

**INDIAN INSTITUTE OF TECHNOLOGY ROORKEE**

**NPTEL**

**NPTEL ONLINE CERTIFICATION COURSE**

**Biomedical Nanotechnology**

**Lec-03**

**Synthesis of Nanomaterials by Physical and Chemical Methods**

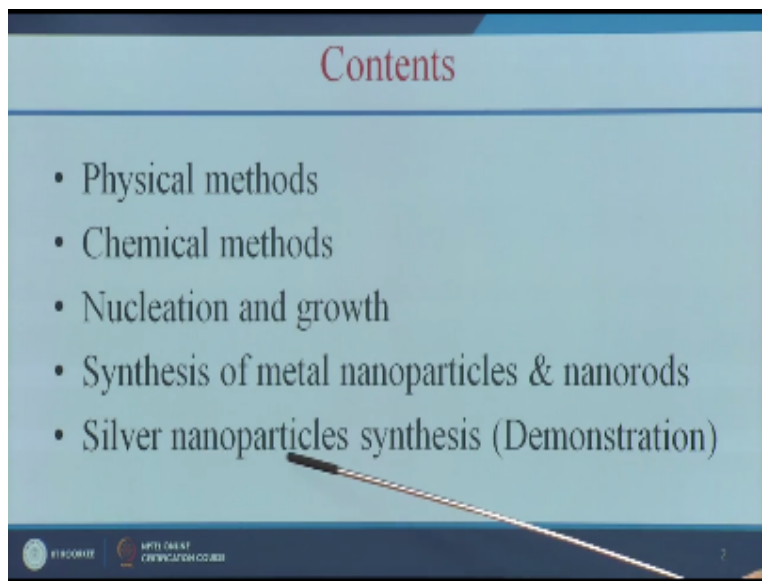
**Dr. P. Gopinath**

**Department of Biotechnology**

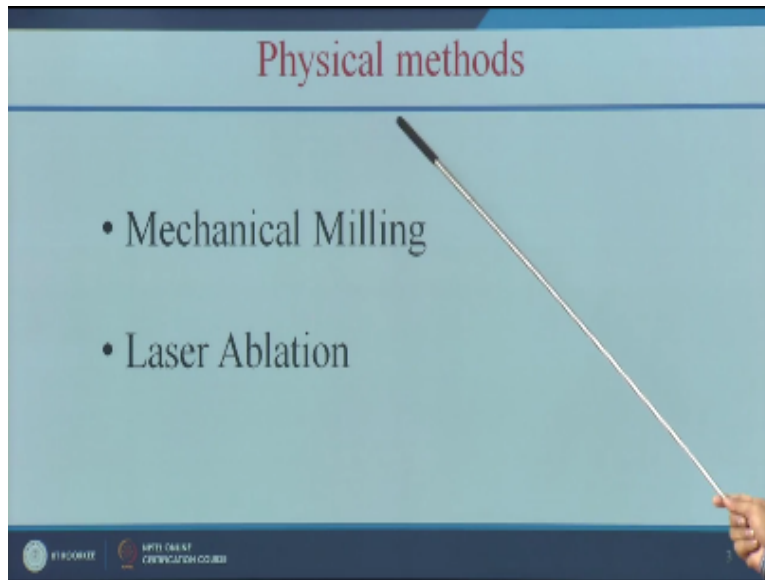
**Indian Institute of technology Roorkee**

Hello everyone today we are going to see the third lecture of this course, the third lecture is on synthesis of nanomaterials by physical and chemical methods.

(Refer Slide Time: 00:33)



So in this lecture we are going to synthesize nanomaterials by physical methods and chemical methods. And we are also going to learn what is nucleation and growth, and how to synthesize metal nanoparticles and metal nanorods. And we are also going to see a small simple experiment to understand how we can synthesize silver nanoparticles in the lab with the available chemicals. (Refer Slide Time: 00:53)

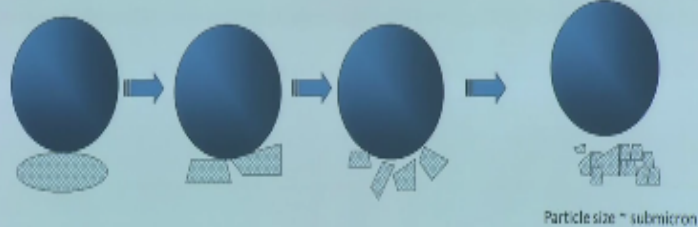


So let us see physical methods, under the physical methods there are several types are available, but in this lecture we are going to mainly focus on mechanical milling and laser ablation.

(Refer Slide Time: 01:04)

## Mechanical Milling

- Nanoparticles from mechanical attrition are produced by a “top-down” process
- Nanoparticles formed in a mechanical device, generically referred to as a “mill,” in which energy is imparted to a coarse-grained material to effect a reduction in particle size.



The diagram illustrates the mechanical milling process in four stages. It starts with a large blue sphere representing a bulk material. In the second stage, the sphere is shown with a smaller, textured area on its surface, indicating the beginning of surface fracture. In the third stage, the sphere is shown with several small, angular particles being released from its surface. In the final stage, the sphere is shown with a large number of very small, submicron-sized particles being released. The text 'Particle size ~ submicron' is located at the bottom right of the diagram.

Particle size ~ submicron


BY COURTESY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY

So we will first see what is mechanical milling. So it is a top-down process you know what is top-down process it means you are making from bulk to nanomaterials and here the nanoparticles formed in a mechanical device is generally referred to as a mill. So here we are going to use the metallic ball, so that is going to break your bulk material into nano-size particle.

(Refer Slide Time: 01:29)

## Principles of milling

- The fundamental principle of size reduction in mechanical attrition devices lies in the energy imparted to the sample during impacts between the milling media.
- This model represents the moment of collision, during which particles are trapped between two colliding balls within a space occupied by mass of powder particles.



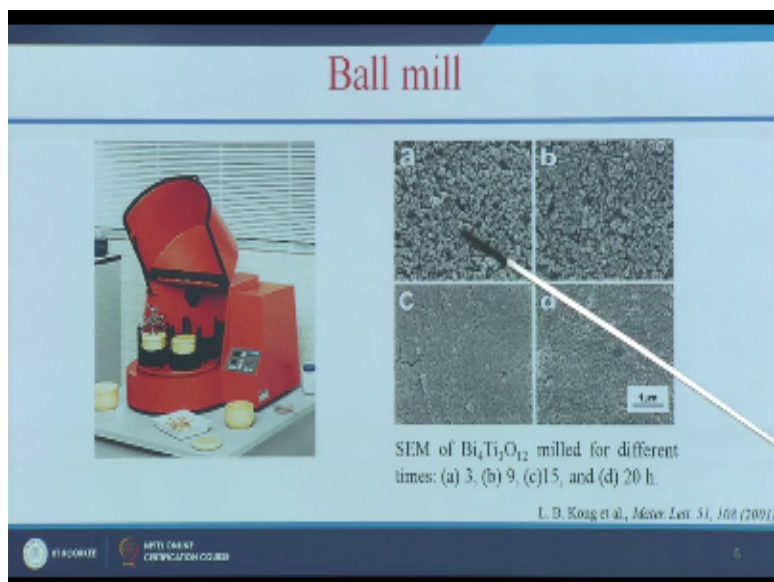
The diagram consists of two parts. On the left, a cross-sectional view of a mill shows two balls (milling media) in contact. Powder particles are shown being trapped in the space between the balls. On the right, a top-down view of a mill drum shows several balls and powder particles. A pencil is visible at the bottom right of the slide.

BYJU'S  
MPTI CAREER  
COUNSELLING

Let us see the principle of milling, so the fundamental principle of size reduction in a mechanical device is the energy imparted to the sample during impacts between the milling media. So this model represents the moment of collision, here you can see here the particles are trapped between the two colliding balls, within that space occupied by the mass of powder particles. So this animation will tell you how the mechanical milling works.

Now here you can see here the metallic balls are rotating, so the metallic drum is rotating and the metallic balls are falling on the powder, and it is going to break the micro sized powder into nano size particles.

