

Effect of pH on morphology and stability of silver nanorods synthesized by seed mediated growth method

A thesis submitted

in partial fulfillment of the requirement for

the award of the degree of

Master of Science

in

PHYSICS



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CERTIFICATE

This is to certify that thesis entitled "**Effect of pH on morphology and stability of silver nanorods synthesized by seed mediated growth method**" submitted by **Khushbu Garg, Roll No. 301604021** 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.



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Declaration

I hereby declare that the work presented in this thesis report entitled "**Effect of pH on morphology and stability of silver nanorods synthesized by seed mediated growth 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 and Science or any other degree.



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Abstract

In this thesis, silver nanorods are prepared by seed mediated growth method. In this method, silver seeds are prepared first and then used as seeds for the preparation of the nanorods. The silver seeds were prepared by the reduction of silver ions with sodium borohydride in the presence of sodium citrate dihydrate as the stabilizer. Effect of pH on the morphology and stability of silver nanorods has been evaluated. Silver nanorods prepared at pH 10.6 are stable. At other pH, either no rods are formed or the synthesized nanorods are unstable and decay with time.

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Chapter 1

Introduction

1.1 Nanotechnology and Nanoscience

Nanotechnology ^[1] deals with matter at nanoscale, in which size ranges between 1-100 nm. It is a study of very small things which can be used in all science fields. Ideal size range of nanoparticles according to nanotechnology is one billionth of a meter. The idea started with the statement “There is Plenty of rooms at the bottom” by physicist Richard Feynman at California Institute of Technology. Nanotechnology creates new devices and materials with several applications in all fields like biomaterials, medicines ^[2], electronics ^[3], etc. Some important research topics in this field are mentioned in table 1.1.

Table 1.1 Current research topics in nanotechnology

Material science	Powders ,coatings, carbon nanomaterials, carbon nanotubes
Energy	Solar power and photovoltaic , LED white light, hydrogen fuel cells
Medicine/biotechnology	Geonomics, drug delivery, nanomedicine
Electronics	Quantum dots, MRAM,NRAM
Devices	Lithography, AFM, MEMS

1.2 Nanoparticles

The word nanoparticle is originated as “nano + particle”; i.e., particles on nanoscale. The word „nano“ comes from Latin word which means dwarf (extremely small). At nano scale particles shows very different properties as compared to the bulk. At this scale particles do not follow Newtonian physics, Quantum mechanics is followed by the nanoparticles. The comparison of relative dimensional scale is presented in fig.1.1.

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

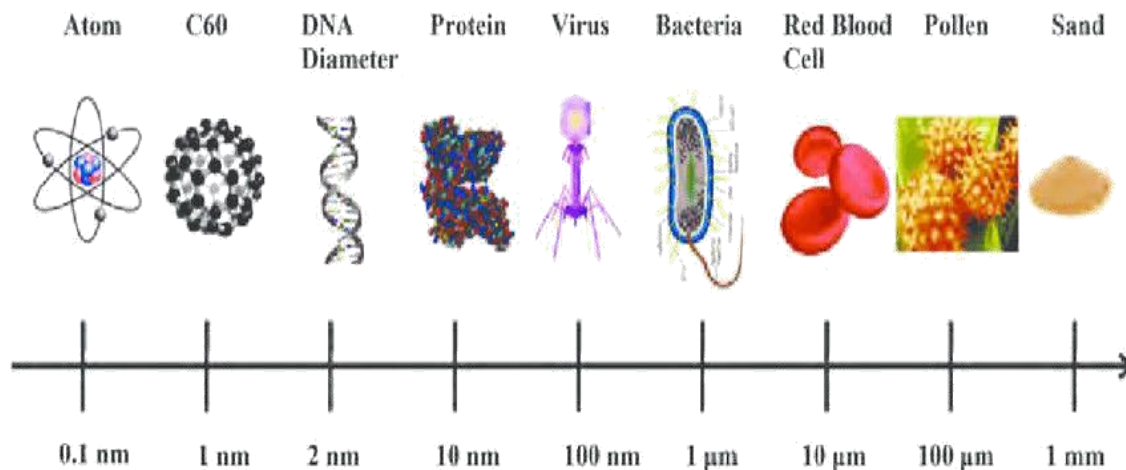


Figure 1.1 Dimension of distinct objects in relative length scale [4]

Size dependence of properties

Most of the properties of solids are size dependent. When properties are measured in nm or micrometre many properties of matter become different. Properties of nanoparticles are far different from bulk material as well as from atoms. This is because of the Quantum confinement of electrons.

1.2.1 Properties of Nanoparticles

1. Optical properties

Optical property of nanoparticles is different as compare to the bulk crystal. Absorption peak shows blue shift (shift towards shorter wavelength) in case of semiconductor nanoparticles because of increase in the energy band gap. Also the colour of nanoparticles changes with the particle size.

2. Melting point

Due to high surface to volume ratio, nanoparticles have lower melting point and lattice constant is also reduced.

3. Mechanical properties [5]

Mechanical strength of nanoparticles is high as compared to bulk materials because in nanomaterials fewer defects are present.

4. Electrical conductivity

Electrical conductivity decreases as the size decreases because of the surface scattering increases at nanoscale.

5. Magnetic properties

At this dimension, ferromagnetic behaviour changes and the material shows superparamagnetism.

1.2.2 Applications of Nanoparticles

Nanoparticles have wide applications in almost all the science fields because at nanoscale properties of materials are very different from bulk material. Some applications are described in table 1.2.

Table 1.2 Applications of Nanoparticles

Energy	Improvement in the efficiency of fuel production from raw materials, carbon nanotubes scrubber, cheaper and more efficient nanostructured solar cell, more efficient and light weight batteries.
Electronics and IT	MRAM, Ultra-high definition displays Flexible, bendable, foldable, rollable, and stretchable electronics, Smaller, faster, and better transistors
Everyday materials and processes	Clear scratch-resistant, or electrically conductive nanoscale films on eye glasses, computer and camera displays, windows, washable, durable “smart fabrics” Light weight cars, trucks, airplanes, boats, and space craft which leads to fuel saving
Medical and healthcare ^[6]	Better imaging and diagnostic tools, treatments for cancer and other diseases, vaccine delivery without the use of needles, single-molecule detection at low cost and high speed
Environmental remediation	Affordable, clean drinking water, low-cost detection and treatment of impurities in water, paper towel, energy-efficient desalination.

1.2.3 Synthesis of Nanoparticles

Nanoparticles can be synthesized ^[7] by two methods:

1. Top-down method: Top-down approach can be defined as from top (larger) to bottom (smaller). In this approach a large piece of material is taken. Then cutting is done to get desired shape and size. Example: Different lithographic techniques (like electron beam and X-ray lithographs), etching, ball milling and grinding techniques.

2. Bottom-up method: Bottom-up approach can be explained as; from bottom to top. In this technique, a nanostructure is developed which is larger than the structure where it is started.

Example: DNA is created from cells by taking molecules and binding them together. Both bottom-up and top-down methods are summarized in fig 1.2.

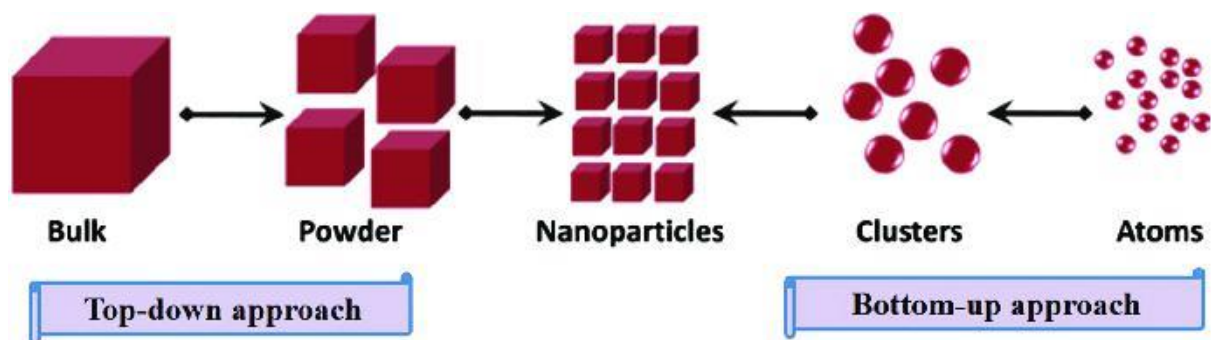


Fig 1.2 Top-down and bottom-up approaches of nanoparticle synthesis ^[8]

1.3 Silver Nanoparticles ^[9]

The biocompatibility and bactericidal activity of silver is highest among all metals. As size decreases the antimicrobial activity of nano silver increases. Because of intrinsic therapeutic properties AgNPs they are widely used in the biomedical field. AgNPs have peculiar electronic, antibacterial and optical properties and thus widely used in various applications like biosensing, electronics, antimicrobial and photonics applications. Nowadays, silver nanoparticles have gained high attention because of therapeutic applications, as it act as anticancer agents. Silver nanoparticles show positive outcomes in the cancer treatment.

