GEDIZ UNIVERSITY INSTITUTE OF NATURAL SCIENCE

SYNTHESIS AND CHARACTERIZATION OF GOLD NANORODS

MASTER THESIS

HAKAN İNAN

Institute of Natural Science

Nanotechnology Graduate Program

Thesis Supervisor : Assistant Prof. Dr. Hadi. Zareie

Anabilim Dalı : Herhangi Mühendislik, Bilim
Programı : Herhangi Program

25 OCTOBER 2012

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Hakan INAN, a **M.Sc.** student of Gediz University, **Institute of Science with** ID no :60071002, successfully defended the **thesis** entitled “**SYNTHESIS AND CHARACTERIZATION OF GOLD NANORODS**”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Defense : **OCTOBER 2012**

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I also would like to thank Fezalar Educational Institute for their tolerance, support and encouragement.

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Abbreviations

CTAB: CetyltrimethylAmmoniumBromide

BDAC: Benzyldimethylammoniumchloride

FCC: Face Centered Cubic

SPR: Surface Plasmon Resonance

LSPR: Localized Surface Plasmon Resonance

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

AFM: Atomic Force Microscopy

NIR: Near Infra-Red Region

ÖZET

ALTIN NANOÇUBUKLARIN SENTEZİ VE KAREKTARİZASYONU

Bu araştırmada Altın Nano çubuklarının sentezlenmesi ve kullanılan malzemelerin üretime etkisi araştırılmıştır.

Üretim basit laboratuvar şartlarında gerçekleştirilmiş olup iki farklı metod denenmiştir.

Bunlardan birinde büyütme çözeltisine tohumlama yöntemiyle ilk çözeltiden bir miktar eklenerek altın çubukların üretilmesi sağlanmıştır.

Bu metodda Altın tuzu, yüzey aktif bir madde olan CTAB varlığında kuvvetli bir indirgeyici olan sodium boro hidrür tarafından indirgenir.
Daha sonrada bu çözeltiden çok az bir miktar alınarak ikinci bir cam şişede hazırlanan ve içerisinde yine altın tuzu, yüzey aktif madde ve zayıf bir indirgeyici olarak ta Askorbik asid ve gümüş nitrat bulunan büyütme çözeltisine eklenir.

Eklenen Gümüş Nitrat miktarıyla oluşan parçaçığın en-boy oranı arasındaki bağlantı Lokalize Yüzey Plasmon Rezonans spektrometresi kullanılarak kanıtlanmıştır.

Ayrıca Taramalı Elektron Mıkroskopu kullanılarak üretilen parçaçıkların şekil ve geometrileri(parçacık veya çubuk) öğrenilmiş ve en-boy oranları yaklaşık olarak hesaplanmıştır.

Bu çalışmada görülmüştür kü altın nano çubukların optik özellikleri kolaylıkla değistirilebilir ve buda basit kimyasal yollarla sağlanabilir.
Burdan yola çıkılarak elde edilecek olan ve 800nm civarında soğurma yapabilen altın çubuk çözeltileri biyolojik ortamlarda rahatlıkla kullanılabilir.(yakın kızıl ötesi ışınlar biyolojik ortama zarar vermemektedir)

Bununla beraber şuda gözlenmlenmiştir ki, tohumlama yöntemiyle altın çubuklar üretildiği gibi hiç çekirdekleşme yapmadan da direk olarak bir kap içerisinde altın çubukların üretimi yapılabilmektedir.

SUMMARY

SYNTHESIS AND CHARACTERIZATION OF GOLD NANORODS

In this research the synthesis methods and the effect of the substances that are used on the production of gold nano-rods have been investigated.

The wet chemical procedure (seed mediated and seedless methods) have been applied. These methods have been used since they are easy to apply and don’t need any extreme experiment media.

In this method, the gold salt is been reduced in the presence of a surfactant, CTAB(cetyltrimethylammoniumbromide), by a strong reducing agent , $NaBH_4$, and then this is used as a seed solution for a second growth solution that contains the gold salt, stabilizer, a mild reducing agent (Ascorbic Acid) and $AgNO_3$ to initiate the formation of gold nano-rods.

The dependence of the rod aspect ratio to the amount of $AgNO_3$ have been confirmed by using LSPR (Localized Surface Plasmon Resonance Spectroscopy) since gold rods have characteristic two peaks on the spectroscopy.

The SEM (Scanning Electron Microscopy) Images of the produced gold rods have been taken and confirmed that the different aspect ratio gold rods have been produced.

Along with that AFM images of the produced gold Nanorods are also taken to re-check the previous measurements.

It has been seen that the length of the gold rod can easily be tuned by chemical means. And rods for the in vivo applications can be produced with that method as well. Gold rods that have absorption peak at about 800nm can be a good candidate for the biomedical applications since it absorbs the wavelength in the NIR (Near Infrared Region).

It is also been proven that along with the seed mediated system another method of seedless production can also be used for the rod formation.

1 Introduction

Gold has been one of the most used and the most valuable metal in the history of the mankind. It has been used mainly as ornament and/or as for decoration purposes. Some artifacts such as Lycurgus Cup from the British Museum have revealed that the gold usage is dated to prehistoric times.

Figure 1 : Lycurgus Cup

Reprinted with permission from reference[1]

Though the gold has been used for centuries it is quite recent that it find itself a place in the academic stage. It is Faraday who has first proposed that this beautiful colour of the gold might be due to the colloidal size of the gold in the solution in 1899. This discovery has been forgotten for couple of decades until when the Turkevich had proposed a way to produce colloidal red coloured gold in 1961[2] and this is the time after which gold started to receive interest from the researchers.

Turkevich had found a way by which one could produce small sized gold particles synthetically by simple reduction. But the real boom has been experienced after the entry of the Electron Microscopy during the last decade of the 20th Century. Furthermore, the unique opto-electronical properties of gold particles along with the ease of preparation methods had contributed a lot to this rush of gold.

On the other hand the biocompatibility of the gold particles have allowed them to be used in vivo studies as well thus opening one more dimension to this multi-disciplinary field of research.

During the first years of the new millennium scientist like MA El-Sayed[3], C. Murphy[4], NR Jana[5], have proposed many protocols to produce gold particle and even the controlling the geometry of it.

Gold particles in Nano size are not only synthesized in the spherical particles but also as shells, stars or cages like structures also have been produced[6]. It is now clearly has been discovered that many optical and electrical properties of the gold particles are dependent to their size[7] which is detailed under chapter 2 of this thesis.

It is been shown that these size dependent properties of the metal are not only valid for the gold but also valid for some other transition metals such as Silver and Platinum. This is explained by the surface plasmon phenomenon that is examined under chapter 3 of this thesis.

Gold nano-particle Silver nano-particle

Figure 2: Gold and Silver Nano Particles

Gold nano-rod Silver nano-rod

Figure 3 : Gold and Silver Nano Rods

1.1 Gold Metal

Gold is in the group of the metals that is named as transition metals. Because of its stability it is also grouped under noble metals. It has 79 protons in its nucleus and 79 electrons when in ground state. And these electrons are distributed into the orbital as follows;

$$\mathrm{Au}_{79}\ \ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ \mathbf{6s^1}\ 4f^{14}\ 5d^{10}$$

Figure 4: Electron Configuration of Gold Metal

Gold is known as its high stability in the air and in the water and is counted as one of the best conductor of heat and electricity as an element. These features of gold could be given to its electronic configuration. It has less number of electrons in the outermost shell and many empty orbital in the 6th energy level for this electron to move freely which gives the gold its most uniqueness.

Metals like gold, silver are also scrutinized widely in many other biological researches as bio-sensor because of a phenomenon known as surface plasmons which is discussed in details in chapter 3.1

1.1.1 The Crystal Structure of the Gold

The Crystal structure of the gold is face centered cubic (fcc). But this is the structure of the bulk gold. When the size of the gold is in the nano domain the structure does also deviate from the fcc.

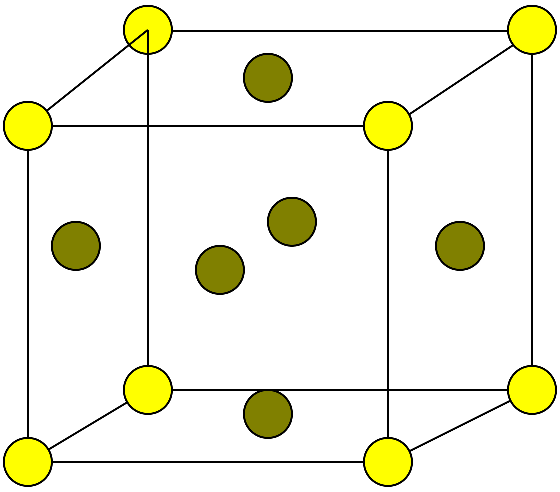


Figure 5: The Crystal Structure(Fcc) of Bulk Gold

1.2 *Synthesis of Gold Nano-particles*

Metal nano-particle synthesis is simply based on the reduction of the metal salt ($HAuCl_4$) in the presence of a stabilizing agent. Reduction is done by a strong reducing agent like $NaBH_4$ / KBH_4 and the stabilizer used generally are either Sodium Citrate or a special surfactant named as Cetyltrimethylammonium bromide (CTAB). [8-15]

The stabilizer is used to prevent the aggregation of the particles due to hydrophobic interaction between corresponding non-polar hydrocarbon tails. In this work CTAB is used instead of Citrate since citrate produces more poly-dispersed rods hence may affect optical properties of the particles.

The structure of Sodium Citrate

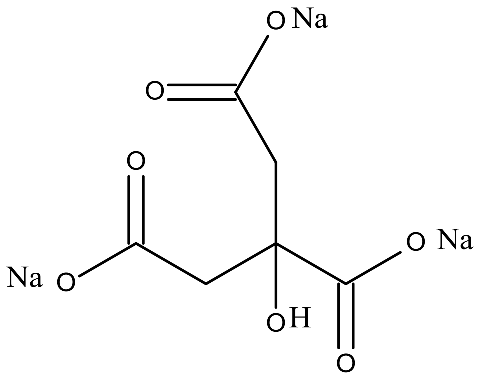


Figure 6: The Structure of Sodium Citrate

1.3 Stabilizing effect of CTAB

CTAB is an amphiphatic substance that has a polar head and a non-polar hydrocarbon tail. Because of this structure it behaves like a surfactant such as oil or soap when dissolved in water. When added to the gold it forms a micelle around the particle and thus prevents the aggregation of the particles and helps grow the controlled size of the rods from the particles.

The structure of CTAB :

$$CH_3\,(CH_2)_{15}\,N+\,(CH_3)_3\,Br^-$$

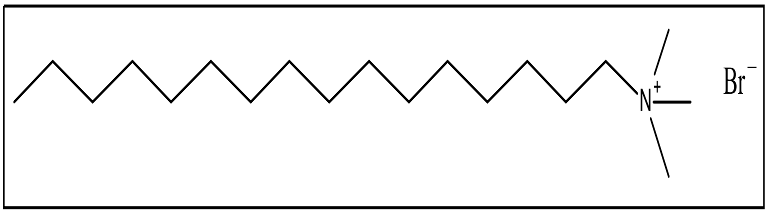


Figure 7: The Structure of CTAB

Murphy et al. have proven that when CTAB is used in the production of Gold particles or Rods it forms a bi-layer structure around the particle or rod which is a type of micelle.

1.4 Micelle

The spontaneous re-arrangement of the amphiphatic (having both polar and non-polar sides within their structure) molecules in aqueous media is named as Micelle. When placed in aqueous media amphiphatic molecules can form different shaped multi-molecular structures according to the molecules used initially.

A micelle is formed in the aqueous media with the help of the non-covalent interactions mainly hydrophobic/hydrophilic ones.

When the amphiphatic molecule is placed in water the hydrophobic (non-polar) side moves away from the aqueous environment thus fold within itself. Meanwhile the hydrophilic (polar) side moves towards water molecules. As a result of this dynamic spontaneous re-arrangement a new multi-molecular structure is formed.

The polar side of the molecule is generally formed from a polar functional organic group and/or a charged ionic part whereas non-polar part is generally formed from long chains of saturated hydrocarbons.

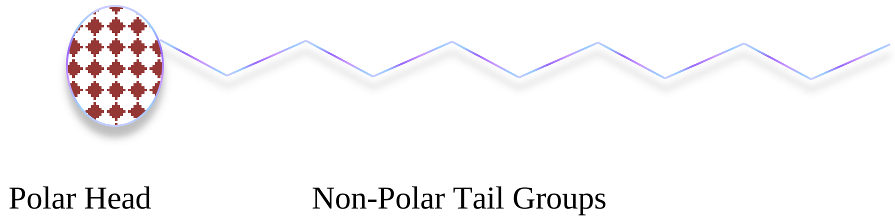


Figure 8: General Amphiphatic Structure

1.4.1 Micelle Formation

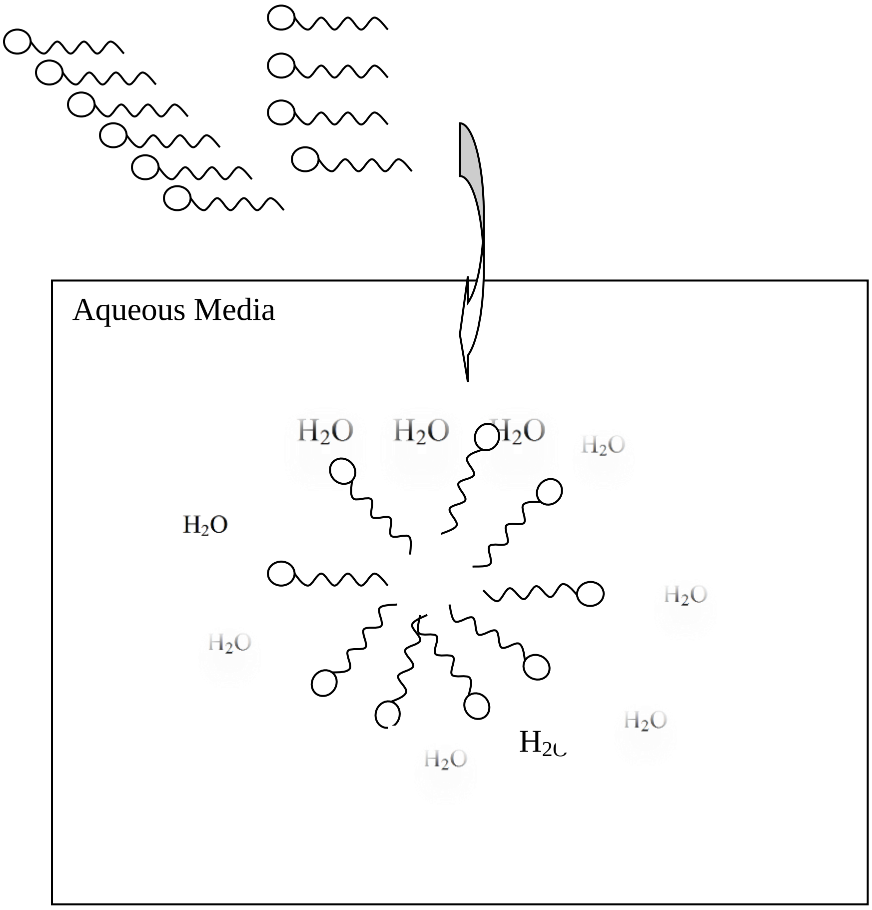


Figure 9: Dynamics of Micelle Formation

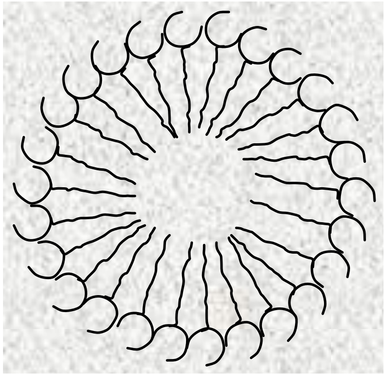


Figure 10: The structure of a Micelle

Micelle After cmc is reached

1.4.2 CMC:

The micelle doesn’t occur immediately after put in water. A critical point of saturation needs to be reached to start forming a micelle. This critical concentration that is needed to form a micelle is named as critical micelle concentration. And it is denoted as “cmc”.