(Refer Slide Time: 02:06)



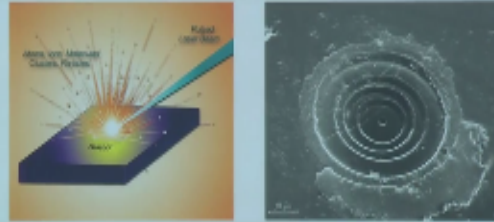
So this is the mechanical milling or ball milling equipments, we can also call it like a ball milling, because we are using metallic balls. And this is a electron microscope picture, so as I told you earlier for seeing these nanoparticles you need a electron microscope. So this is the scanning electron microscope picture, you can see here figure A is after 3 hour of milling, and figure B is after 9 hour of milling, and C is 15 hour and D is 20 hour.

So we can see here with respect to time the particles size is going down, and whenever you take the picture you have to insert the scale bag, so the scale bag is very important which will be useful for calculating the size of the particles.

(Refer Slide Time: 02:49)

# Laser ablation

*Light Amplification by Stimulated Emission of Radiation (LASER)*



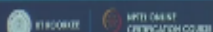
- Using a laser to vaporize material.

So let us see the next method that is, laser ablation. Here you will be using the laser light to vaporize your material.

(Refer Slide Time: 02:56)

## Laser Ablation

- Nanoparticles (NPs) by laser ablation, which involves the generation of NPs by laser ablating a solid target that lies in a gaseous or a liquid environment and collection of the NPs in the form of nanopowder or a colloidal solution.
- It is an easy, fast and straightforward method for NPs synthesis/generation as compared to other methods. It does not require long reaction times or multi-step chemical synthetic procedures.
- It does not require the use of toxic/hazardous chemical precursors for nanomaterial synthesis and thus is an **environmentally friendly** (“green”) and laboratory safe method.



And the nanoparticles by laser ablation which involves the generation of nanoparticles by a laser ablating of a solid target okay. So we can get the nanoparticles in the gaseous or it can be obtained from the liquid environment also. So it depends on the environment, it can get the particles in the nano powdered form, or it can be in a colloidal solution form. And it is one of the easiest and fast method, and here when you compare to the other methods it do not have any long reaction times are it do not have any multiple steps.

And it does not require any toxic chemicals for its synthesis so it is also called as environmentally friendly or green method.

(Refer Slide Time: 03:33)

## Laser Ablation

- In the event that generation occurs in water, the resulting NPs, colloidal solutions are ultrapure. (i.e., they do not contain any counter ions or reaction by-products), and this facilitates the use of these NPs in biological or biochemical *in vivo* applications.
- The produced NPs can easily be functionalized with a ligand of choice, through the subsequent addition of the ligand into the NPs' colloidal solution after its synthesis or by performing the ablation in a suitable solvent.

So in this method the resulting nanoparticles which we are obtaining in the colloidal solutions are ultra pure. So these particles do not contain any counter ions or any reaction by products, so we can use that particle as such for the biological applications. And again we can also add ligand to these particles, we can add the ligand after the synthesis process or we can add the ligand in the suitable solvent itself, so it can be coated on the surface of the nanoparticles.

(Refer Slide Time: 04:03)



## Synthesis of NPs by laser ablation method

- To synthesize Ag (Cu) NPs by LA, a high purity silver (copper) slice is placed on the bottom of glass vessel containing 20 mL of distilled water.
- It is irradiated with focused output of 1064 nm of pulsed Nd:YAG laser (Spectra Physics Inc. USA) operating at fixed energy for 30 minutes.
- This results a yellow color in Ag (light green in copper) colloidal solution.

How to synthesis this nanoparticles by laser ablation, if you want to synthesis silver nanoparticles by laser ablation you need a high purity silver slice. And if you want to make the copper nanoparticles you need a high purity copper slice at the bottom of the glass vessel containing 20ml of water. And if you apply the laser light like 1064 nanometer pulsed Nd:YAG laser and operating at fixed energy of 30 minutes.

So this will result in yellow color in case of silver nanoparticles and it will appear light green in the case of copper nanoparticles.

(Refer Slide Time: 04:39)

## Experimental configurations and equipment

### Generation in Liquids

Synthesis of NPs by laser ablation in liquids the simplest experimental configuration commonly used by many groups around the world is shown in figure .

The target is placed at the bottom of a beaker or a petri dish, which is filled with the liquid and fixed onto an XYZ translational stage. The laser beam irradiates the target vertically.



*Critical Reviews in Solid State and Materials Science, 53: 103–124, 2010*

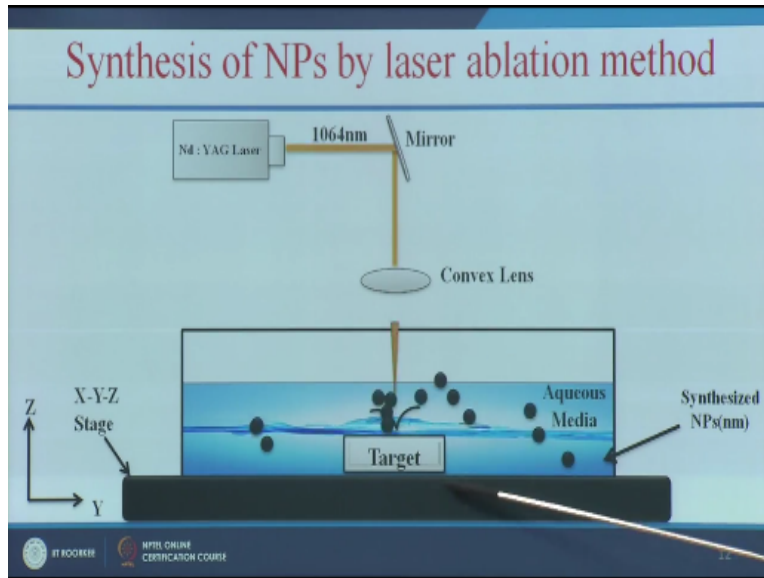


UPTU  
UNIVERSITY OF PETROLEUM & TECHNOLOGY  
UPPER MERUTTI  
CHANDIGARH-150012

11

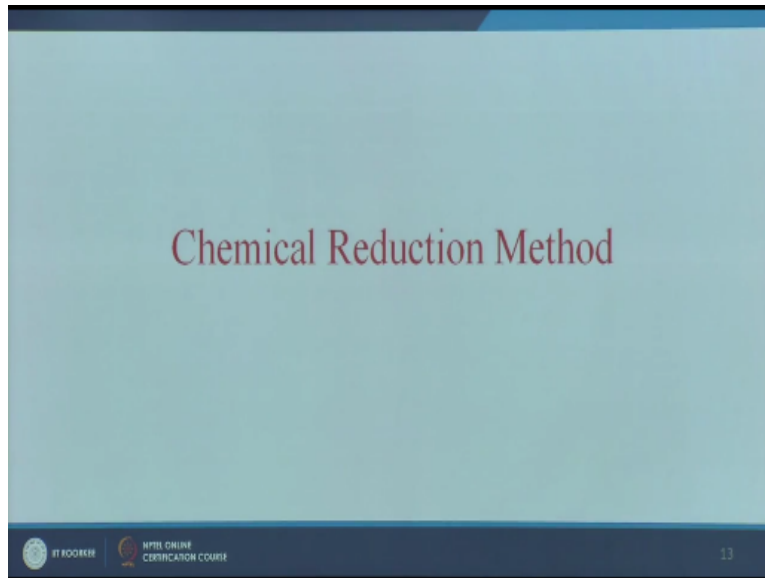
So this is the experimental setup of laser ablation you can see here so the synthesis of nanoparticles by laser ablation liquids it is one of the simplest experimental configuration. And here we are going to keep your metal slice, if you make the silver nanoparticles we are going to give the silver slice, and if you want to make the copper you can keep the copper slice in that here. And when you apply the laser light it will vaporize the material and the nanoparticles can be obtained in the colloidal solution form and here we can use that X Y and Z stage to move the target and you can utilize the complete material for making the nano practices.

