticles are lower than the corresponding bulk materials. Electronic wiring can be done with nanoparticles having low boiling point. For example, polymer.
Electrical function- Nanoparticles are used to make high temperature superconducting materials because of the rise in superconducting transition temperature.
Mechanical Function- Mechanical strength can be increased by mixing nanoparticles with ceramics or metals.
Magnetic function- In the making of soft magnetic materials in the form of nanoparticles and their alloy.

1.2.3 Synthesis of nanoparticles

Top-down and bottom-up are the two fundamental strategies which are used for the synthesis of nanoparticles. In top-down approach, nanoparticles are produced by breaking larger molecules into fine particles. In this bulk material is machined down to nanometer length scale. This method includes catalytic milling, template synthesis and lithography synthesis [10]. Bottom-up approach is considered by researchers for narrow size distributions. It is the basic technique to synthesize metal nanoparticles. In this approach, nanoparticles are building up from atoms or molecules. This is called build-up because material is build up from the bottom: cluster-by-cluster, molecule-by-molecule and atom-by-atom [11]. It is the basic technique to synthesize metal nanoparticles by reducing ions and growth of nanoparticles is controlled by stabilizer or surfactant. This method includes photochemical, electrochemical, template method, seed-mediated and seedless method [10].

Table 1.3 *Different approaches for the synthesis of nanoparticles*

Top-down methods	**Bottom-up methods**
Catalytic milling	Photochemical and electrochemical method
Template synthesis	Template method
Lithography synthesis	Seeded growth and seedless method

1.3 Gold nanoparticles (AuNPs)

In ancient time, Gold nanoparticles were used to form stained glasses and it was assumed that color of the gold suspension was due to the chemicals which are used to make it. In 1857, first sample of pure gold colloid was made by Michael faraday and it was observed that its color is a result of the size of gold particles [12]. Gold always fascinates humankind because of its properties, beauty and vibrant color. It is considered as most precious and desirable often as currency and status metal [13]. Nowadays nanoparticles of gold are studied due to its distinct properties [12]. Gold (Au) is the 3^{rd} member of the 11^{th} group of periodic table. Gold is a soft metal and can be alloyed for strength. It is chemically inert and good conductor of electricity and heat. It is lying below Cu and Ag. But its physical and chemical properties are not calculable according to trends which other members of table observe; this is clear-cut by its bright yellow color [12].

Gold nanoparticles have different properties from corresponding bulk gold. This is because of the reason that the bulk gold has inert nature and it is yellow solid while gold nanoparticles are anti-oxidant and they are wine red in solution form [14]. Gold nanoparticles exhibit different shapes like spherical, nanotriangles, nanoplates, nanoprisms, nanowires and nanorods, etc. Size and shape of gold nanoparticles is different from bulk gold and hence influences their properties. For example-spherical gold nanoparticles have single absorption peak in visible region while gold nanorods exhibit two absorption peaks [7].

Gold nanoparticles have got much attention because of its strong absorption in visible region at different frequencies [15]. They are chemically stable, have unique optical properties and are easy to synthesize. AuNPs have applications in variety of fields like optics, electronics, medicine, energy, etc.

1.3.1 Surface plasmon resonance

It is optical phenomenon which is caused by the interaction between coherent motion of conduction electrons of metals and electromagnetic field. Electrons collectively oscillate at resonance frequency of electromagnetic radiation. At this frequency, nanomaterial absorbs the incident light. Some photons will release in all directions and this process is referred as scattering while other photons get converted into vibrations or phonons of lattice and this process is known as absorption [16]. Distance travelled by electron between scattering collision raises absorption in UV-Visible range. Surface plasmon absorption arises due to the optical excitation of surface plasmon resonance [17]. Optical excitation takes place when frequency of incident photon matches the surface electron oscillation frequency. It depends upon the size and shape of nanoparticles, dielectric constant of matrix and on the metal [18].

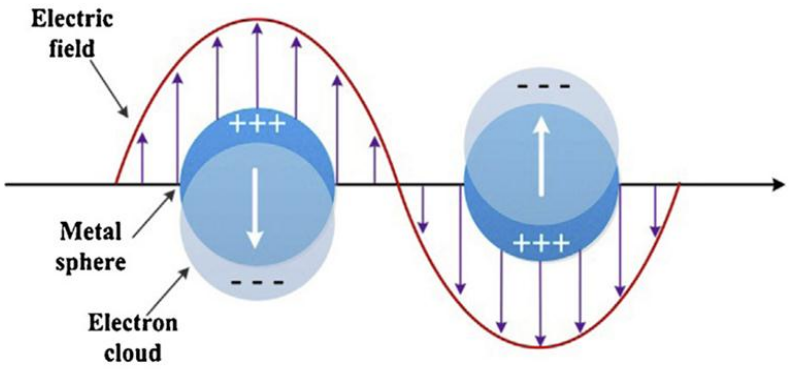


Figure 1.2 *Surface plasmon resonance-collective oscillations of conduction electrons in response to optical excitation*

1.3.2 Shapes of gold nanoparticles

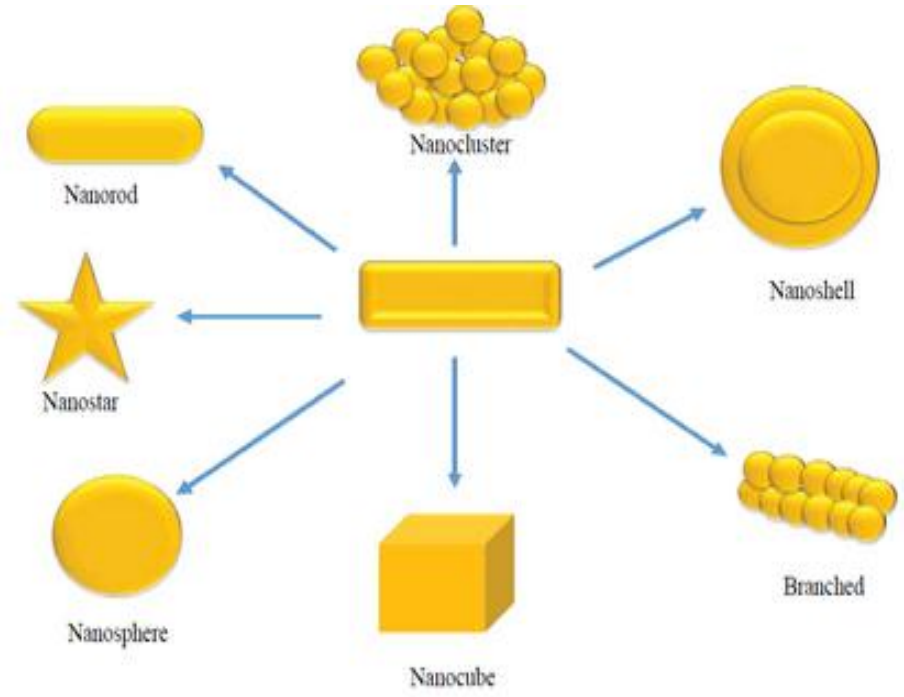


Figure 1.3 *Different shapes of gold nanoparticles*

Nanospheres (AuNS)

Gold nanospheres are commonly known as colloidal gold. Turkevich method and Burst two-phase method are the most commonly used synthetic route for the synthesis of gold nanospheres. Turkevich method was introduced by turkevich in 1951. In this method sodium citrate is used as stabilizing and reducing agent [19]. It leads to the production of AuNPs having diameter around 20 nm [20, 21]. Burst method is another regularly used method for the synthesis of gold nanospheres. It was first introduced in 1994. In this, thiol-ligands are used as stabilizing or capping agent and TOAB (tetraoctyammonium bromide) is used as phase-transfer agent [19]. It is known as two-phase method because it uses both oil and water phase; the reason is that $HAuCl_4$ is insoluble in oil whereas thiol is insoluble in water. To bring $HAuCl_4$ to oil phase, TOAB which is used as phase transfer agent is required [20, 21]. TOAB has two tails, one is hydrophilic and other is hydrophobic. Therefore, it lies at the water and oil interface. While $HAuCl_4$ lies in water because it is hydrophilic group. These form a large complex. By aggregating these

complexes form micelle (inverted) which have hydrophobic tail of TOAB. It is pointed outside. Now these micelles can travel freely in oil phase. Gold ions are trapped in these micelles. After that gold ion reduces from Au^{3+} to Au^{+}. $NaBH_4$ is used for further reduction of gold ion (Au^{+} to Au^{0}) [20, 21].

Gold nanospheres give single absorbance peak which is around 520 nm and it can be tuned up to 600 nm. Due to their high absorption in visible region they may not be useful in biological applications [19].

Nanorods (AuNR)

Nanorods require anisotropic growth so they cannot be easily synthesized like nanospheres. Many methods are used to overcome this issue. Most popular methods which are used for the synthesis of nanorods are template, seed-mediated and seedless synthesis. In template method, synthesis is divided into two categories. One is hard templates and other is soft templates. In hard templates, gold precursor is reduced inside the template or gold precursor can deposits electrochemically on templates. Aluminium oxide membranes are used in hard templates. Whereas soft templates are the surfactant and rodlike micelles. Both of these promote anisotropic growth of particles. This method was first introduced in 1989 [22].

Another most widely used technique is seed-mediated technique. In this seed is used for the reduction of gold salt. It is a two-step process. In first-step, seed is prepared and it results in reduction of gold ion from Au^{3+} to Au^{+} using ascorbic acid. In the second step, seed is used in growth solution for further reduction of gold salt from Au^{+} to Au^{0}. Seed acts as catalyst in this mechanism whereas ascorbic acid acts as weak reducing agent [24]. This multi-step method is used to minimize the impurity amount in nanorod [23]. On the other hand, seedless method is one-step method. It produces nanorods in single step. Both nucleation and growth occurs in one-step. No seeds are required in this method. In this method, strong reducing agent '$NaBH_4$' is used in place of seeds for the reduction of gold salt from Au^{3+} to Au^{0} [24]. Both these method results in anisotropic nanoparticles and CTAB (cetyltrimethylammonium bromide) is used to promote the anisotropic growth because CTAB is less sticky to edges than sides of growing nanorods which result in assembling the gold ions at the end of the rod. They are useful in cancer therapy and drug delivery applications [23].

Nanoplates (AuNP)

Nanoplates can be synthesized by two most widely used methods: seed-mediated method and seedless method. Pluronic F-127 is used to produce gold nanoplates. In seed-mediated method, seeds are used in the growth solution to reduce gold salt. In this method, nanoplates are produced in multi-steps. On the other hand seedless is a one-step method. Nanoplates are produced in single step. $NaBH_4$ is used in the growth solution to initiate the reaction. It is a strong reducing agent. It reduces gold salt from Au^{3+} to Au^0. Both nucleation and growth occurs in one-step. No seeds are required in this method. It is easy to execute than seed-mediated method and also economic.

Nanocubes/cages (AuNC)

Nanocages is the another category of gold nanoparticles, which falls in the list of nanomaterials. For synthesis of nanocages gold ions are reduced onto nanocube of silver which is oxidized and leaves hollow gold cube. By reduction of silver nitrate which is done by $NaBH_4$, these silver nano-cubes are synthesized. Seed-mediated method is used for the synthesis of nanocages [19].

Nanostars (AuNst)

In-vivo imaging, spiked gold nanospheres are used. These are also known as nanothorns, nanourchins, nanocrystals and nanostars. There are two most common approaches for the synthesis of gold nanostars. First approach is seed-mediated method and second is one-step method. Reducing agent and gold salt results in anisotropic growth of the gold into branches or arms, which thus forms star shape [19].

Unusual optical properties of gold nanostarsar are useful in infrared absorption. By increasing sharpness of tips, length and number of branches, peak resonance increases but the nanostar sizes are irrelevant. This can be tuned from 1000 to 1800 nm. Because of its biocompatibility, optical tenability which is far ranging and larger surface area makes it useful in the field of medicine [19]. Pluronic F-127 is used to produce gold nanostars.

