Physics of Renewable Energy Systems
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Lecture 41
Synthesis of Nanomaterials

Hello, in the previous lecture, I gave you a brief introduction to the field of nanomaterials and nanotechnology and how do we define nanomaterials. We are defined nanomaterials as a material which has one of its dimensions in the range of 1 to 100 nanometres, it is possible to have one of the dimensions in this range, two can be in this range or all three of the dimensions can be in this range of 1 to 100 nanometres.

And depending upon this confinement effect, we had given the definition of nanomaterials and the various types of nanomaterials that are there. More so, the quantum well, the quantum wire and quantum dot type nano structures.

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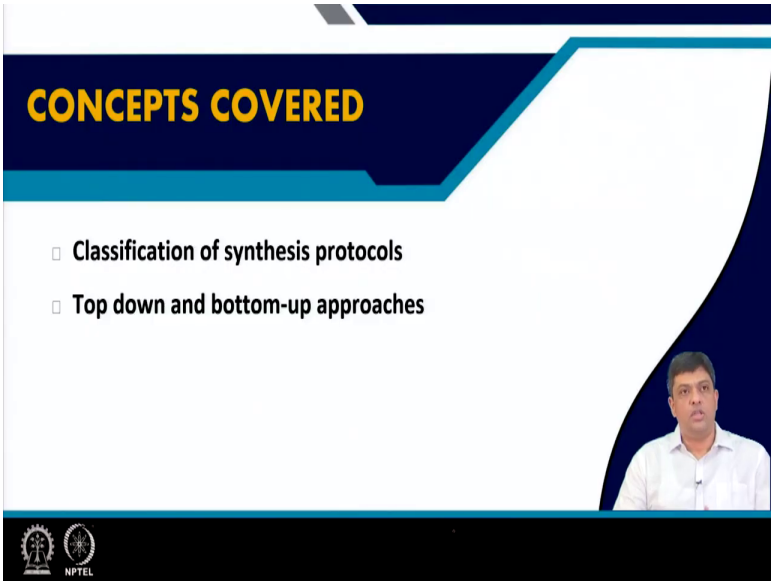

In today's class we will focus on the synthesis protocols and the classification of synthesis protocols. These are the synthesis methods which are used to fabricate nanomaterials and it is imperative that if you want to have the correct physics of materials, then the chemistry of materials must be correct. There are two broad approaches which are followed to classify the

synthesis protocols these are top down approaches and bottom up approaches and the details about this will be covered today.

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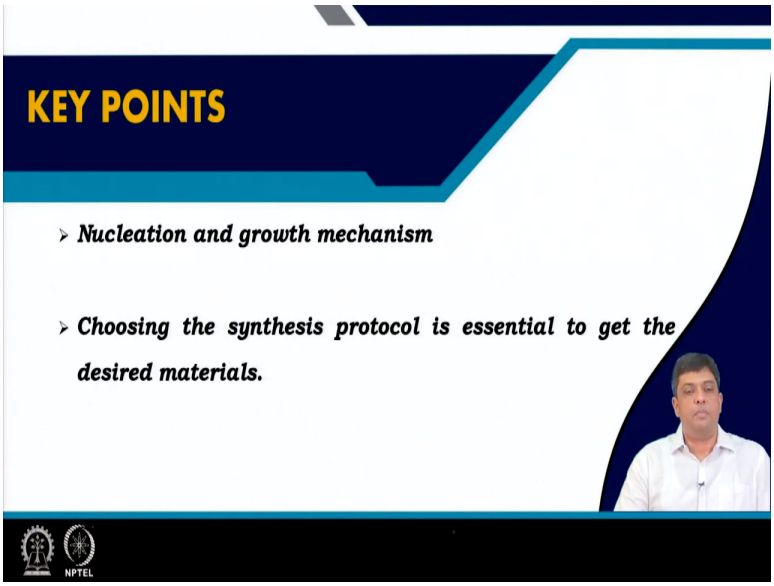

And by the time you will finish this lecture, you will understand the concepts of nucleation followed by growth mechanism which lead to the stabilization of nanomaterials and it is only the choice of the synthesis protocols which will lead to the desired material with the required properties which you want.

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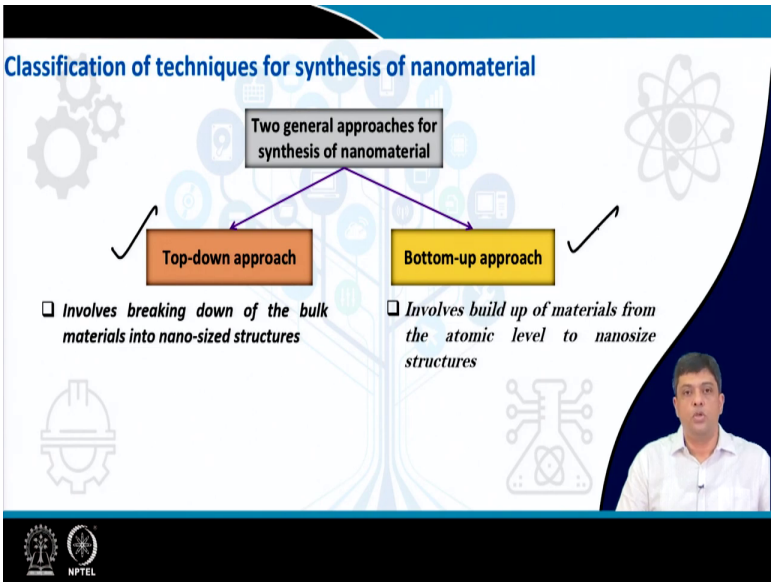

The synthesis protocols are broadly classified under two broad headings, the top-down approaches and bottom up approaches. The top down approach involves the breaking down of the bulk material into its nano size structure or the bottom up approach involves the buildup of a material from the atomic level and then scale up to the height of nano size structures.