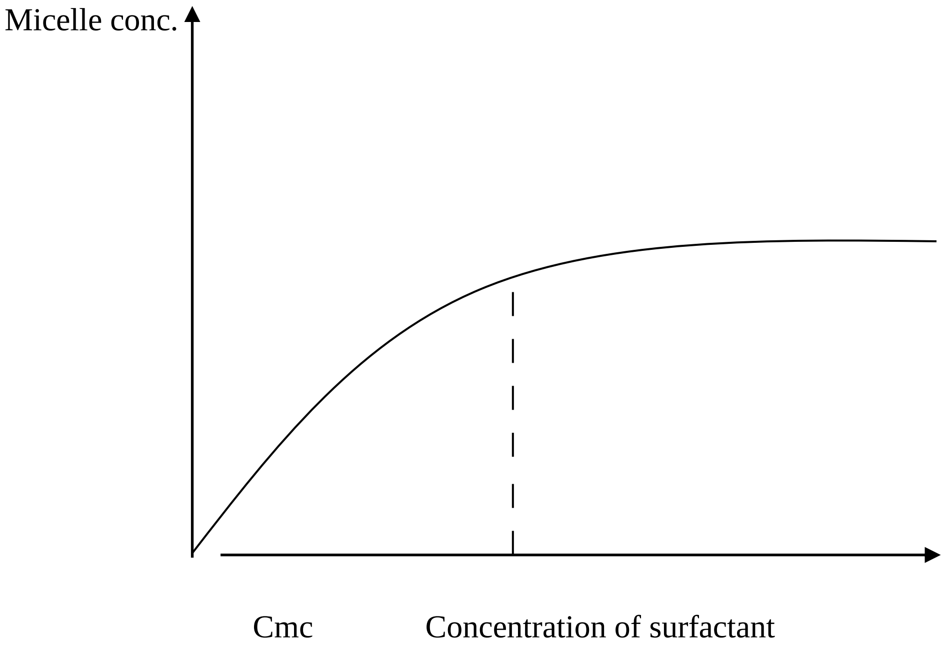
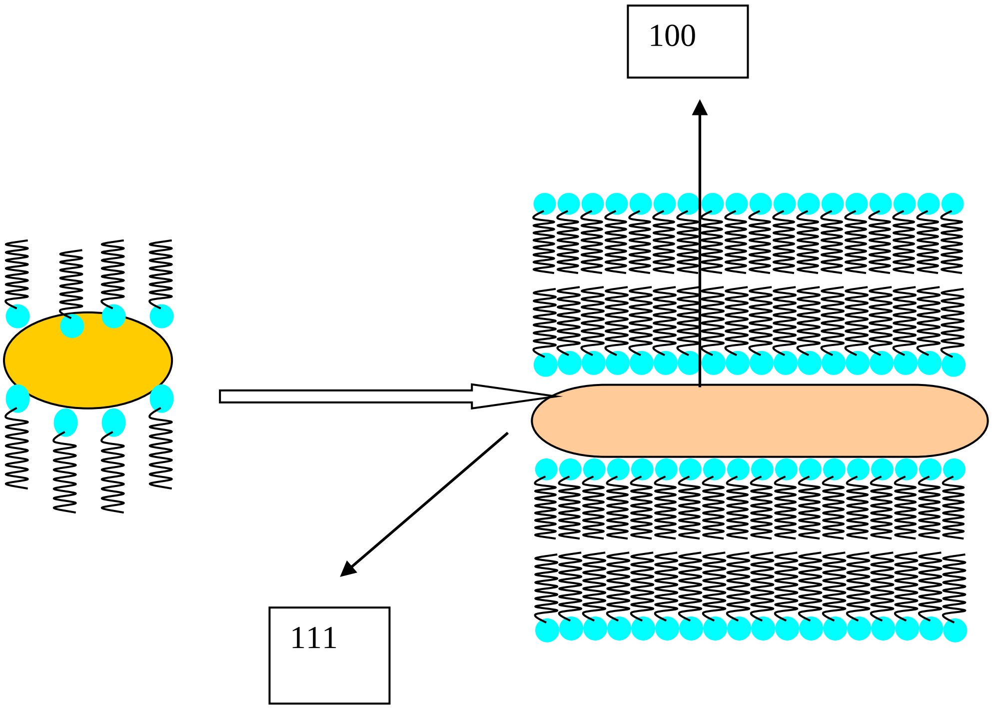


Figure 11 : Concentration of surfactant vs. Micelle Concentration

1.5 Bi-layer structure of CTAB :

It is an example of micelle formation.



Gold Nano Particles Gold Nano Rods

Figure 12: Bi-layer structure of CTAB formation on rods

1.6 Crystal Structure of Gold Nanorods

The crystal structure of gold Nanorods is very much different than the fcc bulk structure. It has been identified by researchers that the crystal structure of gold rods are twinned pentahedrals with 111 and 100 directions. The CTAB is preferentially attached to the 100 face. [16]

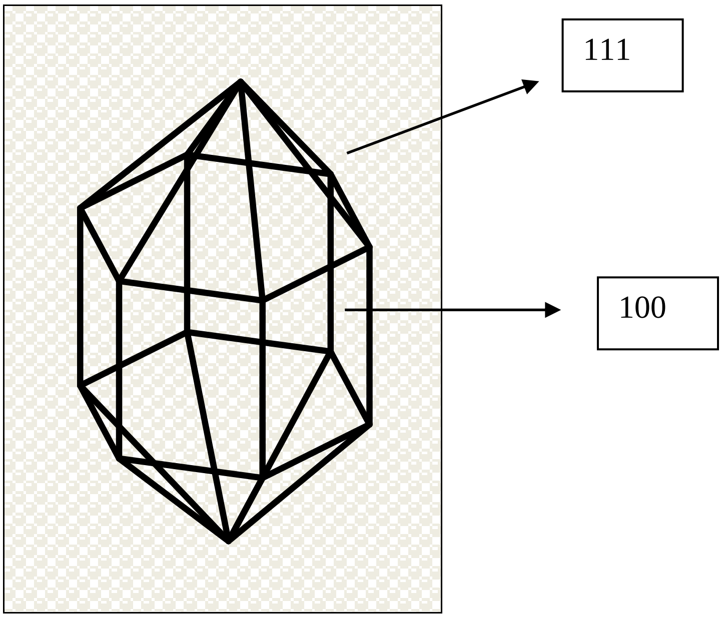


Figure 13: Crystal Structure of Gold Nanorods

2 Synthesis of Gold Nano Rods

Three paths are used for the synthesis of Gold Nano Rods: [8-15]

2.1 *Electrochemical Synthesis:*

The reduction is done in an electrochemical cell. The electrochemical reaction is the result of transferring of electrons from an reducing agent to the oxidizing agent. This free electron can easily be utilized for the reduction of gold salt at the same time. This process makes use of the free redox reaction electron.

For this purpose an electrochemical cell must be set as in the following figure;

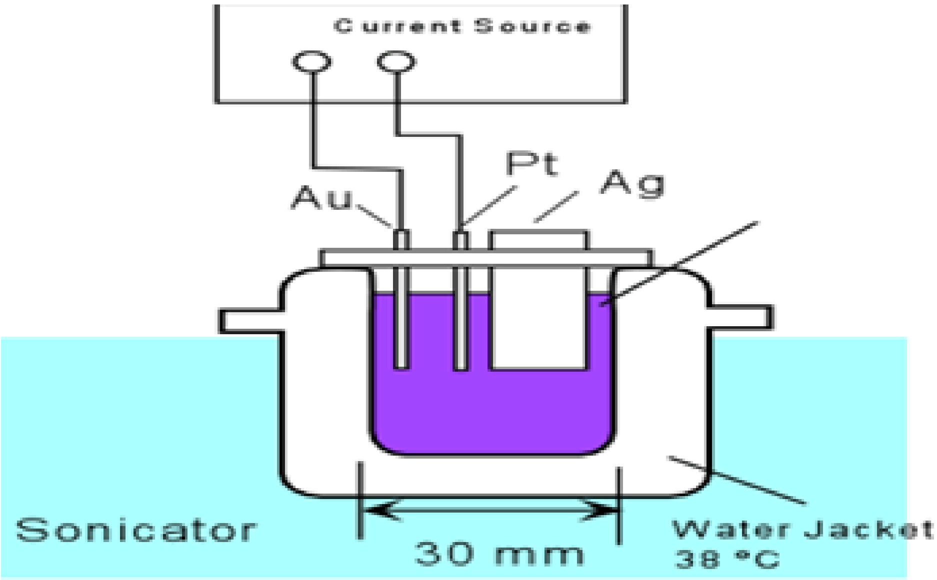


Figure 14 : Electrochemical Cell Setup

Reproduced from the reference [17]

2.2 *Photochemical Synthesis:*

The mother solution (Gold Salt and Stabilizer CTAB) is prepared and irradiated with UV light for a proper period of time and thus reduction of the gold salt is done.

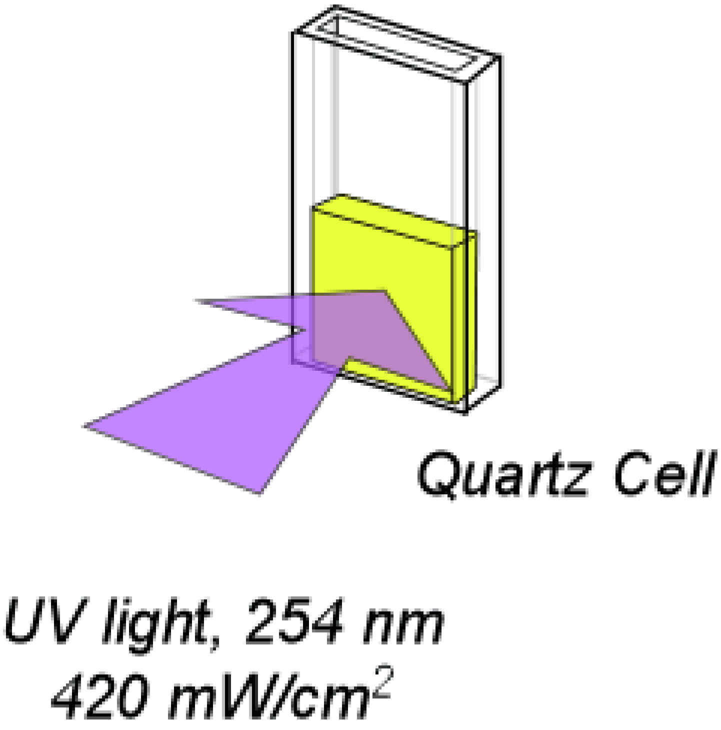


Figure 15 : Photochemical Cell Setup

Reproduced from the reference[17]

2.3 *Wet Chemical Synthesis:: Seed Mediated Synthesis or Seedless Synthesis*

Wet chemical synthesis is generally used because of ease of preparation, requirement of the mild environmental conditions and simple chemical processes. Different shaped nanoparticles can be prepared by the reduction of the gold salt depending on the growth conditions.

Step 1

$$HAuCl_4 + \text{Surfactant} \xrightarrow{\text{strong reduction}} \text{Seed Au} \tag{2-1}$$

Step 2

$$\text{Growth Solution} + \text{Seed} \xrightarrow{\text{Mild Reduction}} \text{GOLD NANO RODS} \tag{2-2}$$

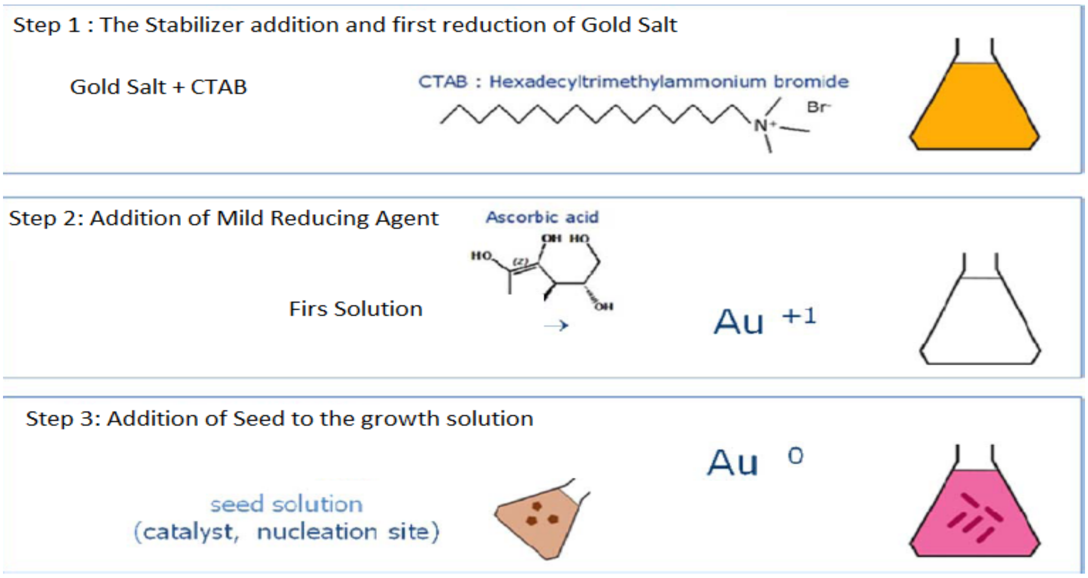


Figure 16: Schematic Representation of the Synthesis

Reproduced from the reference[15]

2.4 Seed Mediated Synthesis of Gold Nanorods

Gold Nanorods have different geometry when compared to spherical nano-particles. Slightly revised method has been opted to produce rod like gold nano structures. This method makes use of the seeded growth path for the production of rods.

In this pathway firstly the particles are produced and used as seeds. A minuscule amount from this seed solution is added to a second solution known as growth solution to initiate the formation of gold nano rods.

$HAuCl_4$ initially reduced by a strong reducing agent borohydride in the presence of CTAB.

Secondly a growth solution of $HAuCl_4$ and CTAB is prepared and a second reduction is done by a mild reducing agent, Ascorbic Acid. To initiate the rod formation a small amount of seed solution is added at this stage.

Equation showing the general reaction overview;

Step 1:

$$HAu^{3+}Cl_4 + CTAB \xrightarrow{NaBH_4} Au^{1+}CTA \tag{2-3}$$

Step 2:

$$HAuCl_4 + CTAB + AgNO_3 + \text{Ascorbic Acid} \xrightarrow{Au\{1+\}CTA} Au_m \tag{2-4}$$

2.5 *Aspect Ratio Controlled Rods Synthesis*

The ratio of the length to the width of a particle is known as the aspect ratio. [5, 6, 18-21]

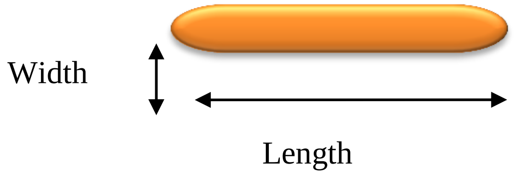


Figure 17: Aspect Ratio

Aspect Ratio Calculation:

A.R = length / width

Different aspect ratio gold Nanorods can be prepared by varying the amount of $AgNO_3$ that is added to facilitate rod formation in to the growth solution.