1.3.1 Optical Properties of Silver Nanoparticles

The efficiency of absorbing and scattering light of AgNPs is unique. By controlling size, shape and refractive index, the absorption and scattering properties of silver nanoparticles can be tuned.

1.3.2 Surface Plasmon Resonance

It is an optical phenomenon which is due to interaction between the conduction electrons of metals and the electromagnetic field. The collective oscillation of electrons is in resonance with the frequency of EM radiation. Nanomaterials absorb the incident light at this frequency. Some photon will move in all directions and scattering occurs while rest of the photons changed into phonons of the lattice and thus absorption occurs. Between scattering collision, the distance travelled by electrons increases the absorption in UV-VIS range. Surface plasmon^[10] absorption occurs due to the optical excitation of SPR. Optical excitation occurs when frequency of incident photons and frequency of oscillation of surface electron are in resonance. The schematic diagram of surface plasmon resonance is shown in figure 1.3.

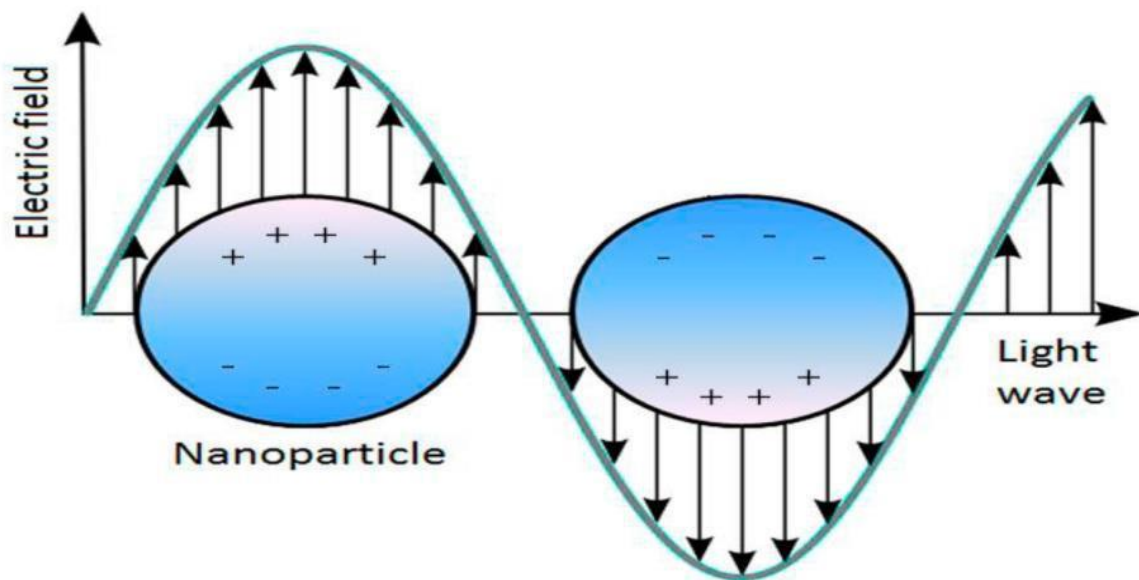


Fig.1.3 Surface Plasmon Resonance in Metal Nanoparticles^[11]

1.3.2 Different Shapes^[12] of Silver Nanoparticles

The properties (physical and chemical) of metal nanoparticles are effected by their experimental conditions, the interaction between metal ions and reducing agents, and adsorption of the stabilizing agent with the metal nanoparticles. By changing process of synthesis, reducing and stabilizing agents, shape, size and distribution of the nanoparticles can be controlled.

The shapes of the nanoparticles determined by their interaction with the stabilizers and method of synthesis. Also the reaction rate is effected by the shape of the synthesized nanoparticles.

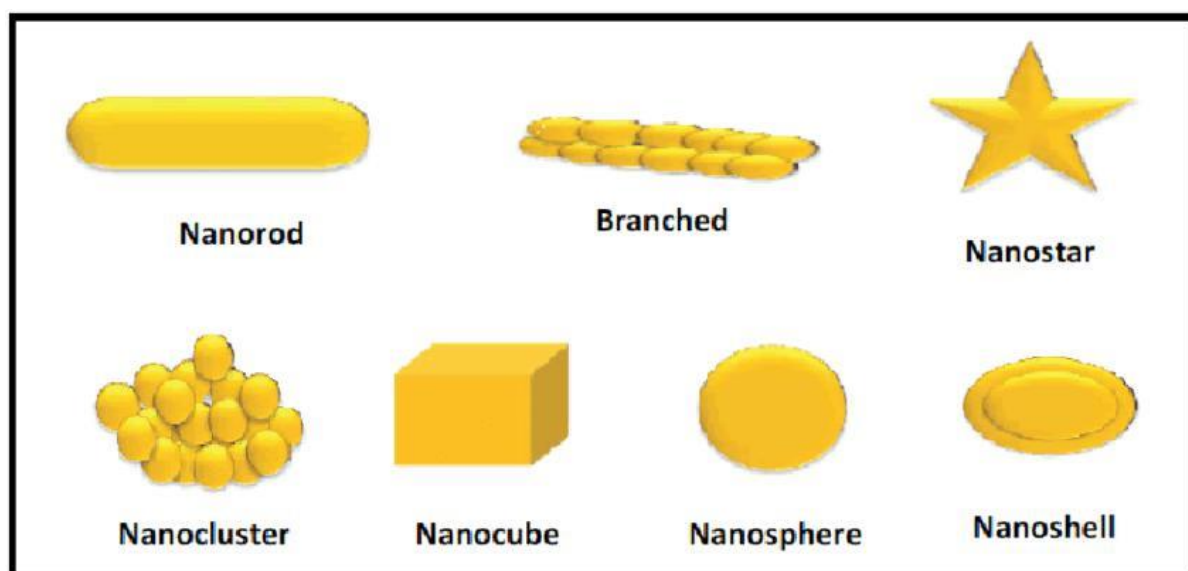


Fig. 1.4 Different shapes of nanoparticles^[13]

Nanosphere (NS)

By taking silver nitrate in less amount with L-ascorbic acid in aqueous solution in presence of CTAB and ammonia, uniform spherical morphology of silver particles are formed in few minutes. The plasmon absorption peak is nearly at 422 nm shown by UV-VIS spectroscopy. Spherical particles are thermodynamically more stable as they have minimum surface to volume ratio.

Nanorods (NRs)

Nanorods are one of the morphology of nanoscale matters. Silver nanorods can be defined as elongated silver nanoparticles and have range from 10 to 120 nm with the specific surface area. They can be prepared from metals or semiconductors. Standard aspect ratio is about 3-5. Nanorods are synthesized by direct chemical synthesis. Ligands work as shape control agents and connect distinct facets of nanorods with divergent strengths. This allows distinct faces of nanorods to develop at different rates, which produces an elongated object. Nanorods can be prepared by many methods. Seed mediated ^[14], template ^[15] seedless are the synthesis methods which are commonly used for silver nanorods synthesis.

Seed mediated technique is the most commonly used technique. In seed mediated method seed is used for reducing silver salt. The process occurs in two-steps. First small particles are formed which then used as seed to prepare nanorods. As this method is a multistep method therefore can be used to reduce the impurity. On the contrary, seedless method is single-step method. It synthesizes nanorods in one step. Both the processes of nucleation and growth takes place in single step. In this method, no seeds are required.

1.4 Surface Plasmon Resonance in Nanorods ^[16]

For surface plasmon, restoring force is related to charge accumulated at the surface of particles, it will be effected by the geometry of particles. For nanorods the accumulation of charge at the surface of nanoparticles will be different for the oscillation of electrons along rod axis (longitudinal plasmons) and along perpendicular direction (transverse plasmons). The charge accumulation will be maximum for transvers plasmons and minimum for the longitudinal plasmons. For nanorods, resonant frequency of transverse plasmons is at the same position as for spherical nanoparticles while resonance of longitudinal plasmons shows red shift (towards larger wavelength) when the aspect ratio increases.

We get two peaks for the nanorods in UV spectroscopy, one corresponding to the transverse surface plasmon and the other corresponding to the longitudinal surface plasmon.

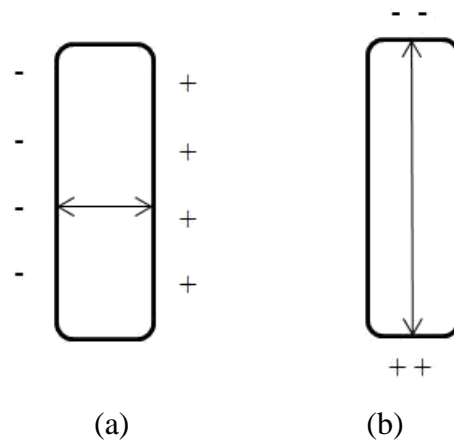


Fig. 1.5 (a) Charge accumulation for transverse surface plasmon (b) charge accumulation for longitudinal surface plasmon

1.5 Applications of Silver ^[17] Nanorods

Silver nanoparticles (AgNPs) are widely used in the various fields, which include medical, food, consumer, and industrial purposes, by reason of their remarkable physical and chemical properties. These include high electrical conductivity, optical, thermal, biological ^[18] and electrical ^[19] properties. Due to their unique properties, they have been used for many applications:-

1. Medical and dental application

- Bone cement
- Implantable devices
- Toothpaste
- Surgical gowns
- Face masks
- Wound dressing and burn treatment
- Disinfecting medical devices
- Coating plastic catheters
- Coating of endotracheal tube

2. Other applications

- Food storage packaging
- Cosmetics
- Textile coatings, socks and athletic cloathing
- Water treatment
- Air and water filters
- Packaging
- Detergents and soaps

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Chapter 2

Literature review

Several methods are used for the synthesis of silver nanoparticles. This chapter reviews different synthesis process of silver nanoparticles. Seed mediated method is most commonly used method to produce silver nanoparticles.

