Effect of pH on morphology and stability of gold nanorods synthesized by seedless method

A thesis submitted

in partial fulfillment of the requirement for

the award of the degree of

Master of Science

in

PHYSICS

Submitted by:
Tamanna
Roll No: (301604038)

Under the supervision of

Dr. Bhupendra Chudasama

Associate Professor
School of Physics and Material Science
Thapar Institute of Enginerring and Technology (TIET), Patiala
Punjab-147004

JUNE 2018

CERTIFICATE

This is to certify to that thesis entitled "**Effect of pH on morphology and stability of gold nanorods synthesized by seedless method**"submitted by **Tamanna, Roll No. 301604038** in partial fulfillment of requirements for the award of the degree **M.Sc.** in **Physics** from the School of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala is a record of candidate's own work carried out by her under my supervision and guidance. The matter embodied in this report has not been submitted in part or full to any other institute for award of any degree.

Dr. Bhupendra Chudasama
Associate Professor
School of Physics and Material Science
Thapar Institute of Engineering and Technology, Patiala

Declaration

I hereby declare that the work presented in this thesis report entitled "**Effect of pH on morphology and stability of gold nanorods synthesized by seedless method**"by me in partial fulfilment of the requirements for the award of degree of **Master of Science** in **Physics** to Thapar Institute of Engineering and Technology, Patiala is an authentic record on my own work carried out under the supervision of **Dr. Bhupendra Chudasama**, Associate Professor, School of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala. The matter presented in this report has not been submitted in any other university/institute for award of Master of Science or any other degree.

Tamanna

Tamanna
(Regd No: 301604038)

Acknowledgement

I would like to express my deep sense of gratitude to Dr. Bhupendra Chudasama, Associate Professor School of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala for his invaluable suggestion, excellent supervision, and constant encouragement, thought provoking and unabashed discussion in nurturing the work and during the preparation of manuscript throughout the research work.

My sincere thanks to Dr. Manoj Sharma, Professor and Head of School of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala for providing me opportunity to conduct this work and bring it out in the present form.

I also thank and regards to Miss Purnima Sharma, Miss Navjot Kaur and Miss Yashpreet School of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala for helping in this work.

The greatest thanks goes to my family members for their infinite support at each and every part of my life. Above all I express my indebtness to the almighty for all his blessings.

LIST OF FIGURES

LIST OF TABLES

Abstract

In this thesis, gold nanorods are prepared by seedless method. In this method, we synthesize two series of gold nanorods. In the first series gold nanorods are prepared by seedless route at two different pH. In the second series, two samples of gold nanorods are synthesized under identical conditions simultaneously at pH-2.2 and they are presented at different pH matching with series-1. Stability of gold nanorods is observed over 36 days with UV-Visible spectroscopy and photon correlation spectroscopy. Both series of gold nanorods shows impressive stability. No significant difference is observed in the stability of gold nanorods that are synthesized at different pH or stand at different pH.

Table of Contents

Chapter 1 Introduction

Chapter 2 Literature Review

Chapter 3 Synthesis and Characterization

CHAPTER 4 Results and Discussion

Chapter-1
Introduction

1.1 Nanotechnology

Nanotechnology is the development of technology at atomic, molecular or macromolecular levels in the length scale of 1-100 nm. The concept of nanotechnology first comes around 1959. Nanotechnology has the ability to construct materials, systems and devices with atomic precision[1]. Nanotechnology is the technology of small things. Nanotechnology combines various fields of physics like solid state physics, biochemistry, chemical engineering and material science etc. Sometimes, nanotechnology also termed as molecular manufacturing.

There are many different fundamental area of nanotechnology. Nanotechnology plays an important role in microelectronic revolution.

$$1 \text{ nm} = 10^{-9}\text{m}$$

There are many ways to visualize nanometre

- Atom ~ 0.1 nm.
- Width of DNA ~ 2 nm.
- Fullerenes (C60) ~ 1 nm.

1.2 Why Nanoscale?

Every material has different physical and chemical properties at nanoscale rather than at larger scale. Nanoscale is very important because many naturally occurring phenomenon are observed only at nanoscale and some of these phenomenon's are:-

1. **Quantum effects**

At nanoscale, quantum effects become dominating which decides the properties of nanomaterials. Properties of the material changes as we change the size of the particle. Quantum confinement is one of the important phenomenon occurs at nanoscale. It is more prominent in case of semiconductors as compared to metals [2].

2. **High Surface Area**

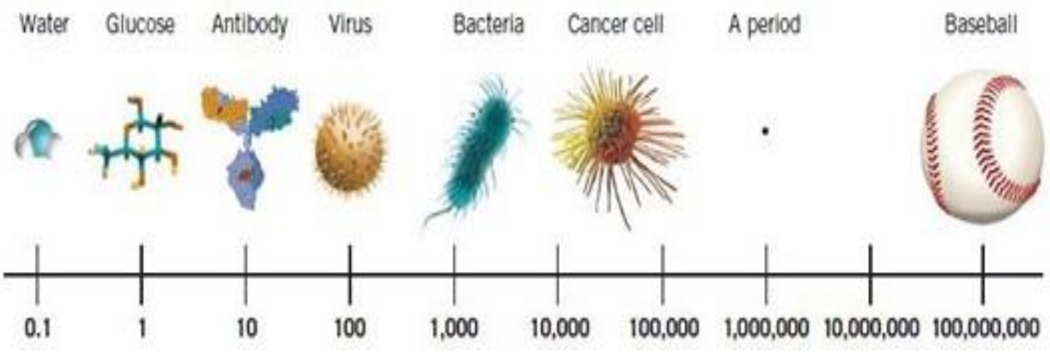
The surface to volume ratio of nanomaterials is high. It means that surface area of materials is large at nanoscale as compared to surface area of materials at bulk scale. Nanomaterials having larger surface area help to create better catalyst.

3. **Majority of biological processes occurs at nanoscale**

Nanometer scale plays very important role in many biological systems. Principle of self assembly shows how biology relates with the nanoscale. Using nanoscale we can easily design the structures having similar size scale as that of biological systems. Working of cells is occurring at nanoscale [3]. For example, DNA the building block of our life is 2 nm in size. In the same way many other biological processes also occurs at nanoscale.

1.3 Nanoparticles

Nanoparticles are defined as objects having size between 1-100 nm and their size is quite different from that of bulk materials. Presently used biomaterials are synthesised using, titanium, gold and silver etc. [4]



Size (nm)

Fig 1.1 Comparison of size scale [5]

1.3.1 Properties of Nanoparticles

1. Melting Point: Nanoparticles melts at lower temperature as compared to bulk material due to the reason that nanoparticles has large surface to volume ratio as compared to bulk material.

2. Magnetic Properties: The confinement of electrons in nanoparticles may leads to different magnetic property [6]. The magnetic properties of nanoparticles are shown by their influence only at very low size scale (10-20 nm).

3. Mechanical Properties: Nanoparticles have different mechanical properties as compared to bulk materials [7]. Due to the better mechanical properties of nanoparticles they can be used in many technical applications.

4. Optical Properties & Electronic properties: The optical properties and electronic properties of nanoparticles are not independent. They are dependent on each other. Metal nanoparticles like gold nanoparticles have size dependent optical properties. The optical properties of nanopaticles are different from that of bulk crystals [8]. This is because of Quantum confinement of electrons.

1.3.2 Applications of Nanotechnology

Medicine and drug delivery	Nanoparticles show its ability to deliver drugs. Many semiconductors and metal nanoparticles are used for cancer therapy. Gold nanoparticles provides a novel class of photo thermal agents which are used for the treatment of tumours[9]. Nanogold is also used in drugs detection.
Surgery	Using nanotechnology, many surgical instruments and robots are made which are called nanobots[10]. They are used to perform surgeries on any part of the body.

Electronics	Nanoelectronics refer to use of nanotechnology on electronic components like transistors. Many techniques are used for the production of microelectronic devices which includes screen printing, inkjet printing techniques etc. Among these techniques, inkjet printing was considered to be a functional technology for micro scale patterning in microelectronic devices for metallic traces[11].
Fuel Cells	Nanotechnology is being used to reduce the cost of catalysts used in fuel cells to produce hydrogen ions from fuel. Using nanotechnology many nanomaterials are produced which will make fuel cells lighter and more efficient.

1.3.3 Approaches of Nanomaterials Synthesis [12]

1. **Top-down Approach** (larger to smaller)
2. **Bottom-up Approach (**smaller to bigger)

- **Top-down Approach:** Top-down approach means slicing or cutting a bulk material so that we will get nano sized particles. This approach is similar to making of a statue with stone.

  Example:-Grinding, Ball milling, etching, X-Ray Lithography, etc.

- **Bottom-up Approach:** refers to approach of building up of a material through atom by atom, molecule by molecule and clusters by clusters, etc. where devices 'create themselves' by self-assembly.

  Example:-Lithography, chemical routes, self-assembly.