(Refer Slide Time: 05:18)



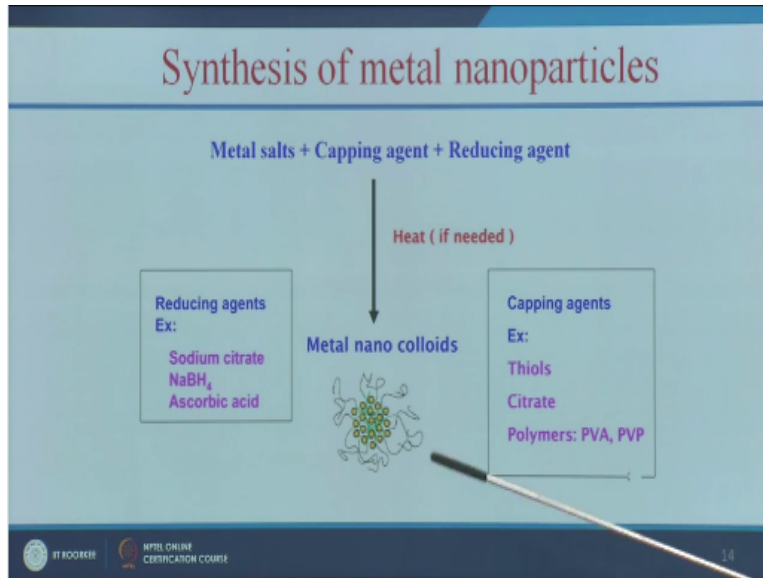
So this summation will give a clear idea how the laser ablation works can see here this YAG laser is applied to the metal target for example if you want to make the silver nano particle you will be keeping this silver metal here and if you want to make the copper nano particle you will be keeping the copper metal here when you apply this laser light it will vaporize the metal and this nano particle will be collected in the aqueous media and using this X, Y and Z stage we can move this target to the X, Y and Z direction.

(Refer Slide Time: 05:47)



So you understood how we can make nano particle with physical methods using mechanical as well as laser ablation so now we will see how we can make nano particle by chemical method.

(Refer Slide Time: 05:57)



For synthesizing nano practical by chemical method we need 3 important components first one is metal salt and second one is reducing agent and third is capping agent so these are some of the examples for reducing agent sodium citrate sodium borohydride and ascorbic acid and these are some of the examples of capping agents Thiols Citrate and Polymers like polyvinyl alcohol and PVP okay.

So what happens here is so this reducing agent will reduce your material salt into metal nano particle but this metal nano particles are highly unstable so it will try to join together and form the agglomeration or aggregation so to make the nano practice stable we have to add a capping agent or stabilizing agent that will prevent the aggregation or agglomeration.

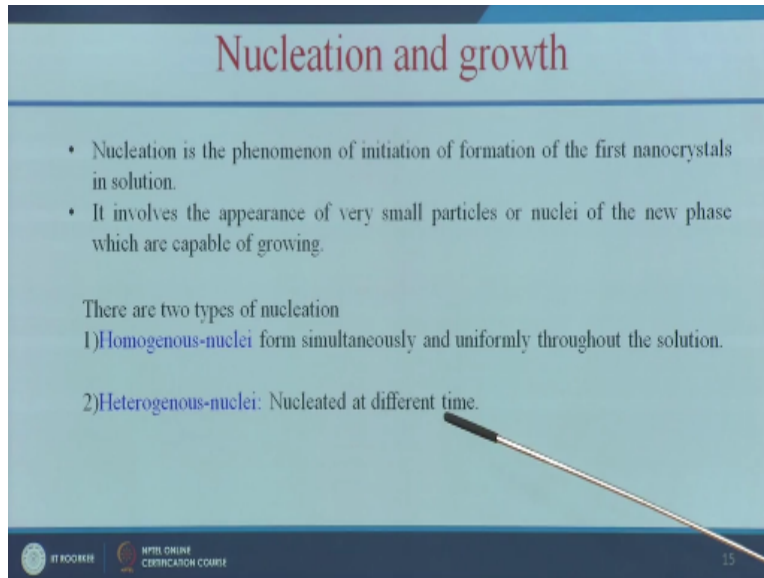
(Refer Slide Time: 06:42)

## Nucleation and growth

- Nucleation is the phenomenon of initiation of formation of the first nanocrystals in solution.
- It involves the appearance of very small particles or nuclei of the new phase which are capable of growing.

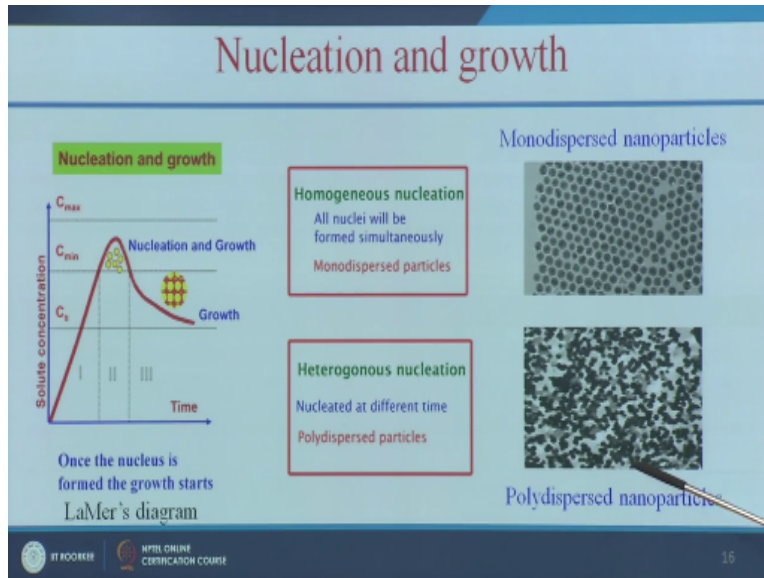
There are two types of nucleation

- 1) Homogenous-nuclei form simultaneously and uniformly throughout the solution.
- 2) Heterogenous-nuclei: Nucleated at different time.



So synthesis of any nano materials involves two important step one is nucleation and other growth, so what is nucleation so nucleation is phenomena of imitation of formation first nano crystals in the solution. So it involves the appearance of very small particles or nuclei of the new phase which are capable of growing so for bio how nucleus is important similarly for nano particle this nuclei is very important there are two type of nucleation first one is homogenous nuclei it form simultaneously uniformly throughout the solution and next one is heterogeneous nuclei so it nucleated at different time point.

(Refer Slide Time: 07:21)

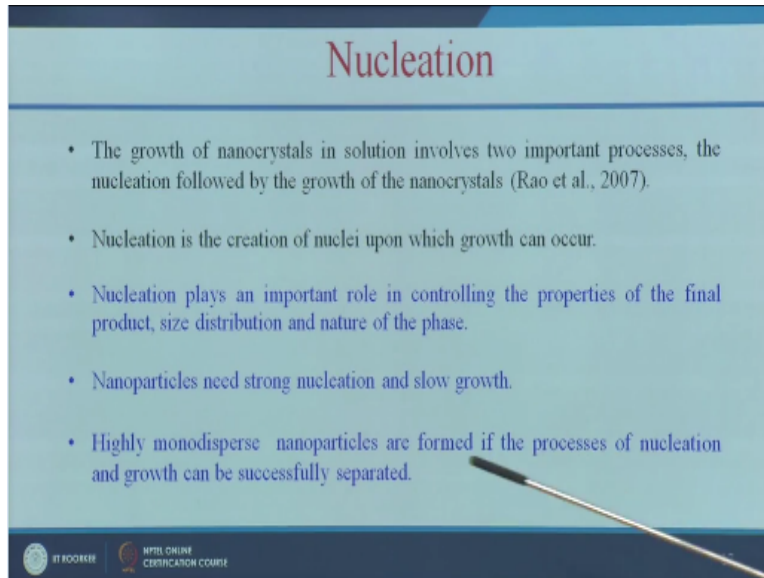


Let us see here this picture is LaMer's diagram adverse time versus solute concentration so once the nucleus is formed then the growth will start so if the nucleation is homogeneous nucleation that means all the nuclei forms simultaneously you will get mono dispersed particles mono dispersed means uniform size particle and if the nucleolus is heterogenous nucleated at different time that is means is poly dispersed practice that means it do not get the uniform size particles so when you see that nano particles under transmission electron microscope you can see here uniform size particles that is called as mono dispersed particles and it is un uniform size that is poly dispersed nano particles.