Synthesis of Silver nanoparticles

Author name	Title	Results
Gil-Jae Lee, et.al. Materials Chemistry and Physics (2004) 84:197–204.	Preparation of silver nanorods through the control of temperature and pH of reaction medium	<ul style="list-style-type: none">• Silver nanorods were prepared by theseed mediated method.• In first step seed of 6 nm were prepared.• In second step these seeds were used to produce nanorods.<ul style="list-style-type: none">• By varying pH aspect ratio can be controlled.
Kholoud M.M., et.al. Arabian Journal of Chemistry (2010) 3, 135–140	Synthesis and applications of silver nanoparticles	<ul style="list-style-type: none">• Silver nanoparticles can be prepared by reduction of silver ions in aqueous solution.• To avoid the agglomeration of nanoparticles, protective agents are used that can be absorbed on nanoparticle surface.
Wiley, B.; et.al. Accounts of Chemical Research Acc. Chem. Res. 2007, 40, 1067– 1076.	Synthesis Of Silver Nanostructures with Controlled Shapes and Properties.	By controlling the crystallinity, wide range of shapes with single synthetic process were produced.

<p>Animesh K Ojha, et.al. Journal of Nanobiotechnology 2013; 11: 42.</p>	<p>Synthesis of well–dispersed silver nanorods of different aspect ratios and their antimicrobial properties against gram positive and negative bacterial strains</p>	<ul style="list-style-type: none"> • Silver particles with an intermediate aspect ratio ($R = 1.8$) has highest antimicrobial activity. • Nano-size is a reason for generating reactive oxygen species for damage to the microbial. • The synthesized nanorods were characterized by the UV-VIS spectroscopy and TEM. Each solution of nanorods show two absorption bands which corresponds to longitudinal and transverse modes of the surface plasmon.
<p>Jakab, et.al. ACS NANO 2011, 5 (9), 6880–6885</p>	<p>Highly Sensitive Plasmonic Silver Nanorods</p>	<ul style="list-style-type: none"> • Sensitivity of Silver nanorods was almost two times higher than the gold nanorods in spectral range of 600-700 nm. • Increasing nanorod width leads to higher sensitivity.
<p>Gang Wei, et.al. J. Phys. Chem. B 2005, 109, 8738-8743</p>	<p>One-Step Synthesis of Silver Nanoparticles, Nanorods, and Nanowires on the Surface of DNA Network</p>	<ul style="list-style-type: none"> • Nanoporous DNA network can adsorb silver ions with greater efficiency because of electrostatic interaction between the silver ions and the phosphate backbone of DNA strand. • Silver nanoparticles are unstable so that they can easily move along the DNA strand. • Increasing the reduction time results formation of longer, higher aspect ratio nanowires.
<p>Rucha Desai, et.al. Nanoscience and Nanotechnology Letters 2012, Vol. 4, 30–34,</p>	<p>Size Distribution of Silver Nanoparticles:UV-Visible Spectroscopic Assessment</p>	<ul style="list-style-type: none"> • One peak nearly at 400 showing the spherical shape of nanoparticle • The second band above 600 nm emerges from the coupling of surface plasmons to these aggregated particles which shows other shapes of nanoparticles

<p>Xi-Feng Zhang, Int. J. Mol. Sci. 2016, 17, 1534</p>	<p>Silver Nanoparticles: Synthesis, Characterization, Properties, Applications, and Therapeutic Approaches</p>	<ul style="list-style-type: none"> • Chemical method for synthesis includes three components, which are metal precursors, reducing agents, and stabilizing agents. • Reduction of the silver salts involves two stages (1) nucleation (2) growth. • Advantage of the chemical methods is ease of production, high yield, low cost.
<p>Neil Shirtcliffe, et.al. Journal of Colloid and Interface Science (1999) 211, 122–129.</p>	<p>Reproducible Preparation of Silver Sols with Small Particle Size Using Borohydride Reduction: For Use as Nuclei for Preparation of Larger Particles</p>	<ul style="list-style-type: none"> • A peak was usually observed at between 390 and 395 nm • Varying the molar ratio of silver to borohydride concentration effects the results.
<p>Nikhil R. Jana, et.al. Chem. Commun., 2001,0, 617-618</p>	<p>Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio</p>	<ul style="list-style-type: none"> • AgNRs of varied aspect ratio were synthesized by using seed mediated approach in a rodlike micellar media. • Spheroidal nanorods were unstable and converted into spheres within 10 min in the absence of CTAB. • Silver ion reduction by ascorbic acid in the presence of CTAB yielded only few rods in the absence of seed, which varied in aspect ratio.
<p>Haiying Xu, et.al. Photon. Res. (2017) Vol.5,2327-9125</p>	<p>Synthesis of high-purity silver nanorods with tunable plasmonic properties and sensor behavior</p>	<ul style="list-style-type: none"> • AgNRs are synthesized by seed mediated method which shows LSPR and TSPR band nearly at 830nm and 350nm respectively. • With increasing AgNO₃ up to 30 μL, LSPR <p style="font-size: small; margin-left: 20px;">blue shift from ~745 to ~680 nm.</p> <ul style="list-style-type: none"> • Further increase in

		<p>AgNO₃ from 35 to 140 μL causes the redshift of</p> <p style="text-align: right;"><small>LSPR band ~680 nm</small></p> <p style="text-align: center;"><small>-1000 nm</small></p>
<p>Mahmoud A. Mahmoud and Mostafa A. El-Sayed J. Phys. Chem. Lett. 2013, 4, 1541–1545</p>	<p>Different Plasmon Sensing Behavior of Silver and Gold Nanorods</p>	<ul style="list-style-type: none"> • AgNRs of nearly 20 nm diameter and different lengths, which were increased up to 100 nm by increasing reduction time, were prepared by seedless synthetic approach. • Linear relationship between AgNRs aspect ratios and LSPR peak position was observed experimentally and which is also confirmed theoretically.

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Chapter 3

Synthesis and Characterization of Silver Nanorods

3.1 Introduction

Different methods are adopted for the synthesis of different shapes of silver nanoparticles. These methods include Irradiation methods, Tollens method, photochemical, seed mediated method, electrochemical etc. The most commonly used method is seed mediated method for synthesis of the silver nanoparticles ^[1].

3.2 Materials

CTAB (cetyltrimethylammonim bromide) was purchased from SDFCL. Silver nitrate (AgNO₃) was purchased from Sigma-Aldrich and ascorbic acid was purchased from Sigma. Sodium borohydride was purchased from Aldrich. All solutions were prepared in millipore ultrapure water.

Table 3.1 List of chemical used in the synthesis of silver nanorods with formulas

Chemicals	Formulas
CTAB	C ₁₉ H ₄₂ BrN
Ascorbic acid	C ₆ H ₈ O ₆
Silver nitrate	AgNO ₃
Sodium hydroxide	NaOH
Sodium citrate	Na ₃ C ₆ H ₅ O ₇
Sodium borohydride	NaBH ₄

3.3 Seed mediated method ^[2]

In this method, first small particles are prepared, which are later used as the seeds for the preparation of the nanorods. Providing the controlled number of seeds and growth conditions that prevents any further nucleation. By varying ratio of seeds to metal salt, the size of particle can be controlled. Actually, the difficulty in finding an appropriate growth condition

that prevents further nucleation during growth stage restricts the application of these methods. These conditions include weak reducing agent to reduce metal salt without presence of seeds. Initial addition of seeds has two advantages

- It increases overall reduction rate, and thus the growth rate.
- Particle size is controlled by changing the ratio of the metal salt to seeds.

Silver seeds were formed by the reduction of silver nitrate with sodium borohydride in presence of citrate which acts as stabilizer. Secondary nucleation throughout the growth stage was prevented by controlling growth conditions by using weak reducing agent (ascorbic acid) and CTAB in an aqueous solution. The reaction pH of solution was varied to control aspect ratio and uniformity of rods. The optical and structural properties of AgNPs were characterized by DLS (dynamic light scattering) and UV –Visible spectroscopy. These characterizations are discussed later in this chapter.