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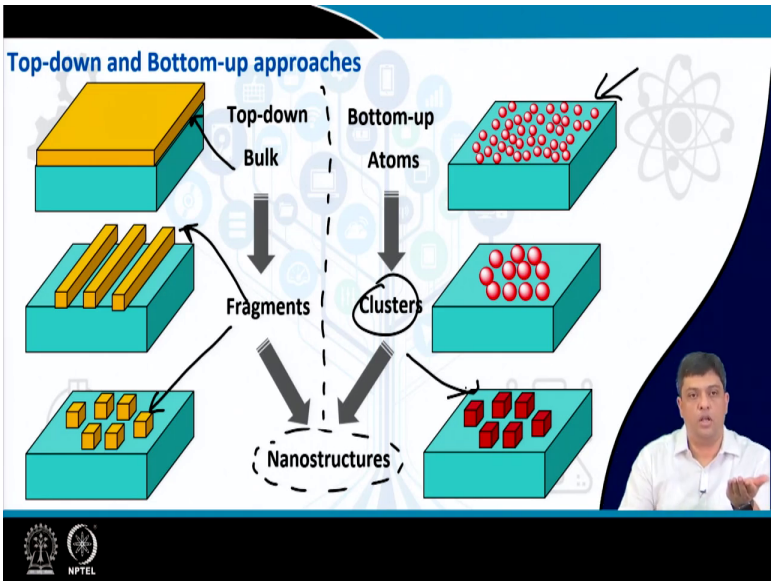

To understand these two protocols, let us have the two schematics to explain these two top down or bottom up approaches. The final aim is to get a nano structure. So, in top down approach, you already have the bulk material, what you do you actually reduce this bulk material to smaller

fragments and then you go on reducing the size of the bulk material and what you obtain is the desired nano structure at the end.

So, you already have the material and then you crush it down to the smaller fragments or the particles just like what you do in a mill. So, a milling process. You can have the wheat going in and what you get out of the milling process is the flour. Whereas in the bottom up approach, you start with the constituents that is the raw material and then they react to give clusters and finally these clusters are treated me as a function of pressure or as a function of temperature or any other related thermodynamic parameter and then you end up getting the nanostructures. So, bottom up it is built up, top down is crushed and go down.

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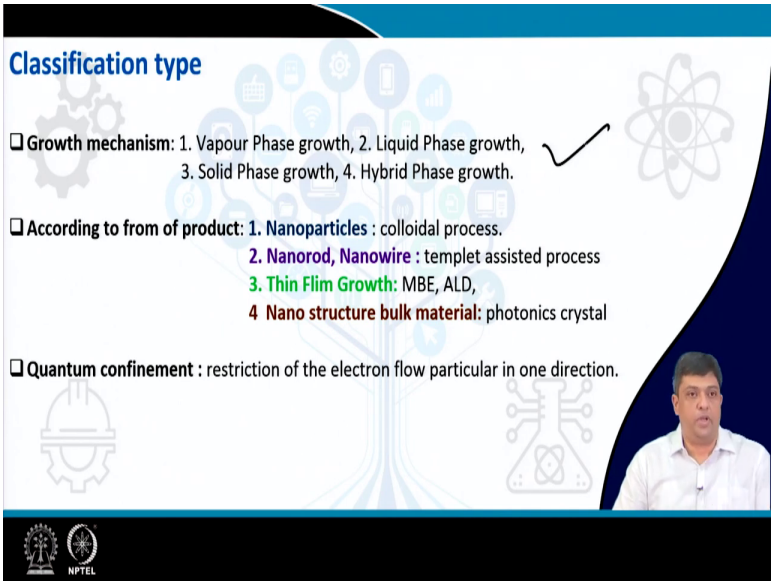

Based on the growth mechanism, there are the techniques can also be classified under different headings so that the top down bottom up is the most common way of classifying the synthesis protocols. There are other protocols which are used to classify the synthesis protocols that are relevant to nano material synthesis. So, based on the particle growth mechanism, you can have the vapour phase growth, the liquid phase growth, the solid phase growth or the hybrid phase growth.

Depending upon the form of the product you get you can have nanoparticle synthesis, nano rod synthesis, thin film rods or nanostructured materials. Depending upon the confinement effect that is in which of the directions you are restricting the flow of the electron you can have the growth mechanisms.