1.4 Surfactant

Surfactants are the organic compounds which contain at least one hydrophilic (polar) group and one hydrophobic (non-polar) group. Hydrophilic group interact strongly with water molecules so

it is referred as “water-loving” and hydrophobic group interact weakly with water molecules so it is referred as “water-hating” or “oil-loving”. They are also called surface active agents [30]. They reduce the interfacial energy or lower the surface tension. Surfactants are often described as amphiphilic molecules which mean they love everything [25]. Surfactants carry one non-polar and one polar group which are represented as:

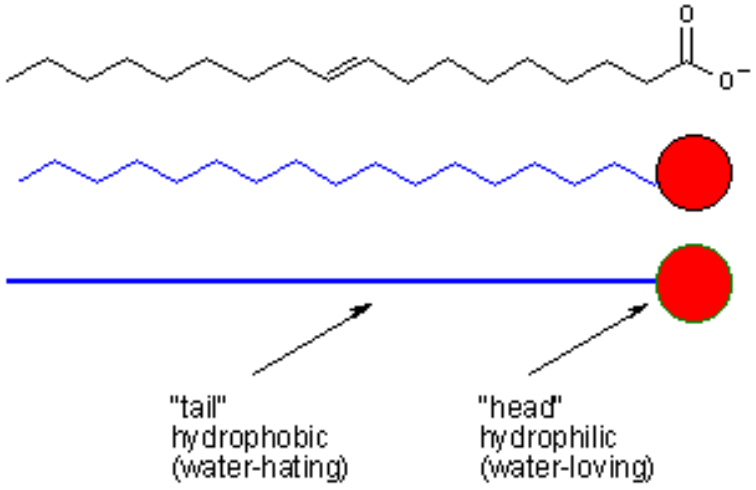


Figure 1.4 *Typical structure of a surfactant*

In aqueous solution, surfactant molecule migrates to the solid/water and air/water interfaces and minimizes the contact between water and hydrophobic groups. This process changes the properties at interface. It is known as adsorption. There is another way to minimize the contact between water and hydrophobic group which is known as aggregation. In this process, water molecule aggregates in bulk solution with its head group (hydrophilic) pointed towards solvent. Aggregates are referred as ‘micelles’ and aggregation process is known as ‘micellisation’. Micelles starts to form at very low concentration termed as CMC or critical micelle concentration [30]. In simple term, adsorption of surfactant molecules at the surface or interface lowers the surface tension, which results in change of interfacial properties of the system. Higher surfactant adsorption leads to the larger reduction in surface tension. Degree of adsorption depends on the structure of surfactant and nature of the interface [31].

1.4.1 Types of Surfactants

Surfactants can be classified according to charge present at hydrophilic portion. Following are different types of surfactants:

- Anionic Surfactant
- Non-ionic Surfactant
- Cationic Surfactant
- Zwitterionic Surfactant
- Gemini Surfactant

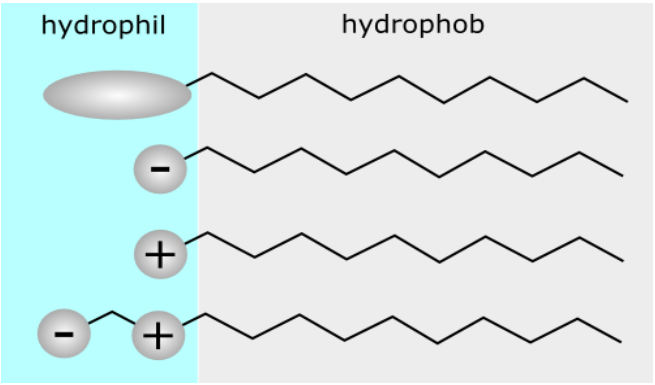


Figure 1.5 *Different types of Surfactant*

Anionic Surfactant

Hydrophilic head group contains negative charge or anionic functional group such as sulfonate, sulfate, carboxylates and phosphates. These types of surfactants are known as anionic surfactants [29]. In aqueous solution, anionic surfactants attaches with the polyethylene glycol, water-soluble polymer and form complex aggregate [26].

Cationic Surfactant

Surface acting agent contains positively charged functional group or cationic functional group at its hydrophilic portion such as primary, secondary and tertiary amines. These types of positively charged head groups are known as cationic surfactant [29]. These surfactants are used in number of technical problems. As cationic surfactant is positively charged, therefore they hydrophobize

the surface of material which is negatively charged and also strong adsorption layer is formed by cationic surfactant [27]. Cationic surfactant has less binding than anionic surfactant [26].

Non-ionic Surfactant

Non-ionic surfactant bears no charge at hydrophilic portion. It is a distinct type of surfactant which has uncharged head groups such as long chain alcohols [29].

Zwitterionic Surfactant

Zwitterionic surfactant has two centers of cationic (-ve) and anionic (+ve) surfactant which are attached to the same molecule. In simple term, hydrophilic group carries both negative and positive charge such as sulfobetaines. This is also known as amphoteric surfactant [29].

Gemini Surfactant

Conventional surfactants contain one head group and one tail. But Gemini surfactant has two hydrophilic head group and two hydrophobic groups in the molecule. Gemini surfactants are also known as dimeric surfactant [28].

1.4.2 Importance of surfactants in nanoparticle synthesis

Nanoparticles are the small particles and they are not thermodynamically stable. It is important to stabilize nanoparticles and this can be done by adding surface directing agents. Surfactants are shape-inducing. They help in synthesizing gold nanoparticles in various shapes. Surfactant stabilizes the particle, when it cannot be stabilized by reducing agent [32]. Surfactant plays important role during synthesis, crystallization and stabilization of metallic nanoparticles. These can be used for stabilization of reactants, shape evolution and stabilization of nanoparticles in different solvents. They work as structure-directing agent to induce anisotropic growth in case of GNRs [33]. For example, CTAB is most widely used surfactant in many synthesis methods such as photochemical or electrochemical method, seed-mediated and seedless synthesis etc. It falls under the category of cationic surfactant. Molecular formula of CTAB is $C_{19}H_{42}BrN$. Head group contains trimethyl ammonium and tail portion contain long chain of alkyl group. Through head and tail group, CTAB interacts with the medium. CTAB acts as capping agent. It reduces the growth rate. In aqueous medium, $AgNO_3$ is added to CTAB results in the formation of AgBr. Ag

ion adsorbs on the surface of Au particle in AgBr form and prevents it from growing. In synthesis of nanorods, CTAB is used as capping agent [35]. Length of nanorod is dependent on the length of surfactant tail. Surfactant having larger chains produced long nanorods with high yield while those having shorter chains produced short nanorods. For the rod formation, CTAB and related surfactants such as CTAC (cetyltrimethylammonium Chloride) and BDAC (benzyldimethylcetylammonium Chloride) are used [34].

References

1. Martin C. R., "Welcome to nanomedicine", *Nanomedicine* 1*(2006)* 5.
2. Mihail (mike) ROCO of the U.S national technology.
3. Mritunjai Singh, Shinjini Singh, S. Prasad, "Nanotechnology in medicine and antibacterial effect of silver nanoparticles", *Digest Journal of Nanomaterials and Biostructures* 3**(2008)** 115 – 122.
4. Lydia L. Sohn, *Nature* 394**(1998)** 131-132.
5. ZHANG YuJuan et al.,"Synthesis, properties, and optical applications of noble metal nanoparticle-biomolecule conjugates", 57**(2012)** 238-246.
6. Susie Eustis and Mostafa A. El-Sayed., "Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes", *Chem. Soc. Rev.*, 35**(2006)** 209–217.
7. Tom Mortier, Andr´e Persoons, Thierry Verbiest., "Two-step synthesis of high aspect ratio gold nanorods", *Central European Journal of Chemistry* 4**(2006)** 160–165.
8. Guozhong cao., "Nanostructures and nanomaterials: Synthesis, properties and applications"
9. Satoshi Horikoshi, Nick Serpone., "Microwaves in Nanoparticle Synthesis: Fundamentals and Applications".
10. ZHANG YuJuan et al., "Synthesis, properties, and optical applications of noble metal nanoparticle-biomolecule conjugates", 57**(2012)** 238-246.
11. Tapan K. Sau, Andrey L. Rogach., "Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications", *ISBN:* **(2012)** 978-3-527-65260-0.
12. Catherine Louis, Olivier Pluchery., "Gold Nanoparticles for Physics, Chemistry and Biology", **(2017)**.
13. Peter Priecel, Hammed Adekunle Salami, Romen Herrera Padilla, Ziyi Zhong, Jose Antonio Lopez Sanchez., "Anisotropic gold nanoparticles: Preparation and applications in catalysis"**,** *Chinese Journal of Catalysis* 3**7(2016)** 1619–165.
14. AK Khan, R Rashid, G Murtaza and A Zahra, "Gold Nanoparticles: Synthesis and Applications in Drug Delivery", *Tropical Journal of Pharmaceutical Research* 13**(2014)** 1169-1177.

15. Peter Zijlstra, Craig Bullen, James W. M. Chon and Min Gu., "High-Temperature Seedless Synthesis of Gold Nanorods", *J. Phys. Chem. B* 110**(2006)** 19315-19318.

16. Min Hu,ae Jingyi Chen,a Zhi-Yuan Li,b Leslie Au,a Gregory V. Hartland,c Xingde Li,d Manuel Marqueze and Younan Xia., "Gold nanostructures: engineering their plasmonic properties for biomedical Applications", *Chem. Soc. Rev.*, 35**(2006)** 1084–1094.

17. Anupama B. Kaul., "Microelectronics to Nanoelectronics: Material, Devices and Manufacturability", *ISBN: 978-1-4665-0954-2 2013*.

18. P. K. Giri, D. K. Goswami, A. Perumal., "Advanced Nanomaterials and Nanotechnology", **(2013)**.

19. Vanessa W. K. Ng et al., "Gold: a versatile tool for in vivo imaging", *J. Mater. Chem. B*, 1**(2013)** 9–25.

20. Birol Ozturk et al., "Single-step growth and low resistance interconnecting of gold nanowires", *Nanotechnology* 18**(2007)** 175707.

21. Goulet, P. J. G.; Lennox, R. B. J., "New Insights into Brust−Schiffrin Metal Nanoparticle Synthesis", *Am. Chem. Soc.* 132**(2010)** 9582– 9584.

22. Yu Chang, Ser-sing, Lee, Chien-liang, Wang, C. R. Chris., "Gold Nanorods: Electrochemical Synthesis and Optical Properties", *The Journal of Physical Chemistry B*, 34**(1997)** 6661-6664.

23. Fei Ye., "Wet chemical synthesis of cylindrical gold nanorods", *Stockholm: Skolan för industriell teknik och management, Kungliga Tekniska högskolan* **(2006)**.

24. Moustafa R. K. Ali, Brian Snyder, and Mostafa A. El-Sayed., "Synthesis and Optical Properties of Small Au Nanorods Using a Seedless Growth Technique", *Langmuir* 28**(2012)** 9807−9815.

25. Salwa M.I. Morsy., "Role of Surfactants in Nanotechnology and Their Applications", *Int. J.Curr. Microbiol. App. Sci* 3**(2014)** 237-260.

26. Nagamune nishikido., "Mixed Micelles of Polyoxyethylene-Type Nonionic andAnionic Surfactants in Aqueous Solutions", *Journal of Colloid and Interface Science*, 60***(1977)*** ISSN 0021-9797.

27. Dipti shukla and V.K. Tyagi., "Cationic and Gemini Surfactants: A Review", *J. Oleo Science.*, 55**(2006)** 381-390.

28. Fredric M.Menger and Jason S. Keiper., "Gemini Surfactants", Angew. Chem. Int. Ed. 2000, 39, 1906-1920.

29. Drew Myers., "Surfactant Science and Technology", *ISBN* 13 978-0-471-68024-6**(2006)**.

30. Richard J. Farn.,"Chemistry and Technology of Surfactants", *ISBN* 12 978-14051-2696-0.

31. Tharwat F. Tadros., "Applied Surfactants: Principles and Applications", *ISBN* 13 978-3-527-30629-9.

32. J. Duy, L. B. Connell, W. Eck, S. D. Collins, and R. L. Smith, "Preparation of surfactant-stabilized gold nanoparticle-peptide nucleic acid conjugates," *Journal of Nanoparticle Research*, 12**(2010)** 2363–2369.