3.4 Seed preparation method

An aqueous solution 10 mL which contained 0.25 mM AgNO_3 and 0.25 mM sodium citrate dihydrate was formed. Then, 25 μL of ice-cold 0.1 M NaBH_4 (strong reducing agent) solution was introduced into solution all at once with stirring. The color was instantly changed to light yellow. Sodium citrate dihydrate acts as stabilizer since it cannot reduce silver salt at room temperature (25 °C). This solution was used as silver seed. Within 24 h of its preparation, solution should be used.

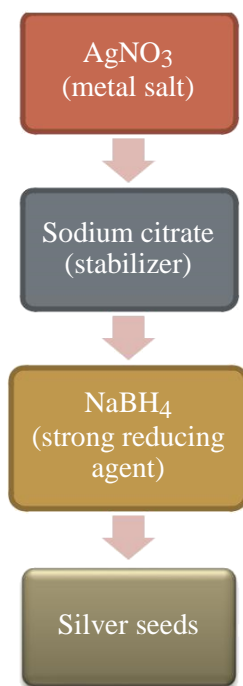


Fig. 3.1 Synthesis protocol for Silver seed

3.5 Synthesis^[3] of Silver Nanorods

For synthesis of nanorods, 20 mL aqueous solution containing 0.1M CTAB was prepared. Then the solution was sonicated for 20 min. and used when the temperature falls to room temperature. Next, growth solution was formed by adding 100 μ L of AgNO_3 (0.05 M) and 1 mL of ascorbic acid in this 20 mL CTAB. Then 100 μ L solution of seed was added to this mixture. At last NaOH (1M) is added to this solution in required quantity to adjust pH. The color of solution was changed into greenish gray. There can be many other shaped nanoparticles present in mixture like spheres, cubes, etc. which are unwanted. Therefore sample centrifuged at 10000 rpm for 10 minutes. After the centrifugation, separate the supernatant and precipitate which are settle down at the bottom of tube with help of the pipette. Next, milipore water about 10 mL was added to the precipitate. This precipitate contained the silver nanorods which are preserved for the further characterizations.

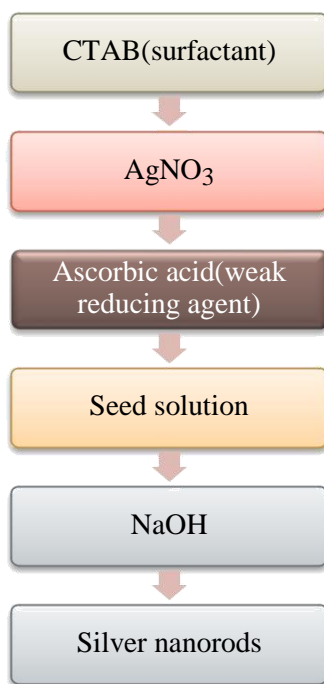


Fig. 3.2 Synthesis protocol for Silver Nanorods

3.6 Instrumentation

UV-Visible-NIR spectrophotometer (Shimadzu, UV-2600), DLS (Brookhaven 90 plus particle size analyser), Mega 17RCentrifuge machine, pH meter and ultrasonic Bath.

3.7 Characterizations

Two techniques were used for characterization of the nanoparticles. These two techniques are:

- UV-Visible-NIR spectroscopy
- Dynamic Light Scattering (DLS)

3.7.1 UV-Visible-NIR spectroscopy

Ultraviolet–visible spectroscopy refers to the absorption spectroscopy or reflectance spectroscopy in ultraviolet-visible spectral region, as it uses light in the visible and alongside ranges. In this region of the EM spectrum, atoms and molecules undergo electronic transitions. Schematic of UV-Visible spectrophotometer is shown in fig. 3.3

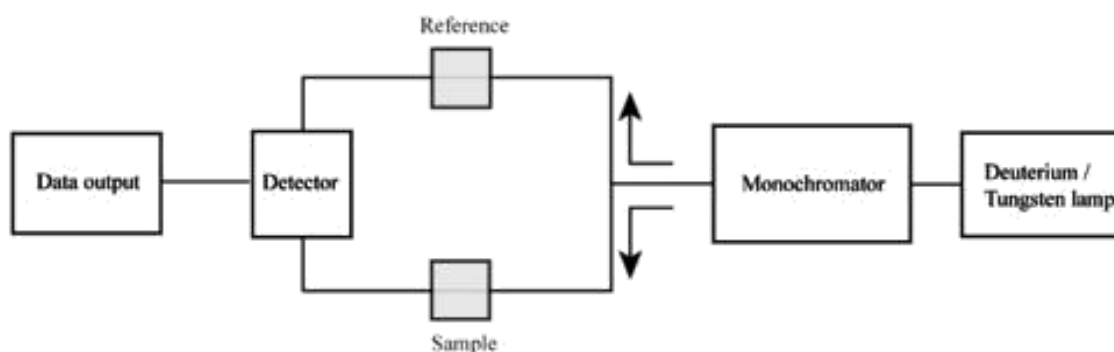


Fig. 3.3 Schematic ^[4] of UV-Visible spectrophotometer

Samples for UV-Vis spectroscopy are mostly liquids, even though absorbance of the gases and of solids can also be studied. Samples are placed in a transparent cell which is known as a cuvette. Cuvette have rectangular shape, and internal width is about 1 cm. Machine used for the UV-Vis spectroscopy was Shimadzu UV- 2600. To get high intensity of light across entire spectrum, two different lamps are used in machine. First lamp is tungsten-halogen lamp which is used for production of Vis-NIR and second lamp is deuterium lamp which is used for production of UV light. Two different slots are present in machine by which two samples can be measured simultaneously. One slot is used to get absorption spectrum of “background” and another is used for testing the sample. Background is medium in which the sample is suspended and for this work water is used as reference. If there is only a single peak in absorption spectra then silver nanoparticles ^[6] produced are spherical in shape. Contrary, if there is more than one peak it shows formation of anisotropic nanostructures.

3.7.2 Dynamic Light Scattering (DLS)

The size of particles can be found by calculating the random changes in intensity of light which is scattered from the solution. This technique is often known as dynamic light scattering (DLS), or photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS). Dynamic light scattering (DLS) is used to find size distribution profile of small particles in solution. In DLS, temporal fluctuations are analysed by means of intensity or photon auto-correlation function. In the analysis of time domain, autocorrelation function generally decays and the faster dynamics due to the smaller particles cause to faster

decorrelation. A monochromatic light source, generally laser, into sample. Then scattered light is collected by photomultiplier and resulting image is projected on a screen. This is known as the speckle pattern, which is then analysed to determine the particle size distribution. Fig. 3.4 explains principle of dynamic light scattering.

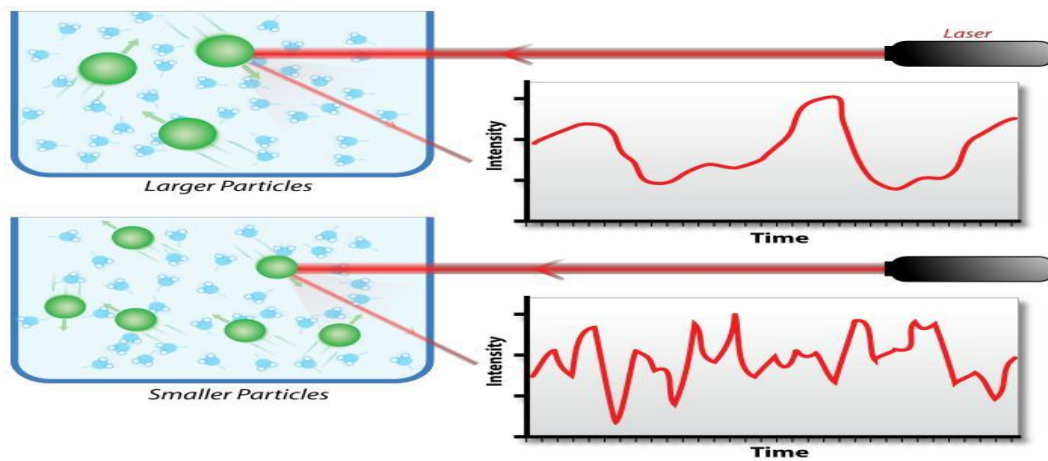


Fig. 3.4 Principle of Dynamic Light Scattering [5]

Reference

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5. https://en.wikipedia.org/wiki/Dynamic_light_scattering#/media/File:DLS.svg
6. Desai, Rucha; Mankad, Venu; Gupta, Sanjeev K.; Jha, Prafulla K. “Size Distribution of Silver Nanoparticles: UV-Visible Spectroscopic Assessment” *Nanoscience and Nanotechnology Letters*, January 2012, Volume 4, Number 1.

Chapter 4

Results and Discussion

4.1 Influence of pH on UV-VIS spectra of Silver Nanoparticles

It was observed that pH plays an important role in defining morphologies and stability of the silver Nanorods. For thesis purpose silver nanorods were synthesized at different pH by following the protocol discussed in the chapter-3. The pH was varied from 10 to 12. UV-Visible absorption spectra of silver nanorods synthesized at different pH is shown in fig. 4.1. All the samples were synthesized at room temperature.