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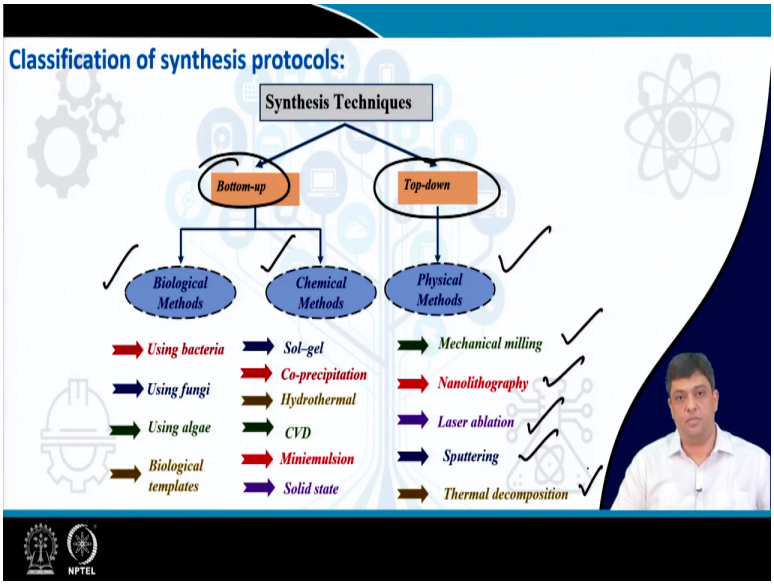

But, just to list some of them, the bottom up and top down approach is are not associated with just one of the material techniques, you will see that these two approaches have large number of synthesis protocols which fall under them. So, these are just the example I am not saying or claiming that this is a comprehensive list, but, this slide is just to prepare, aacha I will just start with this slide.

This slide is just prepared to show you that there are large number of experimental techniques and these techniques can be classified under various sub headings. So, for example, bottom up can be classified under biological methods or chemical methods. Top down approaches can be under physical methods and even under physical methods of the top down approach you can have various kinds of synthesis protocols for example, mechanical milling, lithography, laser ablation, sputtering or thermal decomposition.

Each of these techniques have their own advantages and certain limitations or disadvantages are associated with them. Depending upon the kind of materials you want and also depending upon the availability of the infrastructure, you will choose the synthesis protocol because some of the techniques may actually be very expensive and you may need high end infrastructure to host such a technique for example, lithography.

So, the whole lithographic process or the instrument itself is quite expensive and you need associated infrastructure such as clean room etc. to host this technique so, that you can get nano structures. So, depending upon the availability and also the infrastructure you will choose the synthesis technique but you should understand that there are large number of techniques by which you can get nanomaterials.

So, if you venture into this area do not worry even if you have less number of synthesis protocols or instruments by which you can make nanomaterials because, by tuning the synthesis conditions, you can actually play with the morphology, the structure and the characteristics of these materials. And you can always make newer materials even with the simplest of synthesis protocols. And the protocol which is simple, but gives a high performance material is actually most desired and accepted.

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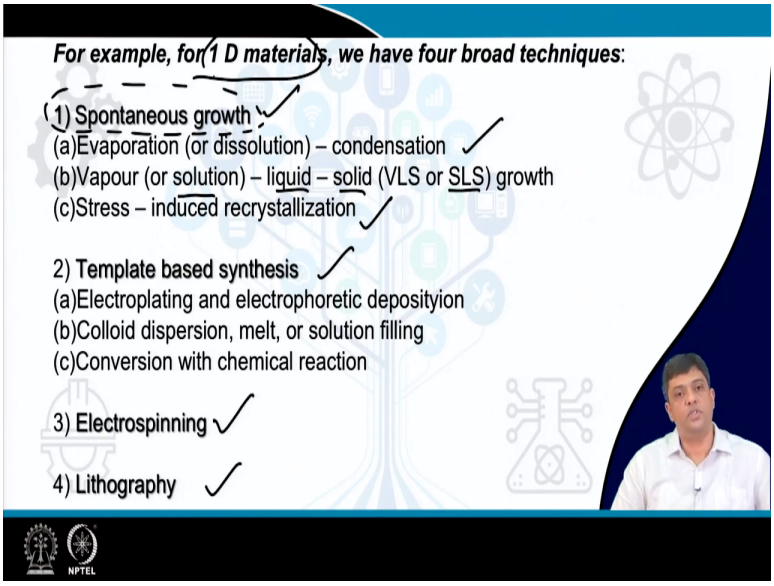

For example, just to give you understanding to what I said, if you want to make a 1D structure then even 1D structures can be made using various kinds of techniques which are put under four broad sub headings. The first subheading is the spontaneous growth type synthesis protocols which involve evaporation, condensation, or dissolution and then subsequent condensation-based protocol or vapor liquid solid growth or solution liquid solid growth mechanisms or you can have stress induced recrystallization.

So, these are kept under spontaneous growth protocols, then there are template based synthesis where you use a template to replicate the structure of the template and obtain the desired material. So, these are template based synthesis, you can use electro spinning or lithography to obtain 1D nanostructures. So, there are techniques which can be used to make 1D materials and there are techniques they use to make 2D materials or 0D materials, but, it is not so, that one kind of technique cannot lead to different kinds of material.

So, if you look at lithography, lithography itself can give you 0D, 1D and 2D structures, electrospinning can do the same, it is just that 1D structures are mostly made using these four kinds of synthesis protocols, but other materials can also be obtained.