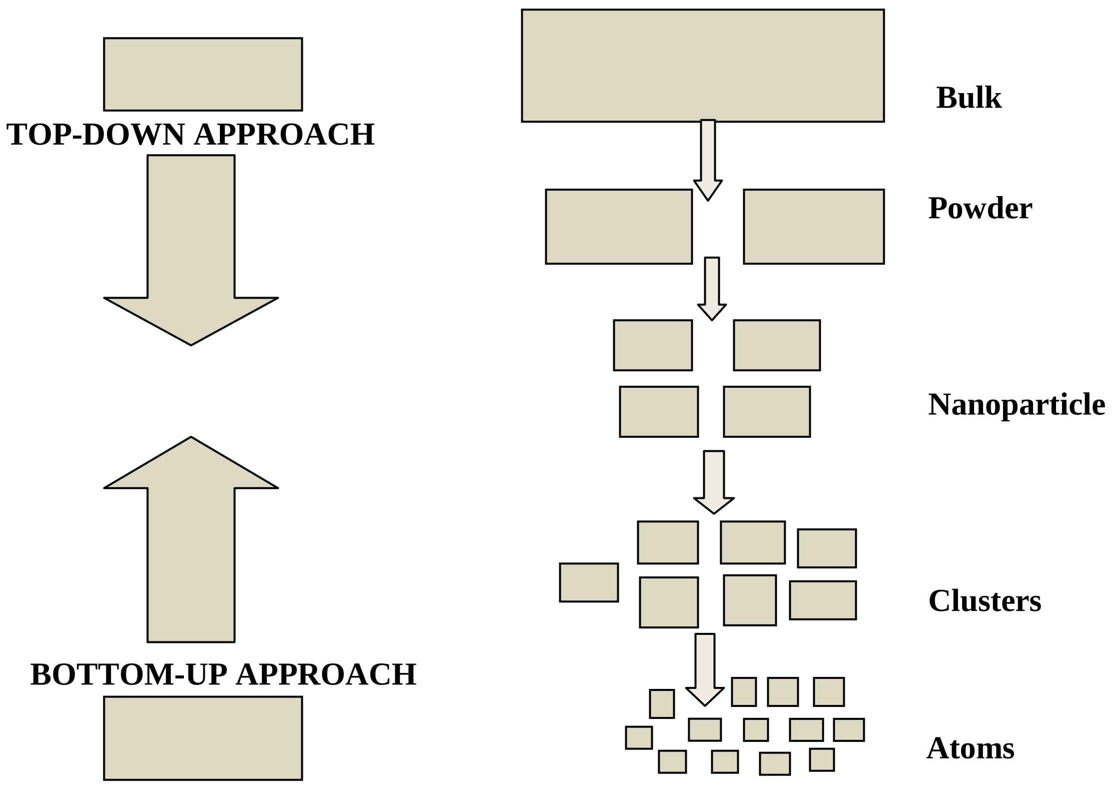


Fig 1.2 Top-down and bottom-up approach for synthesis of nanomaterials

1.4 Gold Nanoparticles

Gold nanoparticles are the group of atoms which are up to 100 nm in diameter and they also have unique optical properties. Gold nanoparticles are used in many medical applications like diagnostics and therapy. The optical properties of gold nanoparticles is decided by Surface Plasmon resonance, which occurs due to the collective excitation of conduction electrons from visible to infrared region, depending upon shape and size of particles[13].When nanoparticles are spherical in shape, we get single Plasmon band in the visible region. But, when nanoparticles are of anisotropic shape like rod, we get two Plasmon resonance bands one is longitudinal band and other is the transverse band.

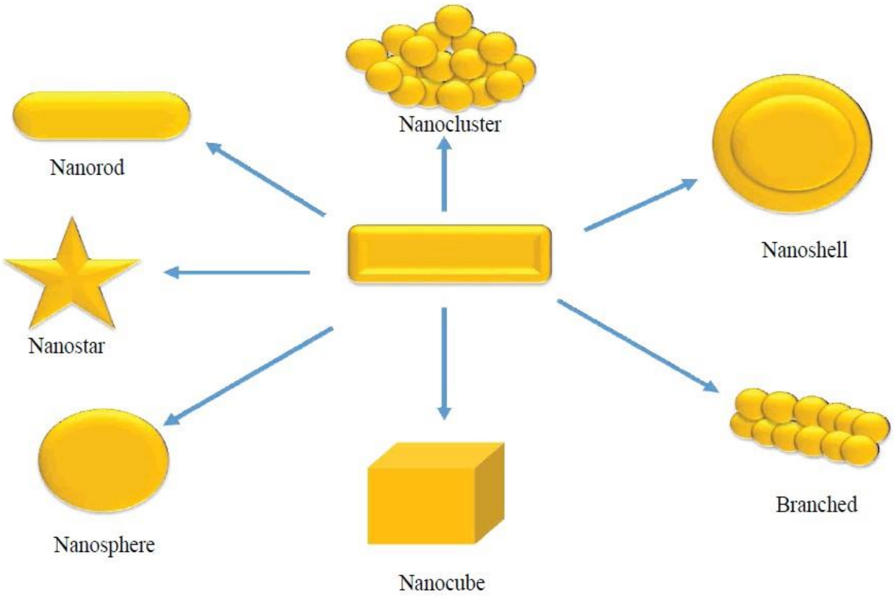


Fig 1.3 Various Shapes of Gold Nanoparticle[14]

1.4.1 Surface Plasmon Resonance [15]:-When electromagnetic radiation of specific frequency is incident on nanoparticles, then excitation of free electrons on the surface of nanoparticles occur which causes absorption of these electromagnetic radiations. This optical property of nanoparticles is called as Surface Plasmon resonance. The specific frequency of light where this occurs is dependent on the shape and size of nanoparticles.

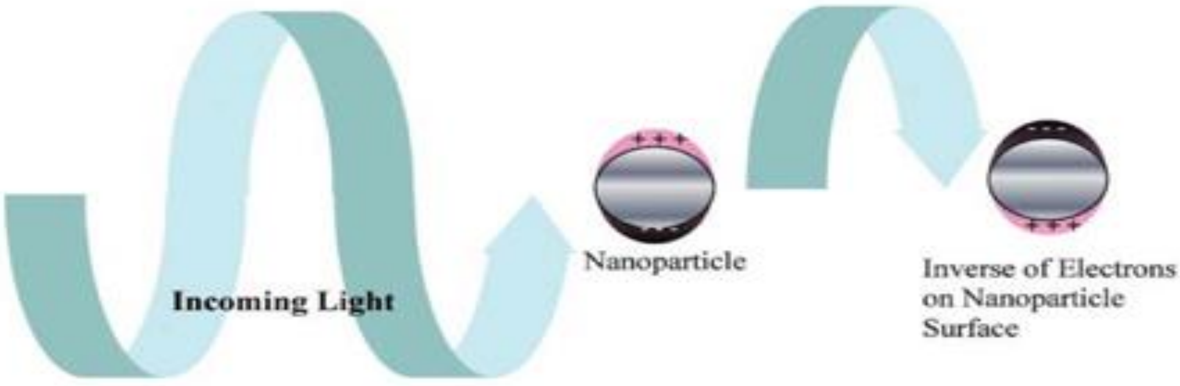


Fig 1.4 Origin of Surface Plasmon Resonance in nanoparticles [16]

A resonance condition occurs from the absorption and scattering of radiation and It depends on the size and shape of metal and the surrounding material.

1.5 Gold Nanorods

Gold nanorods are the rods which are cylindrical in shape and which are less than 10-40 nm in width and up to 100 nm in length. These particles are classified by aspect ratio. Due to anisotropic property of gold nanorods have been achieved lots of attention for optical properties and their applications. There are mainly two Plasmon modes in gold nanorods:

1. The First one is LSPR (i.e. Longitudinal Surface Plasmon Resonance) mode which is associated with oscillations of electron along the length axis of the nanorods.
2. The Another one is TSPR (i.e. Transversal Surface Plasmon Resonance) mode which is due to oscillations of electron along the width of nanorods[17].

1.5.1 Medical applications of Gold Nanorods

- Drug delivery
- Photothermal therapy
- Bioimaging
- Gene delivery
- Antifibrotic therapy
- Hyperthermia

HYPERTHERMIA [18]

Hyperthermia is under consideration as a medical treatment for cancer therapy, in which tissues are exposed to higher temperature than normal temperature for the destruction of abnormal cells. Hyperthermia has been considered as an auxiliary therapy for treatment of various disease states and its potential in cancer treatment is an area of investigation. Gold nanorods have large absorption crossection at near-infrared frequencies. They are excellent candidates as multifunctional agents for various therapies like image-guided therapies which are based on localized hyperthermia.

References

1. G. Ali Mansoori and T. A. FauziSoelaiman., Journal of ASTM International, Nanotechnology – An Introduction for the Standards Community, (2005), 2, 1-22.
2. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen and M. G. Bawendi, J. Phys. Chem., B,CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites, (1997), 101, 9463–9475.
3. Nathaniel L. Rosi and Chad A. Mirkin, Chem. Rev., Nanostructures in Biodiagnostics, (2005), 105, 1547–1562.
4. Dubchak S., Ogar A., Mietelski J.W. and Turnau K., Span. J. Agric. Res., Influence of silver and tianium nanoparticles on arbuscularmycorhiza colonization and acumulation of radiocaesiumin Helianthus anus, (2010), 8(1), 103-108.
5. Chakraborty AK, Roy T and Mondal S, iMedPub Journals, Development of DNA Nanotechnology and uses in Molecular Medicine and Biology,(2016), 1, 2-13.
6. Qi, M., Zhang, K., Li, S., Wu, J., Pham-Huy, C., Diao, X., Xiao, D., He, H., New J. Chem., Super paramagnetic Fe_3O_4 nanoparticles: synthesis by a solvothermal process and functionalization for a magnetic targeted curcumin delivery system, (2016), 40, 4480– 4491.
7. Guo, D., Xie, G., Luo, J., Journal of Physics D, Mechanical properties of nanoparticles: basics and applications, (2014) , 47, 0022-3727
8. Eustis, S., El-Sayed, M.A., Chem. Soc. Rev., 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, (2006), 35, 209–217.
9. El-Sayed H., Huang X., El-Sayed M. A., Cancer letters., Selective laser photothermal therapy of epithelial carcinoma using anti-EGFR antibody conjugated gold nanoparticles, (2006), 239, 129–135.
10. ReitasRA., Int J Surg., Nanotechnology, nanomedicine and nanosurgery., (2005), 3(4), 243–246.
11. Paul Calvert., Chem. Mater., inkjet Printing for Materials and Devices, (2001), 13(10), 3299-3305
12. H. Hahn, Nanostructured Materials, (1997), 9, 3-771.
13. Khlebtsov N.G., Nano Lett, Quantum Electron., (2008), 38, 504–529.
14. Alaqad and Saleh, J Environ Anal Toxicol, “Gold and Silver Nanoparticles,Characterization Routes and Applications towards Drugs”, (2016), 6, 4
15. Rao CNR, KulkarniGU, Thomas PJ, Edwards PP., ChemSoc Rev, Metal nanoparticles and their assemblies., (2000), 29, 27–35
16. Susie Eustis and Mostafa A. El-Sayed, Chem. Soc. Rev., 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, (2006), 35, 209–217
17. Jorge Perez-Juste, Isabel Pastoriza-Santos, Luis M. Liz-Marzan a, Paul Mulvaney., Chem. Rev., Gold nanorods., Synthesis, characterization and applications, (2005), 249, 1870-1901.
18. Terry B. Huff, Ling Tong, Yan Zhao, Matthew N. Hansen, Ji-Xin Cheng, and Alexander Wei., NIH Public Access., Nanomedicine, Hypothermic effects of gold nanorods on tumor cells, (2007), 2(1), 125–132.