33. Sergio Gomez-Grana, Fabien Hubert, Fabienne Testard, Andres Guerrero-Martínez, Isabelle Grillo, Luis M. Liz-Marzan, and Olivier Spalla., " Surfactant (Bi)Layers on Gold Nanorods", *Langmuir* 28**(2012)**1453–1459.

34. Peter Priecel, Hammed Adekunle Salami, Romen Herrera Padilla, Ziyi Zhong, Jose Antonio Lopez-Sanchez, "Anisotropic gold nanoparticles: Preparation and applications in catalysis" *Chinese Journal of Catalysis* 37 **(2016)** 1619–1650.

35. Pascal Granger, Vasile I. Parvulescu, Serge ., "Perovskites and Related Mixed Oxides: Concepts and Applications, Volume 1".

36. Marek Grzelczak et al., "Shape control in gold nanoparticle synthesis", *Chem. Soc. Rev.*, 37**(2008)**1783–1791.

Different methods are used for the synthesis of gold nanoparticles. This chapter reviews different synthesis methods of gold nanoparticles. Seed-mediated technique is the most widely used technique to synthesize gold nanoparticles and it is also preferred by experimentalist.

2.1 Synthesis of Gold nanoparticles

Author name	**Title**	**Results**
Tapan K. Sau et al., *Journal of Nanoparticle Research* 3**(2001)** 257–261	Size controlled synthesis of gold nanoparticles using photo chemically prepared seed particles [1]	• Gold nanoparticles of size in the range of 5 to 110 nm were prepared by using two-steps seed-mediated process. • In first step, seeds of average diameter from 5-20 nm were prepared. • In second step, ions of Au (III) were reduced to Au (0) by ascorbic acid in the presence of seeds.
Nikhil R. Jana et al., *Langmuir* 17**(2001)** 6782-6786.	Seeding Growth for Size Control of 5-40 nm Diameter Gold Nanoparticles [2]	• To prepare nanoparticles which are in range of 5-40 nm with narrow size distribution, seeded growth approach is used. • By varying ratio of seeds, particle size can be controlled. • Secondary nucleation can avoid by step by step enlargement of particles.
Babak Nikoobakht and Mostafa A. El-Sayed	Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-	• In single surfactant system, to grow nanorods to desired length growth solution containing silver was used. • By this nanorods of aspect ratio in

Chem. Mater. 15**(2003)** 1957-1962.	Mediated Growth Method [3]	range of 1.5-4.5 were produced. • To produce longer nanorods in range of 4.6-10 nm, binary surfactant mixture (BDAC and CTAB) was used.
Tapan K. Sau and Catherine J. Murphy, *Langmuir 20(***2004)** 6414-6420	Seeded High Yield Synthesis of Short Au Nanorods in Aqueous Solution [4]	• Silver ion is the crucial factor in the maximum production of short GNRs. • Longer GNRs can be produced in the absence of the silver ion. • Short nanorods between 20-100 nm were synthesized. • Short nanorod plays important role for sensor application as in visible region.
Anand Gole and Catherin J. Murphy *Chem. Mater. 16***(2004)** 3633-3640.	Seed-Mediated Synthesis of Gold Nanorods: Role of the Size and Nature of the Seed [5]	• Aspect ratio of rods depends upon the seed size. • Average diameter is in between 4-18 nm. • With Increase in seed size, aspect ratio of rods decreases.
Linfeng Gou and Catherine J. Murphy *Chem. Mater. 17(***2005)** 3668-3672.	Fine-tuning the shape of Gold nanorods [6]	• Seed-mediated method is used for the synthesis of GNRs but there are still some unreduced ions left, which are used for fine tuning of structure and hence for optical properties of GNRs. • Gold ions are reduced by the oxidized form of ascorbic acid. • CTAB helps in fine-tuning of shape.
Peter Zijlstra et al., *J. Phys.*	High-Temperature Seedless Synthesis of	• Seedless method for synthesis of GNRs is demonstrated at high temperature up

*Chem. B 110(***2006)** 19315-19318.	Gold Nanorods [7]	to 97 °C. • With increase in temperature, rod length decreases. • Activation energy calculated on all facets is 90 (10 kJ mol^{-1}). • High temperature synthesis gives the attractive method for large scale creation of GNRs.
Muhammad Iqbal, Yong-Il Chung and Giyoong Tae, *J. Mater. Chem.*, 17**(2007)** 335–342.	An enhanced synthesis of gold nanorods by the addition of Pluronic (F-127) via a seed mediated growth process [8]	• CTAB and Pluronic F-127 – A binary surfactant system was used in the absence of $AgNO_3$ to avoid reshaping of nanorods upon storage. • Nanorods of high shaping aspect ratio were produced by adding Pluronic F-127. • Blue shift in plasmon resonance absorption can be prevented by Co-surfactant system.
Junyan Xiao and Limin Qi, *Nanoscale*, 3**(2011)** 1383–1396.	Surfactant-assisted, shape-controlled synthesis of gold nanocrystals [9]	• Surfactant can interact with reacting species and hence it influences the reaction regime. • Surfactant plays important role in shape controlled synthesis. • To protect nanocrystals, surfactant acts as capping agent.
Jing Cheng, Lan Ge, Bin Xiong and Yan He, *Journal of the Chinese*	Investigation of pH Effect on Gold Nanorod Synthesis [10]	• pH affects the stability of CTAB on gold surface. • It also affects the reducing power of ascorbic acid. • Therefore, pH plays important role on

Chemical Society, 58**(2011)** 822-827.		morphology of nanorods.
Paula C. Angelomé et al., *Chem. Mater.* 24**(2012)** 1393−1399.	Seedless Synthesis of Single Crystalline Au Nanoparticles with Unusual Shapes and Tunable LSPR in the near-IR [11]	• To induce highly anisotropic Au nanoparticles CTAC was used. • By changing reagent concentration and reaction temperature, LSPR of particles can tune from 600-1400 nm. • Also by changing these two factors, different shapes were obtained.
Moustafa R. K. Ali et al., *Langmuir* 28**(2012)** 9807−9815.	Synthesis and Optical Properties of Small Au Nanorods Using a Seedless Growth Technique [12]	• Seed plays important role for obtaining large gold nanorods but in seedless process as a substitute $NaBH_4$ was used. • Growth time increases with decrease in pH as reduction rate decreases with pH. • Nanorods with smaller size were produced by increasing the CTAB concentration. • Smaller nanospheres were synthesized by increasing $NaBH_4$ to the solution in the non-availability of silver ions.
Leonid Vigderman and Eugene R. Zubarev, *Chem. Mater.* 25**(2013)** 1450−1457.	High-Yield Synthesis of Gold Nanorods with Longitudinal SPR Peak Greater than 1200 nm Using Hydroquinone as a Reducing Agent [13]	Seed-mediated synthesis presents number of limitations: • LSPR peak longer than 1000 nm is difficult by this technique. • 15 % poor yield of gold conversion (ionic to metallic) due to use of ascorbic acid.

		• Hydroquinone is used in place of ascorbic acid to overcome the problem at low yield.
Xiaolong Xu et al., *J. Mater. Chem. A*, 2**(2014)** 3528.	Seedless synthesis of high aspect ratio gold nanorods with high yield [14]	• By using seedless method, width of nanorods was reduced (8-2.8 nm). • For synthesis of thinner GNRs, seedless process is necessary. • Seedless method is simpler and economic than seeded method.
Jianping Lai et al., *Nanotechnology* 25 **(2014)** 125601.	One-pot synthesis of gold nanorods using binary surfactant systems with improved monodispersity, dimensional tunability and plasmon resonance scattering properties [15]	• In this, binary surfactant mixture of CTAB and NaOL was used for synthesis of AuNRs. • It results in formation of thin and thick gold nanorods up to 37 nm. • This is not possible by using single surfactant in conventional seedless method.
Soonchang Hong et al., *Bull. Korean Chem. Soc.* 35**(2014)** 1737.	Kinetically Controlled Growth of Gold Nanoplates and Nanorods via a One-Step Seed-Mediated Method [16]	• Size and shape of gold nanoparticles (nanorods, nanospheres, nanoplates) depends upon the addition rate of ascorbic acid. • By adding less amount of ascorbic acid, GNPs produced were of large dimension. • For production of anisotropic GNPs, activation energy was higher than isotropic GNPs.
AK Khan, R Rashid, G	Gold Nanoparticles: Synthesis and	• Gold NPs have wide application in medicinal field because of its small

Murtaza and A Zahra, *Tropical Journal of Pharmaceutical Research July* 13**(2014)** 1169-1177.	Applications in Drug Delivery [17]	size, stability, high aspect ratio, optical, chemical and physical properties, etc. • It is used in drug delivery system and cancer therapy. • Side-effects of drugs can be minimized by using Au nanoparticles.

References

1. Tapan K. Sau, Anjali Pal, N.R. Jana, Z.L. Wang and Tarasankar Pal., **"**Size controlled synthesis of gold nanoparticles using photochemically prepared seed particles*", Journal of Nanoparticle Research* 3**(2001)** 257–261.
2. Nikhil R. Jana, Latha Gearheart, and Catherine J. Murphy., "Seeding Growth for Size Control of 5-40 nm Diameter Gold Nanoparticles", *Langmuir* 17***(*2001)** 6782-6786.
3. Babak Nikoobakht and Mostafa A. El-Sayed., "Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method", *Chem. Mater.* 15***(*2003)** 1957-1962.
4. Tapan K. Sau and Catherine J. Murphy., "Seeded High Yield Synthesis of Short Au Nanorods in Aqueous Solution", *Langmuir* 20***(*2004)** 6414-6420.
5. Anand Gole and Catherine J. Murphy., "Seed-Mediated Synthesis of Gold Nanorods: Role of the Size and Nature of the Seed", *Chem. Mater.* 16***(*2004)** 3633-3640.
6. Linfeng Gou and Catherine J. Murphy., "Fine-Tuning the Shape of Gold Nanorods", *Chem. Mater.* 17***(*2005)** 3668-3672.
7. Peter Zijlstra, Craig Bullen, James W. M. Chon and Min Gu., "High-Temperature Seedless Synthesis of Gold Nanorods", *J. Phys. Chem. B* 110***(*2006)** 19315-19318.
8. Muhammad Iqbal, Yong-Il Chung and Giyoong Tae., "An enhanced synthesis of gold nanorods by the addition of Pluronic (F-127) via a seed mediated growth process", J. Mater. Chem., 17**(2007)** 335–342.
9. Junyan Xiao and Limin Qi., "Surfactant-assisted, shape-controlled synthesis of gold nanocrystals", *Nanoscale* 3**(2011)** 1383–1396.
10. Jing Cheng, Lan Ge, Bin Xiong and Yan He., "Investigation of pH Effect on Gold Nanorod Synthesis", *Journal of the Chinese Chemical Society* 58**(2011)** 822-827.
11. Paula C. Angelomé, Hamed Heidari Mezerji, Bart Goris, Isabel Pastoriza-Santos, Jorge Pérez-Juste, Sara Bals and Luis M. Liz-Marzán., "Seedless Synthesis of Single Crystalline Au Nanoparticles with Unusual Shapes and Tunable LSPR in the near-IR", *Chem. Mater.* 24**(2012)** 1393−1399.

12. Moustafa R. K. Ali, Brian Snyder, and Mostafa A. El-Sayed., "Synthesis and Optical Properties of Small Au Nanorods Using a Seedless Growth Technique", *Langmuir* 28**(2012)** 9807−9815.

13. Leonid Vigderman and Eugene R. Zubarev., "High-Yield Synthesis of Gold Nanorods with Longitudinal SPR Peak Greater than 1200 nm Using Hydroquinone as a Reducing Agent", *Chem. Mater.* 25**(2013)** 1450−1457.

14. Xiaolong Xu, Yuanyuan Zhao, Xiangdong Xue, Shuaidong Huo, Fei Chen, Guozhang Zou and Xing-Jie Liang., "Seedless synthesis of high aspect ratio gold nanorods with high yield", *J. Mater. Chem. A* 2**(2014)** 3528.