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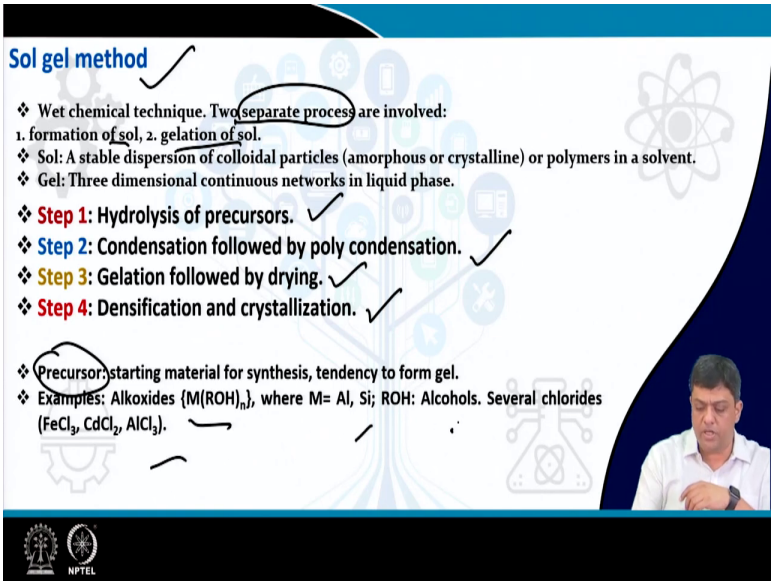

Let us one by one look into the simple techniques which are routinely used and you can use these techniques to obtain the materials which have been discussed with you in this course. So, we have discussed a large number of metal oxides, we have discussed large number of semiconductors and these kinds of techniques can be used to fabricate such materials. So, one of the most common technique is the sol gel method. It is a wet chemical technique. So, it involves chemical reactions, but in the aqueous phase. So, or it has chemical which are actually fluidic in nature.

So, it is not solid, solid reaction, but wet chemical reactions. So, two processes occur in this protocol. First is the formation of sol and second is the generation of this also sol, so sol formation gelation gel and therefore, the technique is called Sol gel technique. What is sol, sol is a stable dispersion of colloidal particles in a solvent and gel is a three-dimensional continuous network in a liquid phase.

Once you have stabilized this condition, the processes which are involved are the hydrolysis of the precursors, the condensation followed by poly condensation, generation followed by drying of this gel, and then densification and crystallization, be it be temperature induced or be it be pressuring. So, you start with the precursors, the reacting materials and ensure that these materials form a gel and then you can follow the processes from step two to step four to get the desired material. So, you can get large number of materials using this protocol.

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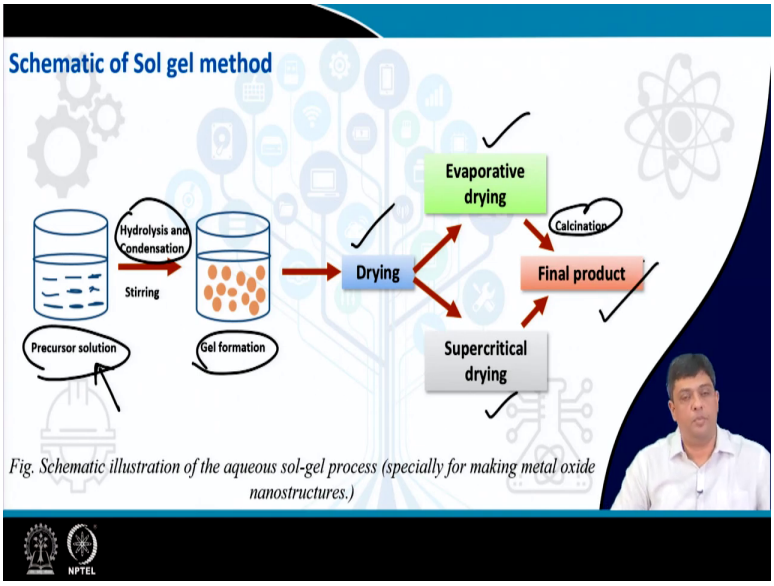

So, if you want to understand schematically so you have the precursor solution. So, wet chemical and then you perform the process of hydrolysis and condensation while you were stirring the solution so as to maintain homogeneity and obtain a gel. The gel is dried you can have evaporative drying or supercritical drying and then calcite as I had discussed earlier, what is calcination, calcination is the process by which you ensure the completion of the reaction and formation of the material.

It is not densification of the material, sintering defines the process of densification of the material. So, calcination is the temperature or the process by which you are going to ensure that the material has formed. So, you calcine and you obtain the final product.

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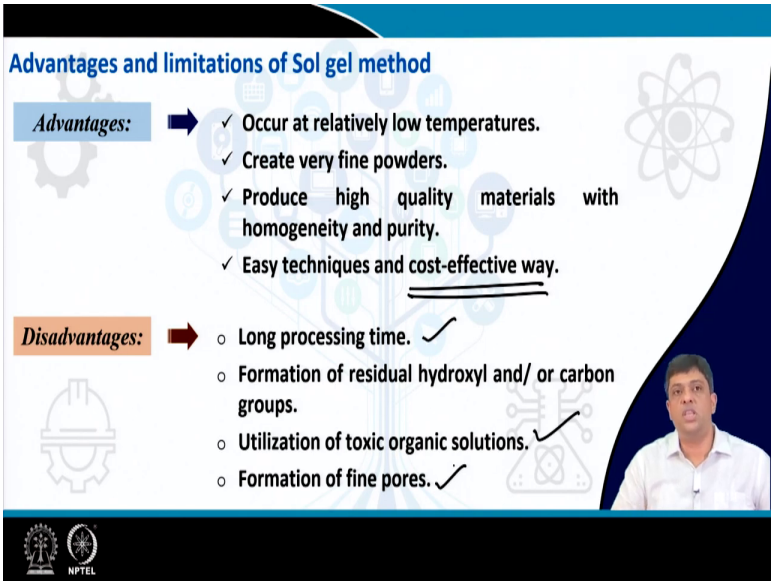

The advantages which are there with sol gel are, you are actually working at low temperatures. So, if you are working at low temperatures, then you can get fine powders and you can control the degree of agglomeration because even if you are making small particles, but if you allow all these small particles to come together an agglomerate then what you will see is a big chunk and that would appear to be a bulk big particular bulk sized system.