Chapter 2

Literature Review

Many methods has been developed for synthesis of gold nanoparticles. This chapter gives reviews of different methods of synthesis of gold nanoparticles .Mostly, seedless method has been used for the synthesis of gold nanoparticles.

2.1 Synthesis of gold nanoparticles

Author name	Title	Results
Peter Zijlstra, et.al., J. Phys. Chem. *B*u, (2006), 110, 19315-19318	High-Temperature Seedless Synthesis of Gold Nanorods[1].	• Gold nanorods by seedless method has been synthesised at high temperatures upto 97°C. • Rod length decreases with increase in temprature but width of rod remain constant. • Average activation energy become 90(10 kJ mol-1 for all facets.

Moustafa R. K. Ali, et.al., Langmuir, (2012), 28, 9807–9815	Synthesis and Optical Properties of Small Au Nanorods Using a Seedless Growth Technique[2].	• Small size gold nanorods having width in range from 2.5- 3 (nm) in one and 4 - 5.5 (nm) in other setting are synthesized by seeless growth method of different aspect ratios. • As pH decreases , growth time increases. • As the concentration of CTAB concentration increases it produces smaller size nanorods .

Parveer Kaur , et.al., J. Mater. , (2017),52,11675–11687	Seedless co-surfactant-based dimensional and optical tunability of gold nanorods with simultaneous pH regulation[3].	• Reduction from Au(I) to Au (0) occurs due to NaBH4 which speed up the growth of gold. nanorods. • The Intensity of both LSPR and TSPR bands is higher in seedless method as compared to seeded method. • Highaspectratio gold nanorods are obtained with medium yield in binary cosurfactant system . • The influence of both binary surfactants and pH on dimensions and plasmonic properties of gold nsnorods by seedless method is also proposed.
XiaolongXu, et.al., J. Mater. Chem. A, (2014), 2, 3528–3535	Seedless synthesis of high aspect ratio gold nanorods with high yield[4].	• Gold nanorods with high aspect ratio, high yield and smooth morphology are obtained by seedless method. • Width of the gold nanorods which are synthesised by seedless

		method should be smaller than seed-mediated method. • The width could be adjust by adding various amounts of $NaBH_4$ .Also aspect ratio could be adjust by varying pH. • Gold nanorods with normal aspect ratio has been developed using seedless method by 0.06 M CTAB.
PaulaCAngelome, et.al., Chem. Mater., (2012), 24, 1393−1399	Seedless Synthesis of Single Crystalline Au Nanoparticles with Unusual Shapes and Tunable LSPR in the near-IR[5].	• Highly Anisotropic gold nanoparticles are obtained using CTAC. • LSPR of gold nano particles which are obtained can tuned from 600-1400 nm by changing temperature of the reaction or concentration of reagents. • By changing temperature of reaction and the concentrations of reagents gold nanoparticles of different shapes with high yields are

		obtained.
Wenjing Wang, et.al., (2016), 27, 0957-4484	Seedless synthesis of gold nanorods using resveratrol as a reductant[6].	• Gold nanorods with aspect ratio 4.3 are obtained. • Two LSPR peaks at 520nm and 830 nm are obtained. • There is a shift in LSPR peaks towards smaller wavelength which shows weaker reducibility of resveratrol as compared to many reductants. • Monodispersity of gold nanorods was improved due to resveratrol. • The growth of gold crystals and reduction of Au(I) to Au(0) is caused due to resveratrol.
Anand Gole, et.al., Chem. Mater., (2004), 16, 3633-3640	Seed-Mediated Synthesis of Gold Nanorods: Role of the Size and Nature of the Seed[7].	• Aspect ratio of gold nanorods increases size of seed decreases. • Dimensions of gold nanorods changes as function of size of

		seed . • Dependence of size of seed on shape and size is known.
Linfeng Gou, et.al., Chem. Mater.,(2005), 17, 3668-3672	Fine-Tuning the Shape of Gold Nanorods[8].	• Gold nanorods are synthesized by the seed-mediated method, but still some unreduced gold ions are left , which can be utilized as a substrate for the fine-tunning of the structural properties of gold nanorods. • Ascorbic acid in oxidized form has ability to reduce gold ions . • For fine-tuning of the shape of gold nanorods CTAB is used. • The optical properties of gold nanorods are influenced by their modified shapes.
Babak Nikoobakht, et.al., Chem. Mater. ,(2003), 15, 1957-1962	Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth	• In single surfactant (CTAB) mixture, gold nanorods with aspect ratios (1.5 - 4.5) are obtained.

	Method[9].	• In single surfactant mixture, the length of gold nanorods can be controlled by changing silverion content in growth solution. • Binary surfactant (BDAC and CTAB)mixture was used to obtain gold nanorods with high aspect ratio (4.6-10).
Jing Cheng, et.al., Journal of the Chinese Chemical Society, (2011), 58, 822-827	Investigation of pH Effect on Gold NanorodSynthesis[10].	• Gold nanords are prepared using seed-mediated method at different pH. • Morphology of goldnanorods is dependent on pH of growth solution. • UV-Vis spectral change indicates that the gold nanorod growth pathway was different at different pH. • CTAB micelle's stability was affected by pH and morphology of final

		products also changes.
Goldie Oza, et.al., Adv. Appl. Sci. Res., (2012), 3(2),1027-1038	Tailoring Aspect Ratio of Gold Nano Rods: Impact of temperature, pH, silver ions, CTAB concentration and centrifugation[11].	• A metallo-micellar complex of Gold Au(III) with CTAB is formed which results into stable nuclei of gold. • When Au (III) – CTAB in optimum concentration is added , there will be reduction from Au (III) to Au (I) which is due to Ascorbic acid. Further reduction from Au (I) to Au (0)is observed in gold seeds • This method separates gold nanorods from other shapes after centrifugation of gold nanorods.
AK Khan, et.al., Trop J Pharm Res, (2014), 13 (7), 1169-1177	Gold Nanoparticles: Synthesis and Applications in Drug Delivery[12].	• Many applications of gold nanoparticles like targeted drug delivery, imaging and therapeutics has been found in field of

		medicines. • Gold nanoparticles can be used in cancer therapy. and also in drug delivery system. • Side effects of many drugs have been reduced by gold nanoparticles.

References

1. Peter Zijlstra,CraigBullen, James W. M. Chon, and Min G, J. Phys. Chem. *B*u, High-Temperature Seedless Synthesis of Gold Nanorods, (2006), 110, 19315-19318.
2. Moustafa R. K. Ali, Brian Snyder, and Mostafa A. El-Sayed, Langmuir, Synthesis and Optical Properties of Small Au Nanorods Using a Seedless Growth Technique, (2012), 28, 9807−9815.
3. Parveer Kaur and Bhupendra Chudasama, J.Mater., Seedless co-surfactant-based dimensional and optical tunability of gold nanorods with simultaneous pH regulation, (2017),52, 11675–11687.
4. XiaolongXu, abYuanyuanZhao, aXiangdongXue, aShuaidongHuo, aFei Chen, aGuozhangZoua and Xing-Jie Liang, J. Mater. Chem. A, Seedless synthesis of high aspect ratio gold nanorods with high yield,(2014), 2, 3528–3535.
5. PaulaCAngelome, HamedHeidariMezerji, Bart Goris, Isabel Pastoriza-Santos, Jorge Perez-Juste, Sara Bals,and Luis M. Liz-Marzan, ., Chem. Mater., Seedless Synthesis of Single Crystalline Au Nanoparticles with Unusual Shapes and Tunable LSPR in the near-IR, (2012), 24, 1393−1399.
6. Wenjing Wang , Jing Li , ShijieLan , Li Rong , Yi Liu , Yu Sheng , Hao Zhang and Bai Yang, Seedless synthesis of gold nanorods using resveratrol as a reductant , (2016), 27, 0957-4484.
7. AnandGole and Catherine J. Murphy, Chem. Mater., Seed-Mediated Synthesis of Gold Nanorods: Role of the Size and Nature of the Seed, (2004), 16, 3633-3640.
8. Linfeng Gou and Catherine J. Murphy , Chem. Mater., Fine-Tuning the Shape of Gold Nanorods, (2005), 17, 3668-3672.
9. BabakNikoobakht and Mostafa A. El-Sayed, Chem. Mater. , Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method, (2003), 15, 1957-1962.
10. Jing Cheng , LanGe , Bin Xiong and Yan He , Journal of the Chinese Chemical Society, Investigation of pH Effect on Gold NanorodSynthesis, (2011), 58, 822-827.
11. Goldie Oza, Sunil Pandey, Ritu Shah, MayureshVishwanathan, RohanKesarkar, Maheshwar Sharon and Madhuri Sharon, Adv. Appl. Sci. Res., Tailoring Aspect

Ratio of Gold Nano Rods: Impact of temperature, pH, silver ions, CTAB concentration and centrifugation, (2012), 3(2), 1027-1038.

12. AK Khan, R Rashid, G Murtaza and A Zahra, Trop J Pharm Res, Gold Nanoparticles: Synthesis and Applications in Drug Delivery, (2014), 13 (7), 1169-1177.