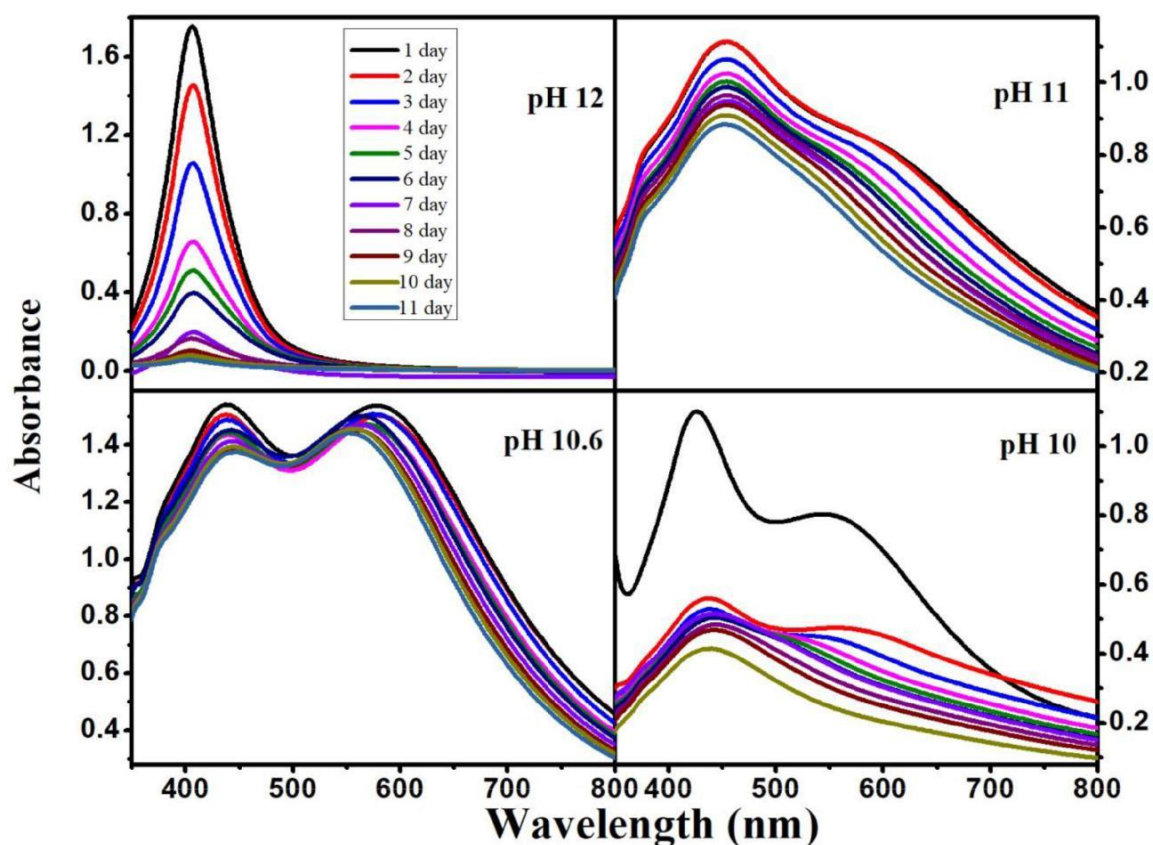


Fig 4.1 UV-Visible absorption spectra of as-synthesized silver nanoparticles prepared at pH 10, 10.6, 11, 12 recorded over 11 days

Silver nanoparticles prepared at pH 12 show single peak in range of 400 to 410 nm in UV-Visible spectra which confirms the spherical shape of silver nanoparticles. In case of PH 11 single peak (440-460nm) and hump (550-600 nm) was observed indicating that this sample contains spheres and some other anisotropic shaped nanoparticles. Sample at pH 10 and pH 10.6 shows two peaks in UV-Visible spectra which confirms the formation of rod shaped silver nanoparticles, first peak corresponds to

LSPR band and second peak corresponds to the TSPR band of nanorods. Rods prepared at pH 10 are not stable. They decay in spheres with time. Two plasmon bands get converted into a single plasmon band which is centred around 450 nm, indicating the conversion of nanorods into nano spheres. Nanoparticles synthesized at pH 10.6 show two distinct plasmon bands confirming the formation of nanorods. Further, these nanorods do not decay with time. Hence it is confirmed that silver nanorods when prepared at pH 10.6 gives stable morphology. At other pH either rods do not form or their morphology is unstable decaying to spheres.

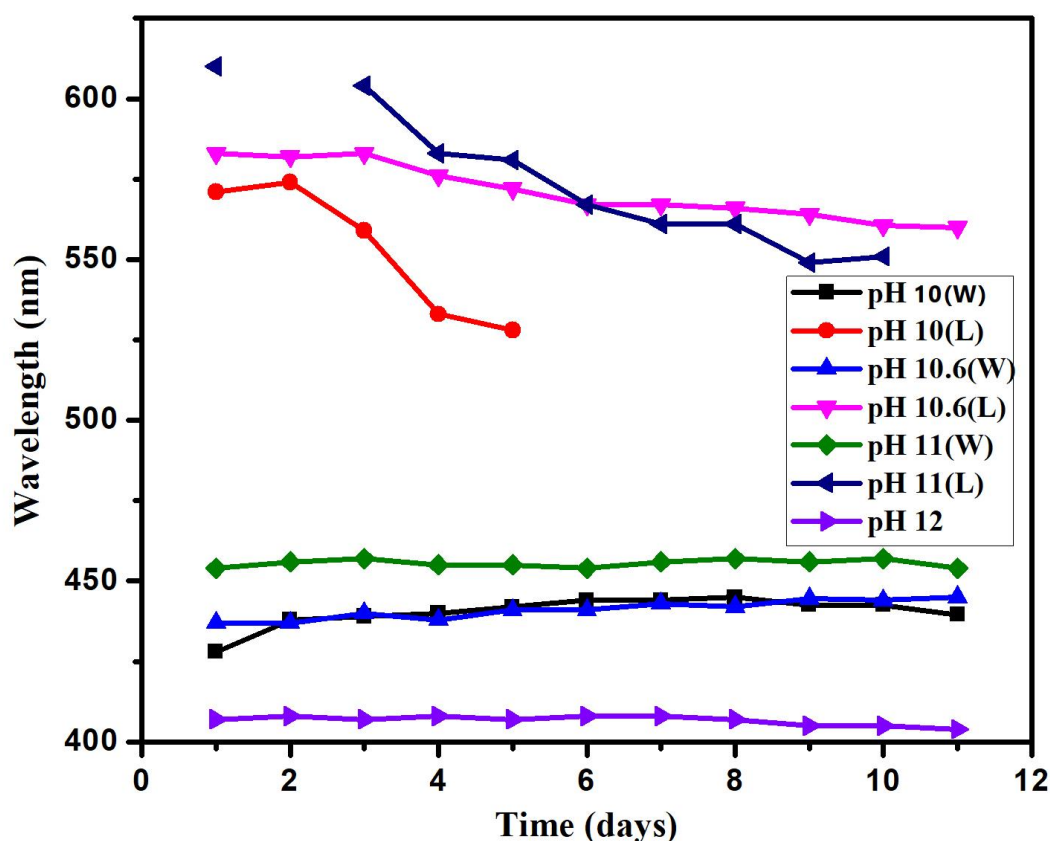


Fig.4.2 λ_{\max} corresponding to LSPR (L) and TSPR (W) band of as-synthesized silver nanoparticles recorded over 11 days

To further analyze this time dependence of LSPR and TSPR band of nanorods, the λ_{\max} position of nanoparticles corresponding to their width (W) and length (L) also plotted in this fig. 4.2. The TSPR band of nanoparticles do not show considerable shift with time as the TSPR band position of rods and plasmon band of nanospheres overlap. A gradual decay in the plasmon band position (LSPR) is observed which refers to the changes in the width of the nanorods. Percentage change in the plasmon bands were calculated from these shifts and it is observed that silver nanorods synthesized at pH 10.6

shows minimum (< 4%) shift over 11 days, indicating it is most stable amongst all synthesized samples.