15. Jianping Lai, Ling Zhang, Wenxin Niu, Wenjing Qi, Jianming Zhao, Zhongyuan Liu, Wei Zhang and Guobao Xu., "One-pot synthesis of gold nanorods using binary surfactant systems with improved monodispersity, dimensional tunability and plasmon resonance scattering properties", *Nanotechnology* 25 **(2014)** 125601.

16. Soonchang Hong, Jesus A. I. Acapulco Jr., Hee-Jeong Jang, Akshay S. Kulkarni and Sungho Park., "Kinetically Controlled Growth of Gold Nanoplates and Nanorods via a One-Step Seed-Mediated Method", *Bull. Korean Chem. Soc.* 35**(2014)** 1737.

17. AK Khan, R Rashid, G Murtaza and A Zahra., "Gold Nanoparticles: Synthesis and Applications in Drug Delivery", *Tropical Journal of Pharmaceutical Research July* 13**(2014)** 1169-1177.

3.1 Introduction

Different methods are used for the synthesis of various shapes of gold nanoparticles. These methods are electrochemical, photochemical, burst method, seed-mediated, etc. The most widely used technique for the synthesis of AuNPs is seed-mediated growth method. In seed-mediated, nanoparticles are obtained by separating nucleation from the growth stage. Small seeds get nucleated first and then these small seeds grown into large particles by slow reduction process. This method is a multi-step method. In the first step, seed solution is prepared by reduction of Au(III) to Au(I). Seeds are of reddish-brown in color. In the second-step, seeds are required for the further reduction of gold salt from Au(I) to Au(0). As ascorbic acid is a weak reducing agent, it cannot reduce the gold salt from Au(III) to Au(0). It reduces the gold salt from Au(III) to Au(I). Further reduction to Au(0) is done by adding seeds. Therefore, seeds play an important role in reduction of gold salt [1].

Varying the ratio of the concentration of the gold ions to the seeds, size of AuNPs can be determined. But in growth solution every seed do not grow. When the concentration of seed is too high then only few of seeds grow while most others do not grow. Through this process, the gold nanoparticles which are obtained have a size 10 nm. Therefore, AuNPs of size less than 10 nm cannot be synthesized by seed-mediated method. To overcome this drawback seedless technique is generally used. This method is necessary for the synthesis of thinner AuNPs [2]. The seedless method is simpler than the seed-mediated technique. It is a one-step process. Only one step is required for the synthesis of AuNPs which is easy to perform. In seedless method, seed preparation is not required. $NaBH_4$ is directly added to the growth solution. As $NaBH_4$ is a strong reducing agent, it reduces the gold ions from Au(III) to Au(0). In this method, Growth and nucleation both occurs in the same solution. $NaBH_4$ plays important role in the formation of gold nanoparticles [1]. Therefore, the method which we followed for the synthesis of gold nanoparticle is seedless method. By using this method, gold nanorods and gold nanostars using different surfactants (CTAB and Pluronic F-127) are produced. After the synthesis, optical and structural properties of gold nanoparticles were characterized by UV-Visible-NIR spectroscopy, DLS

(Dynamic Light Scattering) and TEM (Transmission Electron Microscopy) analysis. These all are discussed in detail in this chapter.

Seedless Method:

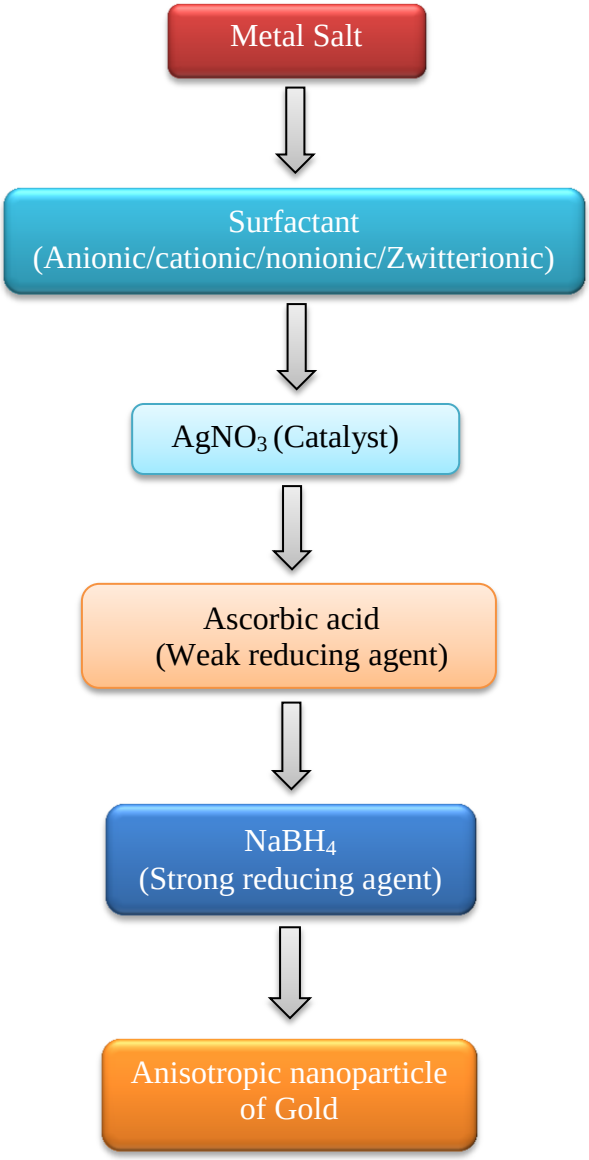


Figure 3.1 *Synthesis protocol for anisotropic gold nanoparticles*

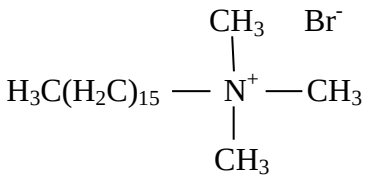
3.2 Materials and Instrumentation

Materials

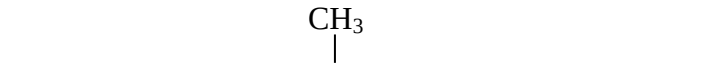
CTAB (cetyltrimethylammonium bromide) and Pluronic F-127 was purchased from SDFCL and Sigma, respectively. Chloroauric acid ($HAuCl_4$) was purchased from Sigma-Aldrich. Silver nitrate ($AgNO_3$) was also purchased from Sigma-Aldrich. Ascorbic acid (AA) was purchased from Sigma. Sodium borohydride ($NaBH_4$) was purchased from Aldrich. All chemicals were used as received for the synthesis of AuNPs. All solutions were prepared with Millipore water.

Chemical Structures

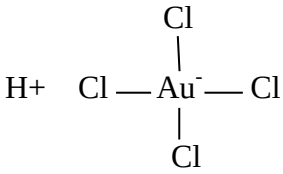
CTAB



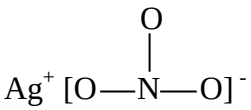
Pluronic F-127



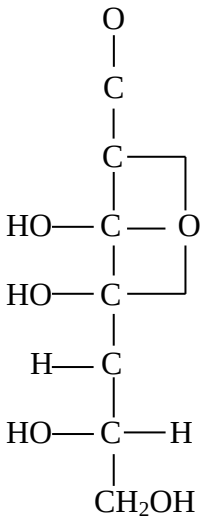
$HAuCl_4$



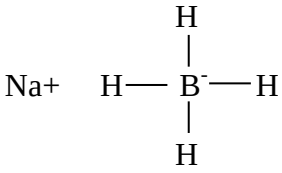
$AgNO_3$



Ascorbic acid



$NaBH_4$



Instrumentation

UB-Visible-NIR Spectrophotometer (Shimadzu, UV-2600), DLS (Brookhaven 90 plus particle size analyzer), Mega17R Centrifuge Machine, pH meter and Ultrasonic Bath.

Stock solution Preparation

For 1mM hydrogen tetrachloroaurate: 1 g of $HAuCl_4 .3H_2O$ was dissolved in 250 mL distilled water having concentration of 10 mM. This solution can be kept for years as a stock solution. Further, 1mL of stock solution was diluted to 100 mL to get 1mM concentration.

3.3 Synthesis of gold nanoparticles

3.3.1 Gold Nanorods

Preparation of gold nanorods

Cetyltrimethylammonium bromide (CTAB) is extensively used for the synthesis of AuNRs. Concentration of CTAB decides the shape of NRs. In this experiment, 0.1M CTAB was taken in 20 mL of water. Then it was dissolved by sonication for 20 min. After that growth solution was prepared by taking 5 mL of CTAB and adding it to 5 mL of $HAuCl_4$ (1 mM) and 0.2 mL of $AgNO_3$ (4 mM). Ascorbic acid (0.1M) was added to this mixture till it turns colorless and at the end 5 μL of $NaBH_4$ (10mM) was added to the solution. The solution color changes from colorless to pink which shows the formation of AuNRs. There can be variety of other nanoparticles present in the mixture such as spheres, cubes, etc which are not desired. Therefore, the sample was centrifuged at 8500 rpm for 900 seconds. After centrifugation, precipitates settle down at the bottom of centrifuged tube and supernatant was removed carefully from the tube with the help of pipette. 9 mL of Millipore water was added to the precipitate. By centrifugation, all the undesirable products can be separated out from the solution. GNR's thus obtained were preserved for further characterizations.

3.3.2 Gold Nanostars

Preparation of Gold nanostars

Pluronic F-127 is widely used for synthesis of Au nanostars. 10mM pluronic F-127 was dissolved in 20 mL of water. Growth solution was prepared by taking 5 mL of pluronic F-127 and adding it to 5 mL of $HAuCl_4$ (1mM) , 0.2 mL of $AgNO_3$ (4mM) and 45 μL of ascorbic acid (10mM). At the end 1 μL of $NaBH_4$ (10mM) was added to the mixture. The solution color changes from colorless to blue which shows the formation of Au nanostars. Solution was centrifuged at 8500 rpm. After centrifugation, precipitates settle down at the bottom of centrifuged tube and supernatant was removed carefully from the tube with the help of pipette. 9 mL of Millipore water was added to the precipitate and sample was preserved for further characterization.

3.4 Characterization

Three different techniques were used for the characterization of nanoparticles. These three techniques are:

- UV-Visible-NIR Spectroscopy
- Dynamic Light Scattering (DLS)
- Transmission Electron Microscopy (TEM)

3.4.1 UV-Visible-NIR Spectroscopy

To characterize metallic nanoparticles, UV-Visible-NIR Spectroscopy is used. Function of UV-Visible spectrometry is to measure the degree of light absorption at various wavelengths in ultraviolet, visible and NIR. This can be achieved by irradiating sample with light whose intensity and wavelengths are known and by measuring intensity of transmitted light.

The machine used for UV-Visible spectroscopy was Shimadzu, UV-2600. There are two different lamps in the machine which are used to get strong intensity of light over entire spectrum (UV-Visible-NIR). The first lamp is tungsten-halogen lamp and the second lamp is deuterium lamp which is used for the production of Visible-NIR and UV, respectively. There are two different slots in the machine which are used to measure two samples simultaneously. One slot is used to measure absorption spectrum of "background" and another is used to test the sample. Background is a medium in which sample is suspended and in this work water is used as reference.

Absorption peaks are shown in the spectra. If there is only one peak in the absorption spectra then spherical gold nanoparticles are produced. On the other hand, if there is more than one peak in the absorption spectrum, it may because of the formation of anisotropic nanostructures [3].

3.4.2 Dynamic Light Scattering (DLS)

The machine used for the measurement of particle size was Brookhaven 90Plus. By measuring random changes in intensity of light which is scattered from a solution or suspension, size of particle can be determined. This technique is known as dynamic light scattering. It is also known

as photon correlation spectroscopy (PCS) and quasi-elastic light scattering (QELS). It is the most popular and fastest method to determine the particle size in colloidal suspensions which are in submicron or nano size range. This technique offers the accurate estimation of size distribution and size of the particle. By Stokes-Einstein relationship, size of particle can be determined.

$$d = k_B T/6\pi \eta_o D$$

Where D - diffusion coefficient, k_B – Boltzmann constant, T – absolute temperature, η_o – viscosity of solvent, d – radius of particle [4].