Chapter 3

Synthesis and Characterisation

3.1 Introduction

3.1.1 Synthesis of Gold Nanorods

It is found that gold nanorods have many applications in field of bio-imaging, plasmon resonance spectroscopy, optoelectronics, drug delivery, diagnosis [1-3]. Various methods have been used for the synthesis of gold nanorods. Mostly seed mediated growth method is used for synthesis of gold nanorods but many modifications are needed in this method for the synthesis of gold nanorods because this method involves many steps and this become very complex process which is not easy to reproduce and yield is also low. To overcome these limitations seedless growth technique is proposed in which nucleation and growth stages are combined [4]. This is one-step synthesis in which we tuned the LSPR band from visible to NIR with high yield as compared to seeded method. In seedless method, the nucleation and growth process take place together without temporal separation. Using this seedless synthesis of gold nanorods we will study the pH controlled tunablity of LSPR band of gold nanorods in BDAC-CTAB co-surfactant system. As we know that $NaBH_4$ acts as strong reducing agent, so it reduces Au(I) to Au (0) and $NaBH_4$ is also responsible for the growth of gold nanorods[4]. After synthesis of gold nanorods, the optical properties and structural properties of gold nanoparticles can be determined by

1. Dynamic light scattering (DLS)
2. UV-Visible-NIR Spectroscopy

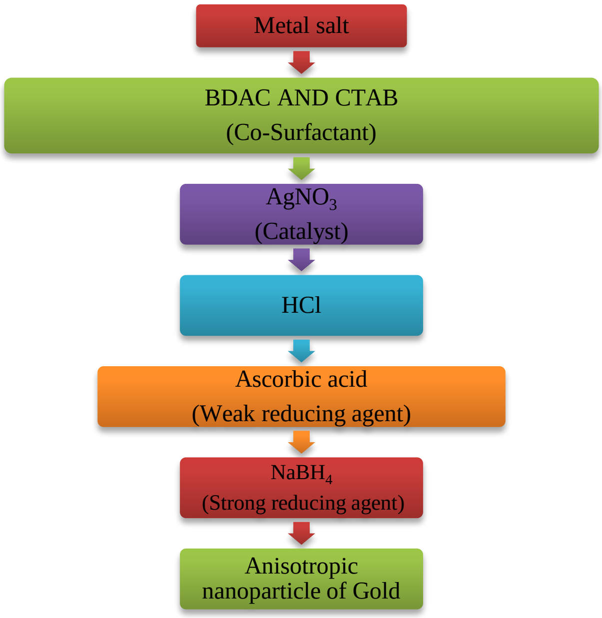


Figure 3.1 Synthesis protocol of anisotropic nanoparticles of gold nanorods

MaterialsCTAB (cetyltrimethylammonium bromide) and BDAC (benzyldimethylhexadecylammonium chloride hydrate) purchased from Sigma-Aldrich. Chloroauricacid ($HAuCl_4$) 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 solutions were prepared with Millipore water.

Stock solution preparation

For preparing 1mM of hydrogen tetrachloroaurate dissolve 1 g of $HAuCl_4$.$3H_2O$ in 250 mL of distilled water which have concentration of 10 mM. The solution prepared can be stored for years as stock solution. To get 1 mM concentration again 1 mL of this stock solution was diluted by 100mL.

CTAB (cetyltrimethylammonium bromide) is necessary for the growth of gold nanorods and stabalizing them after synthesis. When BDAC (benzyldimethylhexadecylammonium chloride) is mixed with CTAB, we get longer nanorods. In this procedure, first we will prepare a growth solution by adding 5.0 mL water with 0.1 g CTAB and 0.15M BDAC and this mixture is sonicate for dissolution of CTAB for 25 min at 40℃. Now add this growth solution to 5.0 mL of $HAuCl_4$ (1mM) and 0.2 mL of $AgNO_3$ (4mM). Then adjust pH of growth solution between 2.5-1.3 with HCl. Then add 0.1M ascorbic acid dropwise to the growth solution till the growth solution become colourless. Now, add freshly prepared 15 µL (0.01 M) $NaBH_4$ to colourless growth solution which will start the growth of the gold nanorods. Colour of growth solution changes from pink to dark red in 24 h.

We synthesize two series of four samples with two pH-1.3 and 1.9. In T1 series gold nanorods are prepared at two different pH. In T2 series identical samples are synthesised at pH 2.2 and after their growth the solution pH is adjusted to an identical value as used for series T1. Sample details along with synthesis conditions are summarized in table 3.1.

Table 3.1 Sample codes and Synthesis conditions

pH	T1	T2
1.3	T1-1.3	T2-1.3
1.9	T1-1.9	T2-1.9

Here T1 series refers to samples which are prepared at two different pH while T2 series refers to samples which are prepared under identical conditions but presented at two different pH.

3.2 Characterisation

Many techniques are used for characterization of nanoparticles. Three out of these techniques are

1. Dynamic light scattering (DLS)
2. UV-Visible-NIR Spectroscopy

Instrumentation

UV-Visible-NIR Spectrophotometer (Shimadzu, UV-2600), DLS (Brookhaven 90 plus particle size analyser), pH meter and Ultrasonic bath.

3.2.1 Dynamic light scattering (DLS)[5]

DLS is a technique which is also termed as photon correlation spectroscopy (PCS), It is a technique used for evaluating size of nanoparticles in colloidal suspensions. With this technique we measure diffusion coefficient of macromolecules and colloidal particles in solution. This technique is used for accurate determination of size and size distribution of particle by using Stokes-Einstein equation

$$d = K_B T / 6\pi\eta D$$

D = diffusion coefficient, T = absolute temperature, η= Solvent's viscosity,

d = hydrodynamic radius of particle, K_B= Boltzmann constant.

3.2.2 UV-Visible-NIR Spectroscopy

It is the instrument which deals with the study of optical properties of nanoparticles. It is used to measure the absorption, reflectance and transmittance [6]. This instrument comprises of source, sample and reference beam, monochromator and a photo detector. The source of radiation is tungsten filament, D2 lamp. The detector is mainly a photodiode array.

The objective of this spectroscopy in this study is to see how absorption is dependent on wavelength. It is the only method which we can use for measuring bandgap of nanoparticles. In many metals like gold the plasmon resonance is the cause of their unique optical phenomenon. The UV-spectra gives us surface plasmon resonance peak for gold nanoparticle. This peak can be analyzed for any structural changes of gold nanorods. Hence, it is used in the present study to evaluate the stability of gold nanorods.

References

1. Huang X, Neretina S, El-Sayed MA., Adv Mater., Gold nanorods: from synthesis and properties to biological and biomedical applications, (2009), 21, 4880–4910.
2. Pe´rez-Justea J, Pastoriza-Santosa I, Liz-Marza´na LM, Mulvaney P.,CoordChem Rev, Gold nanorods: synthesis, characterization and applications, (2005), 249, 1870–1901.
3. Faraday M.,Phil Trans R SocLond, The Bakerian lecture: experimental relations of gold (and other metals) to light, (1857), 147, 145–181.
4. Xu X, Zhao Y, Xue X, HuoS, Chen F, Zou G, Liang X, J Mater Chem., Seedless synthesis of high aspect ratio gold nanorodswith high yield, (2014), 2, 3528–3535.
5. Christopher M. Hoo,Natasha Starostin,PaulWest,Martha L.Mecartney.,Journal of Nanoparticle Research, A comparison of atomic force microscopy (AFM)and dynamic light scattering(DLS) methodsto characterize nanoparticle size distributions, (2008), 10, 89–96.
6. Ibrahim Khan, Khalid Saeed, Idrees Khan, Arabian Journal of Chemistry, Nanoparticles: Properties, applications and toxicities, (2017) (Accepted)

Chapter 4

Results and Discussion

4.1 UV-Visible spectroscopy of Gold Nanorods

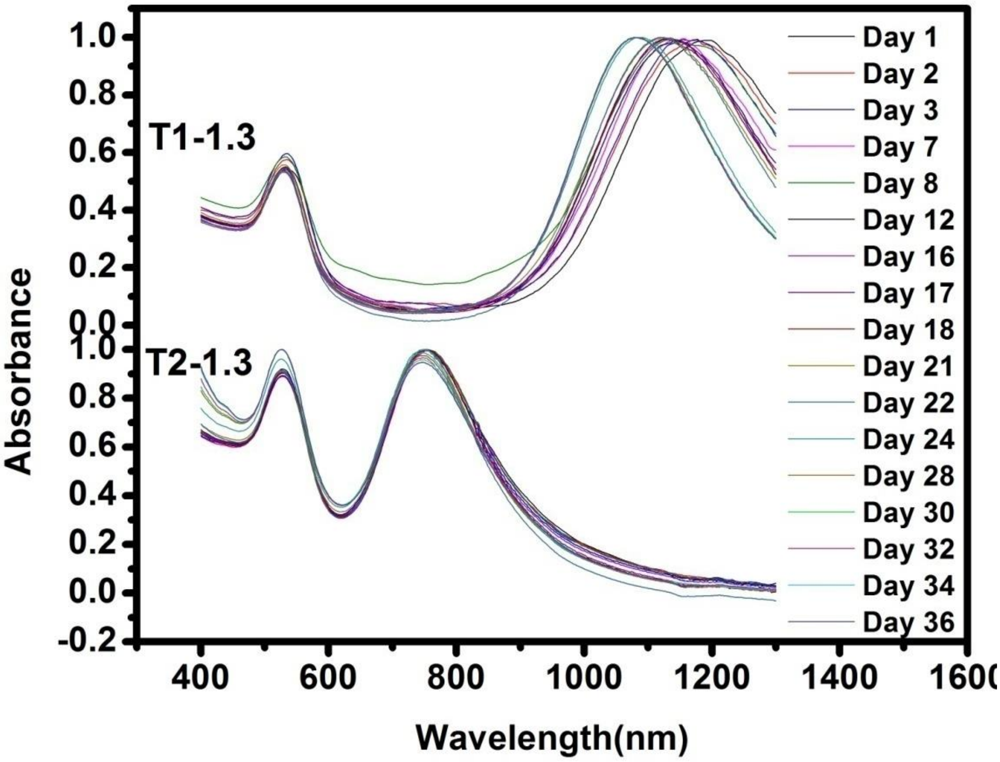


Fig 4.1(a) UV-Visible absorption spectra of AuNRs at pH-1.3 synthesised by seedless Method

UV-Visible spectra of as-synthesized gold nanorods which are aged for 36 days is shown in Fig 4.1(a) UV-Visible spectra show two surface plasmon bands. One is TSPR (Transverse Surface plasmon Resonance) and another one is LSPR (Longitudnal Surface plasmon Resonance) band of Gold nanorods. LSPR band of gold nanorods can be tuned by changing the pH of growth solution and its tunablity depends upon the size and shape of the nanoparticles. The band which appears at higher wavelength corresponds to LSPR while the one that appears at shorter wavelength corresponds to the width of the nanorods. From the spectra in Fig 4.1(a), following can be observed. The LSPR band of T1 series (pH-1.3) is quite high as compared to T2 series sample. This indicates that the length of the nanorods prepared oh pH-1.3 is much larger as compared to those which are prepared of pH-1.3 (T2 series).