Generally the aspect ratio of the rod is increasing by increasing amount of added $AgNO_3$.

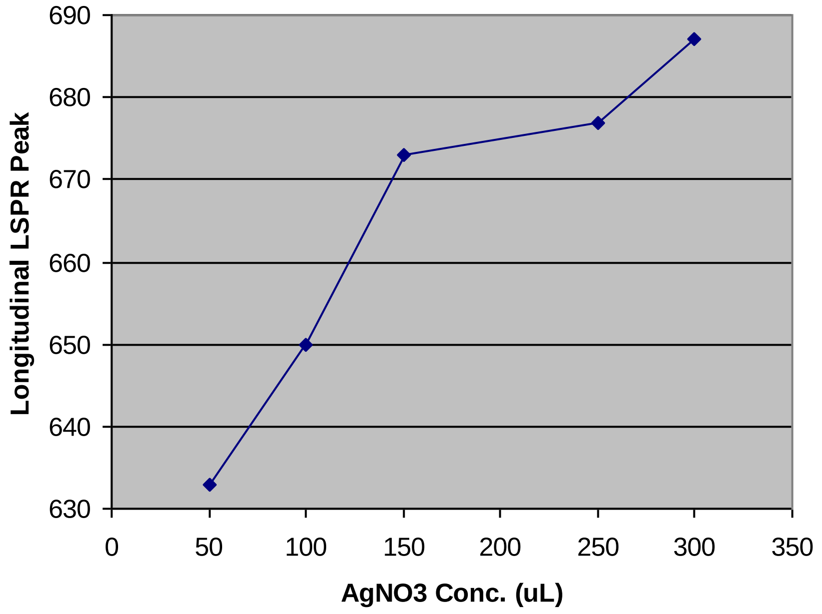


Figure 18: LSPR Peak vs. added AgNO3 concentration

It can easily be seen from the table above that the Longitudinal LSPR Peak maximum varies with the amount of the added $AgNO_3$. But it loses effect after addition of more than 300uL as proposed by El Sayed et. al. [13]

Though the wet chemical synthesis is relatively an easy method it still has many hurdles to overcome since the growth mechanism is too sensitive to the concentration of the starting materials. This also results low reproducibility.

The rods with aspect ratio up to 4 by wet chemistry method can be easily prepared but for the higher aspect ratio different methods have to be applied. Murphy et al. proposed a three step seed mediated system by which the aspect ratio up to 18 could be produced.[22]

In this method three similar growth solutions are prepared in vials and labeled as A , B and C. Firstly seed solution is added into vial A then 1ml from this first vial is taken and transferred to the second vial within 20 seconds and again within 20 seconds all B is transferred into vial C as it is seen in the following figure.

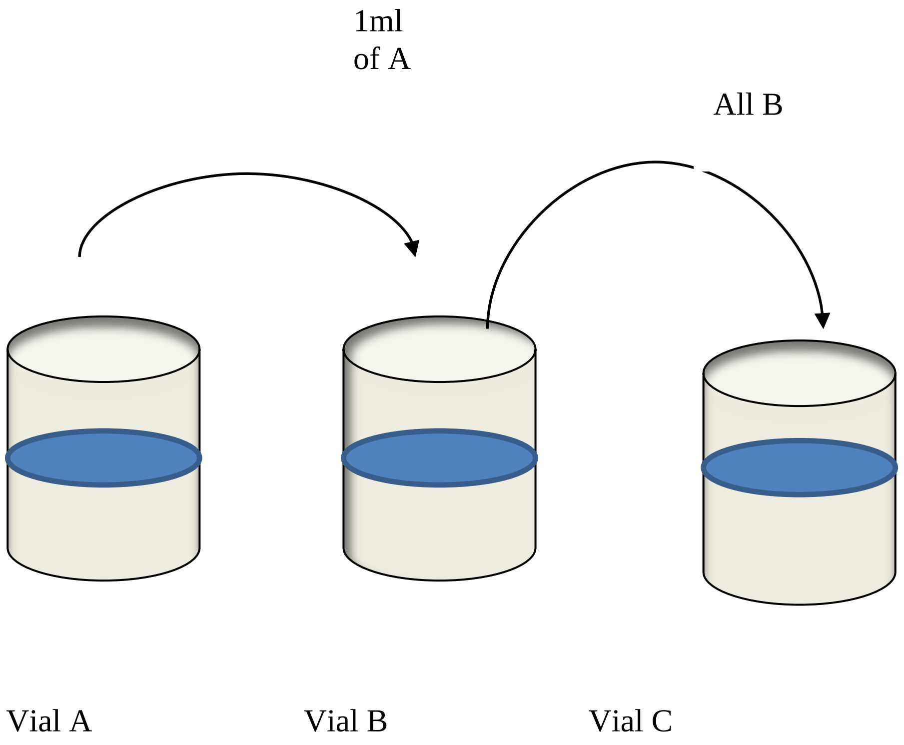


Figure 19: Three step seed-mediated rod synthesis

2.6 Seedless Synthesis Method

In the 2001 Jana et al. have proposed another approach instead of seed method synthesis. According to this method rods are grown without addition of the seed. The reductions are done one after the other in the same medium. In this approach the strong reducing agent NaBH4 is added right after the addition of mild reducing agent Ascorbic Acid in the medium where gold salt and the surfactant are present. [23]

$$HAuCl_4 + CTAB + AgNO_3 + \text{Ascorbic Acid} + NaBH_4 \longrightarrow \text{Rods} \tag{2-5}$$

2.7 Shape Separation after Rod Formation

The shape separation (removing particles and excess substances from the rods) is basically done by ultra-centrifugation. The incubated rod solutions are centrifuged and rods are isolated from the rest and concentrated by multiple consecutive centrifugations. [15, 24]

The higher spin rate is selected for the small particles during centrifugation process.

2.8 Functionalization of Gold Nanorods

CTAB is a poisonous chemical when used in living organism. That’s why for in vivo applications of the rods, CTAB has to be exchanged with non-toxic and a bio-compatible surfactant. [25-31]

PEGylation of the Gold rods is the most commonly used process. In this method the bio-toxic CTAB molecules are exchanged with harmless and biocompatible Poly Ethylene Glycol molecules that is also known as pegylation.[32]

This ligand exchange of CTAB can be done by lipids as well and has been described by Niidome et al.[27]

2.9 Present Applications of the Gold Nanorods

A huge research boom is experienced in the scientific world after the easy preparation methods of gold particles and rods are found. This interest is due to the unique properties of gold metal.[7, 33, 34]

Gold particles have been used in the biomedical field increasingly especially in the field of tumor targeting [35-37], thermal therapy [38, 39], Bio-sensing [40-44] and many other applications.

The Gold nanoparticles and Nanorods are attracting researchers from broad range of field due to their promising features such as ; biocompatibility, simple synthesis processes, size dependent optical properties and control over the size and geometry [14, 37, 45-48].

Controlling the size allows researchers to use Near Infra-Red light (600nm to 800nm) that can penetrate through tissue without harming them.

3 Characterization Methods of Gold Nanorods

Characterization is done by spectroscopic and microscopic methods. A Method called as Localized Surface Plasmon Resonance spectroscopy is used to determine the size and the shape of gold nano rods meanwhile electron microscopy is used to get proper image of rods in nano scale. [8, 14]

3.1 Surface Plasmon Resonance and Localized Surface Plasmon Resonance

The collective oscillation of the electrons on the surface of a metal is known as the Surface Plasmons.[49]

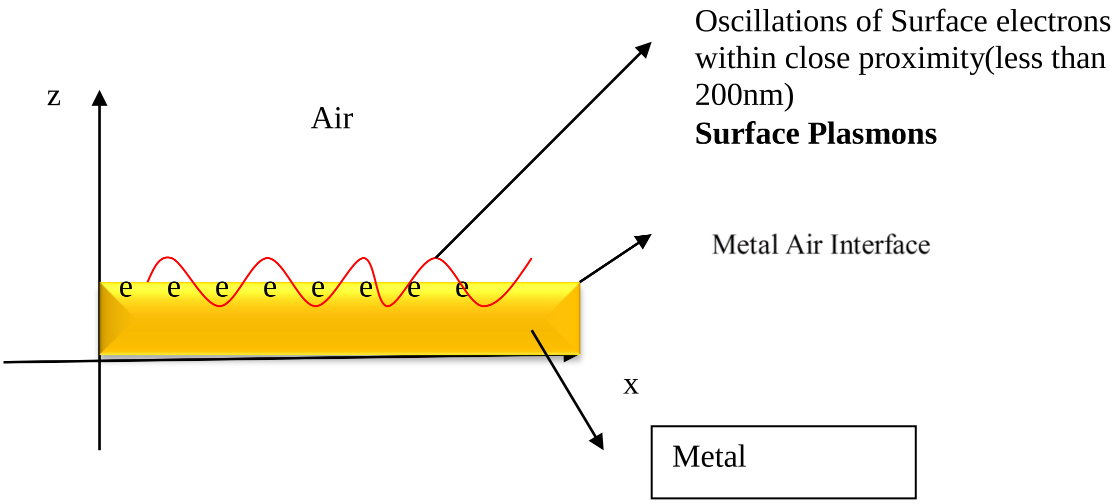


Figure 20: Surface Plasmons

These surface plasmons can be frustrated by an incoming electromagnetic wave such as light.

When an incident light has the wave vector exactly matches to the wave length of the surface plasmons on the metal a coupling occurs and by this coupling a strong absorption is experienced by metallic surfaces.

In a set up known as Kretschman configuration the deviation from total internal reflection of an incident light through a prism under a thin layer of gold film is measured and gives information about the surface of the gold metal. This geometry allows incoming light to interact with the surface plasmons on the gold surface. This entire process is named as Surface Plasmon Resonance (SPR). SPR gives on time information on in-vivo binding processes that occur between a recognition molecule and its target. That's why it is very useful for biological and chemical sensing on the gold surface.

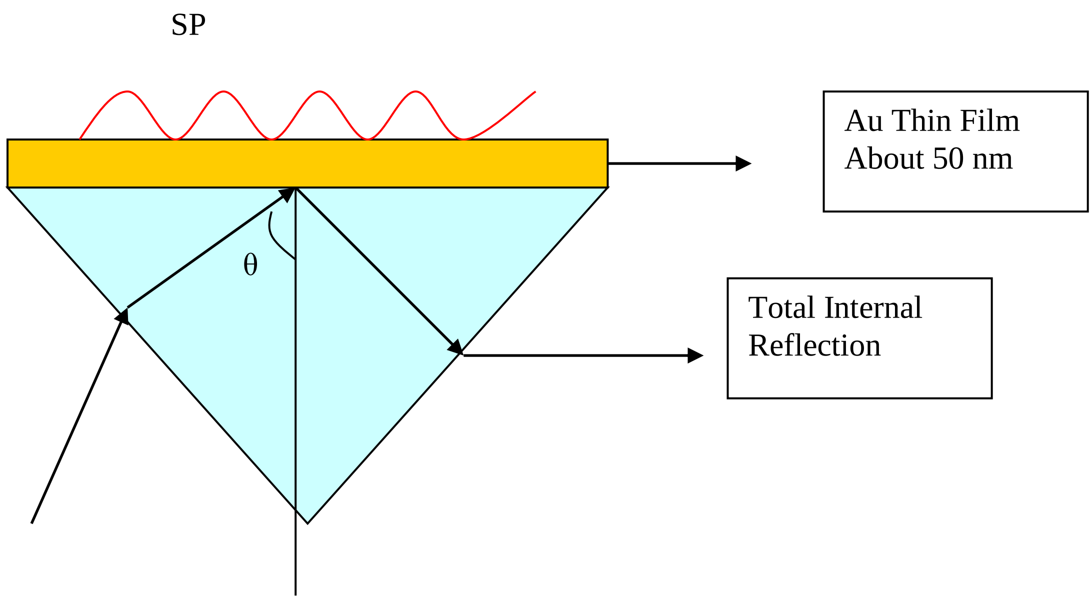


Figure 21: SPR Set-up

The surface plasmons are not confined to only surfaces but also local small sized particles within a bulk metal. A good example for this would be gold nano-particles.

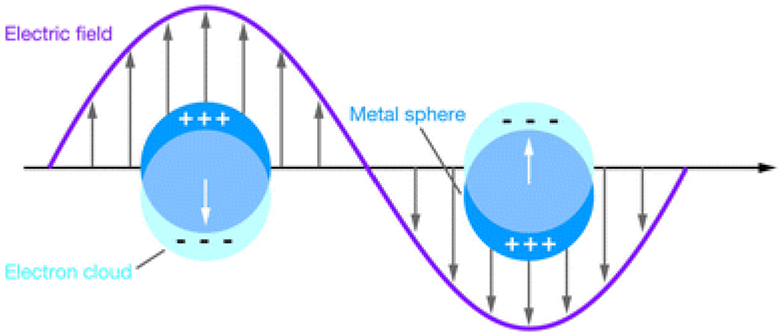


Figure 22: Localized Surface Plasmons

Reproduced from reference[50]

The same phenomenon is observed on the surface of the metal sphere as seen in the above figure and that is quite sensitive to the size and the shape of the particle. When an incident light shun at the metal sphere containing solution a strong absorption is observed due to resonance as explained for the SPR. A qualitative method very much like the Spectro-photometer used commonly almost in every lab.

But here spherical nano particles and rod like nano particles show very different characteristics in terms of absorption of light.

The spherical particles have absorption at only one wavelength whereas rods have two distinct absorption wavelengths. This difference is attributed to the shape differences and explained according to the following figure.

Gold Nano Particles show single absorbance about 520 nm -530nm.