3.4.3 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy provides information about diffraction, spectroscopy and imaging of the sample with a sub-nanometer or atomic spatial resolution. Unlike SEM, it works on different principle but it often gives same results. For TEM, sample preparation is time consuming and complex. When electron beam transmitted through the sample then this beam interacts with the sample. By this the surface characteristics of sample can be visualized [5]. The machine used for TEM images was Philips CM200 transmission electron microscope.

References

1. Moustafa R. K. Ali, Brian Snyder, and Mostafa A. El-Sayed., "Synthesis and Optical Properties of Small Au Nanorods Using a Seedless Growth Technique", *Langmuir* 28**(2012)** 9807−9815.
2. Xiaolong Xu, Yuanyuan Zhao, Xiangdong Xue, Shuaidong Huo, Fei Chen, Guozhang Zou and Xing-Jie Liang., "Seedless synthesis of high aspect ratio gold nanorods with high yield", *J. Mater. Chem. A* 2**(2014)** 3528–3535.
3. Olof Hedkvist., "Synthesis and Characterization of Gold Nanoparticles", (**2013)**.
4. Power, A., Betts, A, Cassidy, J., "Silver Nanoparticle Polymer Composite Based Humidity Sensor", *Analyst*, 135**(2010)** 1645 – 1652.
5. Molpeceres J, Aberturas MR, Guzman M., "Biodegradable nanoparticles as a delivery system for cyclosporine: preparation and characterization", *J Microencapsul*. 17**(2000)** 599–614.

4.1 Gold Nanorods

4.1.1 Variation in CTAB concentration

The formation of gold nanorods depends on the concentration of CTAB. To evaluate the effect of CTAB concentration on optical bands, UV-Visible spectroscopy of as-synthesized gold nanorods was performed *(Figure 4.1).* Higher concentration of CTAB forms GNRs whereas lower concentration of CTAB do not form GNRs. *Figure 4.1* shows that when the concentration of CTAB >=0.1M, only then only two peaks are observed in the UV-Visible spectra. On the other hand, when concentration of CTAB<0.1M then only one peak is observed in the absorption spectra. Two peaks in the absorption spectra show the formation of gold nanorods whereas one peak shows formation of spheres. Position and absorbance of LSPR and TSPR of GNRs are shown in *Table 4.1*.

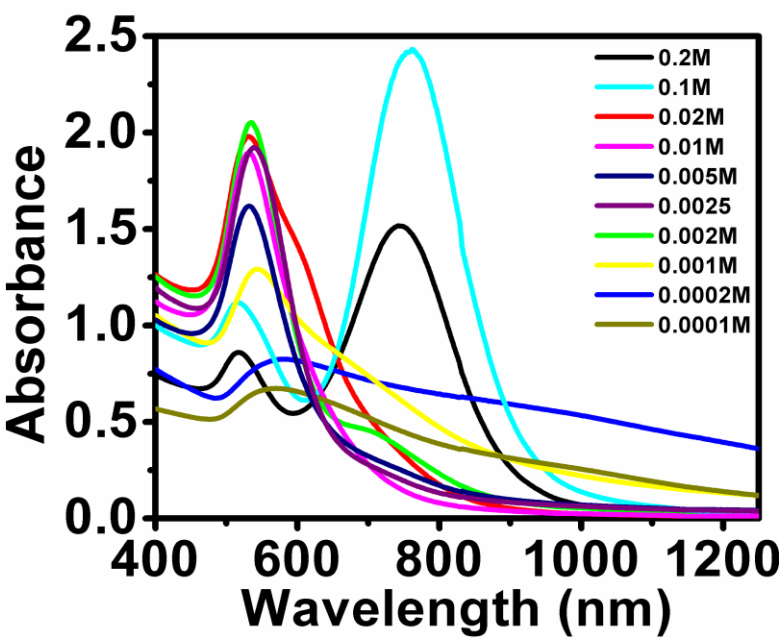


Figure 4.1 *UV-Visible spectra of as-synthesized GNRs using different concentrations of CTAB*

There is no LSPR band observed at other concentrations below 0.1M as shown in the *Table 4.1*. As wavelength and absorbance of 0.1M is higher than 0.2M. Hence, 0.1M is the optimum growth concentration for the synthesis of GNRs.

Table 4.1 *Effect of CTAB on LSPR and TSPR bands of gold nanostructures*

CTAB (M)	**λ_{TSPR} (nm)**	**λ_{LSPR} (nm)**	**Abs_{TSPR}**	**Abs_{LSPR}**
0.2	517	742	0.8609	1.5172
0.1	518	761	1.1186	2.4329
0.02	531	-	1.9814	-
0.01	531	-	1.8942	-
0.005	532	-	1.6201	-
0.0025	539	-	1.9233	-
0.002	535	-	2.0527	-
0.001	543	-	1.2921	-
0.0002	582	-	0.8257	-
0.0001	569	-	0.6744	-

To understand the effect of CTAB concentration on the morphology of GNRs, TEM was performed. TEM image of gold nanorods with 0.1M concentration of CTAB is shown in the *Figure 4.2*. The size distribution histograms were plotted to measure the length and width of the gold nanorods *(Figure 4.3).* Histograms were fitted with lognormal particle size distribution. The length of gold nanorods from TEM images comes out to be 30 nm and width is 7 nm.

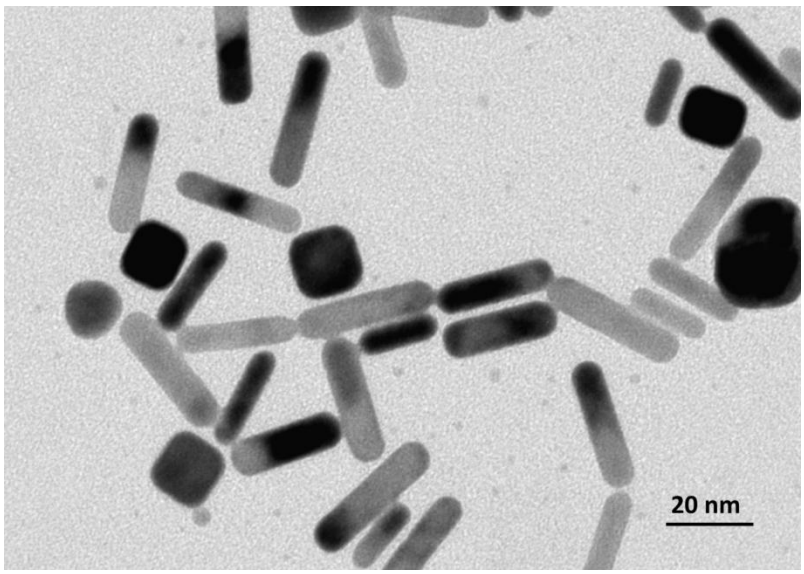


Figure 4.2 *TEM Micrograph of as-synthesized GNRs at 0.1M concentration of CTAB*

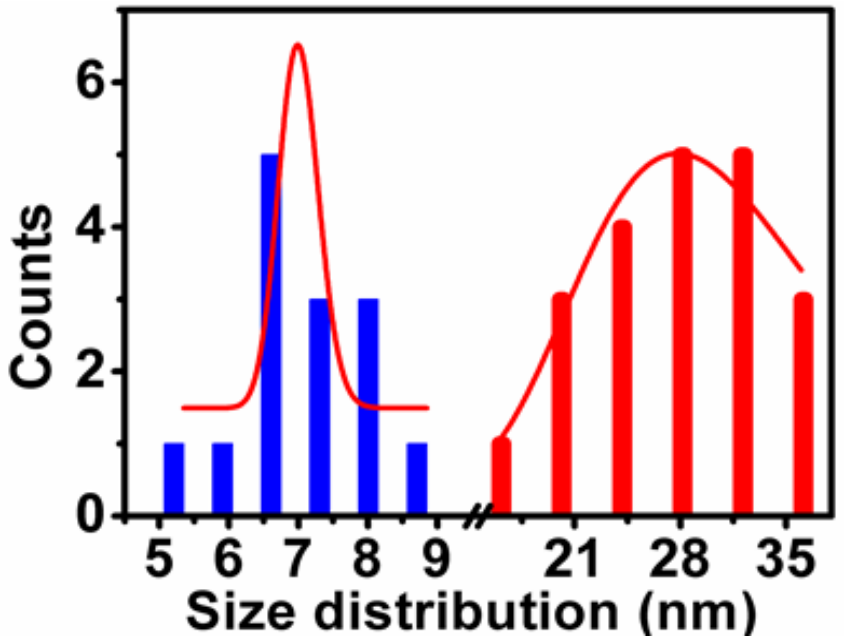


Figure 4.3 *Particle size distribution histogram of GNRs obtained from TEM*

Hydrodynamic size distribution corresponding to length and width of GNRs was determined by dynamic light scattering. As 0.1M is the optimum concentration for the formation of nanorods. So this concentration was used for further analysis. Lognormal size distribution function was used for the fitting of histograms.

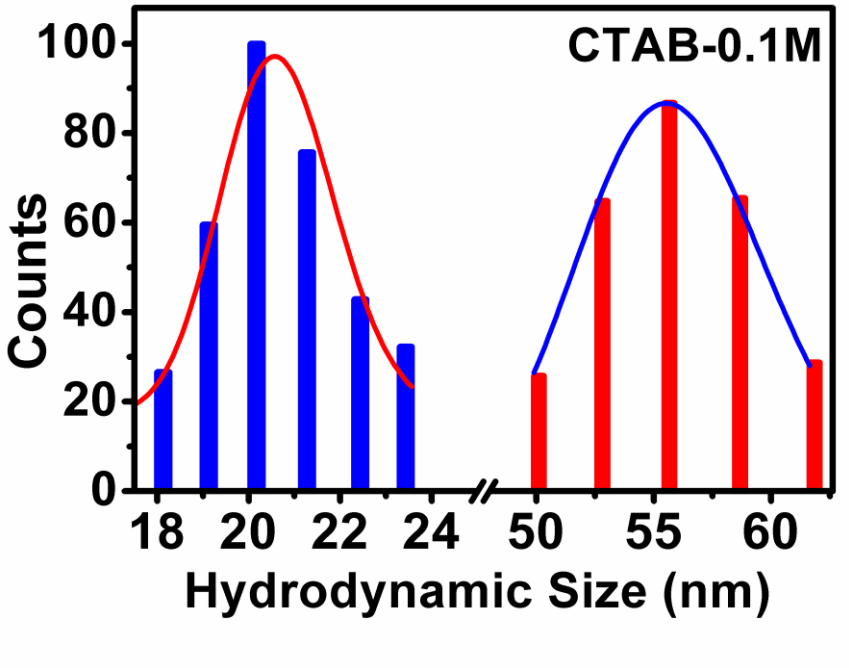


Figure 4.4 *Hydrodynamic size distributions of GNRs at 0.1M concentration of CTAB*

The particle size data was determined from the DLS analysis and hydrodynamic diameter of GNRs at 0.1M concentration of CTAB is shown in *Figure 4.4*. Size corresponding to LSPR band is 55.8 nm and corresponding to TSPR band is 20.5 nm as shown in *Figure 4.4*.

4.1.2 Variation in $NaBH_4$ volume

In seedless synthesis, growth and nucleation both occurs simultaneously. $NaBH_4$ is added to the growth solution to start the reaction as $NaBH_4$ is strong reducing agent. It reduces the gold salt from Au^{3+} to Au^0. Therefore, $NaBH_4$ plays an important role for the effective growth of nanorods. For maximum growth, appropriate amount of $NaBH_4$ should be known.