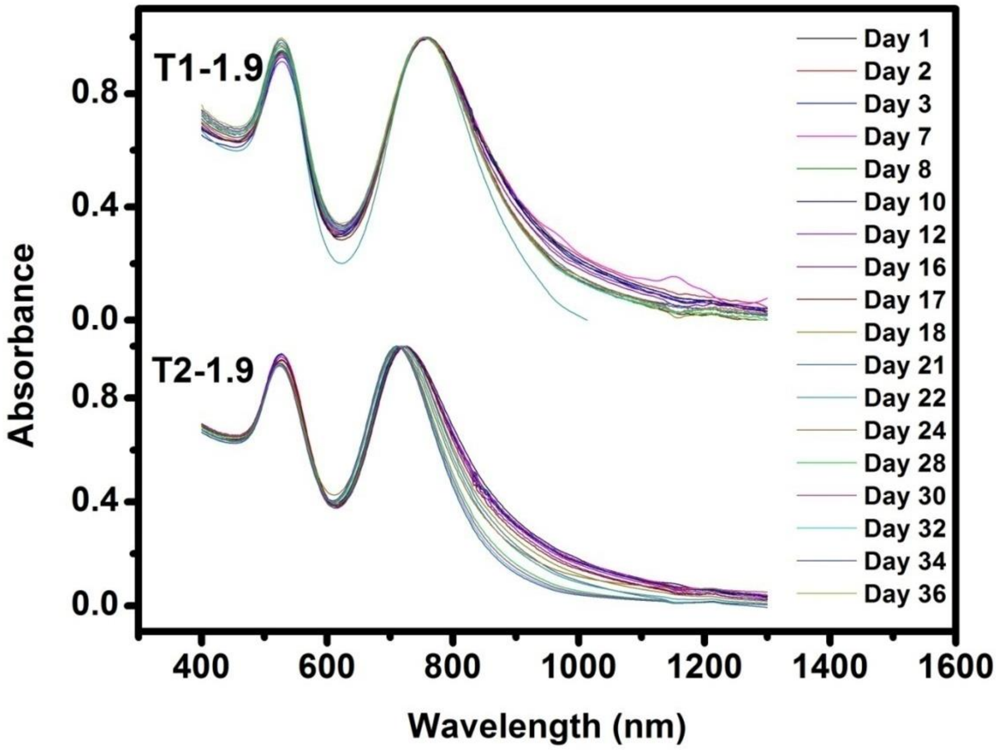


Fig 4.1(b) UV-Visible absorption spectra of AuNRs at pH-1.9 synthesised by seedless Method

In Fig 4.1(b) as well two plasmon band are observed for both the series of samples. However, this time the LSPR band position does not differ significantly for gold nanorods belonging to T1 and T2 series. The LSPR band of T1-1.3 shows significant blue shift while LSPR bands of rest of the samples do not show any drastic change.

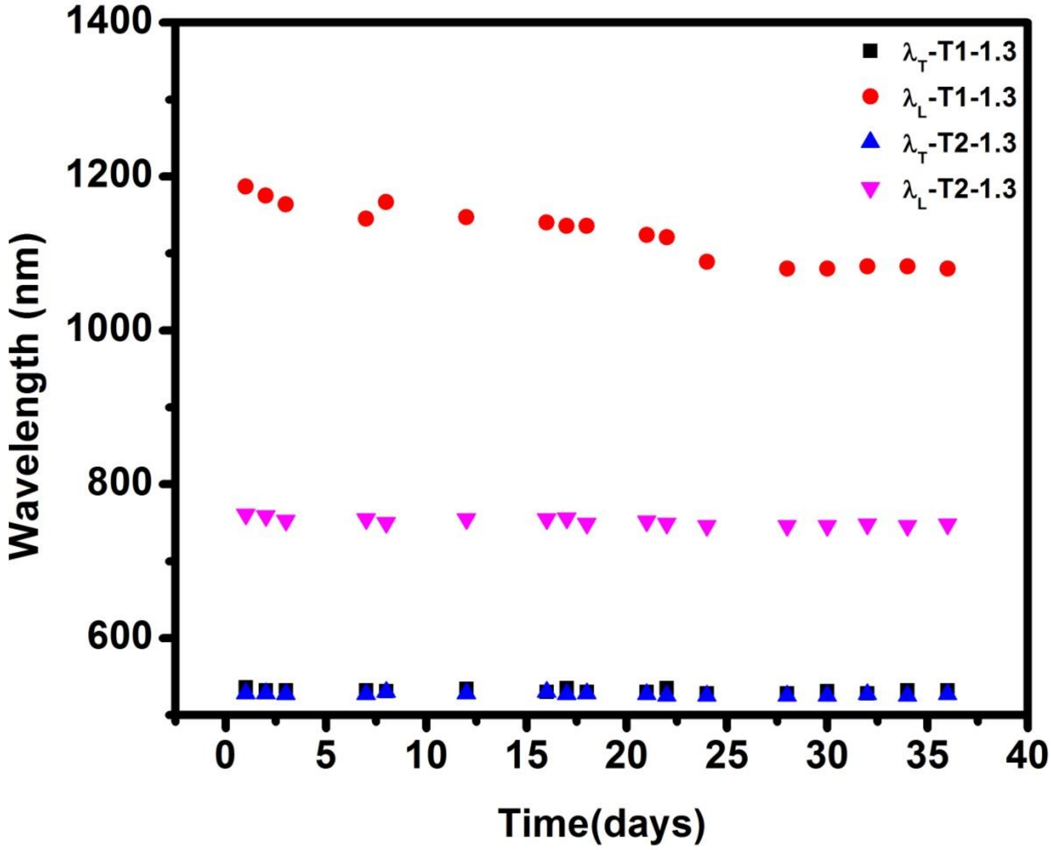


Fig 4.1(c) Variation of λ_{max} with Time at pH-1.3

Here λ_T corresponds to transverse band and λ_L corresponds to longitudinal band. The change in the LSPR and TSPR band positions as a function of time is shown in Fig 4.1(c). The % change in these band positions have been calculated which is reported in table 4.1 . The shift in LSPR band of T2-1.3 sample is minimum (1.97%) while the TSPR band shows a shift of (0.94%). This suggest that sample T2-1.3 has better structural stability as compared to T1-1.3.

Table 4.1 Percentage change in λ_{max} of LSPR (λ_L) and TSPR (λ_T) bands of gold nanorods synthesized at pH-1.3 (T1) and stand at pH-1.3 (T2)

Sample Code	λ_T (%)	λ_L (%)
T1-1.3	1.3	9.01
T2-1.3	0.94	1.97

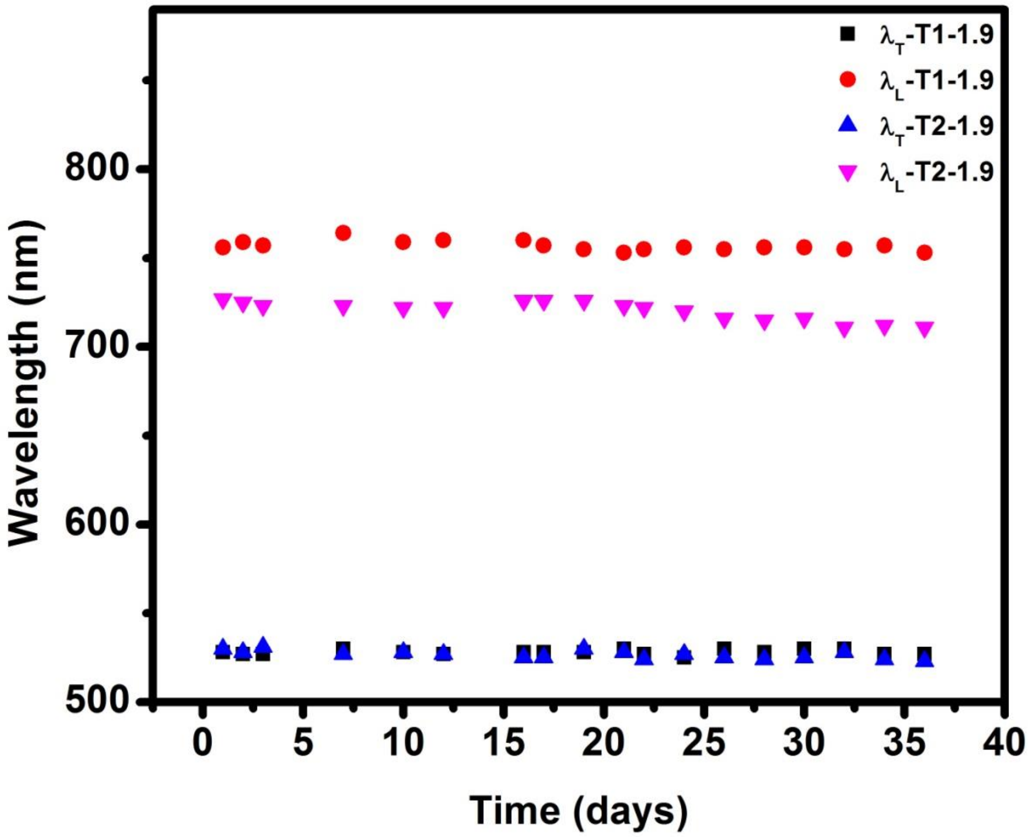


Fig 4.1(d) Variation of λ_{max} with Time at pH-1.9

Here λ_T corresponds to transverse band and λ_L corresponds to longitudinal band. TSPR band for both T1-1.9 and T2-1.9 is almost same and wavelength of both T1-1.9 and T2-1.9 is constant with time which shows stability of TSPR band of gold nanorods. LSPR band of T1-1.9 is more stable than LSPR band of T2-1.9 because percentage change in LSPR band position in T1-1.9 is 1.43% and 2.2% in T2-1.9 which shows that T1-1.9 is more stable than T2-1.9 as shown in table 4.2 but wavelength remains constant with time for both T1-1.9 and T2-1.9 as shown in Fig 4.1(d). Hence no significant difference in the structural stability of gold nanorods corresponding to T1-1.9 and T2-1.9 samples has been observed. Some data points are missing in as shown in Fig 4.2(d) due to high dilution factor.

Table 4.2 Percentage change in λ_{max} of LSPR (λ_L) and TSPR (λ_T) bands of gold nanorods synthesized at pH-1.9 (T1) and stand at pH-1.9 (T2)

Sample Code	λ_T (%)	λ_L (%)
T1-1.9	0.94	1.43
T2-1.9	1.5	2.2

4.2 Effect of pH on Hydrodynamic size of Gold Nanorods

Hydrodynamic size corresponding to the length and width of gold nanorods and its length and width was determined by dynamic light scattering. DLS for both T1 and T2 at both pH 1.3 and 1.9 shows binary distribution which shows formation of nanorods (Annexure 1-4). Mean diameter corresponding to length and width for both T1 and T2 which is obtained by lognormal curve fitting of hydrodynamic size (Annexure 1-4) is shown in Fig 4.2-(a) and Fig 4.2-(b).