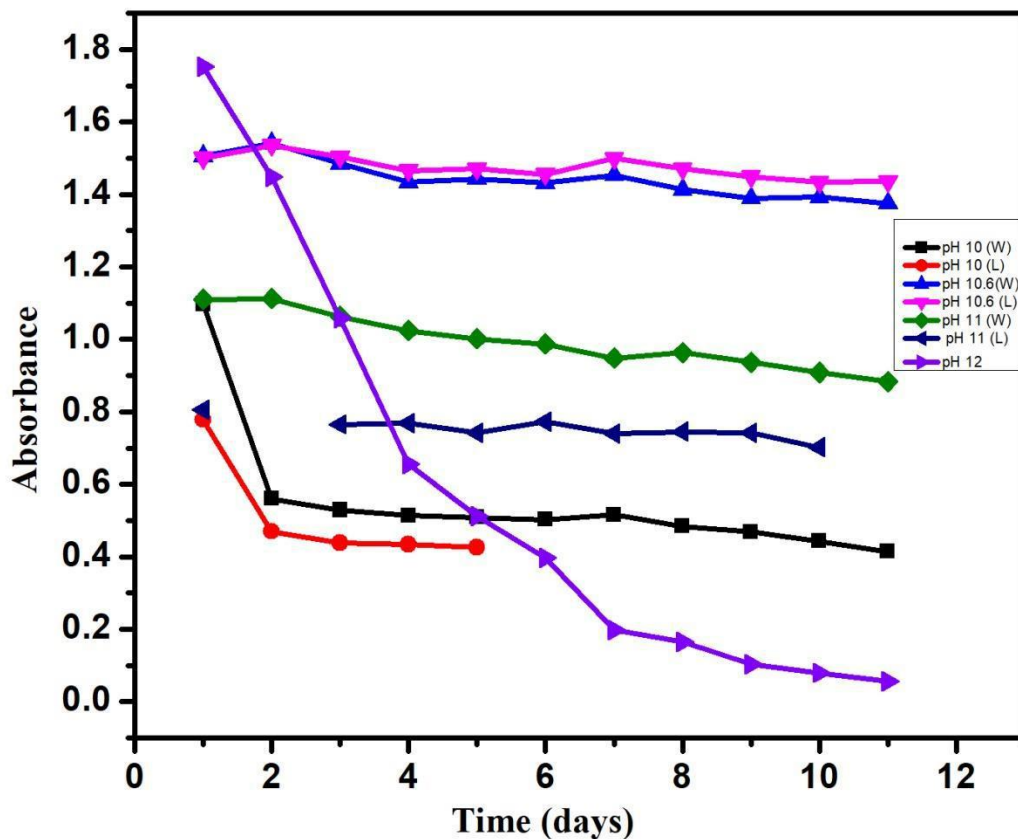


Fig.4.3 Maximum absorbance corresponding to LSPR (L) and TSPR (W) band of as-synthesized silver nanoparticles recorded over 11 days

The maximum absorption corresponds to TSPR and LSPR band of nanoparticles are almost constant with time for all the samples at different pH except at pH 12 which contains only spheres. At 10.6 pH the variation in absorption with time (Table 4.1) is minimum which is consistent with our previous observations. All nanoparticles display gradual decrease in their absorption maxima primarily due to decay in their dimensions or may be because of the clustering of nanoparticles leading to the sedimentation of nanorods.

Table 4.1 Percentage change in absorption max and wavelength max corresponds to LSPR (A_L , λ_L) band and TSPR (A_W , λ_W) of silver nanoparticles recorded over 11 days

pH	A_W (%)	A_L (%)	λ_W (%)	λ_L (%)
10	62.2	45.3	3.82	8.01
10.6	10.74	6.59	1.79	3.94
11	21.40	12.87	0.66	9.67
12	96.78	-	0.98	-

The percentage change in wavelength and absorption gives the information about stability of the nanorods. As the change is very large for the samples synthesized at pH 12 and pH 10, which indicates structural instability of nanorods at these two pH. The change is minimum in case of nanorods synthesized at pH 10.6. This confirms that silver nanorods are most stable at pH 10.6 (Table 4.1).

4.2 Effect of pH on Hydrodynamic Size of Silver Nanoparticles

Hydrodynamic size corresponding to length and width of silver nanoparticles were determined by dynamic light scattering. Mean diameter corresponding to LSPR and TSPR at different pH values which is obtained by lognormal curve fitting of hydrodynamic size (appendix 1-4) is shown in fig. 4.4

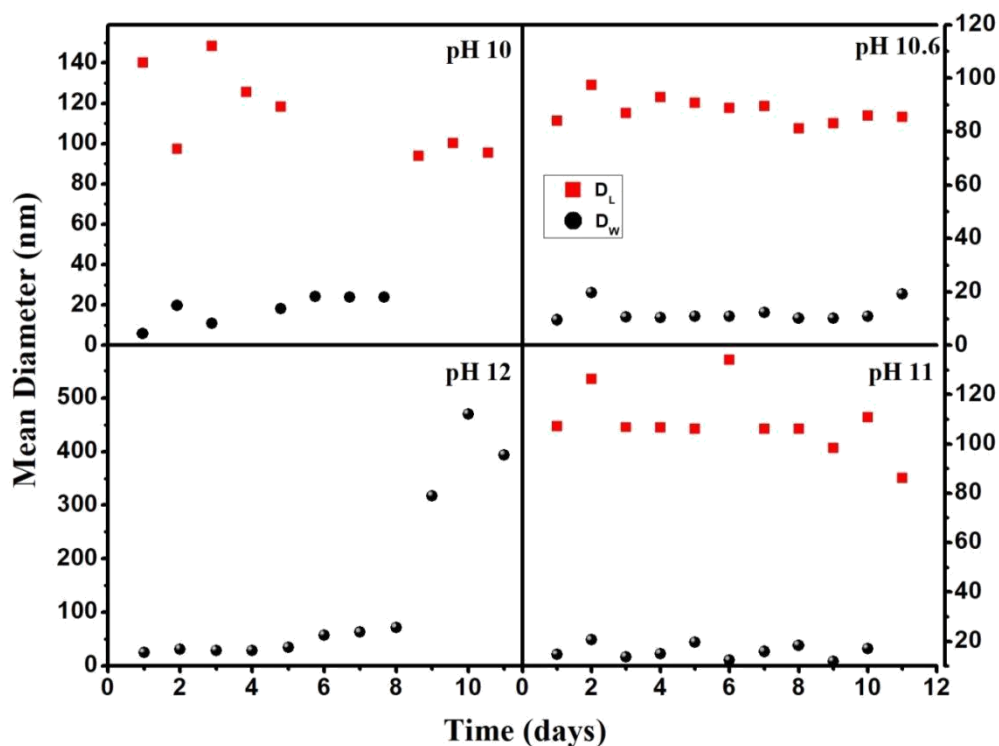


Fig.4.4 Mean hydrodynamic diameter corresponding to LSPR (D_L) and TSPR (D_W) band of as-synthesized silver nanoparticles recorded over 11 days

Here D_L and D_W denotes the mean diameter along length of the nanorods and along the width of the nanorods, respectively. The sample synthesized at pH 10, 10.6 and 11 shows the mean diameter in range of 80 nm to 150 nm and 5nm to 25 nm for length and width, respectively. Some data points of mean diameter along width of silver nanorods at pH 10 are missing. Silver nanorods synthesized at pH 10.6 shows stable mean diameters with time which indicates that nanorods are most stable at pH 10.6. The sample at pH 12 show only single size distribution indicating the spherical shape of silver nanoparticles (Appendix-4).

Table 4.2 Percentage change in mean diameter corresponds to LSPR (D_L) band and TSPR (D_W) of silver nanoparticles at pH 10, 10.6, 11, 12

Ph	D_w (%)	D_L (%)
10	75.67	40.25
10.6	50.41	12.62
11	42.31	35.72
12	94.71	-

The minimum variation in mean diameter of silver nanorods for LSPR band and TSPR band at pH 10.6 and pH 11 respectively. It confirms the highest stability of nanorods corresponding to LSPR at pH 10.6 and corresponding to TSPR at pH 11. These results are shown in table 4.2.