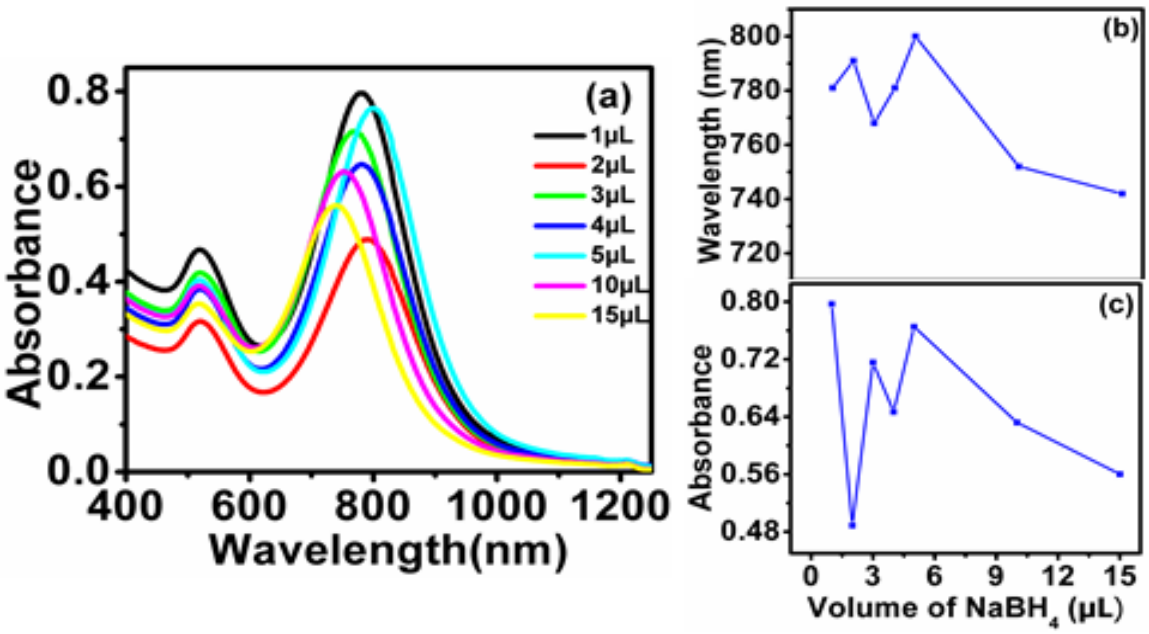


Figure 4.5 *(a) UV-Visible spectra of as-synthesized GNRs with $NaBH_4$ volume (b, c) Variation in LSPR wavelength and absorbance as a function of $NaBH_4$ volume*

UV-Visible spectra shows the rod formation at all concentrations of $NaBH_4$ *(Figure 4.5 a).* With the increase in $NaBH_4$ concentration, there is ambiguous change in the wavelength. *Figure 4.5 (b, c)* shows the effect of variation of $NaBH_4$ on the LSPR band. LSPR band position red shifts from 768 to 800 nm with increase in $NaBH_4$ which then blue shift from 800 to 742 nm with further increase in $NaBH_4$ *(Table 4.2).* When $NaBH_4$ is 5μL, the LSPR band is at 800 nm and absorbance (0.7652) is highest. Beyond 5μL $NaBH_4$, LSPR band blue shift with decrease in absorbance. Hence, 5μL of $NaBH_4$ is the optimized volume for the better growth of GNRs.

Table 4.2 *LSPR and TSPR band positions with corresponding absorbance*

$NaBH_4$ (μL)	**λ_{TSPR} (nm)**	**λ_{LSPR} (nm)**	**Abs_{TSPR}**	**Abs_{LSPR}**
1	519	779	0.4673	0.757
2	520	791	0.3166	0.4889
3	521	768	0.4189	0.7156
4	518	781	0.3844	0.6468
5	519	800	0.4037	0.7652
10	519	752	0.3909	0.6321
15	519	742	0.3537	0.5602

Hydrodynamic size distribution of GNRs synthesized with different volume of $NaBH_4$ is shown in *Figure 4.6* and size of corresponding LSPR and TSPR at different values of $NaBH_4$ is summarized in *Table 4.3*.

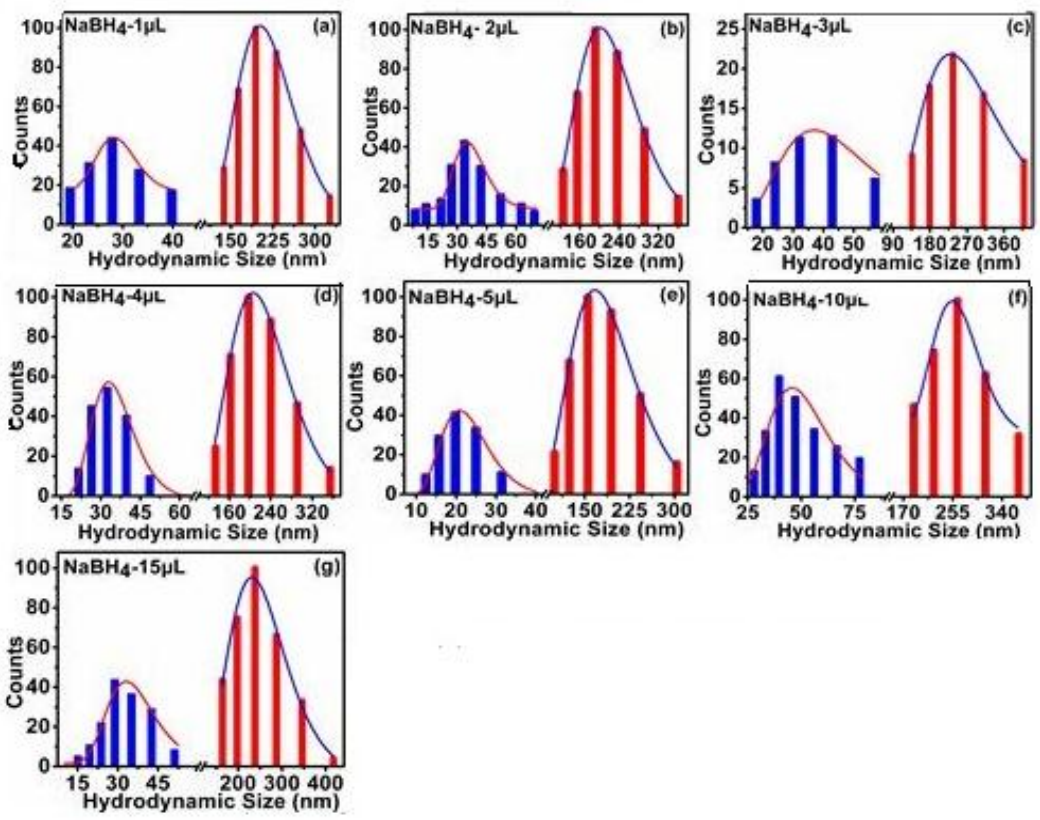


Figure 4.6 *Hydrodynamic size distribution histogram of GNRs at different values of $NaBH_4$*

Hydrodynamic size corresponding to TSPR band varies from 22.49 to 49.8 nm and corresponding to LSPR band varies from 185.71 to 520.03 nm as shown in *Table 4.3*.

Table 4.3 *Hydrodynamic size of GNRs at different values of $NaBH_4$*

$NaBH_4$ (µL)	D_{TSPR} (nm)	D_{LSPR} (nm)
1	28.74	215.8
2	36.74	221.08
3	43.63	271.5
4	34.86	223.12
5	22.49	185.71
10	49.8	260.78
15	35.52	520.03

4.1.3 Variation in pH

GNR's are synthesized at different pH as per the protocol described earlier. pH was varied from 3.5 to 1.3. UV-Visible spectra of GNRs prepared at different pH are shown in *Figure 4.7(a).* It shows two absorbance bands at each pH corresponding to TSPR and LSPR bands. *Figure 4.7(b, c)* shows the effect of variation of pH on the LSPR wavelength and its absorbance. LSPR wavelength red shifts from 778 to 849 nm with the decrease in pH. At pH 3.5 (when no HCl is added to the solution) there is rod formation. Further decrease in pH also shows the rod formation. By adding HCl, pH of the solution decreases but its shape remains same. Therefore, shape of particle is unaffected with the addition of pH.

Table 4.4 *Variation in pH values of growth solution with the addition of HCl*

Amount of HCl (diluted) (µL)	pH
1	3
2.2	2.5
4	2.3
9.3	2
27	1.7
77	1.5
102	1.3

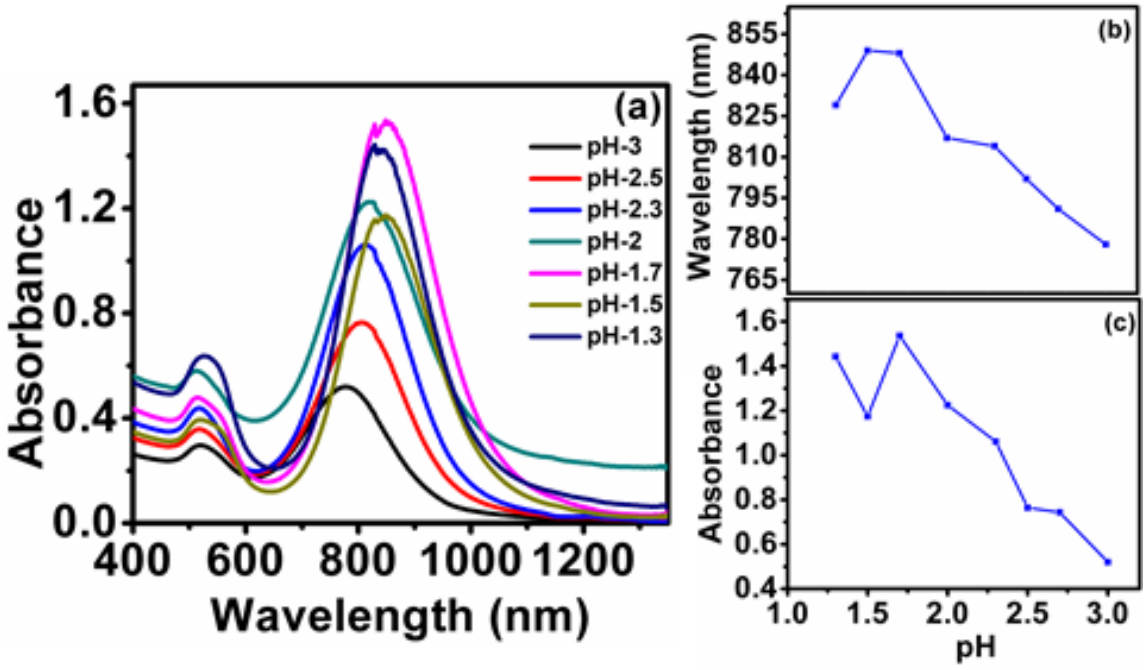


Figure 4.7 *(a) UV-Visible spectra of as-synthesized GNRs at different pH (b,c)Variation in LSPR band position and its absorbance with pH*

Wavelength and absorbance corresponding to LSPR and TSPR bands at different pH are shown in *Table 4.5.*

Table 4.5 *Wavelength and absorbance of GNRs synthesized at different pH*

pH	λ_{TSPR} (nm)	λ_{LSPR} (nm)	Abs_{TSPR}	Abs_{LSPR}
3.5	518	789	0.3784	0.8458
3	520	778	0.2964	0.52
2.5	517	808	0.358	0.7645
2.3	518	814	0.4382	1.0617
2	512	817	0.5803	1.2245
1.7	514	848	0.4784	1.5364
1.5	518	849	0.3935	1.1746
1.3	525	829	0.637	1.443

With the decrease in the pH value, growth rate of GNR's becomes slow. As the growth rate reduces, there is more LSPR band red shift from 778 nm to 849 nm.