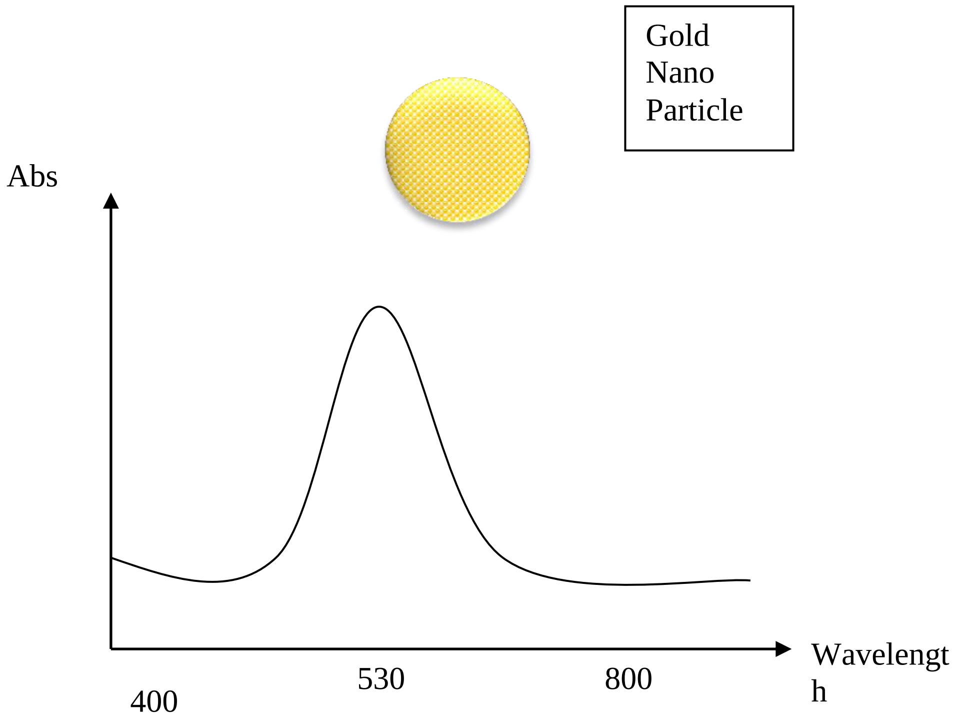


Figure 23: Gold Nanoparticles LSPR Absorption

The Spherical Nano-particles have a single absorption peak at about 520nm but Nano-rods have two peaks one at about 520 nm that is attributed to the transverse dimension of the rod and another peak from 550nm to 1200nm that is attributed to longitudinal dimension of the rod

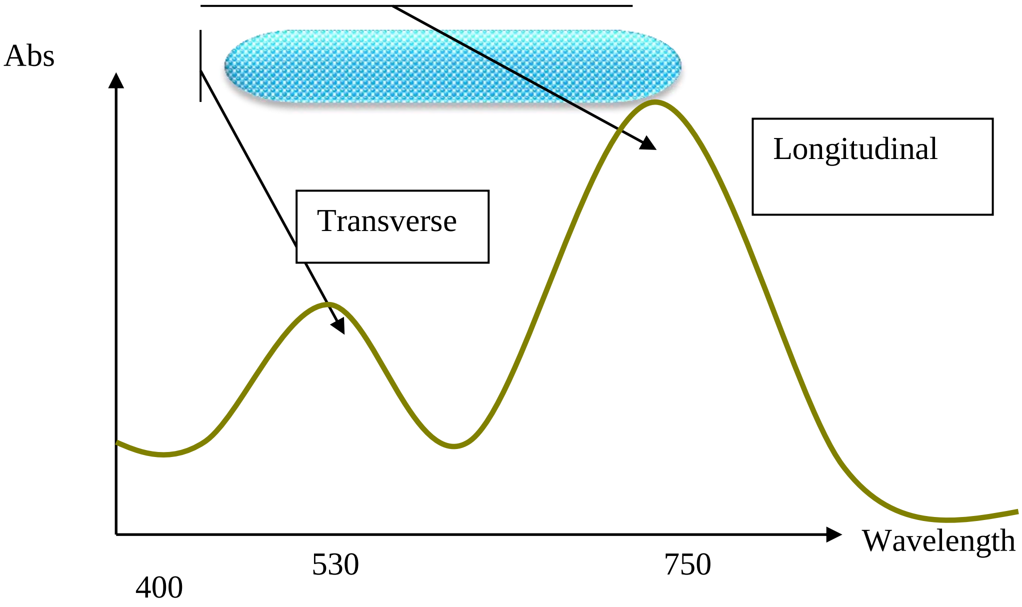


Figure 24: Gold Nanorod LSPR Absorption

LSPR of Au Rods shows two peaks

Another very useful LSPR indication is that the longitudinal LSPR Peak is very much dependent to the size of the rod. Simply the aspect ratio of the rod is increased as the wavelength of the absorption is increases.

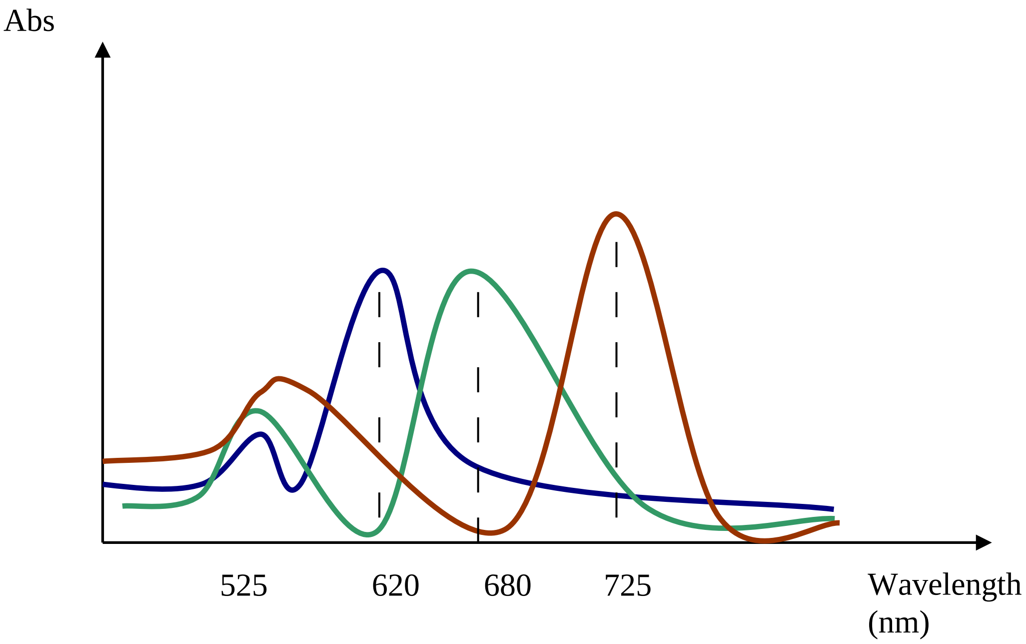


Figure 25: LSPR Peak Dependence to the Aspect Ratio

As the aspect ratio increases, the longitudinal LSPR Peak red shifts that is to say the wavelength shifts towards higher value.

Since the absorption spectra of the metals like Au and Ag falls in the range between 400 - 800 nm(Visible range) they have coloured solutions.

It is also important to note that the colour of the gold nano rod solutions is also varying with the changing aspect ratio. For example the rod with aspect ratio about 2 has blue colour, the rod with aspect ratio about 3 has green colour and the rod with aspect ratio about 4 has brownish colour.

3.2 SEM (Scanning Electron Microscopy)

Electron microscopy has been used since the invention by M Knoll and E Ruska in 1931. Scientists were forced to find another way to look into the world of unseen due to limited resolution of the light microscopy.

The electron microscopy uses electrons to examine the materials rather than using light. Practically certain problems must be overcome to produce an image by electrons.

The electron microscopy basically uses a source for electrons (generally a transition metal wire and / or filament) and then accelerate these electrons and passes through a lenses system to hit a specimen.

The electrons interact with the specimen at the atomic level then produce a form of signal in terms of light and electrons which can be interpreted to identify the structure of the specimen at the resolution of nanometer sizes.

The electrons are generally produced by either thermally or by field emission by using Tungsten(W) filament or LaB_6 crystals. After electrons are ejected from the source it needs to be focused since electrons can also travel like light does. This focusing is done by lenses with the help of coils magnetically.

The focused electron beams are then hit the specimen on the tilted specimen holder to interact with the material. Out of this interaction some of the electrons are deflected or backscattered. The backscattered electrons can be collected and be interpreted to give an idea about the structure of the specimen depending on the atomic number and size.

Some additional coils can be used for raster scanning of the electrons through specimen.

If the electrons are highly energetic they can penetrate through the specimen and can give idea about the crystallographic structure of the material. This method of electron microscopy is known as Transmission Electron Microscopy (TEM). But SEM can only gives` information about the surface of the material.

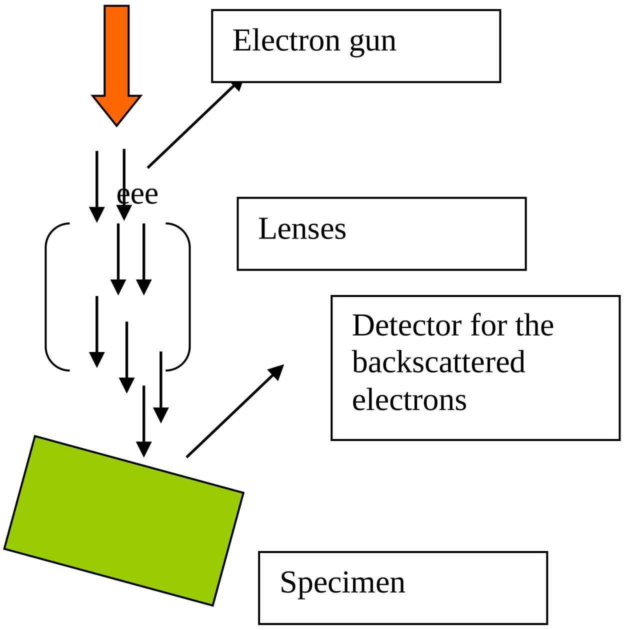


Figure 26 Scanning Electron Microscopy Overview

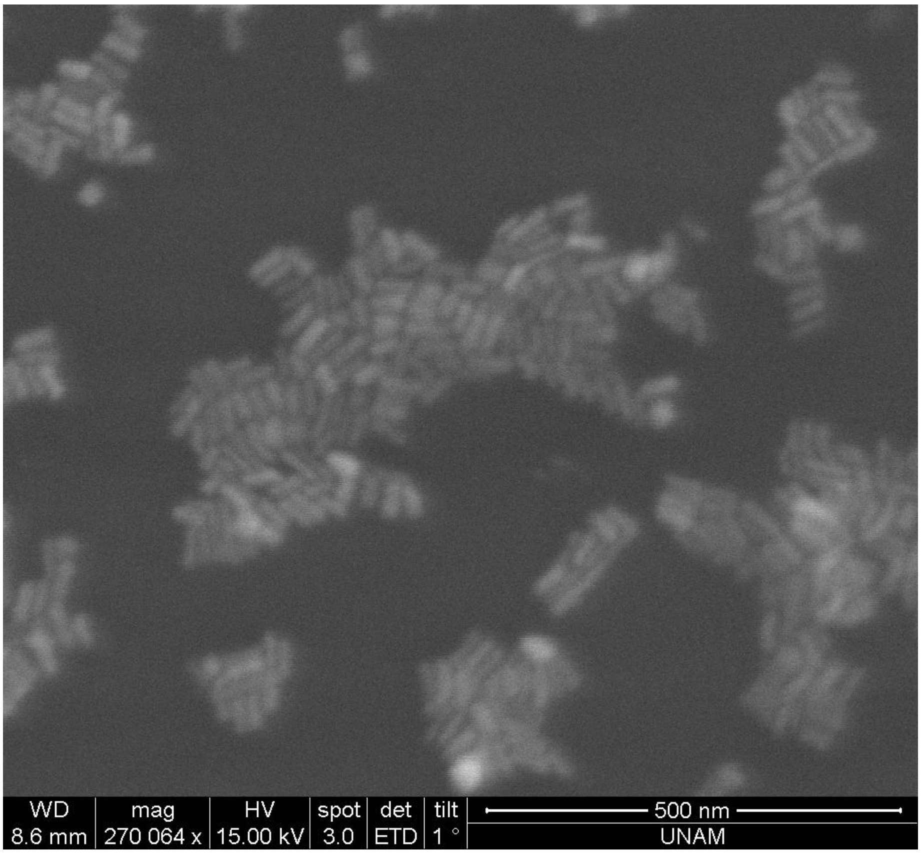


Figure 27: SEM Image of Rods

Scanning electron microscopy images of Gold Nanorods prepared on 26/12/2011. Image is taken at UNAM(Ulusal Nanoteknoloji Merkezi, Ankara/Turkey).

4 Experimental Procedure

All the materials have been used as they have been acquired. No further purification is been done. CTAB, $HAuCl_4$, $AgNO_3$, Ascorbic Acid, $NaBH_4$ and BDAC have been purchased from Sigma Aldrich Co.

Milli Q ultra-pure distilled water used for the solution preparations all the times.

All the experiments were performed at room temperature.

4.1 Preparation of Stock Solutions

Firstly, stock solutions of the materials have been prepared. Required amount of solid substance is weighed and dissolved in proper amount of distilled water to make the desired concentrated stock solutions.

The experiments are performed with the help of these stock solutions as needed.

Table 1: Preparation of Stock Solution[13]

Chemicals	Molar Mass	stock solution conc	volume of the sol	amount of the solid
HAuCl4	**339.79**	1,0 E-3 M	100mL	34 **mg**
HAuCl4	**339.79**	0,5 E-3 M	100mL	17 **mg**
CTAB	**364.45**	0,2 M	100mL	**7,3g**
NaBH4	**37.8**	0,01M	100mL	38 **mg**
Ascorbic Acid	**176.12**	0,0788M	100mL	**1,38g**
AgNO3	**169.87**	4 E-3 M	100mL	**68mg**

4.2 Synthesis of Seed (Gold Particles)

Particles are prepared as per the seed mediated system. Firstly 5ml 0.2M CTAB is taken and added to the vial containing 5ml 0.5mM $HAuCl_4$ solution. And to this mixture under vigorous stirring 0.6ml 0.01M $NaBH_4$ is added. The yellow colour of the mixture has turned to brownish colour immediately.

After 2 minutes of stirring this solution is used as seed solution for the rod formation. After that seed solution is left for next day. In the very next day the brownish colour of the solution has turned to pink indicating the proper formation of gold nano particles. [5, 13, 20, 21, 23, 24]

Table 2: Preparation of Seed Solution

Chemicals	**Stock Concentration**	**Amount added**	**Final Concentration**	
HAuCl4	0,5mM	5mL	2,5 E -4	
CTAB	0,2M	5mL	0,1M	*yellow brownish colour*
	total volume of mixture	***10mL***		
NaBH4	0,01M	0,6mL	5,6 E-4	ice cold with stirring

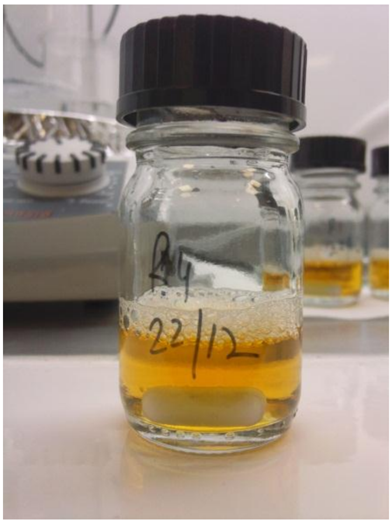


Figure 28: Picture of Initial CTAB+HAuCl4

Initially solution has yellow colour as seen in the above picture but it turns brownish immediately after addition of reducing agent and remains in this colour for a period of time (generally 24 hours) reason of which couldn't be understood as seen in the following pictures.

Figure 29: Picture of mixture after addition of NaBH4

The colour of the seed solution after addition of $NaBH_4$ turns brown from yellow.

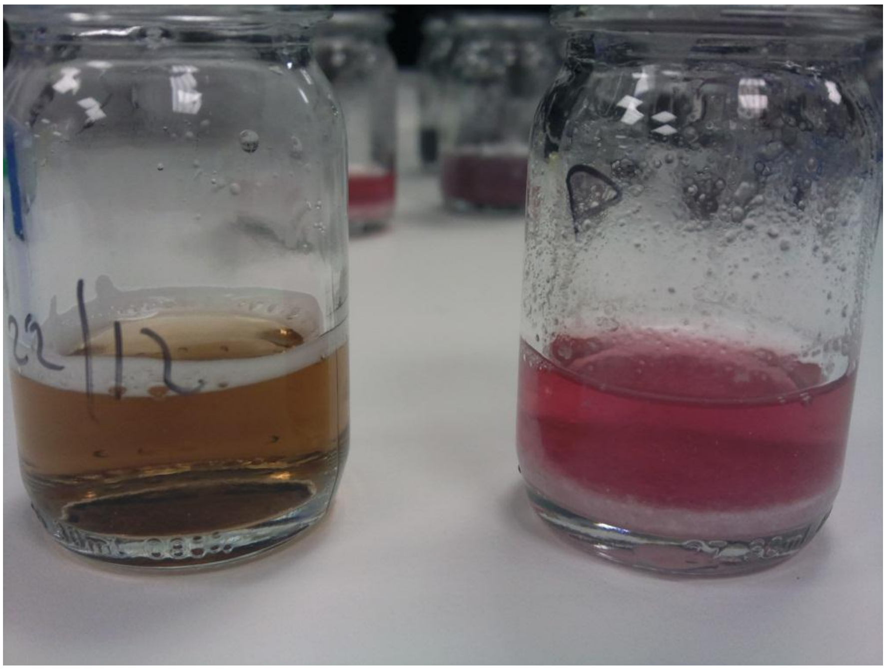


Figure 30: Fresh and aged gold particle solutions

The brownish colour turns pink within 24 hours indicating the formation of the gold particles.