(Refer Slide Time: 08:03)

## Nucleation

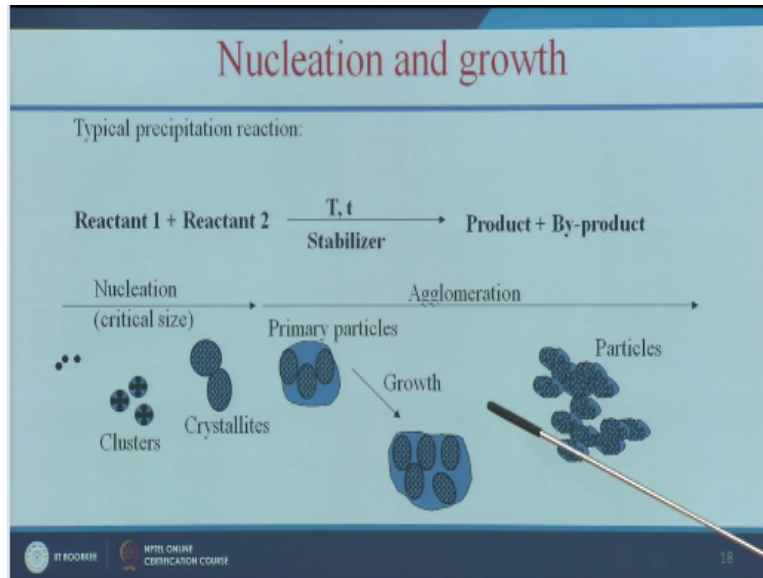
- The growth of nanocrystals in solution involves two important processes, the nucleation followed by the growth of the nanocrystals (Rao et al., 2007).
- Nucleation is the creation of nuclei upon which growth can occur.
- Nucleation plays an important role in controlling the properties of the final product, size distribution and nature of the phase.
- Nanoparticles need strong nucleation and slow growth.
- Highly monodisperse nanoparticles are formed if the processes of nucleation and growth can be successfully separated.



So this nucleation play a very important role in controlling the properties of final product like size distribution as well as the nature of the phase. For making as very small size nano particles you need a strong nucleation and slow growth, so you can get a highly uniformed size particles if the process of nucleation and growth can be successfully separated.

(Refer Slide Time: 08:26)





So this is the typical precipitation reaction so here we are going to use the metal slat and reducing agent so this reducing is going to reduce the metal slat into metal atoms this metal atoms combine and form the clusters this clusters come and form the crystal size so this crystallite will combine and form the primary particles this is the nucleation step and this is the growth step so this primary particles combine and start growing so we have to stop the growth otherwise what happens this all the particles combine and grow like a very big size particle that is agglomerated practice which is not useful we had a small particles for our applications.

(Refer Slide Time: 09:00)

## Aspects of nanoparticle growth in solution

### Arrested precipitation

- Precipitation under starving conditions: a large number of nucleation centers are formed by vigorous mixing of the reactant solutions.
- If concentration growth is kept small, nuclei growth is stopped due to lack of material.

*Particles had to be protected from Oswald Ripening by stabilizers*

### Oswald Ripening

The growth mechanism where small particles dissolve, and are consumed by larger particles. As a result the average nanoparticle size increases with time and the particle concentration decreases. As particles increase in size, solubility decreases.



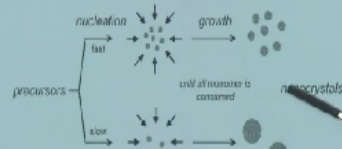
So how we can achieve that by arrested precipitation method what is arrested precipitation here a large number of nucleation centers are formed by vigorous mixing of the reactant solution. So when you make your nano particle we have to mixed vigorously when you mix it vigorously you will have more number of nucleation so this I will show in the last with the a simple experiment how to make this and how to mix it vigorously.

And here if you keep the concentration growth kept small the nuclei growth will be stopped due to lake of material now this called as arrested precipitation and due to stope the particles from the Oswald ripening so how we can stop the Oswald repining by using the stabilizer what is Oswald ripening the growth mechanism where small particles dissolve and are consider by the larger particles what happens is at the result of this average nano particle size get increased with time so and the particle concentration get decreases so if the particle size is increased it decreases at the solubility so this is called Oswald ripening that means it the small particle dissolve and consumed by the larger particles by using this stabilizers agent we can protect it from the also like we can protect the particle from the Oswald ripening.

(Refer Slide Time: 10:18)

## Tuning of the size of nanoparticles

- Tuning of the size of nanoparticles can be achieved by control over nucleation and growth rates, as illustrated in Scheme.
- Fast nucleation provides a high concentration of nuclei, ultimately yielding smaller nanocrystals, whereas slow nucleation provides a low concentration of seeds consuming the same amount of precursors, thus resulting in larger particles.



Schematic representation of the synthesis of CoPt<sub>3</sub> nanocrystals.

*Nanoparticles: From Theory to Application, Edited by Gunter Schmid (2004)*



So how we can tune the size of particle the tuning of the size of the particles can be achieved by controlling the nucleation as well as the growth rate for example fast nucleation will provide high concentration of nuclei, and it will yield at smaller nano crystals but when you use this slow nucleation it provides the low concentration of seeds and again the same concentration of precursors so that results in the larger particles the simple example is we have 5% and we have 50 rupees each will get 10 rupees.

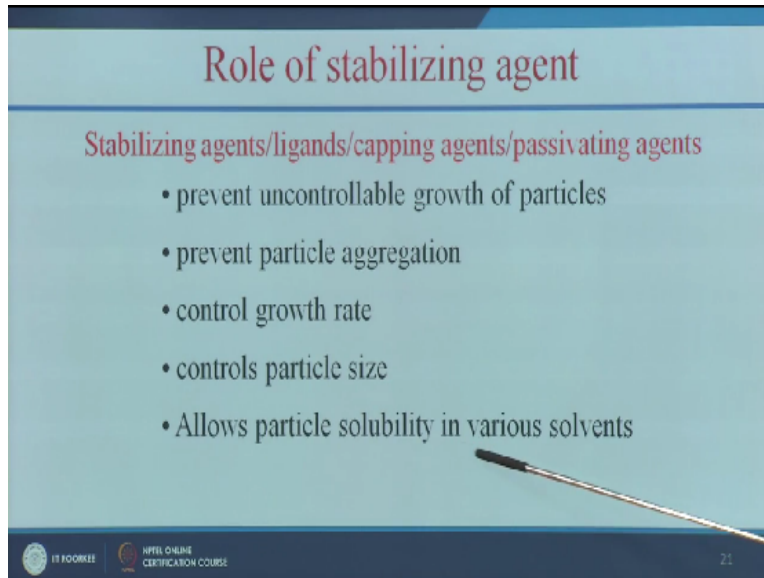
But I and if we have that 2 persons each can share like 24 rupees each, so similarly here you can here if we have the more number of nuclei and the precursors amount is same so what happen this will get a small size particle and doing a slow nucleation you are having only two nucleus but again the precursors is same so everything is consumed and the crystals is size is bigger it is going bigger size.

(Refer Slide Time: 11:13)

## Role of stabilizing agent

Stabilizing agents/ligands/capping agents/passivating agents

- prevent uncontrollable growth of particles
- prevent particle aggregation
- control growth rate
- controls particle size
- Allows particle solubility in various solvents



IIT ROORKEE NPTL ONLINE CERTIFICATION COURSE 21

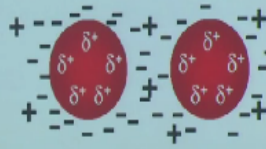
And what is the role of stabilizing agent it is preventing the uncontrollable growth of particles and it will prevent the particle aggregation and it will control the growth rate and also will control the particle size and it will allow the particles solubility in various solvents also.