So, what do you want, that you want small particles which are not agglomerated. So, we are maintaining or avoiding agglomeration you must work at low temperatures. The sol gel technique is also an easy technique and if you are working with simple materials and simple precursors, then it will also cost effective but if the cost of the precursors go up and there are some expensive materials which are there and used as precursors then the cost can be slightly on the higher side.

The disadvantages are it takes appreciable amount of time to get them material you can have the requirement of using toxic organic solutions and you can have systems where fine pores are visible, but you do not want a structure which is porous, but if you want systems where you need porosity then the technique is quite okay.

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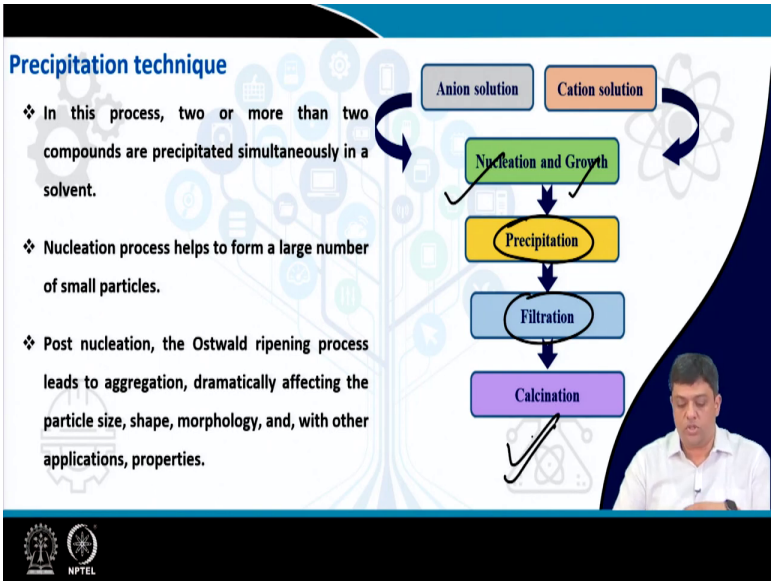

The other technique which you have been hearing right from our school days is the precipitation technique. What do we do in precipitation, you have the anion solution, the cation solution, they are mixed and then they are either as a function of temperature or pressure you induce the nucleation once the nucleation site is setting inside the solution or the in between the reaction coming in from the anion and the cation solutions, then you have the critical radius and beyond that critical radius you see the growth of the particles.

Once the particles are forming, they appear like a precipitate, once you have the precipitate you filter it, once you have the filtered precipitate many a times you need to wash this filtrate using different kind of washing solutions. Be it be water or be it be ethanol, or be it be ethanol depending upon what you want to remove from the precipitate you undertake the process of washing and once you have washed the precipitate you let it dry once, once it is dry, then you initiate the process of calcination.

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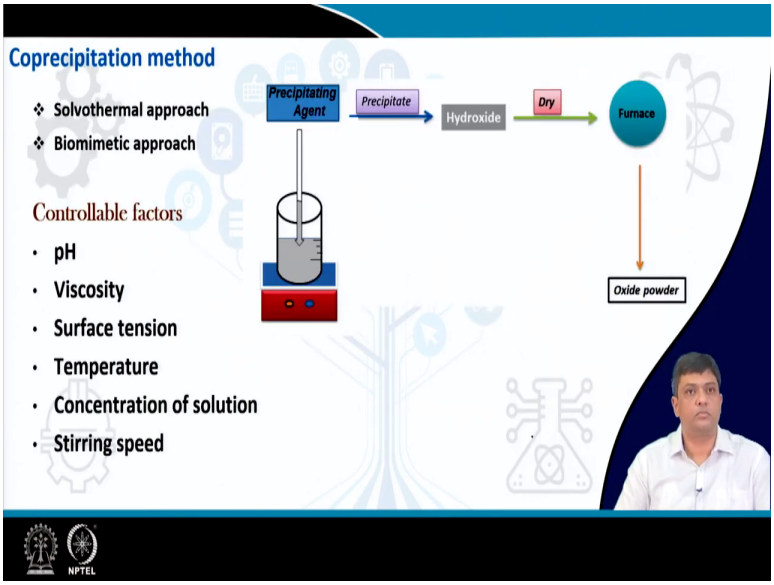

Similarly, you can have coprecipitation method, (cause) coprecipitation means you can ensure that there are two different reactants, but they are precipitating together, so that they form a solid solution that is a single phase matrix. So, it is a solvothermal approach and sometimes it is also biomimetic approach. Here you need to control the pH, the viscosity, the temperature the rate at which you add the acid or the alkaline solution or the precipitating agent, so that you ensure that there is a coprecipitation of the reactor or the reactants or the atoms which you want to precipitate out together. And to ensure homogeneous precipitation, you also need to stir the solution quite vigorously.