4.3 Synthesis of Gold Nano Rods with different aspect ratio

After the seed formation, a growth solution is then prepared as follows;

5ml 0.2M CTAB is taken and added to different amount (50ul-250ul) 4mM AgNO3 and then to the same vial 1mM 5ml HAuCl4 is added. And next 70ul 0.0788M Ascorbic Acid is added. After this step the colour has faded away and the solution have turned colorless.

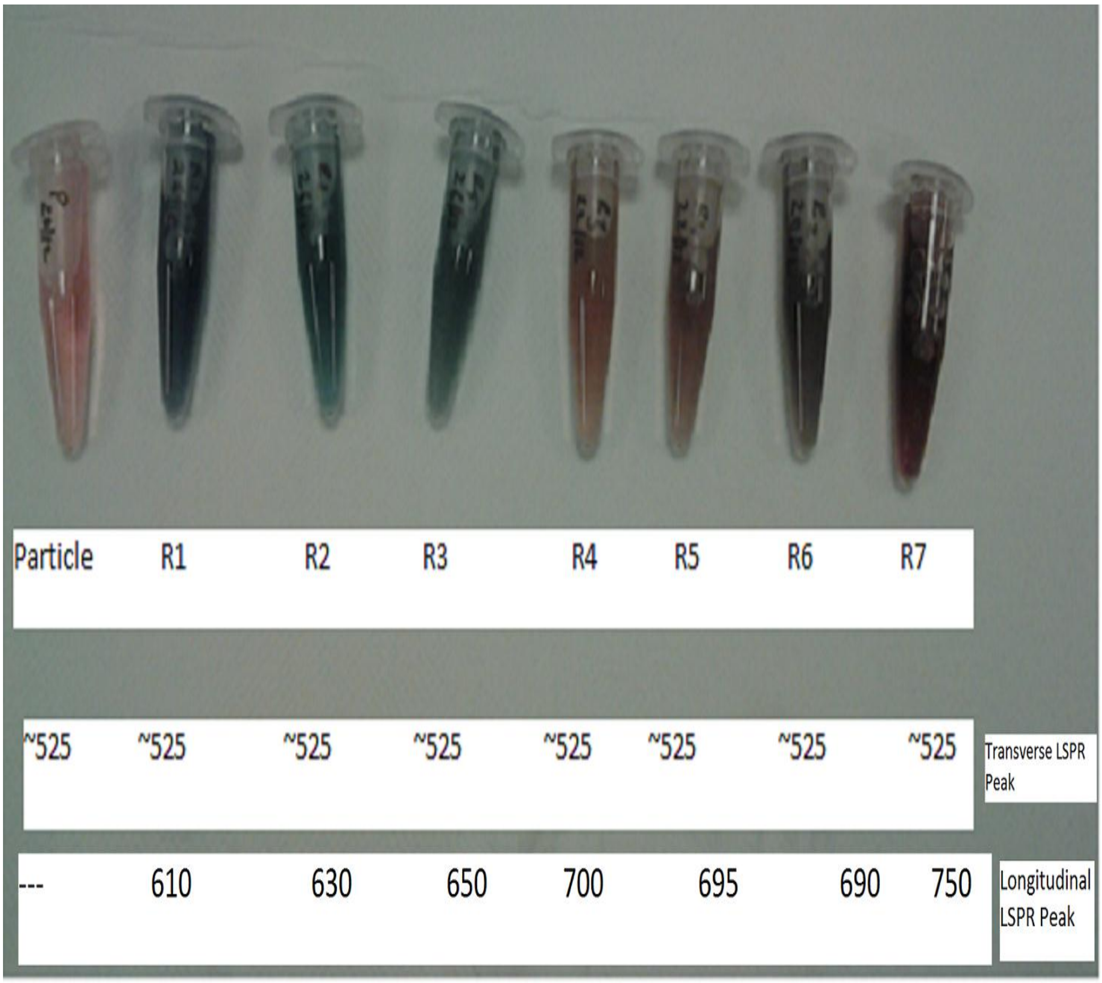
And finally, to initiate the rod formation 12ul Seed solution prepared in the first step have been added to this growth solution. The colors of the solutions started to change within the 10 minutes.

Depending on the aspect ratio of the formed rods the colors of the solutions have also varied from blue to brown.

Table 3: Preparation of Growth Solution

Chemicals	**Stock Concentration**	**Amount added**	**Final Concentration**	
HAuCl4	1mM	5mL	5,0 E -4	
CTAB	0,2M	5mL	0,1M	
AgNO3	4mM	50ul - 250 ul	2,0 E-5 to 1,0 E-4	
	total volume of mixture	***10mL***		
Ascorbic Acid	0,078M	70 uL	5,5 E-4	*turns colorless*
Seed Solution		12 uL		*10-20' colour stable*

depending on the added volume of $AgNO_3$ colour changes
which indicates the different aspect ratio from 2-4



	Particle	R1	R2	R3	R4	R5	R6	R7
Transverse LSPR Peak	~525	~525	~525	~525	~525	~525	~525	~525
Longitudinal LSPR Peak	---	610	630	650	700	695	690	750

Figure 31: Prepared Rods and Their LSPR Data

As seen in the figure the transverse peak is constant at about 525nm while longitudinal peak shifts from 610 to 750nm according to the aspect ratio and this aspect ratio can be controlled by the amount of the added $AgNO_3$.

4.4 Images of selected rod solutions

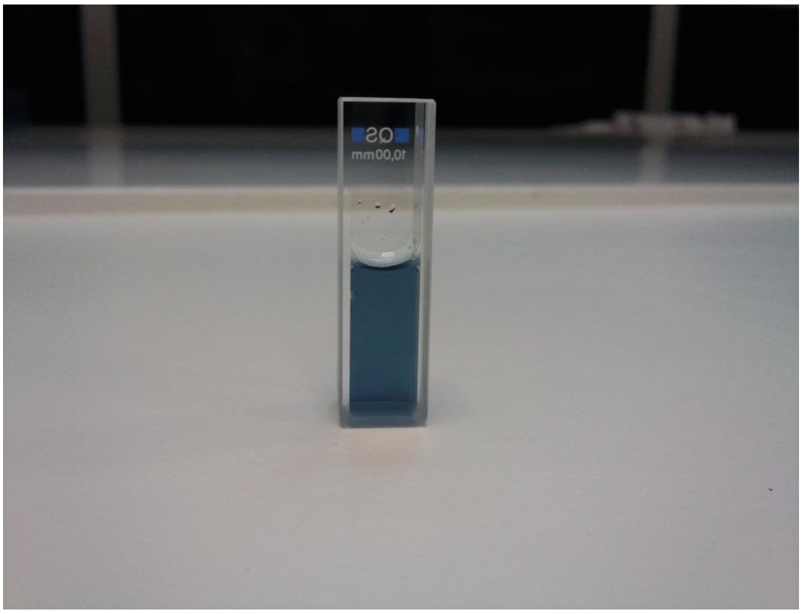


Figure 32: Picture of Rod that has LSPR at 620nm

LSPR longitudinal Peak at about 620nm and blue colour is worth to note.

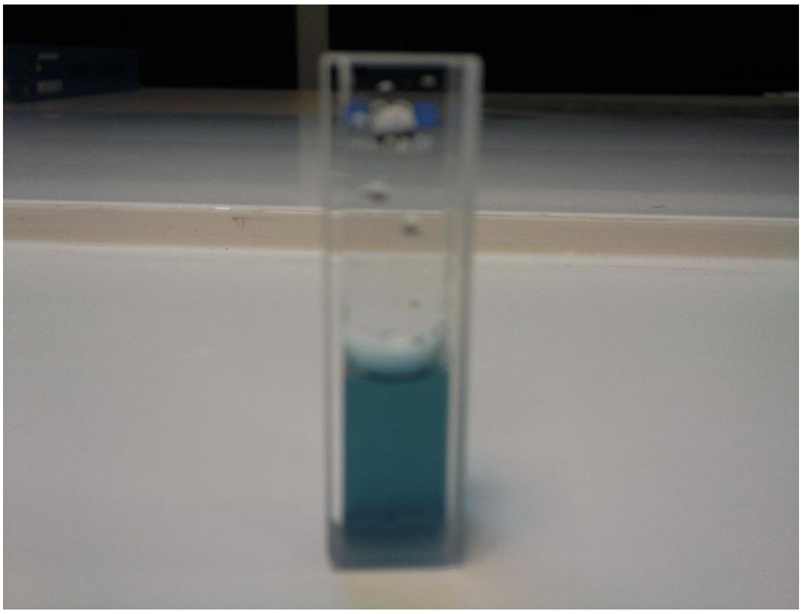


Figure 33: Picture of the rod that has LSPR at 680nm

LSPR Longitudinal Peak at about 680nm and the greenish colour is worth to note.

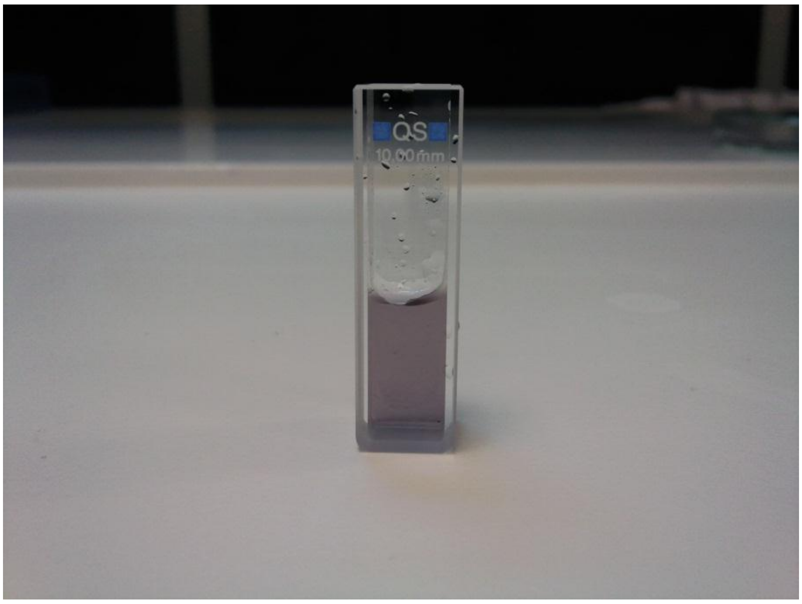


Figure 34: Picture of rod that has LSPR at 720nm

LSPR Longitudinal Peak at about 720nm and the brownish colour is worth to note.

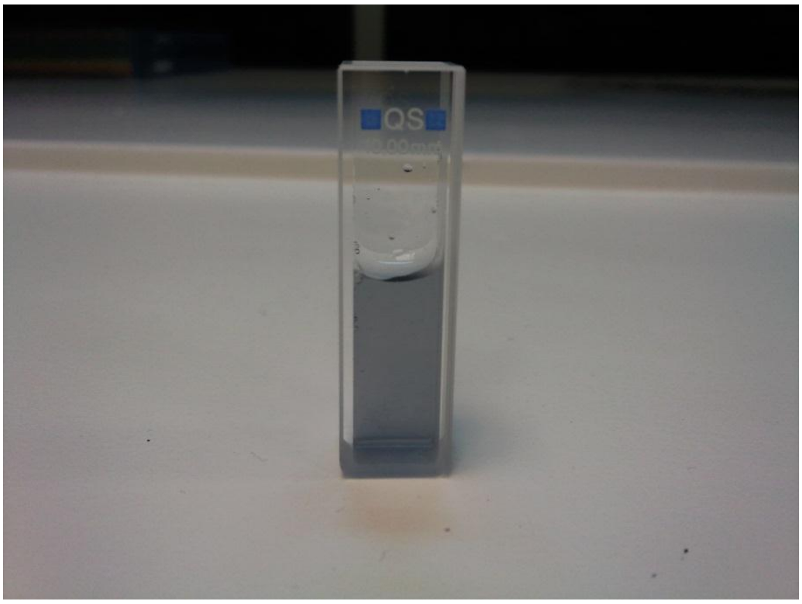


Figure 35: Picture of rod that has LSPR at 690nm

The colors of the different aspect ratio gold Nanorods given in the literature have been produced successfully in our experiment as seen from above pictures. As per the pictures colour varies from blue to the brown.

It is also possible to produce red coloured long aspect ratio gold Nanorods and that is still in the visible range of the electromagnetic spectrum. But there is no distinct colour difference in the rod solutions where the LSPR longitudinal Peak falls above 800nm(High Aspect Ratio) since it is not in the visible range anymore.

4.5 Synthesis of Rods by Seedless Method

It has been proven that the seedless method can also be used to produce gold Nanorods. Jana et al[5] have proved that the gold nano rods can be synthesized by single step procedure in the same vial rather than seed mediated one.

The following table indicates the preparation of the stock solutions that are used for the experiment at this step.

Table 4: Preparation of Stock Solutions for seedless method

Chemicals	Molar Mass	stock solution conc	volume of the sol	amount of the solid
HAuCl4	**339.79**	0.002M	50ml	34mg
CTAB	**364.45**	0.2M	50ml	**3.65g**
NaBH4	**37.8**	0.001M	100ml	3.78mg
Ascorbic Acid	**176.12**	0.084M	10ml	**148mg**
AgNO3	**169.87**	0.0084M	10ml	**14.3mg**

Table 5: Preparation of rods by seedless method

Chemicals	**Stock Concentration**	**Amount added**	**Final Concentration**	
HAuCl4	2mM	5ml	1mM	
CTAB	0.2M	5ml	0.1M	*yellow brownish colour*
	total volume of mixture	***10mL***		

AgNO3	8.4mM	250ul	0.2mM	
Ascorbic Acid	84mM	250ul	2mM	*turns colorless*
NaBH4	1mM	10-100ul	app 10E-6 to 10E-4	rod colors

The seedless rods are prepared in one vial by using above method and the result of this rod has been given in the figure 46. The colour of the solution is observed as pinkish and brownish.

It is worth to note that the concentration of the Gold salt is doubled as compared to the concentration of the gold salt in the previous preparation method.

4.6 Separating of Rods by Centrifugation

Since there is excess amount of CTAB surfactant in the final rod solution the rod solution has to be concentrated and purified from the impurities. This is usually done with centrifugation process.

Ultra centrifugation is used for the separation of the rods from the excess CTAB molecules.

Generally long rods need low rpm (rotation per minute) whereas smaller rods need high rpm ultra-centrifugation.[15]

Figure 36: Micro centrifuge Device

Reproduced from reference[51]

5 Results

The rod formation is a very sensitive process and it is highly dependent to the environmental conditions such as temperature and pH.

It has been found that the reproducibility of the rod formation for the same set of the concentration is quite difficult. But anyhow rods were produced at each trial.