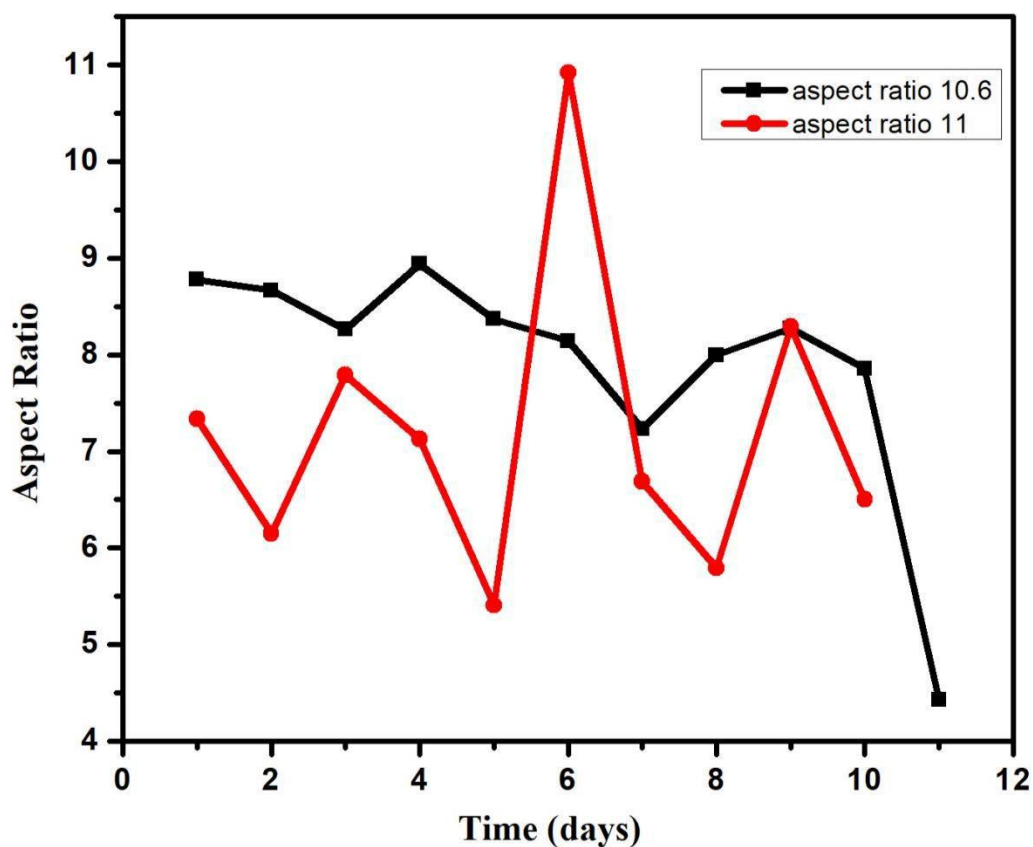


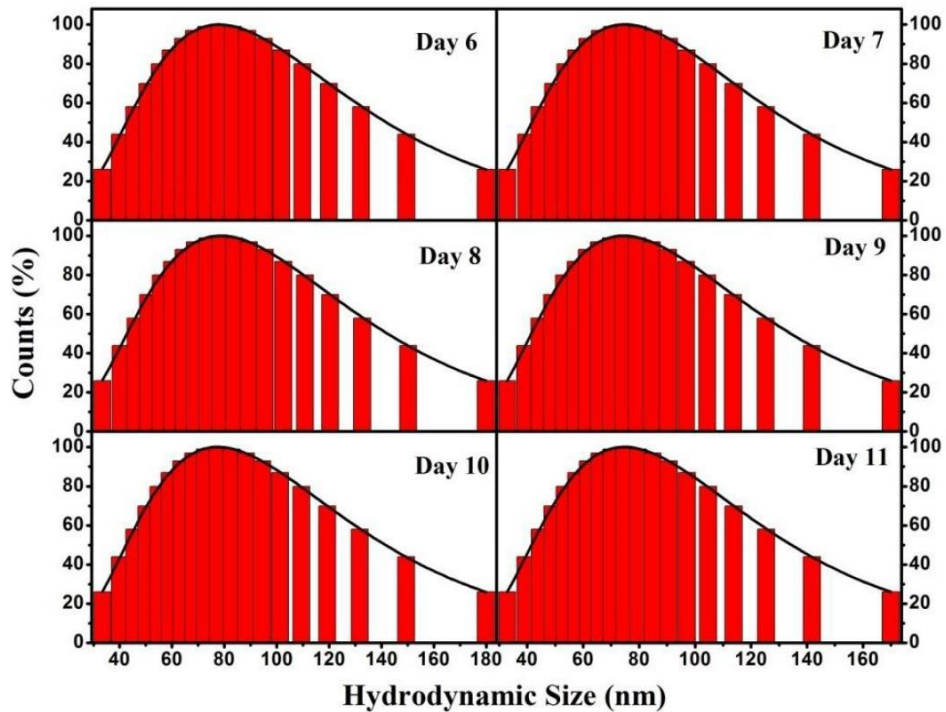
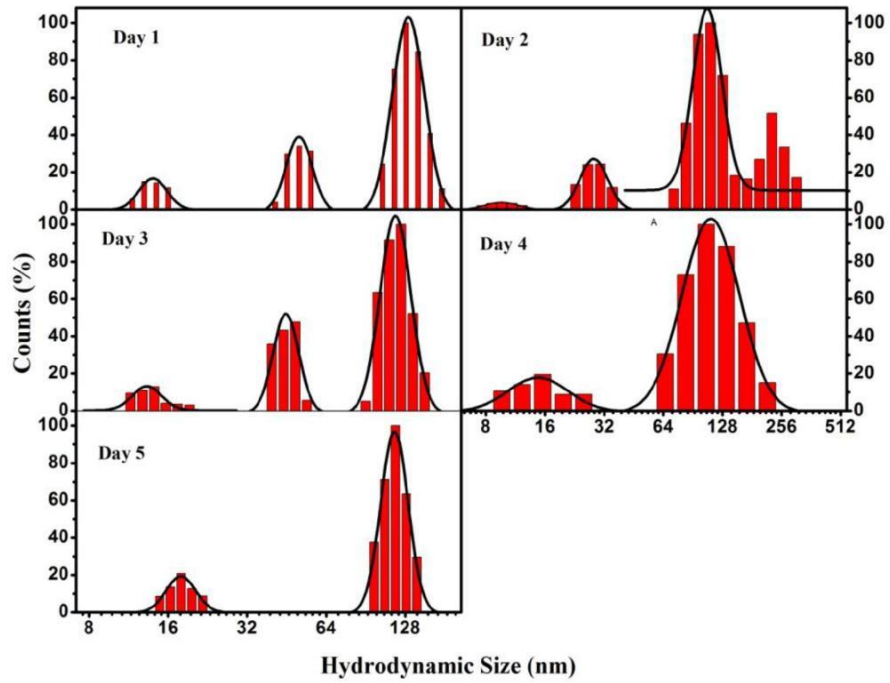
Fig.4.5 Aspect ratio of as-synthesized silver nanoparticles at Ph 10.6 and 11 recorded over 11 days

Silver nanorods synthesized at pH 11 shows more variation in aspect ratio with time as compare to ph 10.6 (fig.4.5). Hence amongst nanorods, those synthesized at ph 10.6 are most stable. This result is in good agreement with those observed in UV-Visible spectroscopy.

Conclusions

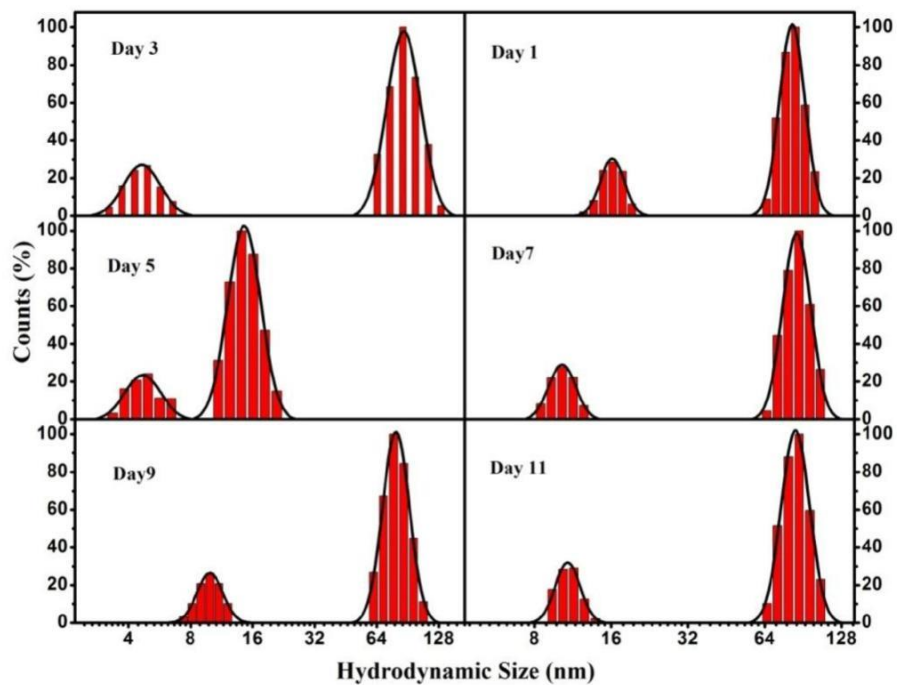
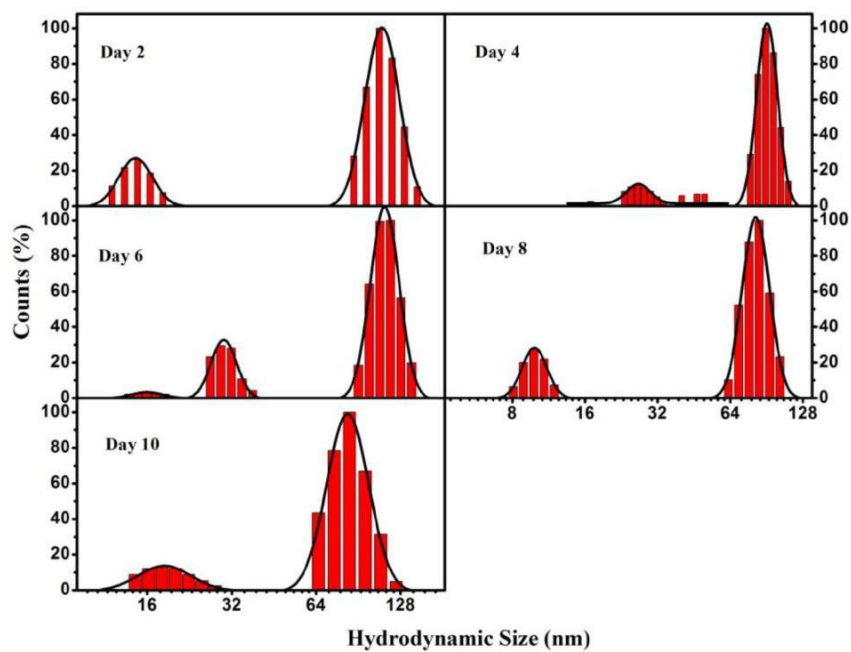
Seed mediated method was used for the synthesis of silver nanorods in aqueous solution at different pH values. The reaction pH plays an important role in defining the morphology and structural stability of nanorods. It is observed that only at pH 10.6 anisotropic silver nanorods are formed while at other pH, either nanospheres are formed or nanoparticles with mixed morphologies are formed. Both UV-Visible and dynamic light scattering studies show that only silver nanorods synthesized at pH 10.6 are structurally stable while others decay into spheres.