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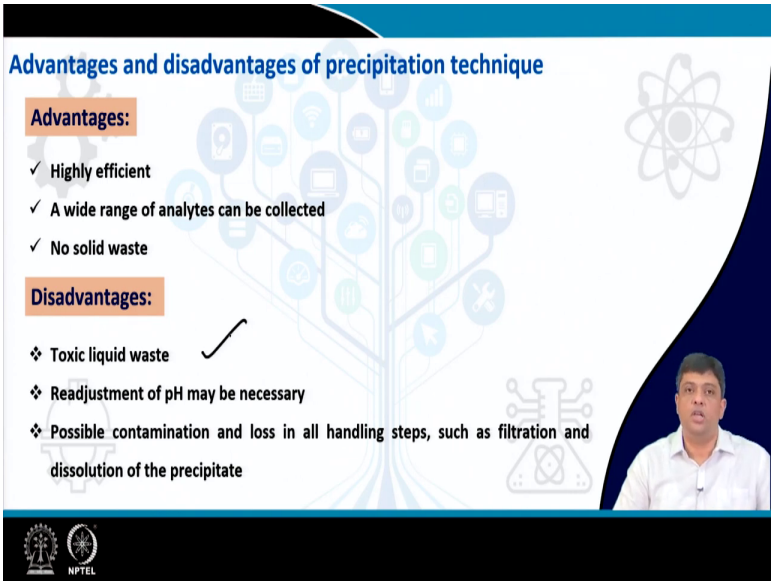

The advantages of the precipitation techniques are that they are quite efficient, chemical based process so quite efficient. A wide range of materials can be prepared, mostly you do not get any solid waste, but the disadvantage is you can have toxic liquid waste and the disposal of this liquid waste is quite tricky, because you cannot just throw it in the washbasin otherwise, the water underneath the wash basin or in the catchment area of that sink or where the water is in going in may get contaminated.

So, there are dedicated processes by which you need to dispose these toxic liquid waste. You need to control the pH level and there is possibility of introducing contamination because there are many steps involved during the preparation of the material using precipitation technique.

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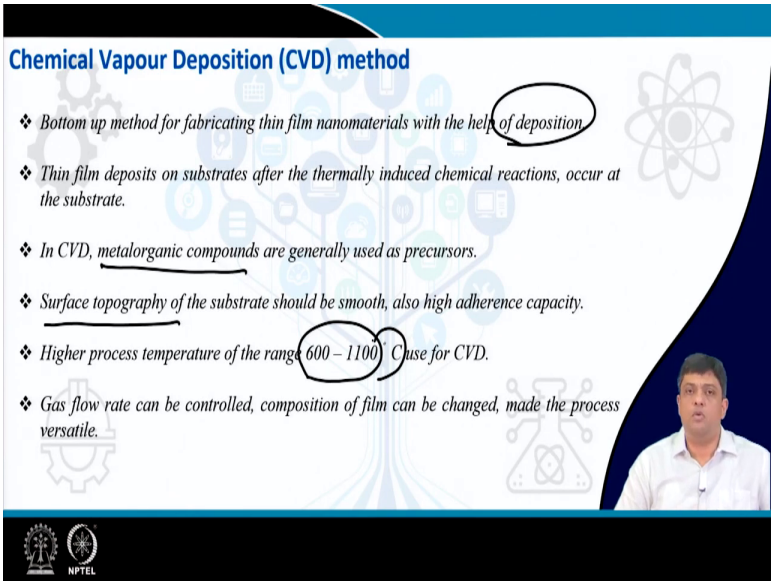

The next technique which is used that is a bottom up technique is the chemical vapor deposition technique. Mostly you have these kind of techniques where you are utilizing the concept of deposition and in these kinds of techniques you can obtain thin films or you use metal or organic compounds as the precursors to have an efficient chemical vapor deposition technique you must ensure that the surface topography of the substrate should be smooth because this is where the material are going to get deposited and then you will induce the growth.

In chemical vapor deposition techniques you have high temperature. So, you use somewhere between 600 to 1000 degrees C and hence this CVD techniques are mostly useful for organic materials or systems which are able to sustain this temperature, but if you are looking into electronic circuit trees and semiconductor materials, which have to be synthesized or the structures which have to be grown at much lower temperatures, then you are looking at PECVD, that is Plasma Enhanced CVD, the process is slightly different from chemical vapor deposition, but the technique remains the same or the concept remains the same.

And those kinds of instruments or the whole process can be undertaken in the temperature range between 100, 250 degrees or so, and hence, you use PECVD for electronic circuitry, but for the kind of materials which we have discussed chemical vapor deposition that is CVD is the most used material.

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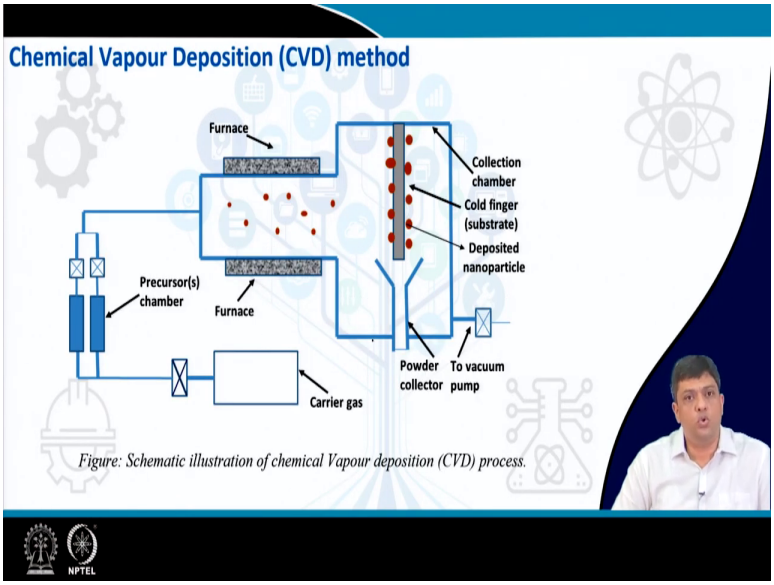

So, what you do you have the precursor chamber. So, you introduce precursors then they get heated in the furnace and then you introduce the carrier gas and using this carrier gas the carrier gas gets dissociated and then you can use the dissociated nucleus as the nucleating sites and from there you can lead to the growth of the materials which will go and get deposited on the substrate.