The effect of the addition of $AgNO_3$ has been shown clearly as it is seen in the Figure-18.

The formation of homogeneous CTAB solution is another big hurdle since it doesn't dissolve in the water completely at room temperature for higher concentrations. That's why a mild heating was always necessary for through dissolving.

Rods have generally started to occur within first 10 minutes after the addition of seed particles and this can be observed from the colour change easily.

The amount of the Ascorbic acid is also found to be very important though it is a very mild reducing reagent. It has been seen that when the molar ratio of the ascorbic acid to Auric Acid is less than 1 the rods are not formed and solution generally remains in yellow colour.

During the experimentation it has been found that the Auric acid solution is very sensitive to the light and decomposes after some time when directly exposed to the light. To prevent this the Auric acid solutions have been prepared in amber bottles and covered with aluminum foil and kept away from the light.

The colors of the solutions have been taken as a good indicator of the prepared material. For example: the initial colour of the CTAB + Auric Acid becomes dark yellow but turns brownish after addition of $NaBH_4$

5.1 Data obtained From the Measurements and Its Interpretation

The following table has been created by using the amount of the added $AgNO_3$ against the LSPR Peaks observed.

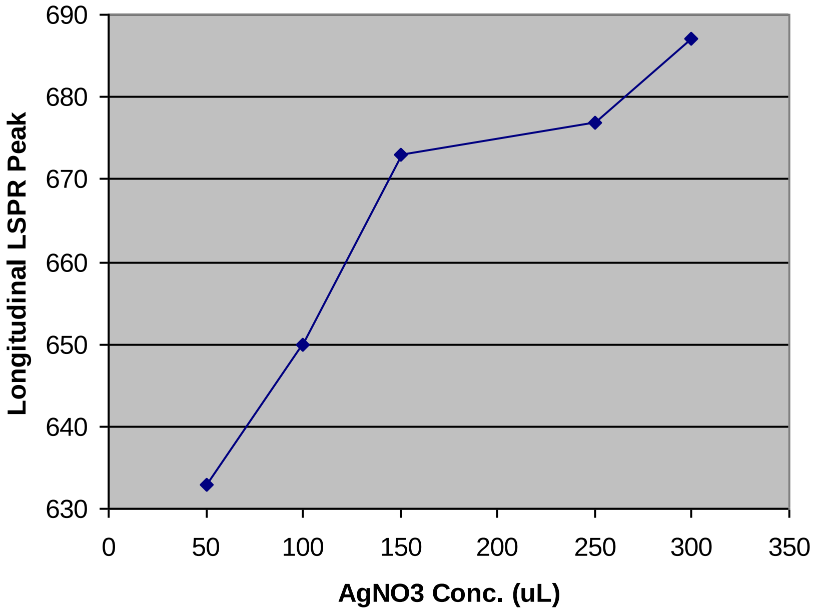


Figure 37: LSPR Peak vs. added AgNO3 concentration

It can be seen from the table above that the Longitudinal LSPR Peak maximum varies with the amount of the added $AgNO_3$. But it loses effect after addition of more than 300uL. [13]

5.2 LSPR Peaks and SEM Images of the samples prepared

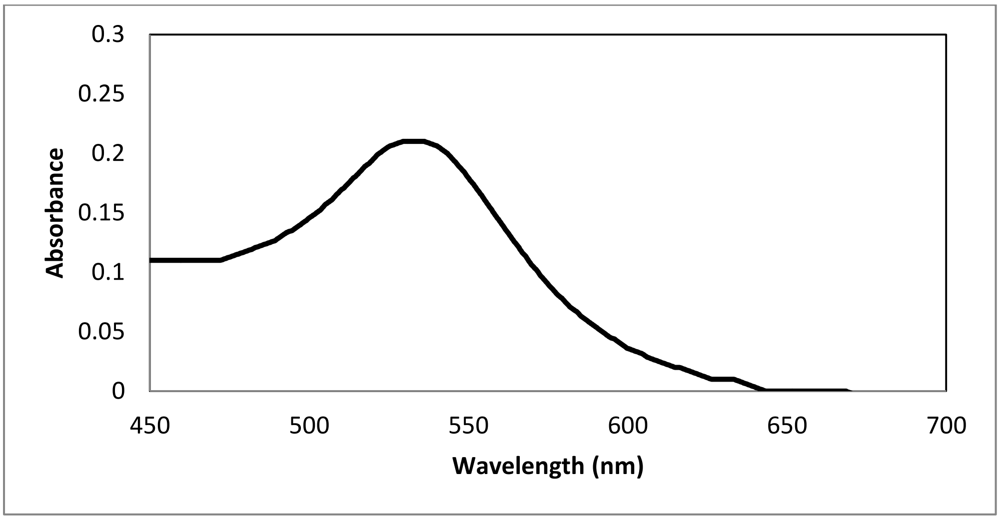


Figure 38: LSPR of Gold Particle prepared on 28/12

The LSPR graph of the particle prepared on 28/12/2011. The absorbance maximum is observed at about 530nm in good agreement with the literature. This single peak seen around 520nm is the characteristics of the gold nanoparticles. This peak has been observed in all the experiment sets as indication of gold particle.

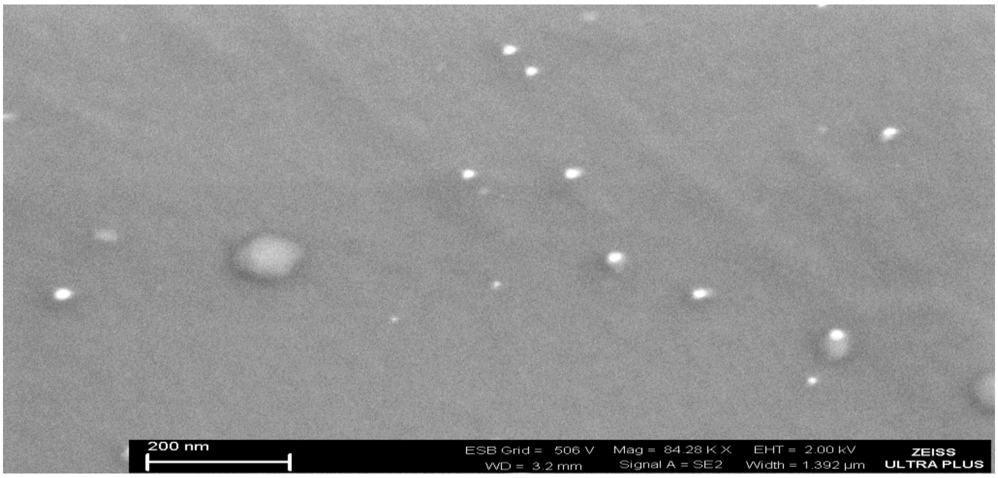


Figure 39: SEM Image of Gold Particle prepared on 28/12

The SEM image of the particle prepared on 28/12/2011.

The bright spots seen on the image are the gold nano particles. The size of these spheres is somewhere between 10 nm to 20 nm as inferred from the image.

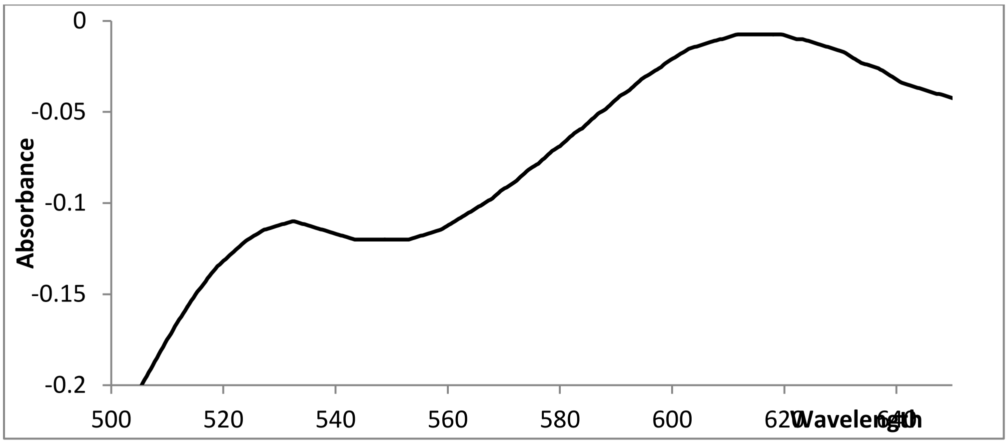


Figure 40: LSPR of Rod-1 prepared on 26/12

R1 26/12. The characteristic double peak has been observed at this sample as the indication of the deviation from isotropy of the particle leading rod shape. First peak is at about 525nm and second peak is observed at about 610nm that stands for the longitudinal Plasmon peak.

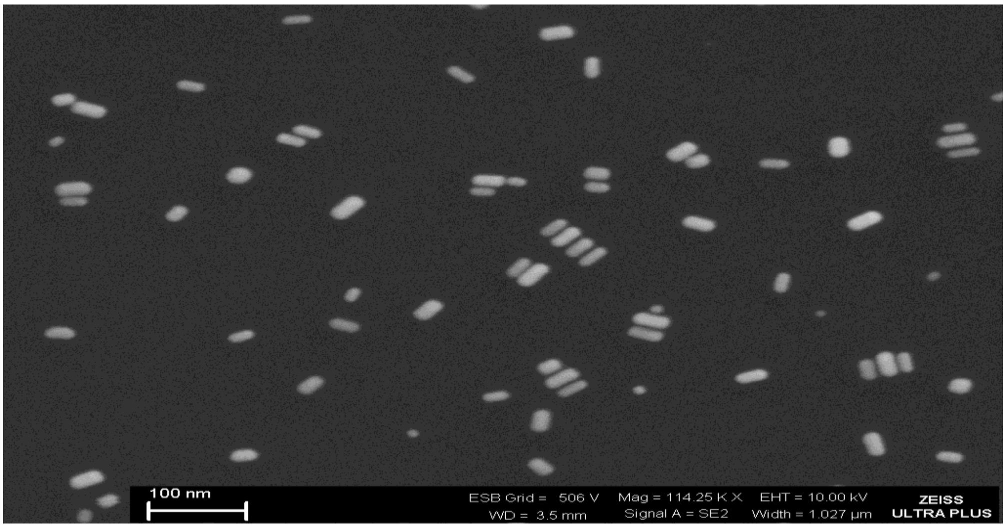


Figure 41: SEM Image of Rod-1 Prepared on 26/12

As it is seen from the figure rods formation is quite acceptable and homogenous. Rods do not stick to each other and there is some distances between rods which is due to stabilizer (CTAB). The colour of this solution is blue and corresponding aspect ratio is about 2.0-2.5 which is in good agreement with the literature values and colors.

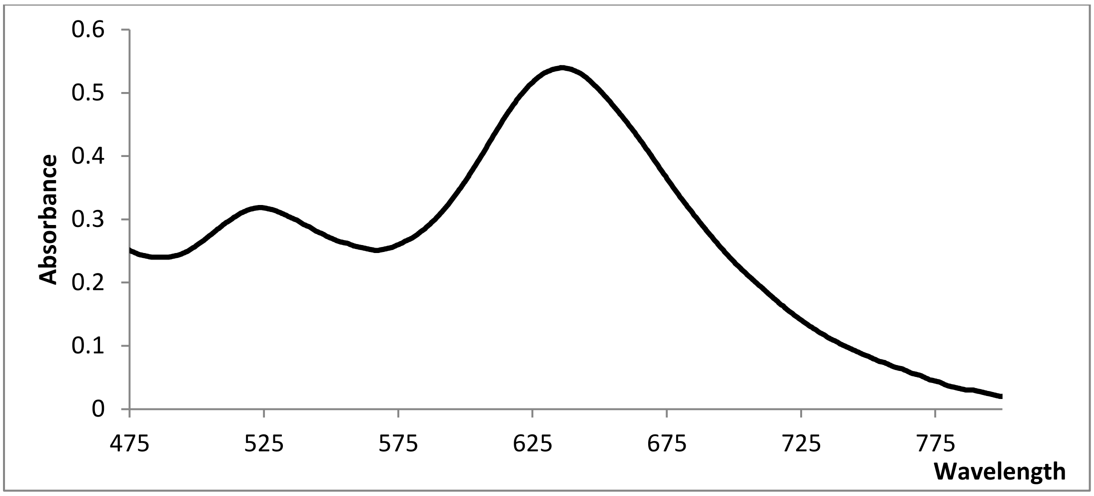


Figure 42: LSPR of Rod-2 prepared on 26/12

R2 26/12. The LSPR graph from the same set of the rods. The longitudinal peak is observed at about 640nm. The red-shift is clearly observed in this graph as the amount of the $AgNO_3$ is increased. The amount of $AgNO_3$ has increased from 50ul to 100ul. All the other substances and concentrations were kept constant.

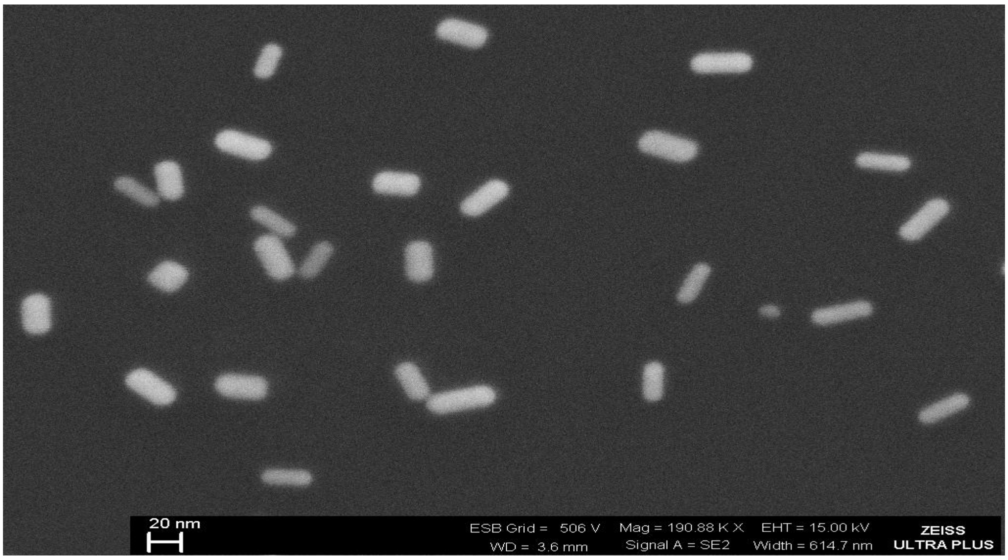


Figure 43: SEM Image of Rod-2 prepared on 26/12

The SEM image clearly shows there are almost only rods in the final solution. The rods length is about 40nm and the width is about 20nm which suggest the aspect ratio about 2. Again it has blue colour as it is expected.