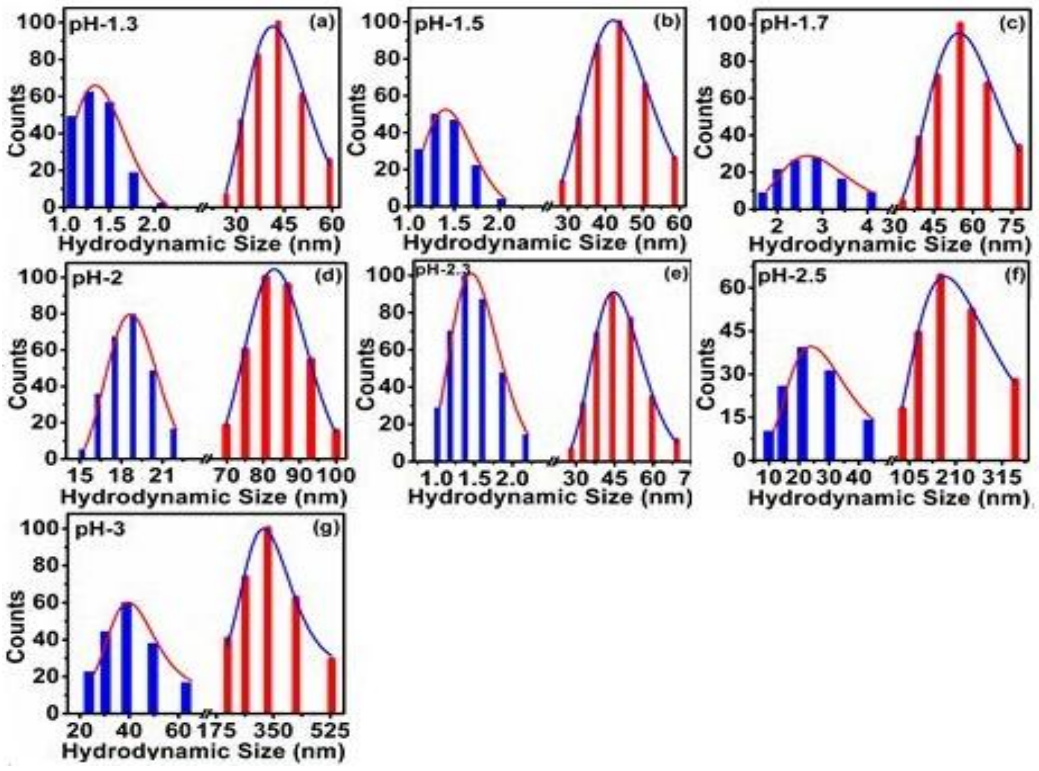


Figure 4.8 *Hydrodynamic size distribution histogram of gold nanorods synthesized at different pH values*

Hydrodynamic size corresponding to TSPR and LSPR of GNRs at different pH values is shown in the following table.

Table 4.6 *Hydrodynamic size of GNRs synthesized at different pH values*

pH	D_{TSPR} (nm)	D_{LSPR} (nm)
1.3	14.9	43.7
1.5	17.13	43.9
1.7	18.9	58.2
2	8.85	83.8
2.3	10.1	46.7
2.7	28.12	230.04
3	41.7	336.41

Hydrodynamic size corresponding to LSPR band varies from 8.85 to 41.7nm and corresponding LSPR band varies from 43.7 to 336.41 nm.

4.2 Gold Nanostars

4.2.1 Variation in Pluronic F-127 concentration

The formation of gold nanostars depends on the pluronic F-127 concentration. To evaluate the effect of pluronic F-127 concentration on optical bands, UV-Visible spectroscopy of as-synthesized gold nanostars was performed. It is shown in *Figure 4.9*. Formation of nanostars is observed only at 0.01 and 0.001M of pluronic F-127 whereas at other concentrations (0.0001M, 0.0005M, 0.005M and 0.0025M) spherical nanoparticles are formed as evidenced from single plasmon resonance peak.

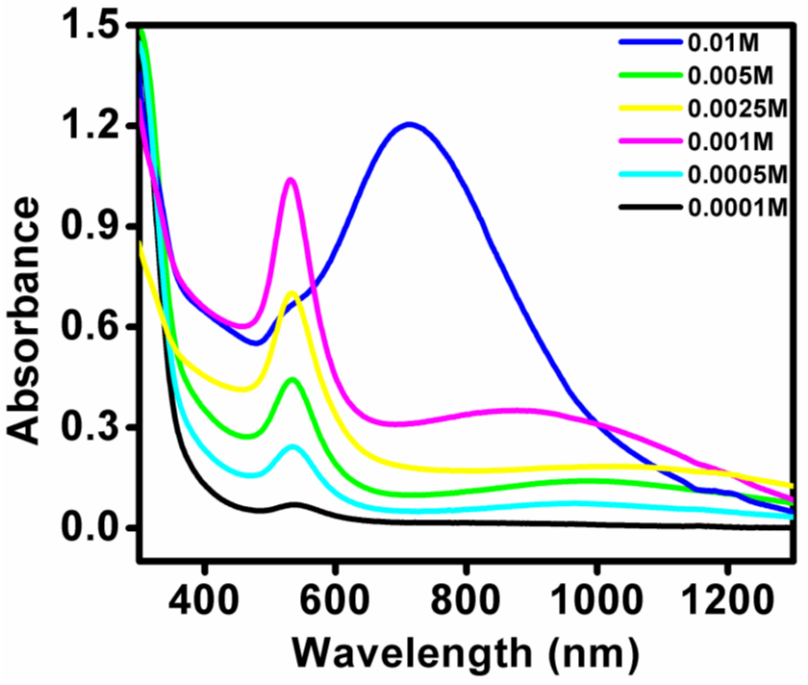


Figure 4.9 *UV-Visible spectra of gold nanostars synthesized with different concentration of Pluronic F-127*

Wavelength position and absorption of TSPR and LSPR bands are shown in *Table 4.7*.

Table 4.7 *Wavelength and absorbance of gold nanostars synthesized at different concentration of Pluronic F-127*

Pluronic F-127 (M)	**λ_{TSPR} (nm)**	**λ_{LSPR}** (nm)	**Abs_{TSPR}**	**Abs_{LSPR}**
0.01	-	709	-	1.2038
0.005	534	-	0.4425	-
0.0025	533	-	0.7007	-
0.001	531	870	1.3094	0.3505
0.0005	535	-	0.2423	-
0.0001	537	-	0.0691	-

From UV-Vis analysis it is observed that 0.01M is the optimum growth concentration for the synthesis of gold nanostars due to high yield of this concentration as compared to 0.001M of pluronic F-127.

To understand the effect of Pluronic F-127 concentration on the morphology of GNRs, TEM was performed. TEM image of gold nanorods with 0.01M concentration of Pluronic F-127 is shown in the *Figure 4.10*.

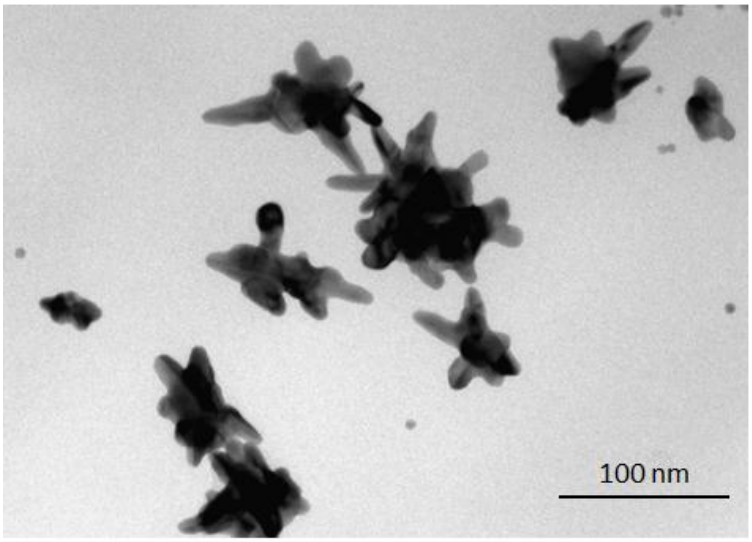


Figure 4.10 *TEM Micrograph of as-synthesized gold nanostars at 0.01M concentration of Pluronic F-127*

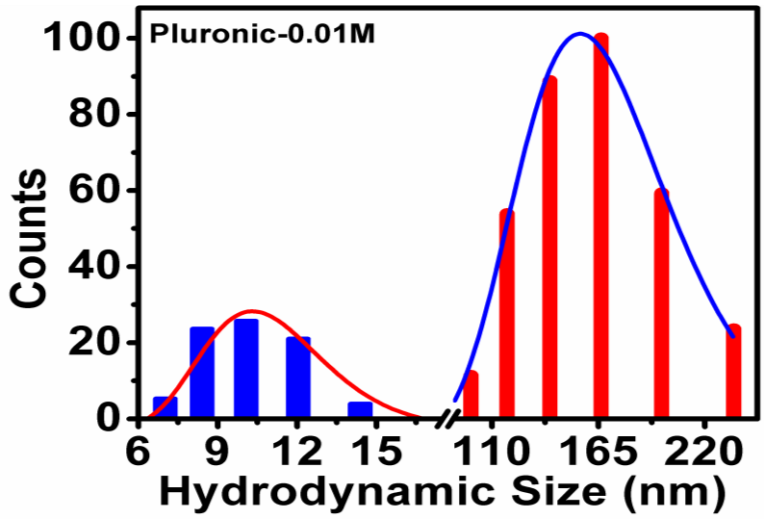


Figure 4.11 *Hydrodynamic size distribution histogram of gold nanostars synthesized at 0.01M concentration of Pluronic F-127*

Hydrodynamic size corresponding to LSPR band is 165.34 nm and corresponding to TSPR band is 10.82 nm.

4.2.2 Variation in $NaBH_4$ Volume

$NaBH_4$ plays important role for the effective growth of nanostars. For maximum growth, appropriate amount of $NaBH_4$ should be known. To investigate this, different volume of $NaBH_4$ such as 1, 2, 3, 4, 5 and 10μL was taken whereas all other experimental conditions were kept constant.

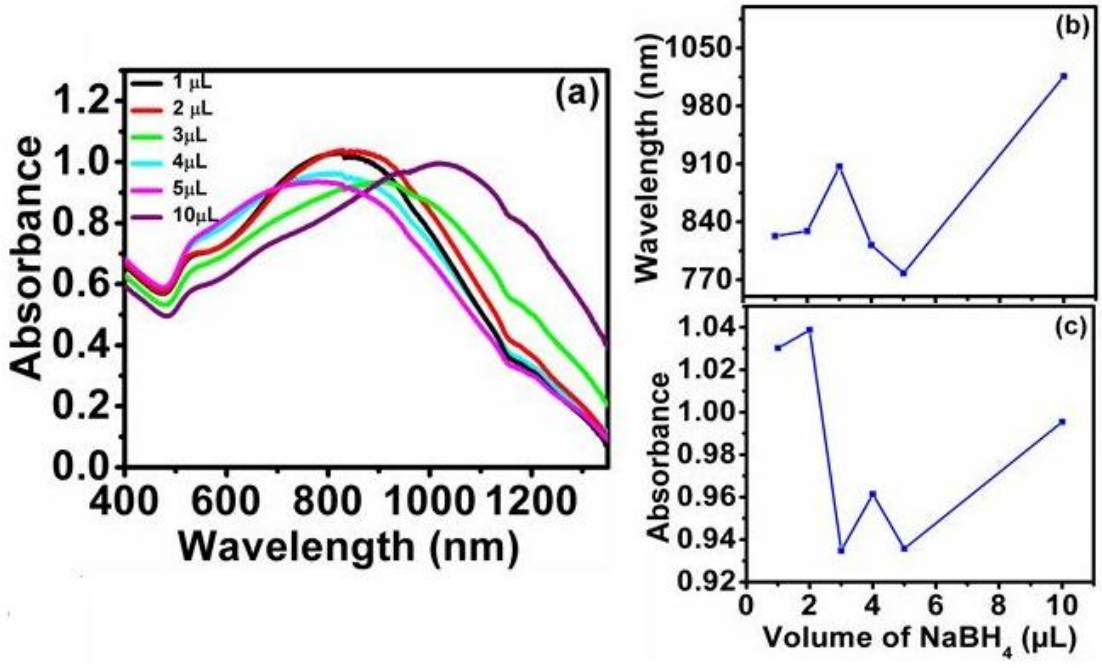


Figure 4.12 *(a) UV-Visible spectra of as synthesized gold nanostars with $NaBH_4$ volume (b, c) Variation in LSPR wavelength and absorbance as a function of $NaBH_4$ volume*

Absorbance peaks observed from UV Visible spectra is shown in *Figure 4.12(a).* UV graph shows nanostar formation at different concentration of $NaBH_4$. With the increase in $NaBH_4$, there is ambiguous change in wavelength. *Figure 4.12(b, c)* shows the effect of variation of $NaBH_4$ on the LSPR wavelength and its absorbance. LSPR wavelength blue shifts from 907 to 778 nm with the increase in $NaBH_4$. *Table 4.8* shows the wavelength and absorbance values at different values of $NaBH_4$.