(Refer Slide Time: 11:29)

## Stabilization of nano clusters against aggregation

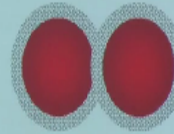
### 1. Electrostatic stabilization

Absorption of ions to the surface. Creates an electrical double layer which results in a Coulombic repulsion force between individual particles



### 2. Steric Stabilization

Surrounding the metal center by layers of material that are sterically bulky.



Examples: polymers, surfactants, etc



IIT ROORKEE



INTEL ONLINE  
CERTIFICATION COURSE

22

Let us see how the stabilization agent works there are two types of stabilization one is electrostatic stabilization the other one is Steric stabilization so what is electrostatic stabilization it means absorption of ions to the surface so it create an electrical double layer so which results in a Coulombic repulsion force between the individual particles so the uniform particles start it will repulse each other so it will give a electrostatic stabilization the next one is Steric stabilization that means the metal is covered by a layer of material.

That was sterically bulky okay so for example polymers and surfactants to be used so that is example for the Steric stabilization.

(Refer Slide Time: 12:13)

Parameters affecting particle growth/ shape/ structure

- Type of capping agent/stabilizers
- Reducing agent
- Concentration of the reactants
- pH value of the solution
- Duration of heat treatment

IT FOOTKEE NPTEL ONLINE CERTIFICATION COURSE 23

So these are the parameters which is going to affect the particle growth shape and structure so what can have capping agent you are going to use what is the reducing agent whether you going to reduce the strong reducing agent or weak reducing agent and what is the concentration of reactants and again the pH value of solution is important and duration of heat treatment in some cases the heat treatment is going to favor the fast nucleation.

(Refer Slide Time: 12:38)

## Metallic nanoparticle synthesis

$$M^+ + \text{Reductant} \longrightarrow \text{Nanoparticle}$$

$$\begin{array}{c}
 M^+ \quad M^+ \\
 M^+ \quad M^+ \\
 M^+
 \end{array}
 + ne^- \longrightarrow \text{M}$$

$M = \text{Au, Pt, Ag, Pd, Co, Fe, etc.}$   
 $\text{Reductant} = \text{Citrate, Borohydride, Alcohols}$

Shipway, A.N., Katz, E., Willner, I. *CHEMPHYSCHM* 2000, 1, 18-52

So this is a typical picture of your metal nanoparticle synthesis can see here if you want to make golden particle you can use the gold metal precursor and you going to reduce using reduce agent so that is going to reduce the metal salt into metal nanoparticle.

(Refer Slide Time: 12:53)

## Synthesis of gold colloids

- Synthesis of a gold colloid in water starting from a solution of **hydrogen tetrachloroaurate** ( $\text{HAuCl}_4$ ) and a solution of **trisodium citrate** ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ).
- Gold colloid with nanoparticles 10-20nm in size.
- In the reaction, the citrate acts as a **weak reducing agent** (reducing  $\text{AuCl}_4^-$  to Au) and as a stabilizer.
- A **layer of citrate anions adsorbs around each nanoparticle** and prevents these from aggregating: the anions electrostatic repulsion keeps the nanoparticle separated.
- In this state, the colloid appears **ruby-red**.



Let us see how we can synthesis gold colloids for synthesis gold colloid in water we have to use this metal precursor hydrogen, tetrachloroaurate and a solution of trisodium citrate it is your reducing agent so here the we can get a gold nanoparticles in the size of 10 to 20nm nanometer and again in this reaction the citrate act like a weak reducing agent and also it act like a stabilizer okay so a layer citrate anions adsorbs around each nanoparticle and it prevent from the aggregating because the citrate ions give the uniform charge to nanoparticles.

By electrostatic repulsion it will be separated out so here the citrate act like a reducing agent as well as it also act like a stabilizing agent so at the finally you will get a ruby-red color when you get the ruby red color you can confirm you got the gold nanoparticle.

(Refer Slide Time: 13:47)



# Synthesis of gold colloids

**Colorful chemistry of Au**

Different sizes of colloidal gold

Band gap depends on particle size

The distinctive colors of colloidal gold and silver are due to a phenomenon known as surface plasmon resonance.

Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed.

INTEL ONLINE CERTIFICATION COURSE
26

So why this metal nanoparticles showing different kind of colors you can see here different size and different shapes showing different kind of colors these are silver and it is why different kind of colors with respect to size and shape and again this is the gold spheres of different size and this gold nano rods and it is also showing different colors. So what is the reason for these colors the reason is the surface Plasmon resonance the metal nano particle will show the surface Plasmon that means the incident light creates oscillation in the conduction electrons on the surface of the nano particles and the electromagnetic radiation is absorbed.

(Refer Slide Time: 14:28)

## Surface plasmon resonance

When a nanoparticle is much smaller than the wave length of light, coherent oscillation of the conduction band electrons induced by interaction with an electromagnetic field. This resonance is called Surface Plasmon Resonance (SPR).

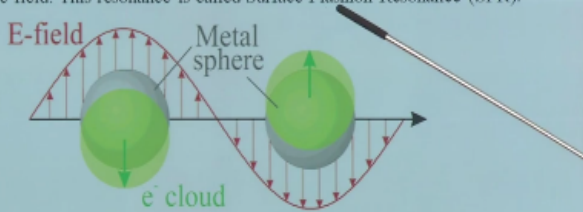
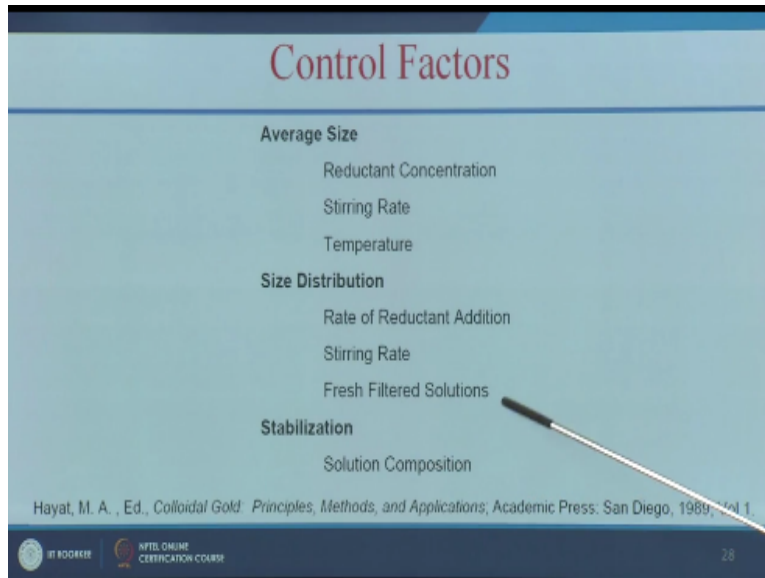


Figure: Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.

BY ROGEREE    NPTEL ONLINE CERTIFICATION COURSE    27

So let us see what is surface Plasmon resonance so when a nano particle is much smaller than the wave length of light, coherent oscillation of the conduction band induced by interaction with an electromagnetic field so this resonance is called surface plasmon resonance.

(Refer Slide Time: 14:46)




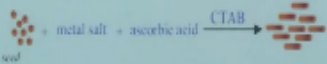
And these are the factors which are going to control the size and the shape of the nano particle. So you can see here the concentration of your reducing agent it is going to control the size of the particles and also the string rate and I again you have to use the fresh solution filter solution will always remained the particles again the stabilizing agent wanted of stabilizing agent you are going to use that is going to decide the size and shape of your Nano particles.