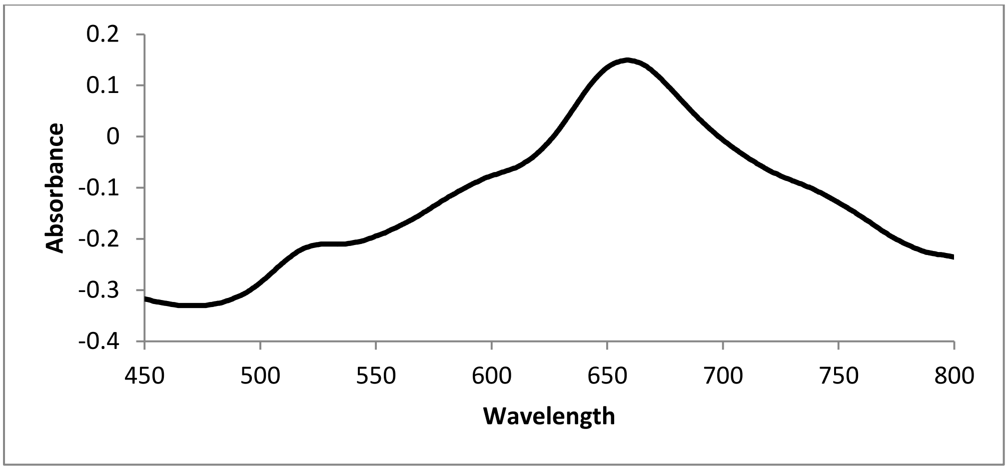


Figure 44: LSPR of the Rod-3 prepared on 26/12

R3 26/12. The graph as the continuation of the set of the rods prepared on 26/12. The Peak here is red shifted (goes towards higher value) even further to 650nm due to increase in the added amount of $AgNO_3$ (150ul is added at this step)

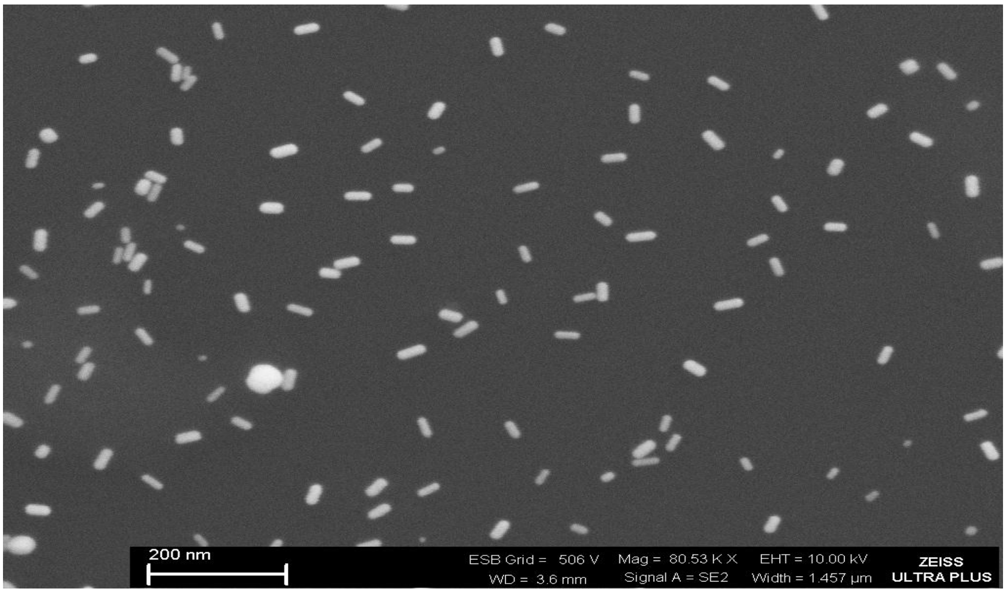


Figure 45: SEM Image of the Rod-3 prepared on 26/12

What we observe from this image is that the aspect ratio of the rods is somewhere between 2.5 to 3.0. This suggests us that the LSPR peak must be around 650nm that has been proven by the above LSPR Graph.

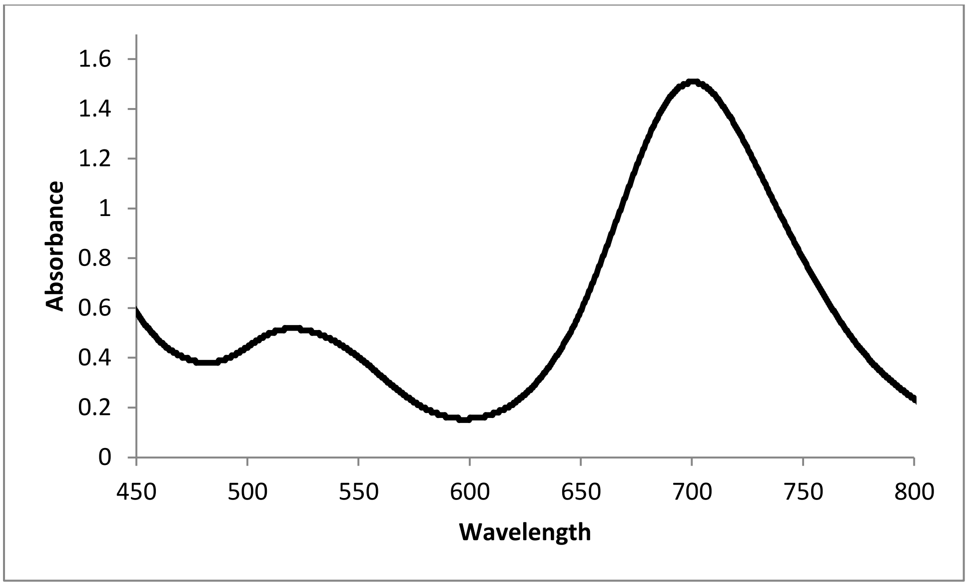


Figure 46: LSPR of the Rod -4 prepared on 22/12

R4 22/12 This set show absorption at about 525nm and at about 700nm. The colour of the solution is the light brown that is good agreement with the literature results.

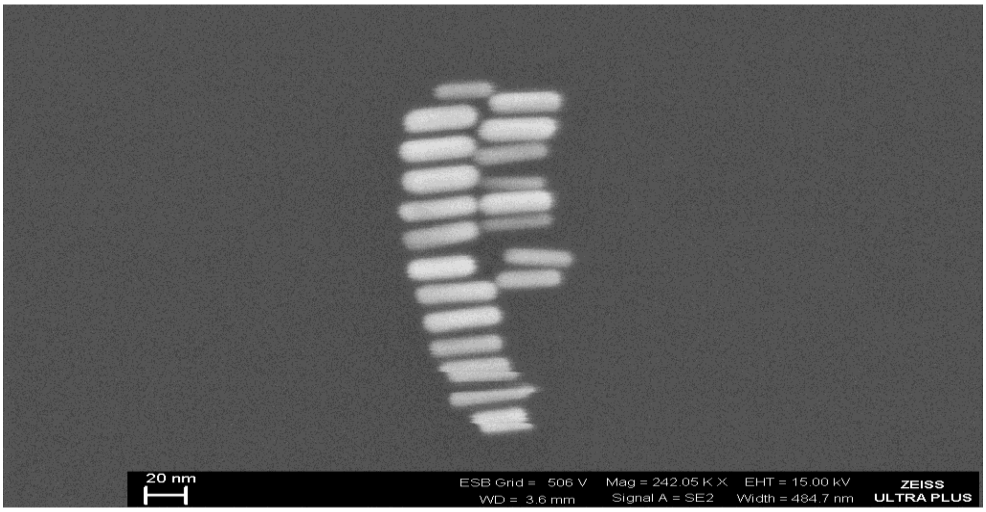


Figure 47: SEM Image of the Rod-4 prepared on 22/12

The approximately calculated aspect ratio of this rod is as follows;
Length is about 40nm and the width is about less than 12nm. So the aspect ratio is 40/15 = 3.4 and the colour of this aspect ratio would be brownish and the longitudinal LSPR Peak is expected around 700nm that is been proven with our results in the above graph.

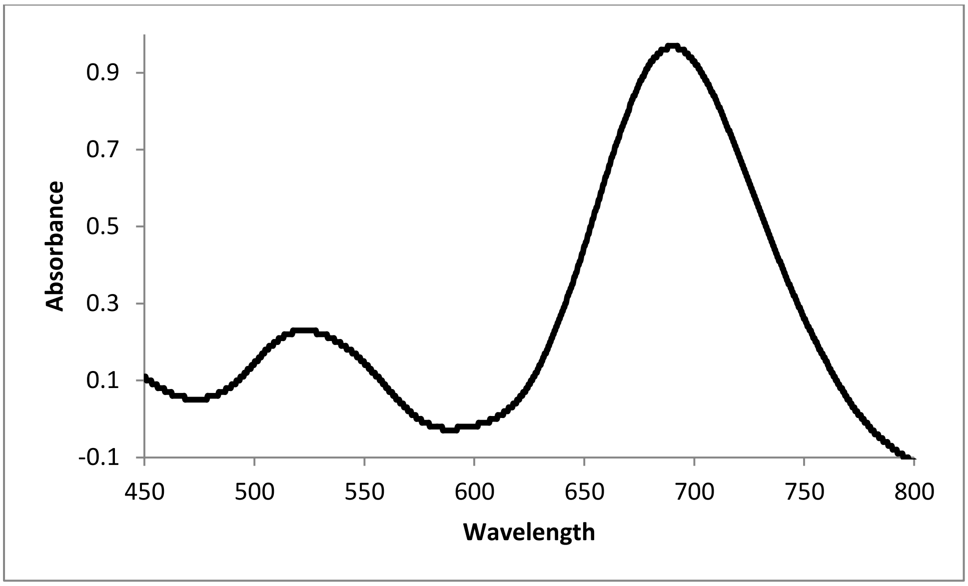


Figure 48: LSPR of the Rod-5 prepared on 22/12

R5 22/12. Similar result is observed for the second trial as well. This is the confirmation of the Rod-4 with the same amount of added $AgNO_3$. The LSPR Peaks are both at about 690nm.

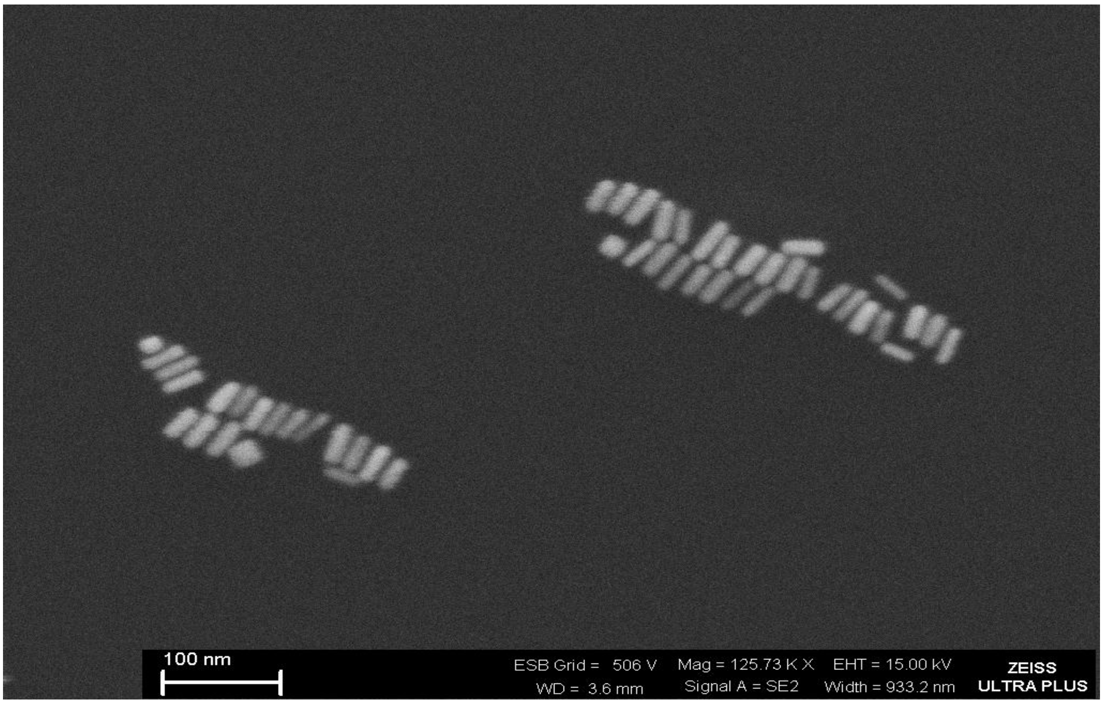


Figure 49: SEM Image of the Rod-5 prepared on 22/12

This image is also confirmation of the aspect ratio of 3-3.5 as calculated for Rod-4.

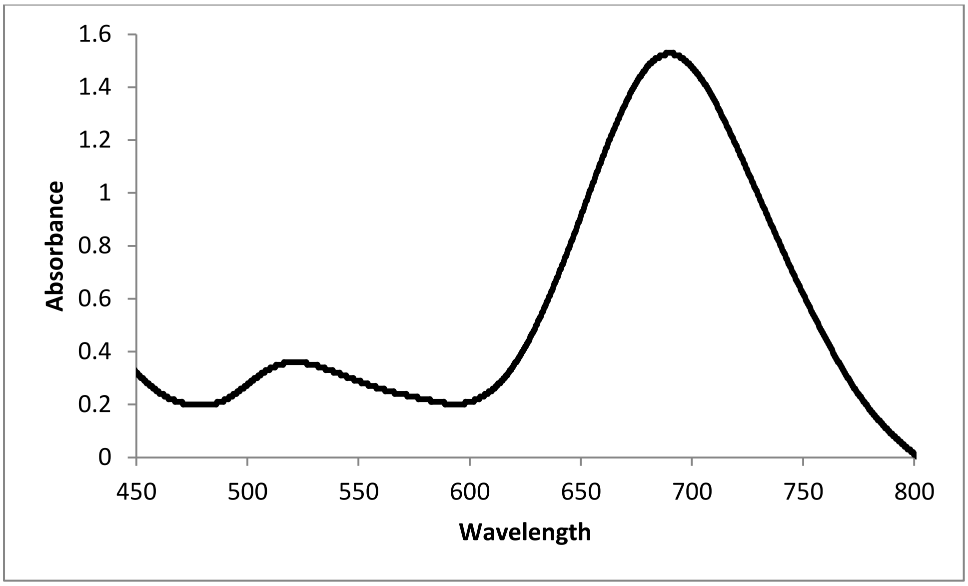


Figure 50: LSPR of the Rod-6 prepared on 20/12

R6 20/12 . Reproduces same results of Rod-5. They are prepared with the same amount of chemicals but on different days.

Figure 51: SEM Image of the Rod-6 prepared on 20/12

This image is also a proof of the aspect ratio about 3-3.5 which is the aspect ratio of the previous rod.

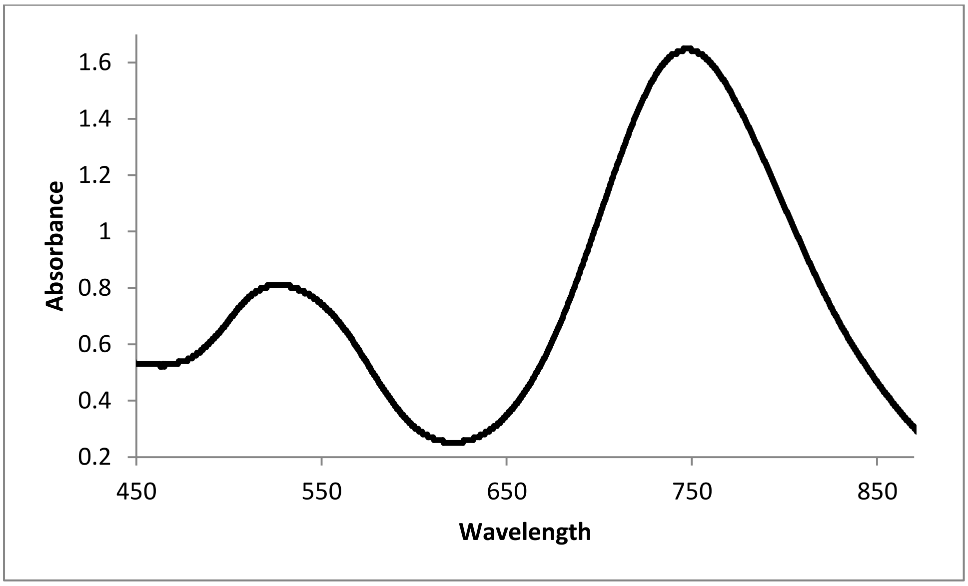


Figure 52: LSPR of the seedless sample prepared on 12/03

Seedless sample, 12/03/2012. This graph is observed for the sample that has been prepared with seedless method. It proves that the rod formation is not only confined to the seed mediated method.