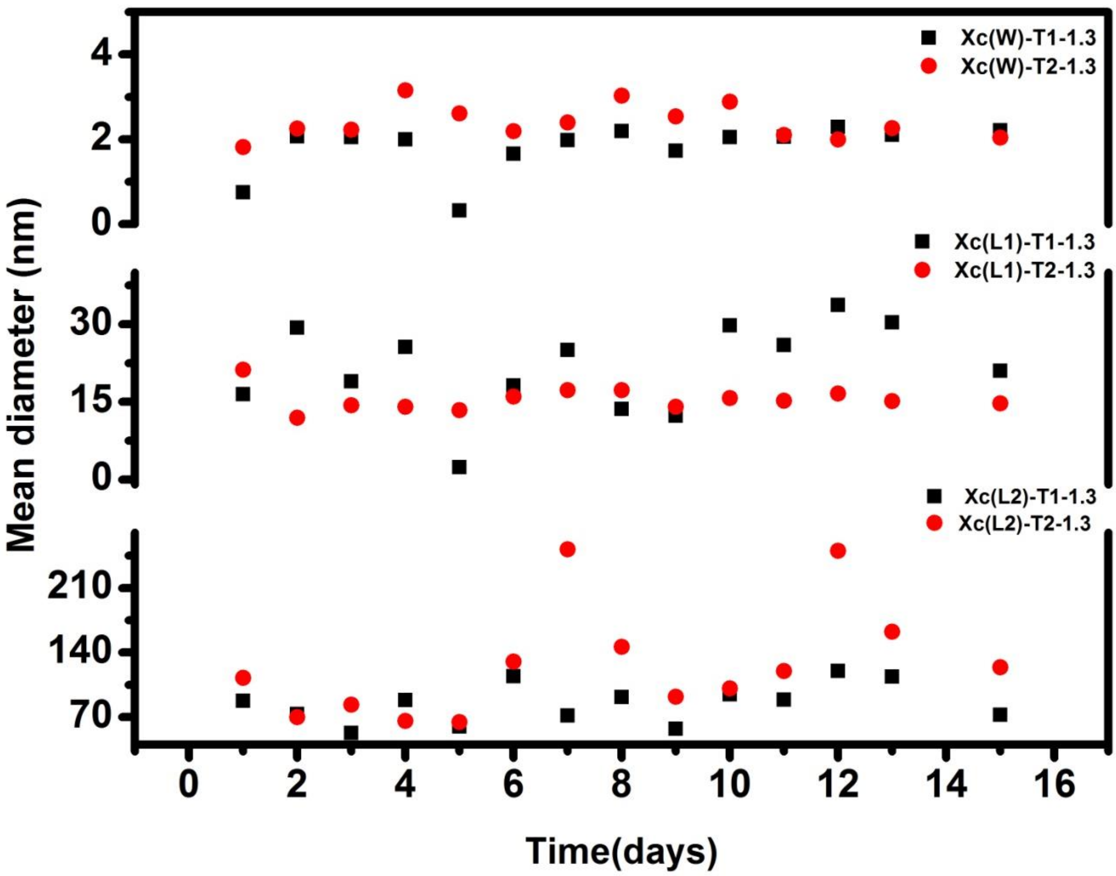


Fig 4.2(a) Variation in Mean diameter with time at pH-1.3

Here $X_c(W)$ denotes mean diameter along the width and $X_c(L1)$ and $X_c(L2)$ denotes mean diameter along length at pH 1.3. The mean diameter is in the range of 1-2 nm for $X_c(W)$ along the width 12-34 nm for $X_c(L1)$ and 53-115 nm for $X_c(L2)$, which is along the length for T1-1.3. The mean diameter is in range of 2-3 nm for $X_c(W)$, 12-22 nm for $X_c(L1)$ and 60-250 nm for $X_c(L2)$ for T1-1.3. Fig 4.2(a) shows that mean diameter remains constant for T2 series. This shows that gold nanorods are more stable for series T2 at pH-1.3.

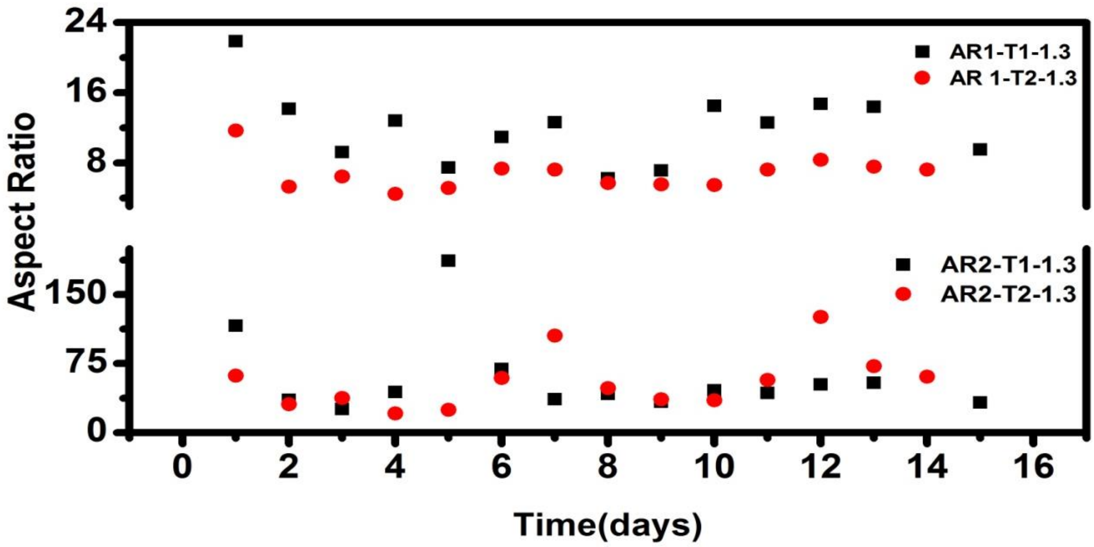


Fig .4.2(b) Variations in aspect ratio with time at pH-1.3

Gold nanorods synthesized in T1 series shows more variation in aspect ratio with time as compare to the gold nanorods synthesized in T2 series which indicates the greater stability of T2 series at pH-1.3.

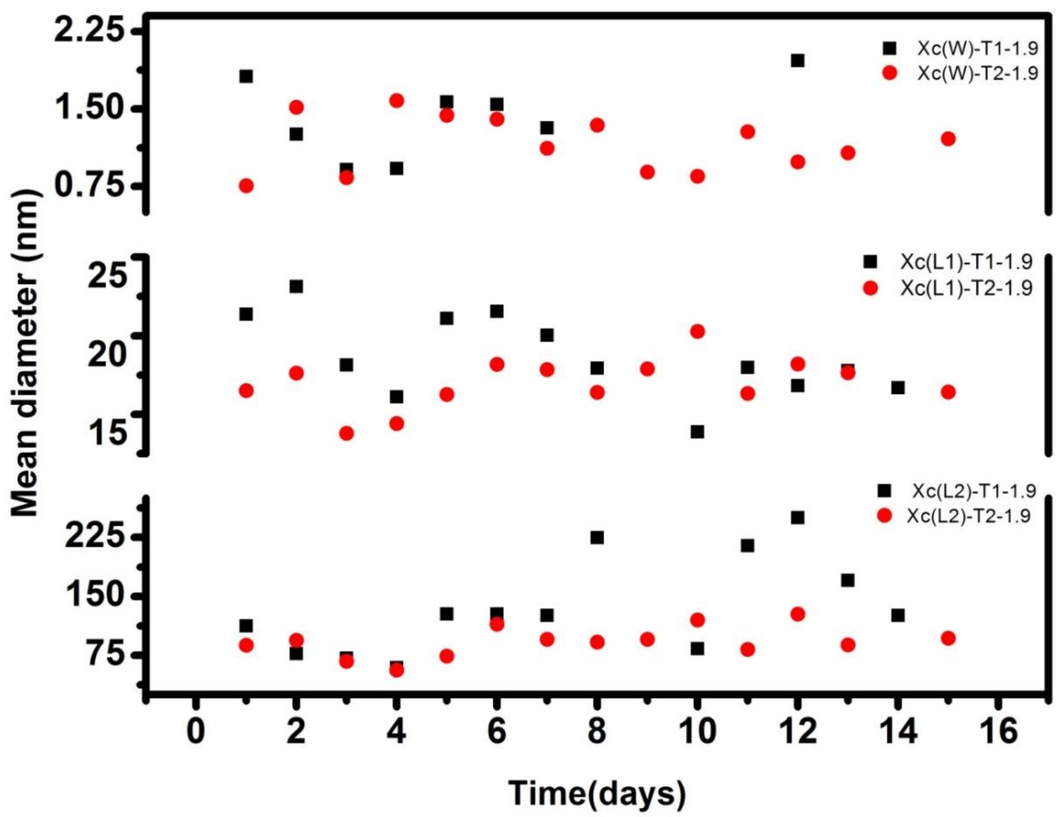


Fig 4.2(c) Variation in mean diameter with time at pH-1.9

The variation in mean diameter for T1-1.9 and T2-1.9 samples is shown in Fig 4.2(c) and corresponding changes in their aspect ratios are plotted in Fig 4.2-(d). No significant difference in the colloidal stability of these samples has been observed from the DLS data in samples T1 and T2.