(Refer Slide Time: 15:09)

## Synthesis of Gold nanorods

**• Formation mechanism**  
Seed-mediated growth for gold and silver

$Au \text{ or } Ag \text{ salt} + NaBH_4 \xrightarrow{\text{citrate}}$ 

Seed Formation


Nanorod Growth

- $NaBH_4$  ; Strong reducing agent
- Citrate ; capping agent (inhibit particle growth)
- Ascorbic acid ; Weak reducing agent
- CTAB ; Rod like template

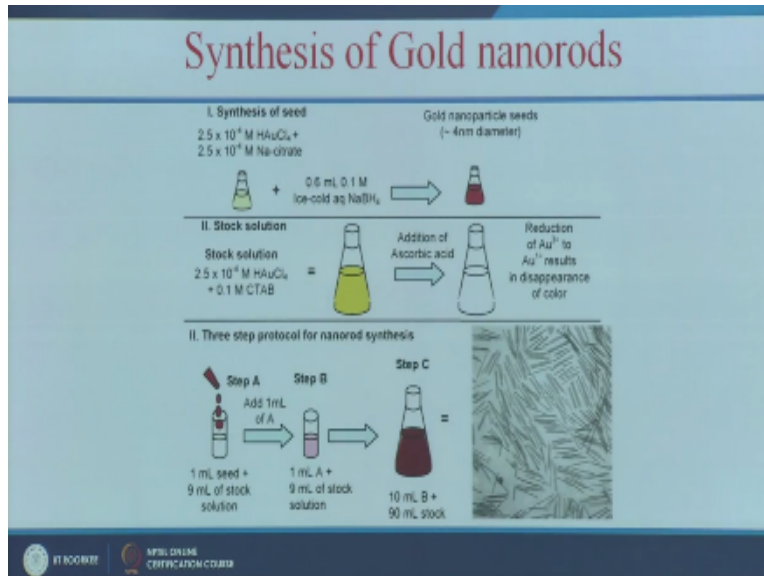
ET 1000078
AFRIL ONLINE CERTIFICATION COURSE
29

So let us see how to synthesize gold, Nano rods, okay. So it is a two step process like you can see here it is a Seed mediator grows for gold and silver here will be using this gold or silver salt if you want to make a silver Nano rods you have to use a silver salt and if you have to use a if you want to make gold Nano rods you have to use a gold as a metal salt and we are going to use the  $NaBH_4$  that is sodium boro hydride.

It is a very good strong reducing agent what happens is, when you use that sodium boro hydride it will reduce its gold into very small size particle and it will get the seed formation okay and here citrate will act like a capping agent, stabilizing agent and it will inhibit the particle growth, so you will get the seed and in next step you will use the seed then you will add the gold or silver salt.

And you will have the weak reducing agent that is ascorbic acid, when you add the weak reducing agent what happens is, here it will favors the growth okay and here you are using a different kind of stabilizer that is CTAB so this CTAB stabilizer it will provide a lot like template so you will get a rod shaped Nano rods you will get in this step okay. So when you use that strong reducing agent you will get the seeds and when you use the weak reducing agent you get the Nano rods okay. And also we have to use the stabilizer this CTAB stabilizer place a major role in formation of Nano rods.

(Refer Slide Time: 16:45)



So this is the synthesis of gold Nano rods so here you can see here in the first step they are going to use that gold solution and sodium citrate and you are going to mix with the sodium borohydride and you will get a Nano particle of four Nano meter, diameter so this is your seed and second step is stock solution here we are going to use the gold solution plus you are adding the CTAB stabilizer and you are going to add the ascorbic acid.

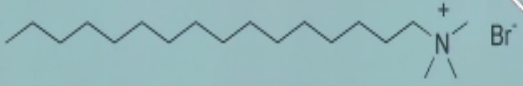
So when you add the ascorbic acid what happens is, it is reducing the gold  $\text{Au}_3^{+2}$ ,  $\text{Au}^{1+}$  it results in the disappearance of color and it is a 3 step protocol for Nano sensors so first step is like you a 1 ml of seed and mix with 9 ml of your stock solution and from here you take 1 ml and mix 9ml of your stock solution and from here you take the 10ml + 90ml of this circulation finally you will get the Nano rods.

(Refer Slide Time: 17:45)

## Synthesis of gold nanorods

Factors related to the growth

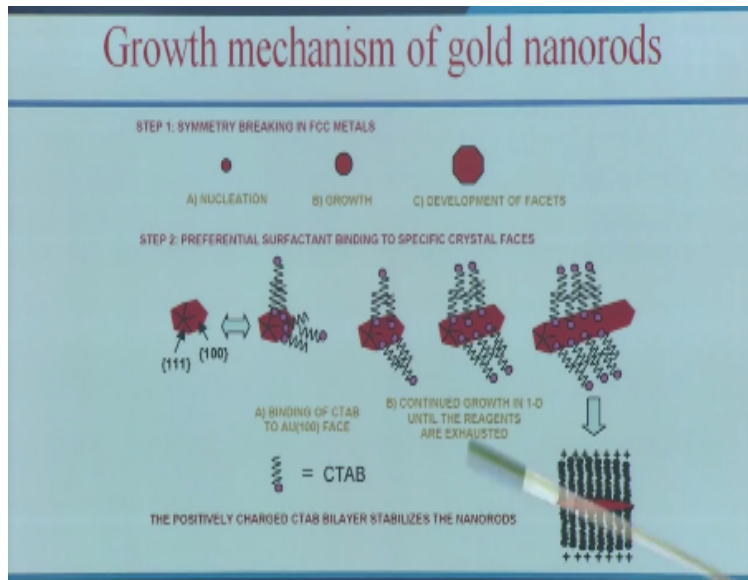
1. Seed size
2. Length of "tails" of CTAB (cetyltrimethylammonium bromide )



The image shows a slide titled "Synthesis of gold nanorods". It lists two factors related to growth: "1. Seed size" and "2. Length of 'tails' of CTAB (cetyltrimethylammonium bromide)". Below the text is a chemical structure of CTAB, which consists of a long hydrocarbon chain (the tail) and a trimethylammonium cation (the head) with a positive charge on the nitrogen atom. A bromide ion (Br<sup>-</sup>) is shown as the counterion. A red arrow points from the text "Length of 'tails'" to the hydrocarbon chain. At the bottom of the slide, there are logos for "ET 600102" and "AFSIL ONLINE CERTIFICATION COURSE" and a page number "11".

So this Nano rods size synthesis depends on the seed size as well as the length of tails that is by the CTAB okay so we have the mode CTAB and other things it is going to play a major role in the Nano rod size and dimension.

(Refer Slide Time: 18:03)



So what is a growth mechanism of gold Nano rods, the first step is nucleation followed by that you will have the growth and followed by that you have the development of phase, so once that faced is form what happens is, this CTAB stabilizer will go and bind to this facer and it will continue to grow in until all the reagents are exist, so this CTAB it is a partially charged by layer and it is a stabilizing Nano rods.

(Refer Slide Time: 18:32)

## Synthesis of gold nanoparticles of different shapes

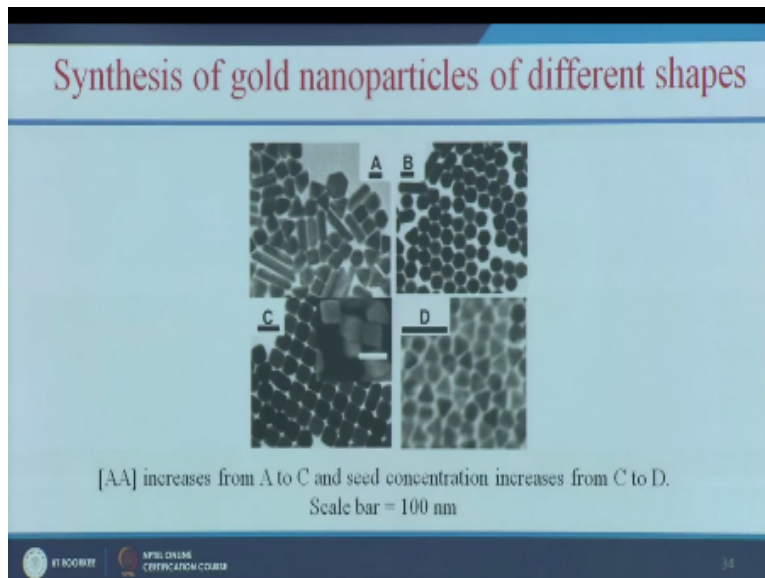
- General idea is the same as the growth of gold nanorods (seed-mediated method)
- Slightly change the conditions when growing nanorods (concentration of different reactants)
- Cubes, hexagon, triangle, tetrapods, branched

T. K. Sau, C. J. Murphy, *J. Am. Chem. Soc.* 2004, 126, 8648-8649

And based on this idea we can make a several size and shape of gold Nano particle only this is you are going to change the concentration of reducing agent and concentration of stabilizing agent by just playing around with this concentration you can get a different kind of shape like cubes, hexagon, triangle and you can have a different kind of shapes.