Now, this is what it is done then you once they have formed you can collect the powder, but also these kinds of processes initially the whole chamber needs to be clean or it has to be purified. So, first you introduce vacuum and then you introduce some kind of gas, made the inert gas then you vacuum again. So, that you remove any kind of moisture or any other gases which have got absorbed on the surface of the reacting chambers. So, there are processes and which are involved in CVD and you need to be careful while running this whole instrument.

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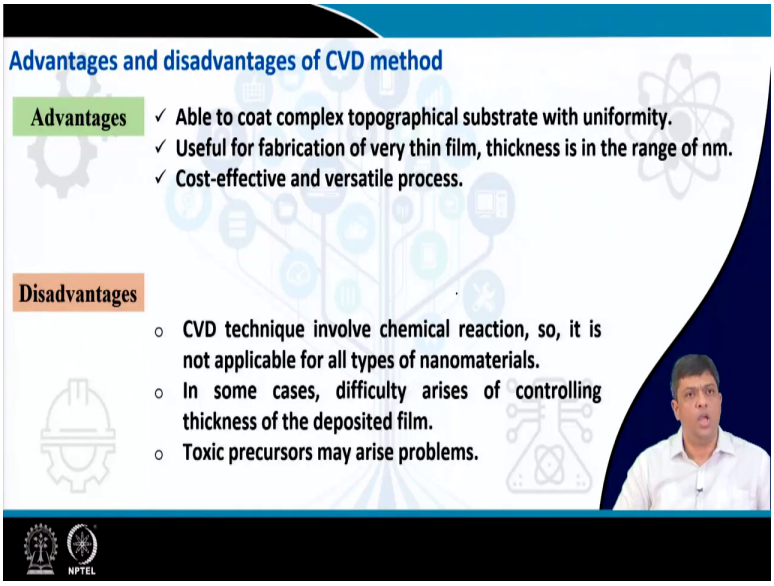

But the process is quite simple, it is the technique is able to code complex topographic substrates with uniformity. So, you can get uniform films or uniform structures growing quite nicely. But the major problem as I said that CVD is mostly at high temperature, you can also have toxic precursors, which are used and that can lead to other limitations.

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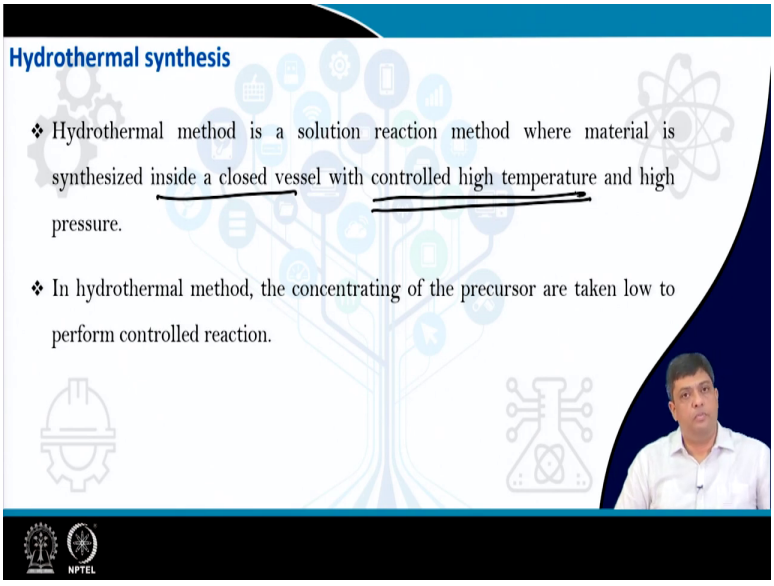

One of the most fast emerging technique is the hydrothermal process where you use materials inside a closed vessel which is controlled in a way that it can go to very high pressures while the

temperature is also rising. So, you have hydro thermal process where the temperature can make can be made to increase and along with that the pressure inside the chamber also is increasing and in a layman language you can say that it is somewhat similar to a pressure cooker type stuff, but this is more scientific and then you are using various kinds of safety precautions and protocols to run this instrument and then you can get large number of materials.

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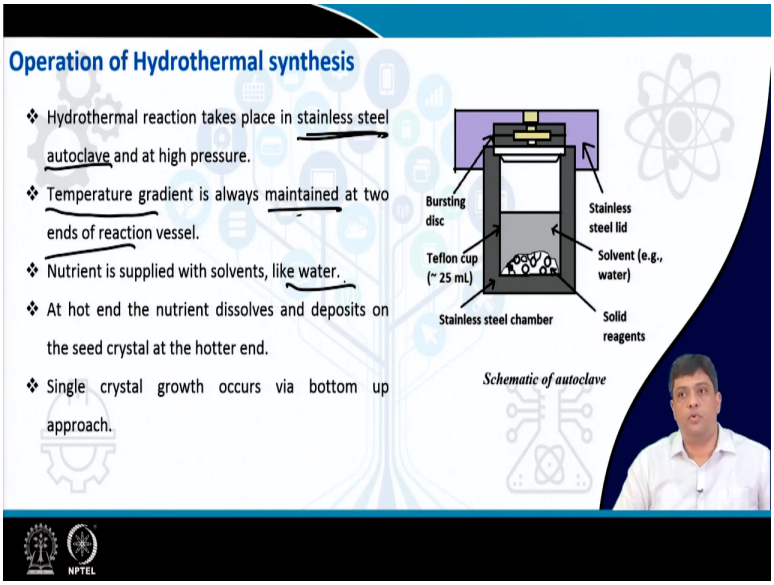