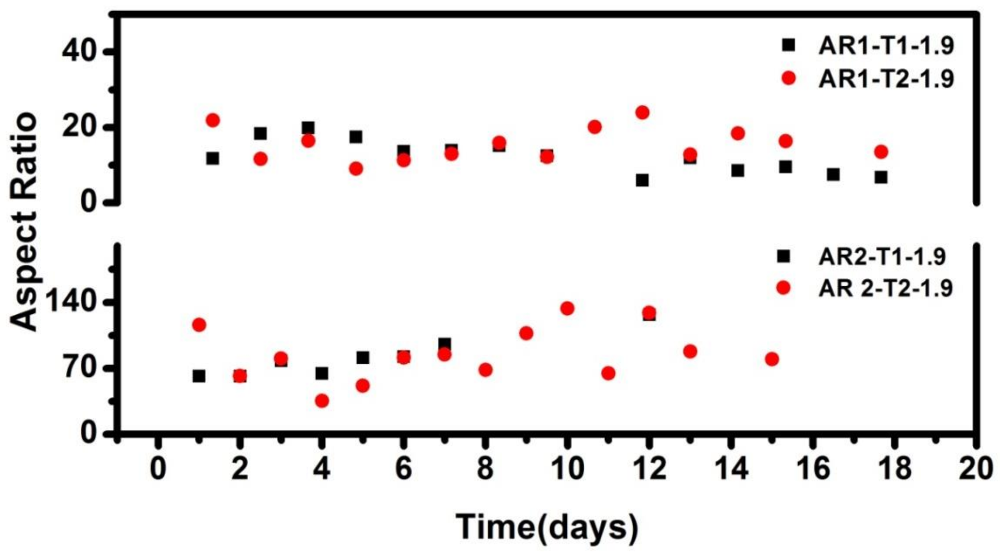
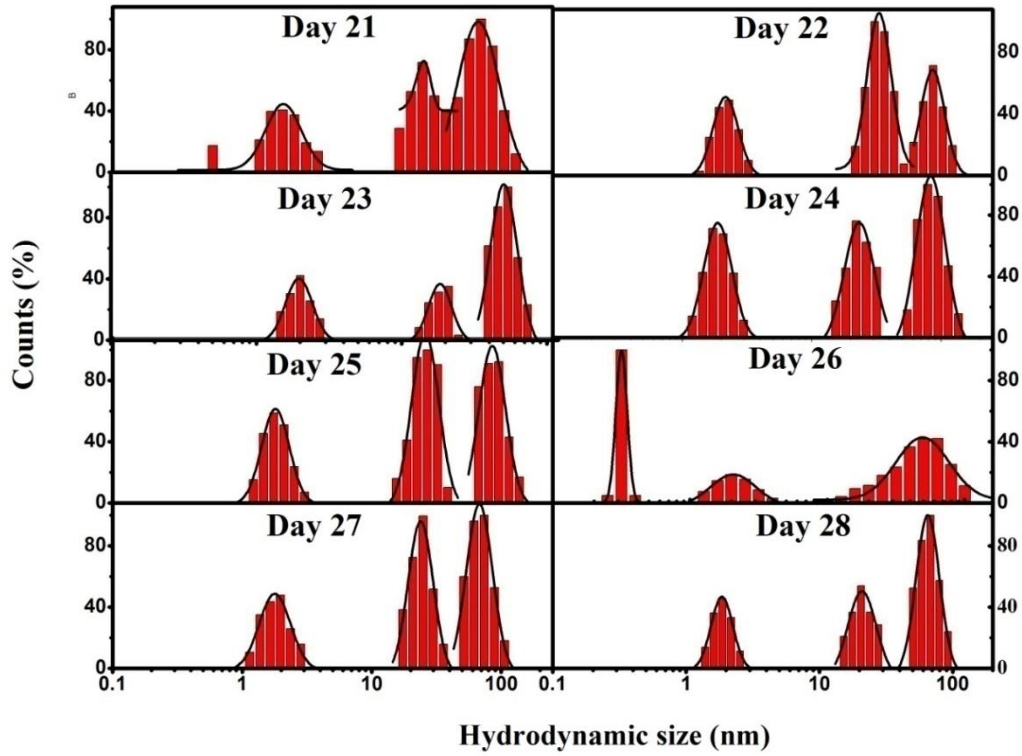


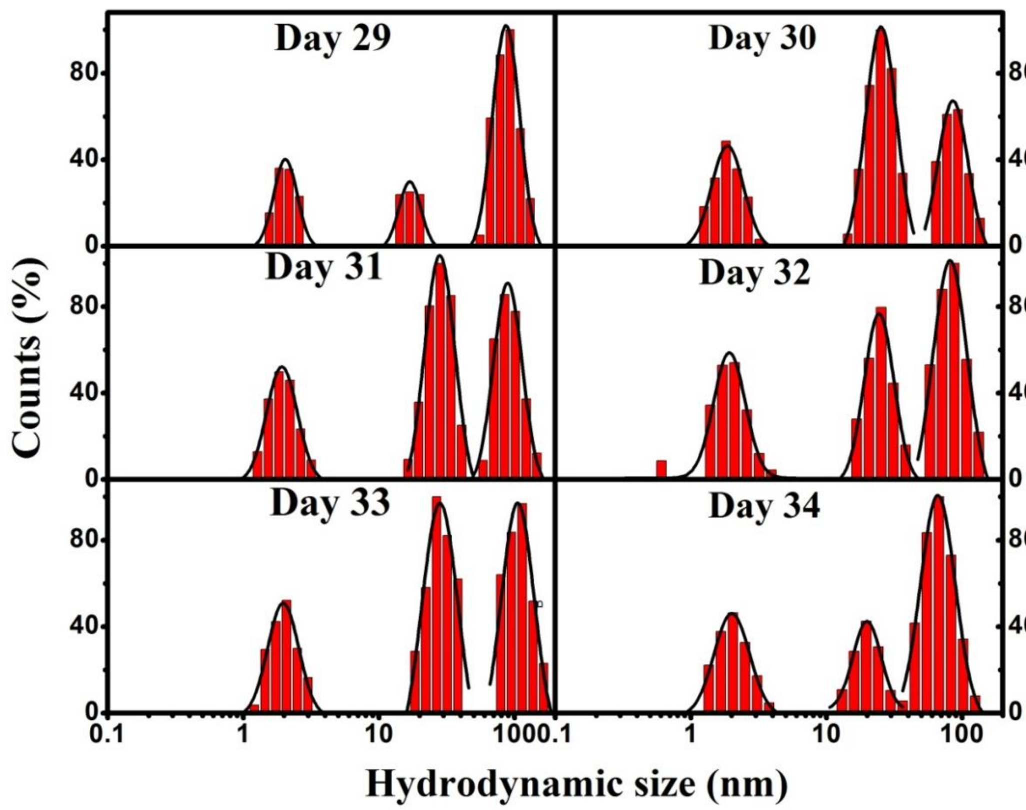
Fig 4.2(d) Variations in Aspect ratio with time at pH-1.9

Conclusions

- Gold nanorods are synthesized by seedless synthesis method at pH 1.3 and 1.9(series T1). Amongst them gold nanorods synthesized at pH-1.3 has higher aspect ratio than those synthesized at pH-1.9.
- Two sets of Gold nanorods are synthesized under identical conditions and they are stored at pH-1.3 and pH-1.9.
- From UV-Visible and dynamic light scattering, structural changes in gold nanorods have been monitored. All synthesized nanorods are stable as no significant changes in their Plasmon bands are observed (except T1-1.3).
- Within this T2-1.3 and T1-1.9 samples show better stability as compared to their counter parts. However, the study remains inconclusive whether the synthesis pH or the solution pH affects the structural stability of gold nanorods.