Table 4.8 *Wavelength and absorbance of gold nanostars at different concentration of $NaBH_4$*

$NaBH_4$ (µL)	λ_{LSPR} (nm)	Abs_{LSPR}
1	823	1.0302
2	829	1.0388
3	907	0.9348
4	812	0.9614
5	778	0.9358
10	1016	0.9958

Hydrodynamic size distribution of gold nanostars with different $NaBH_4$ is shown in *Figure 4.13* Hydrodynamic size corresponding to LSPR and TSPR bands is also mentioned in *Table 4.9.*

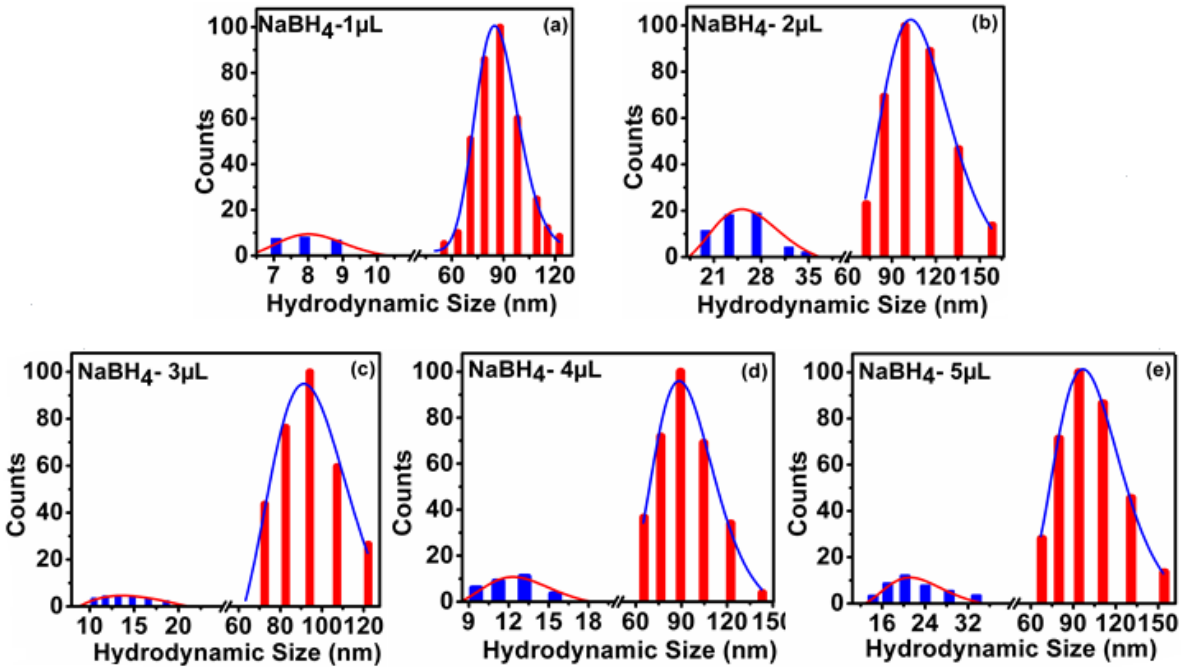


Figure 4.13 *Hydrodynamic size distribution histogram of gold nanostars prepared with different values of $NaBH_4$*

Table 4.9 *Hydrodynamic size at different concentration of $NaBH_4$*

$NaBH_4$ (µL)	D_{TSPR} (nm)	D_{LSPR} (nm)
1	8	86.61
2	26.17	108.18
3	19.63	95.39
4	12.8	63.07
5	22.6	102.47
10	31.5	122.2

Hydrodynamic size corresponding to TSPR band varies from 8 to 31.5 nm and corresponding LSPR band varies from 63.07 to 122.2 nm.

4.2.3 Variation in pH

Nanostars were obtained at different pH values and other experimental conditions were taken as per seedless synthesis. Values of pH were varied from 3.5 to 1.3.With the increase in HCl, pH of the solution decreases.

Table 4.10 *Variation in pH values of growth solution with HCl*

Amount of HCl (diluted) (µL)	pH
1	3
2.6	2.5
4.8	2.3
10.2	2
31	1.7
75	1.5
108	1.3

Absorbance peaks observed from UV Visible spectra is shown in *Figure 4.14(a)*. *Figure 4.14(b, c)* shows the effect of variation of pH on the LSPR wavelength and its absorbance. LSPR wavelength blue shifts from 737 to 663 nm with the decrease in pH. At pH-3.4 (when no HCl is added to the solution) nanostars are formed. Further decrease in pH also shows the nanostar formation.

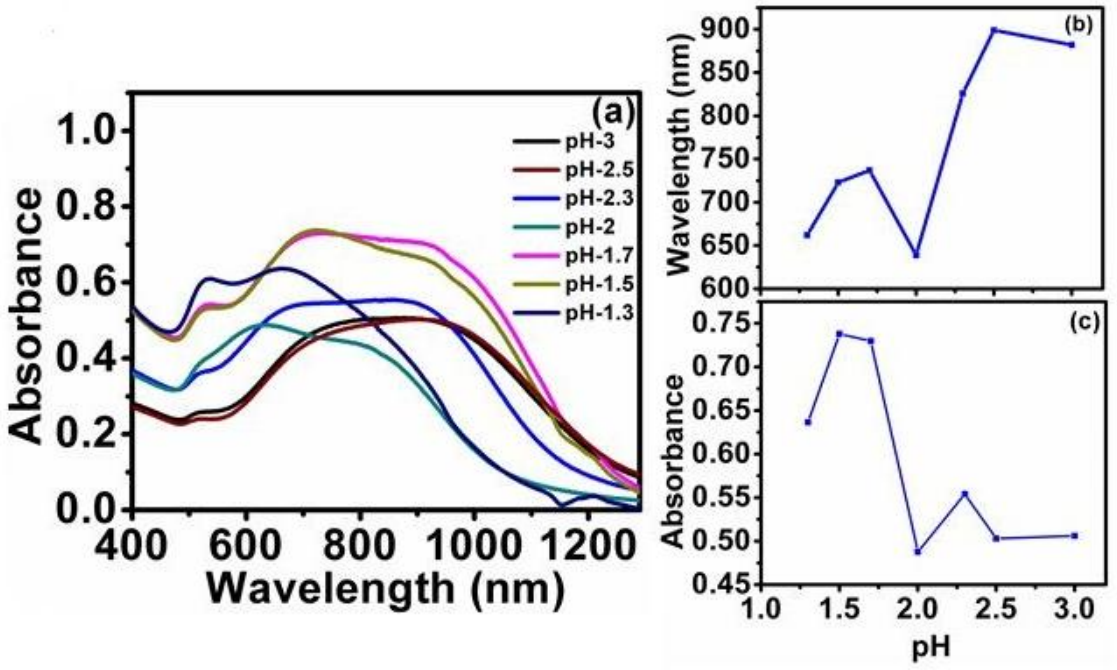


Figure 4.14 *(a) UV-Visible spectra of as synthesized gold nanostars at different pH (b,c) Variation in LSPR wavelength band and absorbance with pH*

Wavelength and absorbance corresponding to LSPR band at different pH values are also shown in *Table 4.10*. With the decrease in the pH, growth rate of the solution becomes slow. As the growth rate decreases, LSPR blue shift from 737 to 663 nm.

Table 4.11 *Wavelength and absorbance of gold nanostars synthesized at different values of pH*

pH	λ_{LSPR} (nm)	Abs_{LSPR}
3	876	0.5071
2.5	899	0.5031
2.3	854	0.555
2	639	0.4877
1.7	737	0.7298
1.5	723	0.7379
1.3	663	0.6369

Hydrodynamic size distribution of pH at different values is shown in *Figure 4.15* and Size of corresponding LSPR and TSPR at different values of pH is summarized in *Table 4.12*

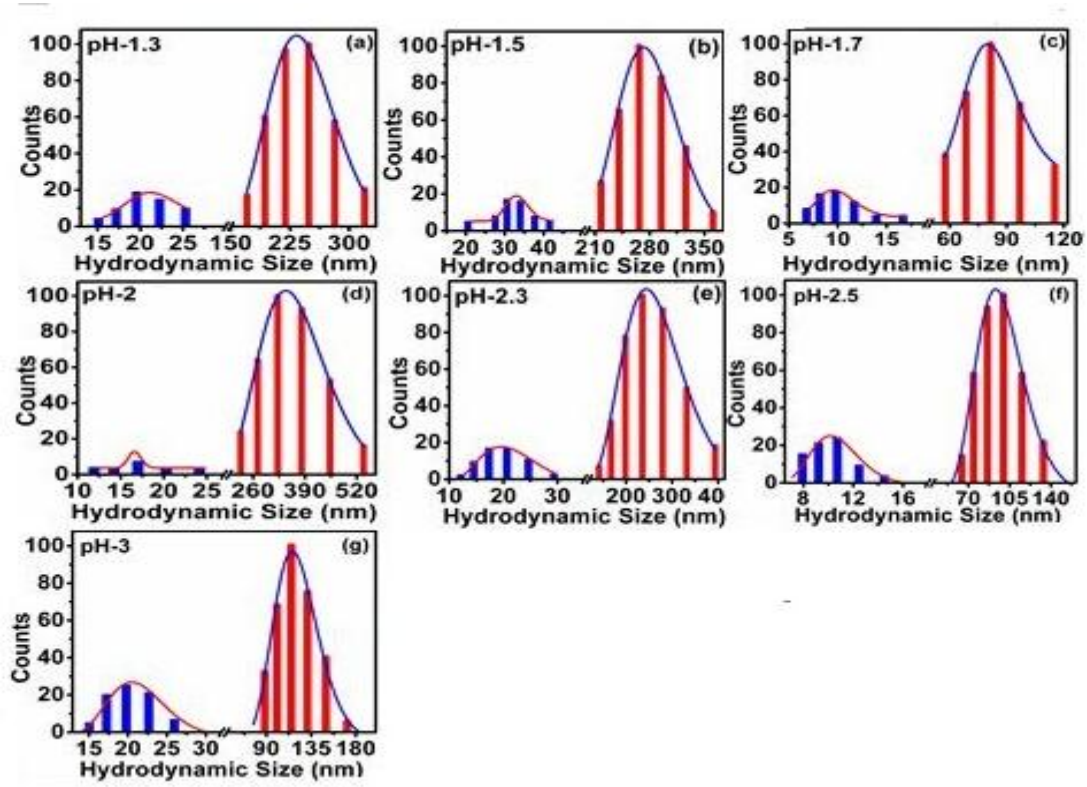


Figure 4.15 *Hydrodynamic size distribution histogram of gold nanostars at different pH*

Hydrodynamic size corresponding to TSPR and LSPR at different pH values is shown in the following table

Table 4.12 *Hydrodynamic size of gold nanostars at different pH*

pH	D_{TSPR}(nm)	D_{LSPR}(nm)
1.3	21.5	241.23
1.5	33.17	277.6
1.7	9.9	82.3
2	16.06	363.6
2.3	21.5	262.12
2.5	10.54	97.40
3	21.12	120.24

Hydrodynamic size corresponding to LSPR band varies from is 9.9 to 33.17 nm and corresponding to TSPR band varies from 82.3 to 363.6 nm.

Conclusion

- Strong effect of surfactant type is observed on the morphology of gold nanoparticles under optimized conditions, gold forms nanorods when CTAB is used as surfactant while pluronic F-127 produces nanostars of gold.
- Nanorods show red shift in LSPR band while nanostars show blue shift in LSPR band with decrease in pH of growth solution.
- Surface plasmon resonance (LSPR and TSPR), hydrodynamic size and aspect ratio can be tuned by varying the synthesis conditions in single step seedless growth.