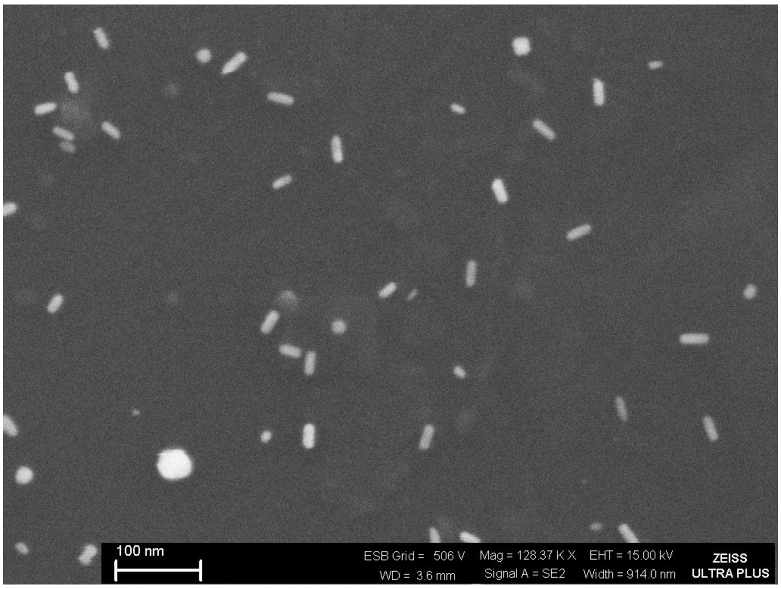


Figure 53: SEM Image of the Seedless sample

The image is somehow not as clear as it is the case for seed mediated rod image. There are some spherical and uneven particles. The colour of the seedless solution was somehow blurry brownish.

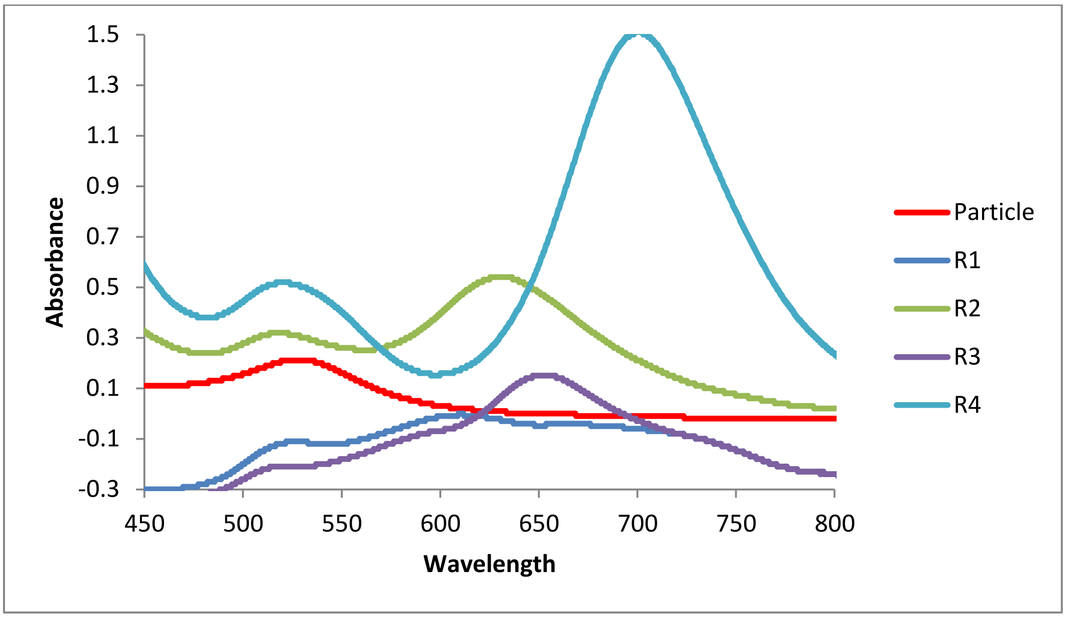


Figure 54: LSPR All Red Shift

This graph is the combination of all four rods with the particle LSPR Peaks versus absorbance. It can be seen that all first absorbance are around 530nm that stands for the transverse dimension of the rods. It is also worth to note that the LSPR Peak of the particle is also at the same value of 530nm.

Secondly, Values of second LSPR peaks are moving towards higher value starting from 620nm for the R1(dark blue) to 700nm for the R4(light blue). This move is also named as red-shift since values are approaching to the red colour wavelength.

5.3 Some additional SEM Images of Rods

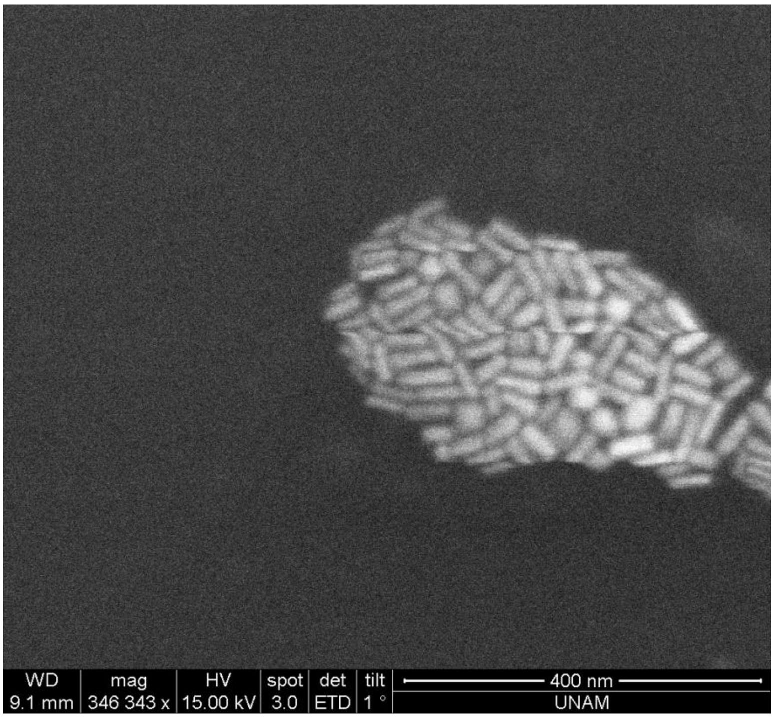


Figure 55: SEM Image of the rods taken from UNAM.

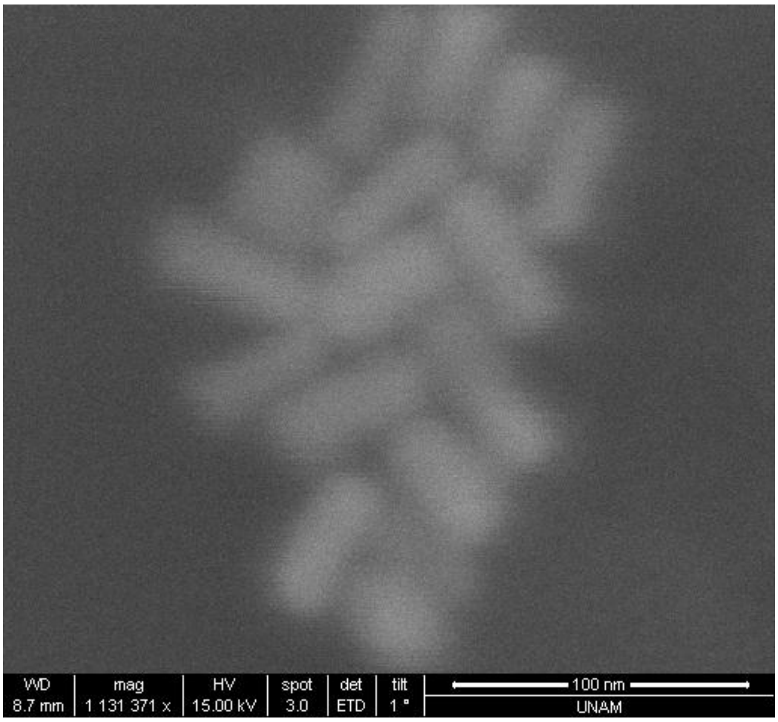


Figure 56: SEM Image of rods from UNAM at 1131371 magnification

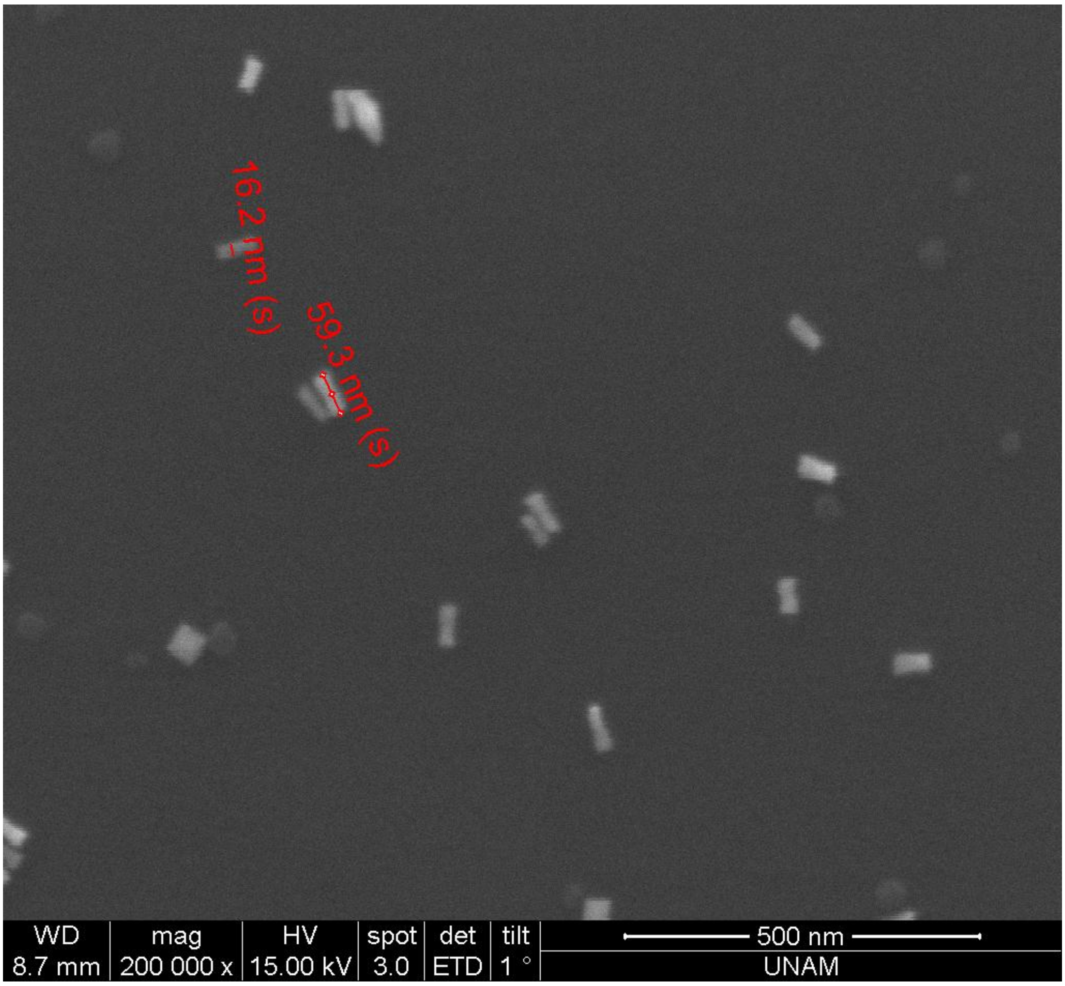


Figure 57: SEM Image of rod from UNAM with dimensions.

SEM of a sample prepared on 26/12 taken at UNAM, showing the dimensions of the rod.

$$\mathbf{AR = 59.3nm / 16.2nm = 3.7} \tag{5-1}$$

6 Conclusion

It has been found that gold nanoparticles and gold Nanorods can be prepared by seed mediated and seedless methods. During the preparation the temperature of the environment and the concentration of the used substances are found to be very sensitive parameters for the production of the Nanorods.

First of all it is been found that when the mole ratio of ascorbic acid to Auric Acid is less than 1 rods are not produced and the solution remains yellow in colour instead of turning brownish.

It is clearly seen that the seed mediated method has many advantages over seedless method. It produces better results. In Seedless method produced rods are poly dispersed and there are many other shapes other than rods.

The LSPR data have proven that gold nanoparticles have absorption at around 520-530nm which shows that particle is spherical meanwhile Nanorods have two characteristic peaks out of which one is about 520-530nm that is for the transverse dimension of the rod and the other one is in a range from 600-800nm stands for the longitudinal dimension of the rod.

A red-shift has been observed in the LSPR Peak of the rods due to increasing aspect ratio. Thus, a solid correlation between the aspect ratio of the rod and the LSPR Peak has been confirmed.

Meanwhile it is also been confirmed that changing the amount of AgNO3 effects the aspect ratio hence it effects the LSPR Peak as well.
But this effect has limitation as such; when the amount of Silver Nitrate is more than 300ul a deviation is observed in the LSPR Peaks suggesting that the aspect ratio increases no more as in good agreement with the work by El Sayed et al.[13]

Though the preparation of gold nanoparticles and rods are found to be easy it has been found that it has many hurdles due to very high sensitivity of the process to the environmental conditions such as temperature.

The SEM Images taken have confirmed the presence of highly mono-dispersed gold Nanorods. The approximately calculated aspect ratios and the taken LSPR Peaks are in good agreement with the literature.

The SEM images have also shown that the obtained nanoparticles are mostly rods not in the other shapes which is attributed to the usage of CTAB instead of Citrate as capping agent as indicated in the literature.

7 Future Prospects

The Gold Nanorods have found many applications in the field of bio-medicine because of its size can be tuned to the dimensions needed. Its interaction with the Near Infra-red light and its manipulation has become an important tool.

The CTAB that is used as the stabilizer have high cyto-toxicity. That's why it needs to be replaced by a less toxic stabilizer for in vivo applications. This research work can be extended to the in vivo application after the exchange of CTAB with a proper stabilizer mainly polyethylene glycol and the lipids.

In vivo application of the Gold Nanorods can vary from the drug delivery to the tumor therapy. Especially, the cancer cell targeting and thermal therapy have drawn huge interest due to easy application and bio-compatibility of the gold rods.

Besides, the electronics applications of the rods are also been investigated.[52]

One very promising field that can utilize the gold Nanorods is the field of data storage. The tunable character of the gold rods can be used to store the data thus increasing storage capacity till 1TB in the commercial CDs / DVDs.[53]

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EXPERIENCE

2010-present	Biochemistry Lecturer, Faculty of Dentistry Ishik University/Erbil
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2004-2006:	Teacher as well as Deputy Director(Founder), Learnium International School, Mumbai

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Foreign languages: English: Excellent speaking, writing, reading skills.

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2005	Participated in the How to teach not to tell by Prof Elenour Duckworth, Harvard University Faculty Workshop for 3 days, Mumbai/India
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