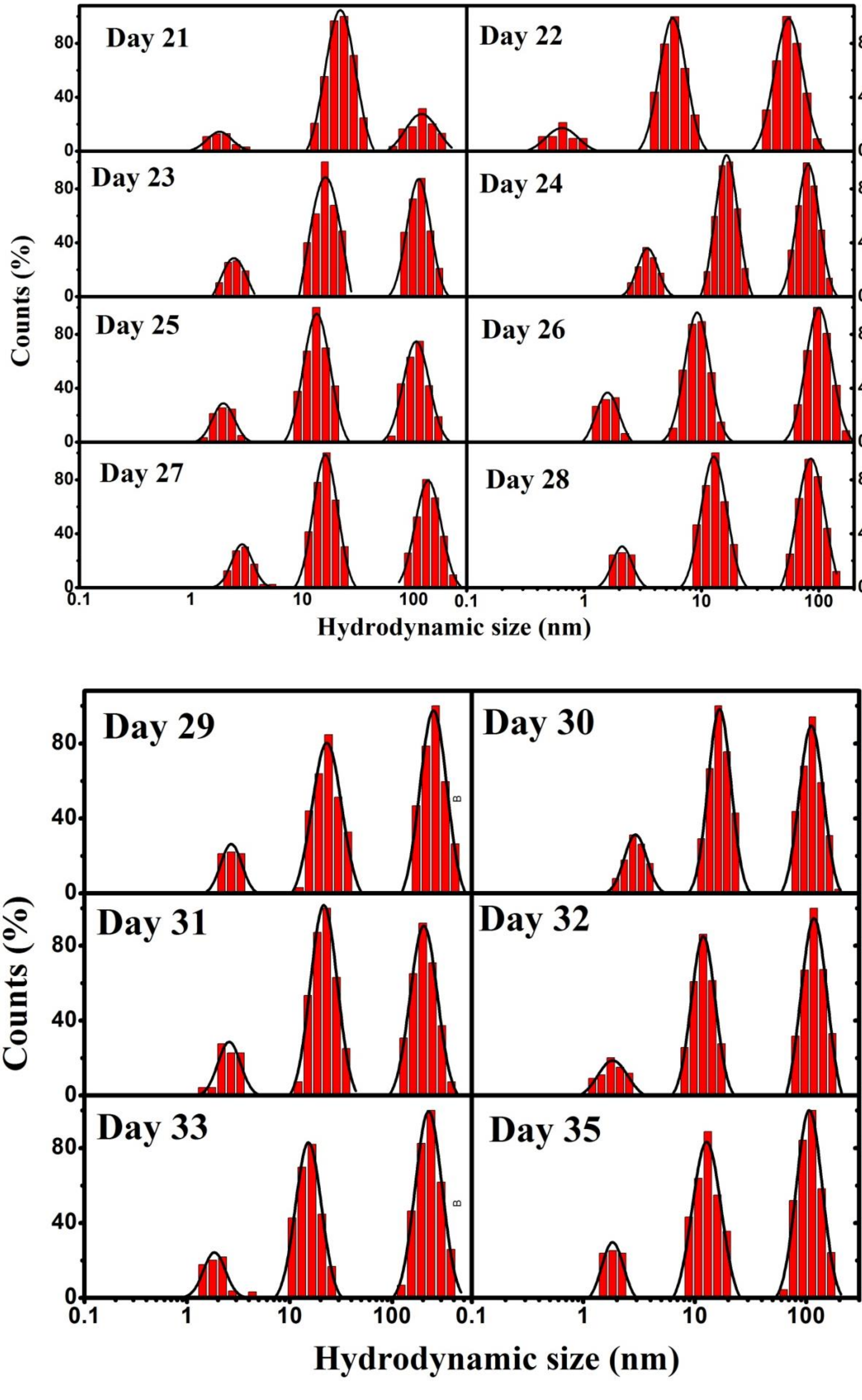
Annexure 1





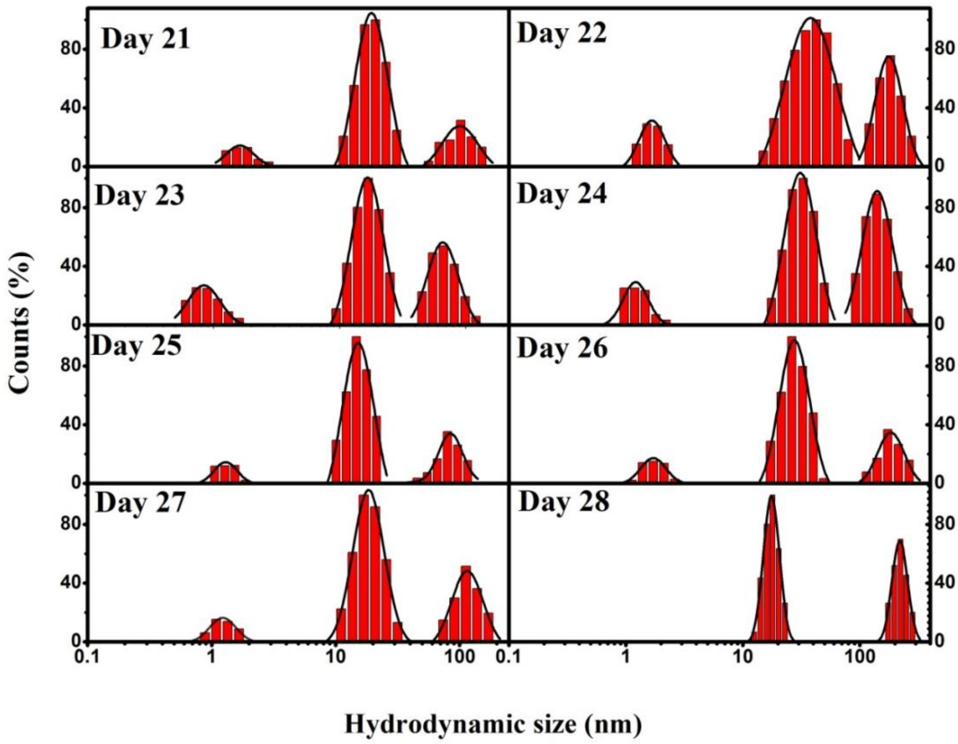
Hydrodynamic particle size distribution of gold nanorods(GNRs)-T1-1.3 fitted with lognormal particle size distribution function recorded over 36 days.

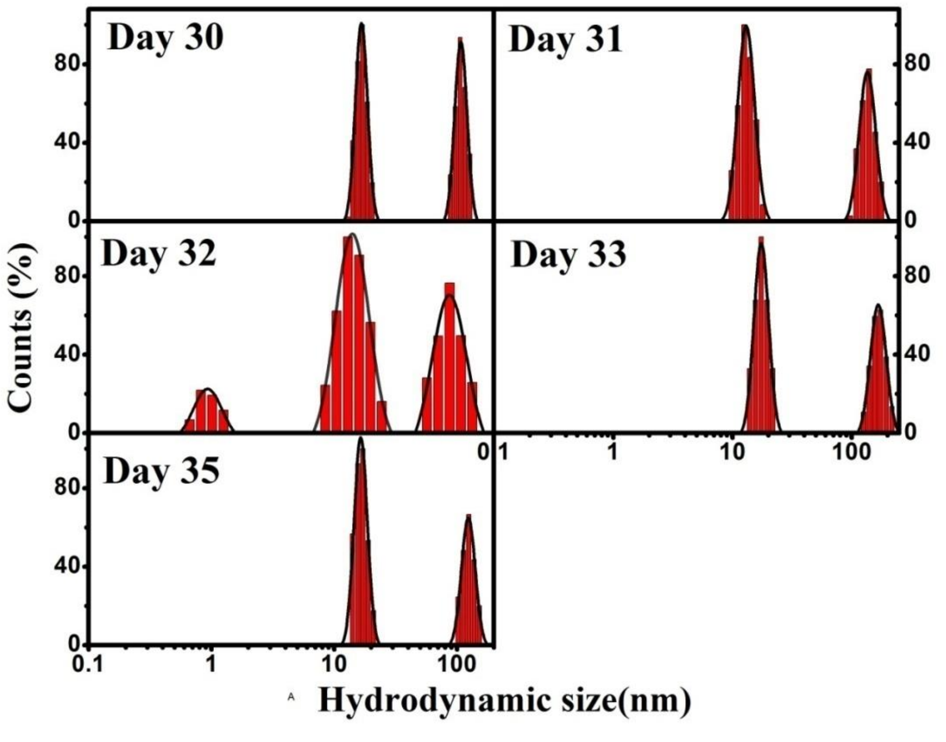
Ann**exure 2**



Hydrodynamic particle size distribution of gold nanorods(GNRs)-T2-1.3 fitted with lognormal particle size distribution function recorded over 36 days

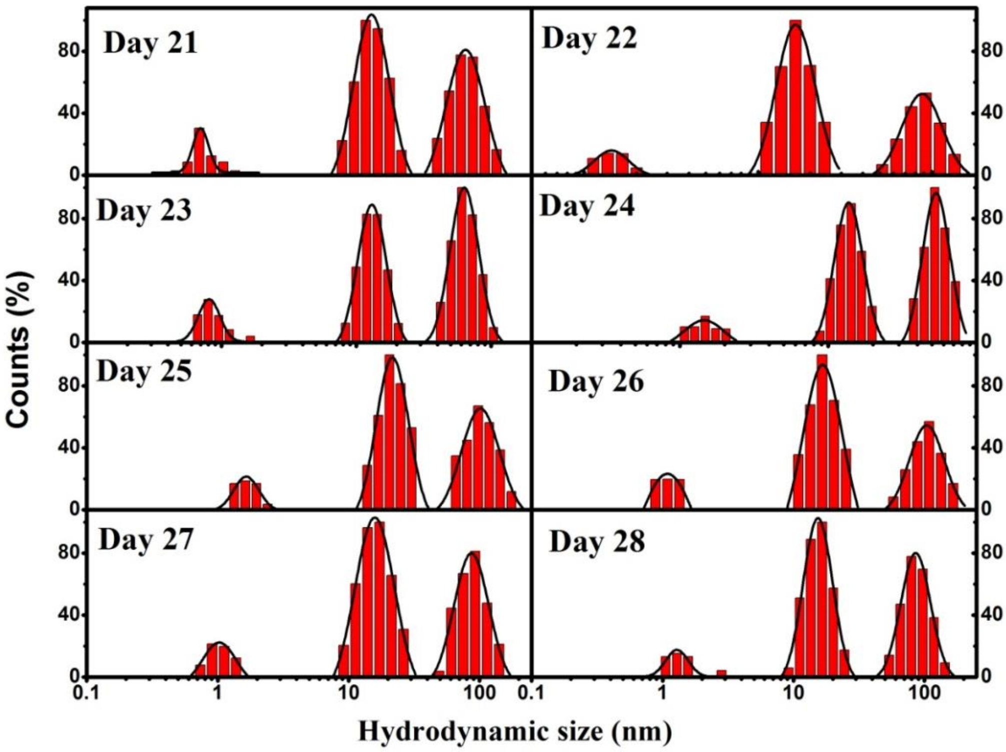
Annexure 3

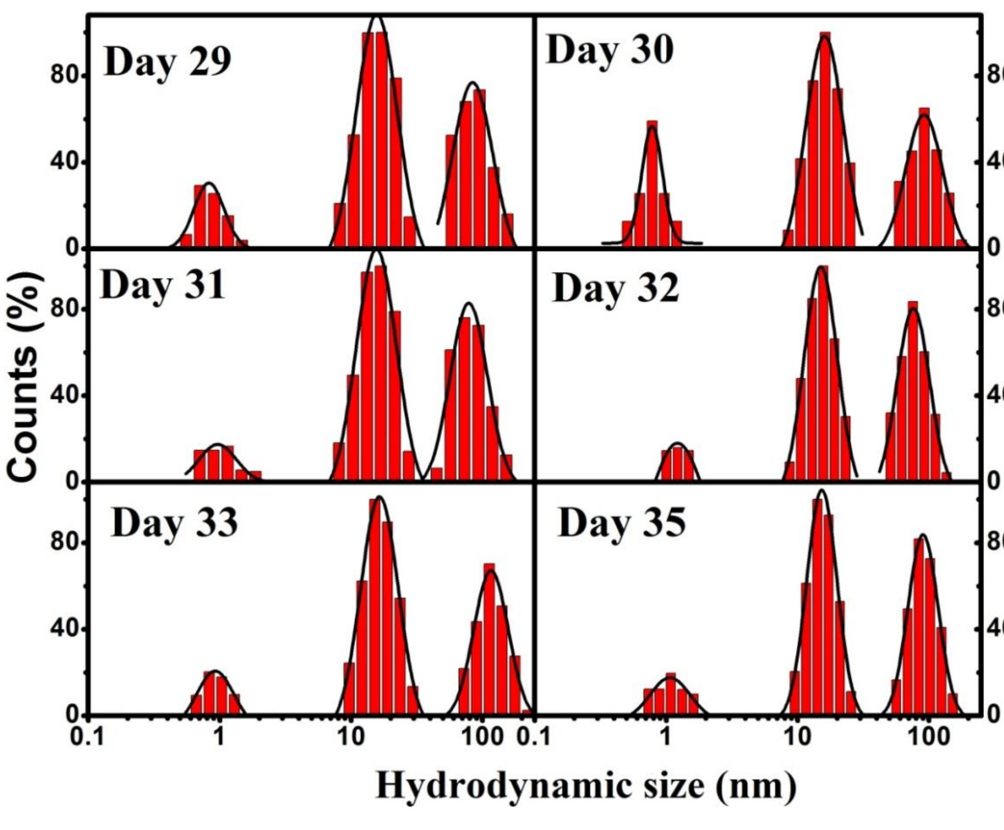




Hydrodynamic particle size distribution of gold nanorods(GNRs)-T1-1.9 fitted with lognormal particle size distribution function recorded over 36 days.

Annexure 4





Hydrodynamic particle size distribution of gold nanorods(GNRs)-T2-1.9 fitted with lognormal particle size distribution function recorded over 36 days.