(Refer Slide Time: 18:53)





So here you can see a simple example, so we are going to use this ascorbic acid and we are going to increasing the concentration of ascorbic acid from  $A \rightarrow C$  so when you increasing the concentration of  $A \rightarrow C$  and we are increasing the seed concentration from  $C \rightarrow D$ , so when you play around this with the ascorbic acid that is reducing agent as well as the seed concentration we will get a different kind of shapes and different kind of size.

(Refer Slide Time: 19:21)

## Synthesis of gold nanoparticles of different shapes

[CTAB]/M	[Au] <sub>seed</sub> /M	[Au <sup>3+</sup> ]/M	[AA]/M	Shape/Profile	Dimension <sup>s</sup>	% Yield
$1.6 \times 10^{-2}$	$1.25 \times 10^{-8}$	$2.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	Cube	66 nm	~ 85
$1.6 \times 10^{-2}$	$1.25 \times 10^{-8}$	$2.0 \times 10^{-4}$	$3.0 \times 10^{-5}$	Hexagon	70 nm	~ 80
$1.6 \times 10^{-2}$	$1.25 \times 10^{-7}$	$2.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	Triangle	35 nm	~ 80
$1.6 \times 10^{-2}$	$1.25 \times 10^{-8}$	$4.0 \times 10^{-4}$	$6.4 \times 10^{-4}$	Cube <sup>s</sup>	90 nm	~ 70
$9.5 \times 10^{-2}$	$1.25 \times 10^{-7}$	$4.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	Tetrapod <sup>s</sup>	30 nm	~ 70
$1.6 \times 10^{-2}$	$1.25 \times 10^{-8}$	$4.0 \times 10^{-4}$	$1.2 \times 10^{-2}$	Star	66 nm	~ 50
$5.0 \times 10^{-2}$	$6.25 \times 10^{-6}$	$5.0 \times 10^{-4}$	$3.0 \times 10^{-5}$	Tetrapod	293 nm	~ 75
$9.5 \times 10^{-2}$	$2.5 \times 10^{-7}$	$4.0 \times 10^{-4}$	$6.4 \times 10^{-4}$	Branched <sup>s</sup>	174 nm	~ 95

So this tabular column will give to a clear idea so if you use this concentration of CTAB and if you use this concentration of AU seed and this concentration of Au<sup>3+</sup> and this concentration of ascorbic acid you will get this kind of different shape so we are going to use this four components and we are going to achieve different kinds of shapes and different size only by changing the concentration of this four components we are achieving different size and different shape.

So if I ask you to select a Nano particle based on size for a catalytic reaction which one you will select, so we will select yes you are right we will select the smallest size so if I ask you to select nano particle from this tabular column for catalytic activities based on the size we have to select the smallest size because the smallest nano particle have highest surface areas to volume issue it will have more catalytic activity.

(Refer Slide Time: 20:20)

## Synthesis and study of silver nanoparticles

The chemical reaction is the sodium borohydride reduction of silver nitrate:

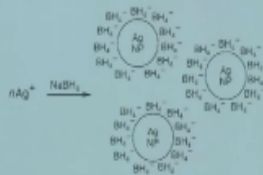
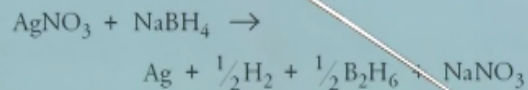
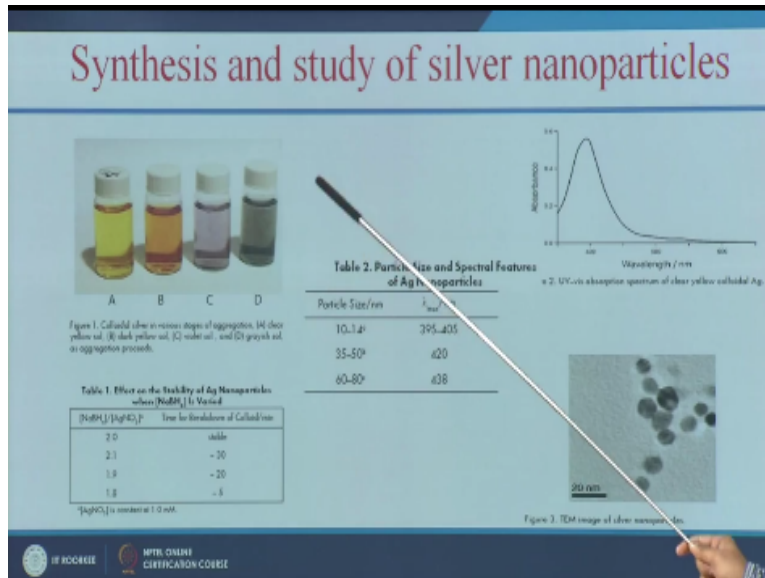


Figure 5. Repulsive forces separate Ag nanoparticles (NP) with adsorbed borohydride.

Journal of Chemical Education • Vol. 84, No. 2, February 20

So let us see how to synthesis silver nano particles okay, so here we can use this silver nitrate  $\text{AgNO}_3$  and your sodium borohydride this is your reducing agent and this reducing agent will act like a also stabilizer can you see here so from  $\text{Ag}^+$  it became  $\text{Ag}^0$  and this borohydride protecting this nano particles from aggregation or agglomeration.

(Refer Slide Time: 20:44)



So in silver nano particle you will get yellow color we can see here these all silver nano particle but these are of different size okay, so you can see here the silver colloids of if you see this is a, if we have a yellow color pale yellow that is like we have a very small size particle and if we have this kind of color that means the particles are aggregated it is not useful for the further applications.

And how do you control and how do you stabilize this nano particle you can see here the ratio between your metal salt and reducing agent is very, very important if the ratio is 2 it is highly stable, if the ratio is 2.1 it is stable for 30 minutes and if the ratio is 1.9 it is stable for only 20 minutes and if the ratio is 1.8 it is stable only for 5 minutes okay. so when you see optimize any synthesis protocol you have to think and you have to optimize, okay so this is very, very important first making a very good stable nano particles.

So when you made the nano particle the first step of your characterization is you will be using this UV visible spectroscopy, I guess most of them know what is UV visible spectroscopy and most of the lab you will be having this UV visible spectroscopy so what you have to do is, you have to transfer this 1ml of solution to a quartz cuvette okay, so you take it to that quartz and you will do the scanning of this solution.

So when you start the scanning from 200 to 800 so you will get the  $\lambda_{max}$  at 400 wave length usually the silver nano particles gives the  $\lambda_{max}$  at 400 nano meter range okay, so if we get this kind of peak you are sure that you got silver nano particle so from the silver nano particle peak

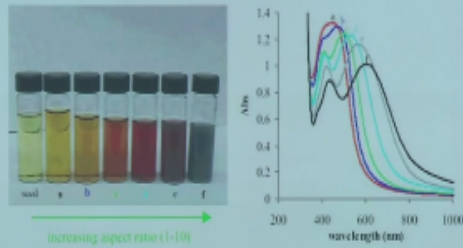
you can approximately calculate the size. For example, if you are getting the  $\lambda$  maths at 395 the particle says approximately 10 to 14 and if we get the peak at 420 the size of the particle is 35 to 50 and if we get the peak at 438 the size of the particle is 60 to 80.