Appendix 1



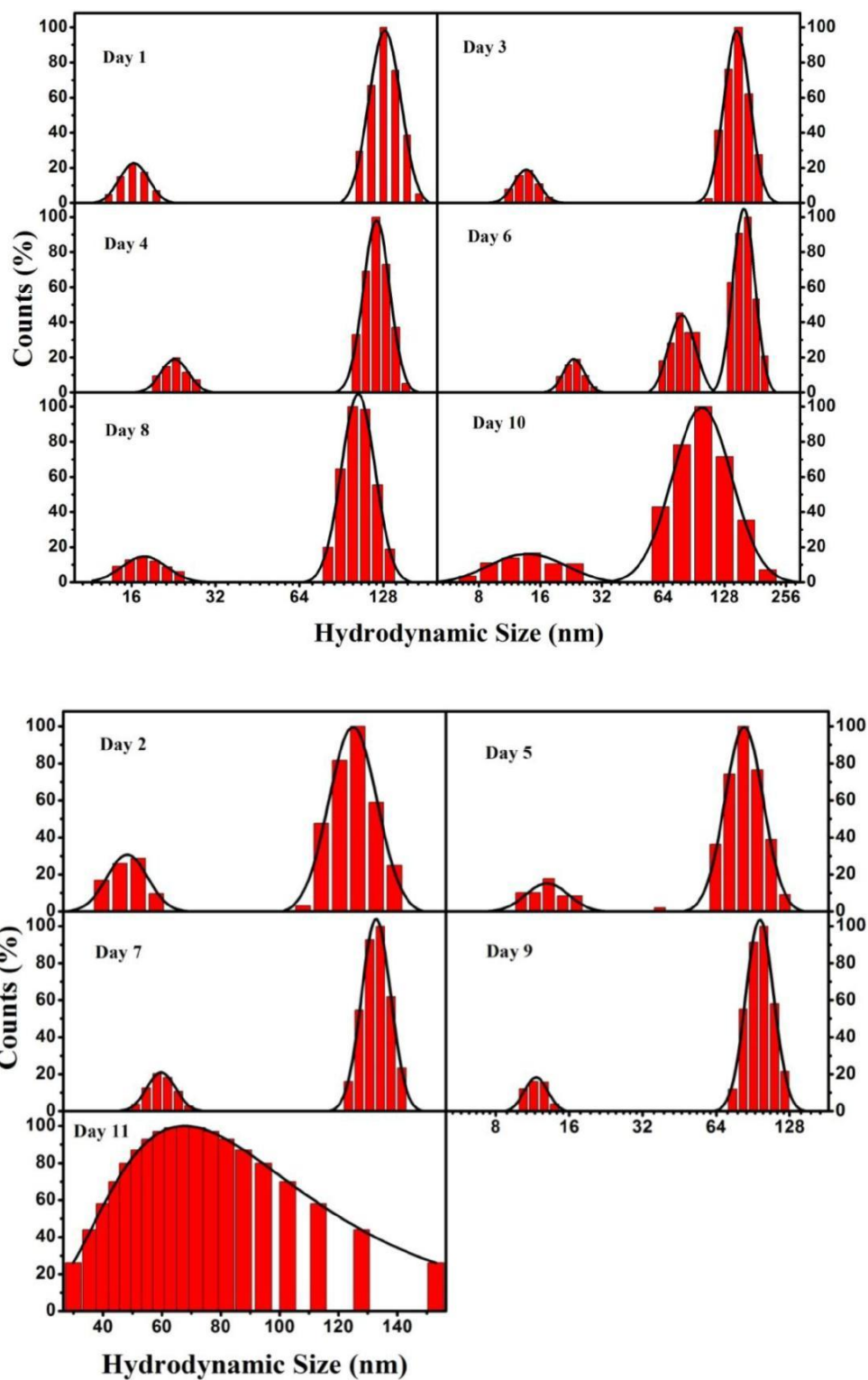
Hydrodynamic particle size distribution of silver nanoparticles prepared at pH 10

Appendix II



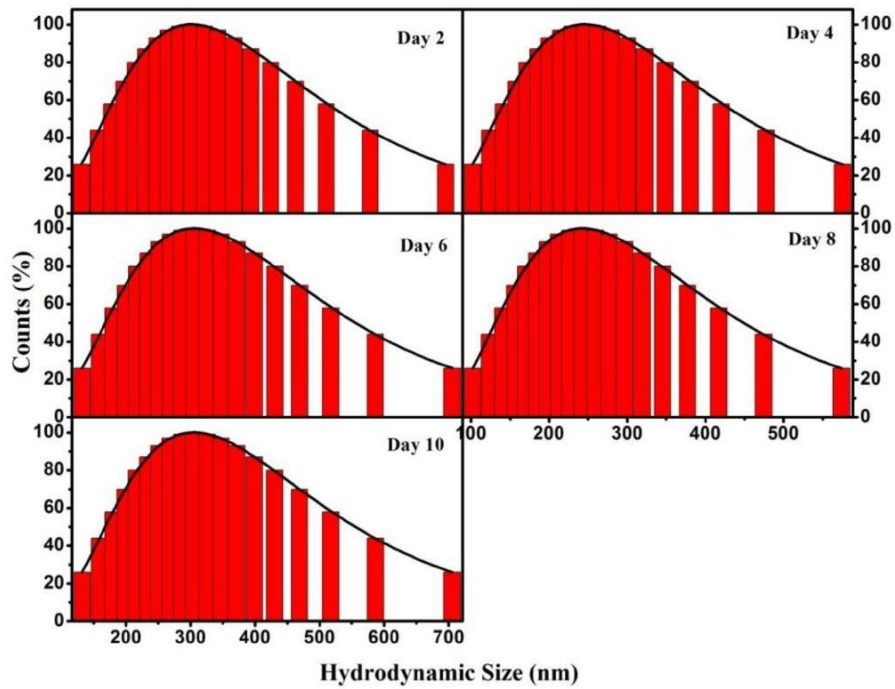
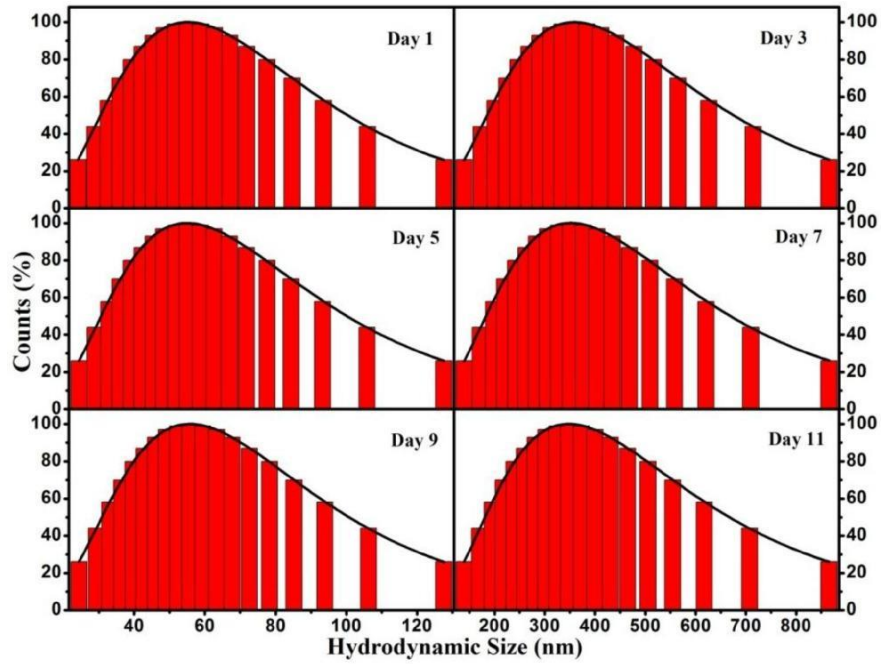
Hydrodynamic particle size distribution of silver nanoparticles prepared at pH 10.6

Appendix III



Hydrodynamic particle size distribution of silver nanoparticles prepared at pH 11

Appendix IV



Hydrodynamic particle size distribution of silver nanoparticles prepared at pH 12