And the next step is you have to take it for the transmission atom microscope you want to see the particle okay, so when you see under this electron microscope you can see the particles size and as I told you earlier when you take any microscope picture we have to include this scale bar. So here you can see this scale bar is 20 nano meter so assume this scale bar is approximately 1cm okay, and when you use this scale bar so when you use this scale bar and it move it to this particle so you can see here this is like 0.5cm.

Though if it is 0.5cm we can calculate it is like 10 nano meter particle, so based on this scale bar we get easily estimate and calculate the particle size. So let us see the nano rod formation so when you use this silver salt and if you make the nano rods what happens is like it will give two peaks.

(Refer Slide Time: 23:49)

## Reduction in solution -Seed mediated growth




Aqueous solution of silver nanoparticles show a beautiful variation in visible color depending on the aspect ratio of the suspended nanoparticles: far left in the photograph, silver nanoparticles 4nm in diameter that are used as seeds in subsequent reactions: a-f) silver nanorods of aspect ratio 1~10.



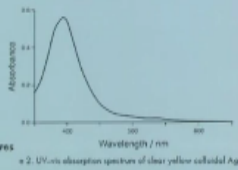
When you see the nano rods under UV visible spectroscopy it will give two peaks and if you see this is red color one is the seed okay, and remaining all are nano rods of different size nano rods so why it is giving two peaks what is the reason.

(Refer Slide Time: 24:05)

# Synthesis and study of silver nanoparticles



**Figure 1.** Colloidal silver in various stages of aggregation. (A) clear yellow sol, (B) dark yellow sol, (C) violet sol, and (D) greyish sol, as aggregation proceeds.



**Figure 2.** UV-vis absorption spectrum of clear yellow colloidal Ag.

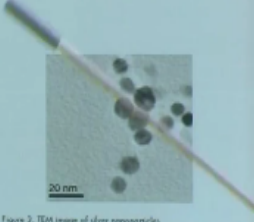
**Table 2. Particle Size and Spectral Features of Ag Nanoparticles**

Particle Size/nm	$\lambda_{max}/nm$
10-15 <sup>a</sup>	395-405
35-50 <sup>b</sup>	420
60-80 <sup>c</sup>	438



**Table 1. Effect on the Stability of Ag Nanoparticles when  $[NaBH_4]$  is Varied**

$[NaBH_4]$ / $[AgNO_3]$ <sup>a</sup>	Time for Breakdown of Colloid/min
2.0	stable
2.1	-30
1.9	-20
1.8	-5

<sup>a</sup> $[AgNO_3]$  is constant at 1.0 mM.



**Figure 2.** TEM image of silver nanoparticles.



37

You can see here the nano particle is giving a single peak but the nano rod is given two peaks so what is the reason the nano rod is giving two peaks because it has two dimension so it has dimension like this as well as like this like longitudinal and transverse so it will give a two peaks transverse as well as a longitudinal peaks okay. So let us see a simple experiment I will demonstrate you how to make nano particles in the lab with the simple chemicals available in your lab okay.

(Refer Slide Time: 24:35)

## Silver nanoparticles (Ag NPs)-Simple method

### Synthesis of Ag NPs by NaBH<sub>4</sub> reduction method:

- Take 1 mL deionized water in a 1.5 mL micro centrifuge tube.
- Add 1.67  $\mu$ L of AgNO<sub>3</sub> (0.1M) to the above tube.
- Immediately add 1.33  $\mu$ L of freshly prepared (2mg/mL) NaBH<sub>4</sub> solution to it.
- Then add 90  $\mu$ L of SDS solution (0.1 M) to the above solution.
- Agitate the micro-centrifuge tube containing all the components vigorously.
- Appearance of yellow color is indicative of the formation of silver nanoparticles.



SPRINGER



SPRING  
CERTIFICATION COURSE

39

So for this we have to use 1ml of deionized water in a 1.5 ml micro centrifuge tube and we will be adding 1.67 micro drops silver nitro solution that is a 0.1m to the above tube and we will immediately add 1.33 m drops for freshly prepared 3mg /ml NaBH<sub>4</sub> solution to it okay. So the sodium boride should be freshly prepared solution and then you add 90m drop at this solution to this above solution it is the stabilizer it is going to stabilize your silver nano particle.

And you have to mix it vigorously then if you see the yellow color that means you are showing that the silver nano particle is formed. So let us see the experiment I will demonstrate you. So now we are going to see how to make silver nano particle by using a simple experiment with the available chemicals in the lab.

The first step is we have to take 1ml of deionized water in a 1.5 ml tube this is a 1.5ml micro tube so here I am going to take 1ml of deionized water, so I am taking 1ml of deionized water in two tubes here to one tube I am going to add a reducing agent and a other tube I am not going to add reducing agent so that you will get a idea the tube which I add a reducing agent in to reduce a silver salt in to silver nano particle the other tube which will do not have the reducing agent it will be transparent.

It do not form any nano particles and from this I am going to remove 93 micro drops water because in this subsequent step we are going to add 90 micro drops SDS and 1.67 of silver nitrate solution and 1.33 of sodium boride solution, so the next step is I am going to add 1.67 micro drops silver nitrate solution so this silver nitrate solution is light sensitive so we have to



use cover with aluminum foil and always wear gloves and also lab coat when you make silver nano particles.

So I am adding this silver nitrate solution to both the tubes so now I am going to add 1ml of water to the sodium boride as I told you earlier the sodium boride should be prepared freshly so what you did is we already measured 2mg per ml that is we are measuring 2ml in a 1.5 ml tube to this I am going to add 1ml of water and I am going to make sodium borohydride freshly.

Just mix it so that the sodium borohydride can dissolve completely and immediately you have to add the freshly prepared sodium borohydride 1.33micro ton to this tube, so I am going to add 1.33 drops sodium borohydride to only one of the tube not to both the tubes. Now I am adding immediately the SDS 90ml drops SDS to both the tubes.

So I am going to mix it vigorously to both the tubes, so now you can observe the yellow color formation that means the nano particle is formed. So you can see here the tube which I added reducing agent it reduces the metal salt into silver particle. You can see here it has become yellow color the other tube that I did not add the reducing agent it is transparent.

That means the silver particle formed in this solution where I added the reducing agent the other tube that there is no reducing agent there is no formation of silver particle. Hope you understood the experiments how we can make nano particles in the lab. The summary of this lecture so in this lecture we have learnt what mechanical milling is and what is laser absorption.

So these are two physical methods and these physical methods how to make nano particles and you learnt mechanical milling is the top on approach okay again the laser absorption is a green method and eco friendly method because they are not using the toxic chemicals and we also learnt how to make nano particle by chemical reaction method.

For chemical reaction method you need three important components and what are the three important components you need metal salt, reducing agent as well as capping agent or stabilizing agent and we also learned nucleation and what is growth. So nucleation is formation of nano solution formed by the growth.

And we also learnt how to make nano particles and metal rods and what is the mechanism of nano dot formation and a simple experiment how to make nano particles in lab with the available

chemicals okay. I will end my lecture here thank you all for listening I will see you in another interesting lecture.

**For Further Details Contact**

**Coordinator, Educational Technology Cell  
Indian Institute of Technology Roorkee  
Roorkee-247 667**

**E Mail: [etcell.iitrke@gmail.com](mailto:etcell.iitrke@gmail.com), [etcell@iitr.ernet.in](mailto:etcell@iitr.ernet.in)  
Website: [www.iitr.ac.in/centers/ETC](http://www.iitr.ac.in/centers/ETC), [www.nptel.ac.in](http://www.nptel.ac.in)**

**Production Team**

**Sarath. K. V  
Jithin. K  
Pankaj Saini  
Arun. S  
Mohan Raj. S**

**Camera, Graphics, Online Editing & Post Production  
Binoy. V. P**

**NPTEL Coordinator  
Prof. B. K. Gandhi**

**An Eductaional Technology Cell  
IIT Roorkee Production  
©Copyright All Rights Reserved**