This is what you have, generally you use a stainless steel autoclave which is at which can sustain high temperatures and high pressure. There is always a temperature gradient which is maintained between two ends of the reaction vessel. So, once you have supplied the nutrients and then use some kind of a medium in which you can disperse these nutrients may it be water or any other kind of liquid medium so that you can ensure homogeneous distribution of these nutrients.

Then at the hot end what will happen the nutrients dissolve and deposit on the seed crystal at a hotter. So, at the seed crystal then the particles can grow from the seed crystal. And many times single crystals are grown using this approach.

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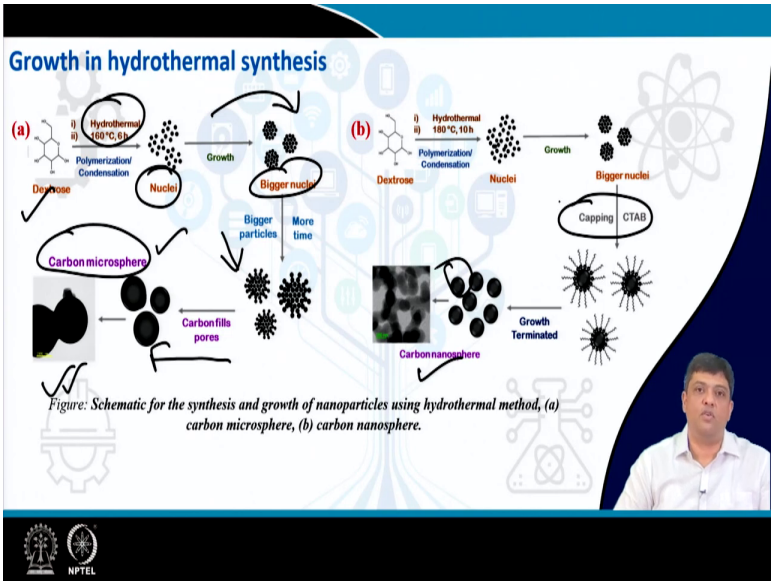

Figure: Schematic for the synthesis and growth of nanoparticles using hydrothermal method, (a) carbon microsphere, (b) carbon nanosphere.

The growth the process in the hydrothermal synthesis is somewhat like the one which we have shown here. So, if you want to get like carbon micro spheres which were discussed in one of the protocols or the modules earlier then we can start with the extras, take it in the hydrothermal jar heated to 116 degrees then you will form nuclei, let these nuclei grow and so the bigger nuclei will grow at the expense of these smaller nuclei's and you give them enough time to grow further and then slowly you will get carbon filled pores and then you let it stabilizes even further and you will get a carbon microsphere.

So, this is what, so playing with time and temperature you can change the dimensions and you can go from larger size to smaller structures. So, you can go from let us say carbon microspheres to carbon nanospheres by changing the temperature, changing the pressure or using capping agents, which do not allow the smaller particles to come together. So, you do not have the condition where the agglomeration is taking place. So, the capping agents are preventing the agglomeration, so smaller particles remain as smaller particles and then you can stabilize these kinds of nano structures.

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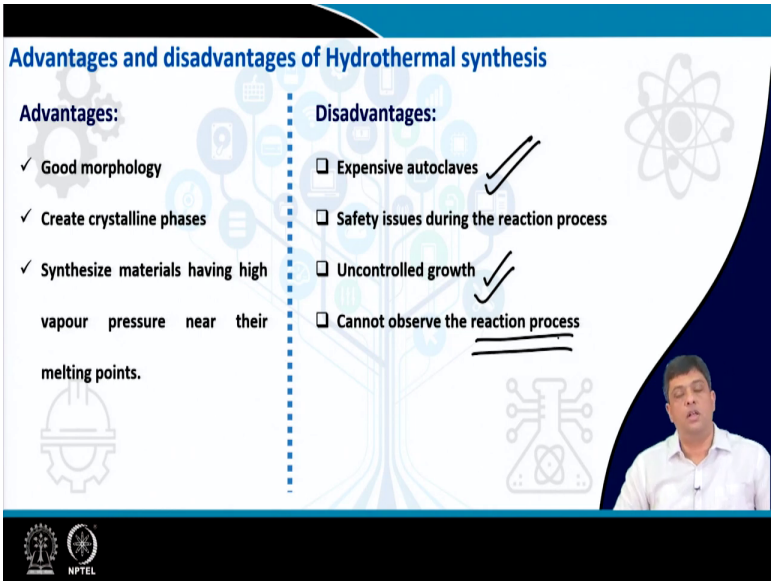

The advantages are you can have quite control morphologies you can have crystalline phases and compared to many other techniques, this is much faster, but the disadvantage is the instrument or the autoclaves are quite expensive, you have to ensure safety protocols and if you are not controlling the temperature and pressure as per the desired conditions, then you will have an uncontrolled growth and the reproducibility will become an issue and online visualize visualization of the reaction process is next to impossible.

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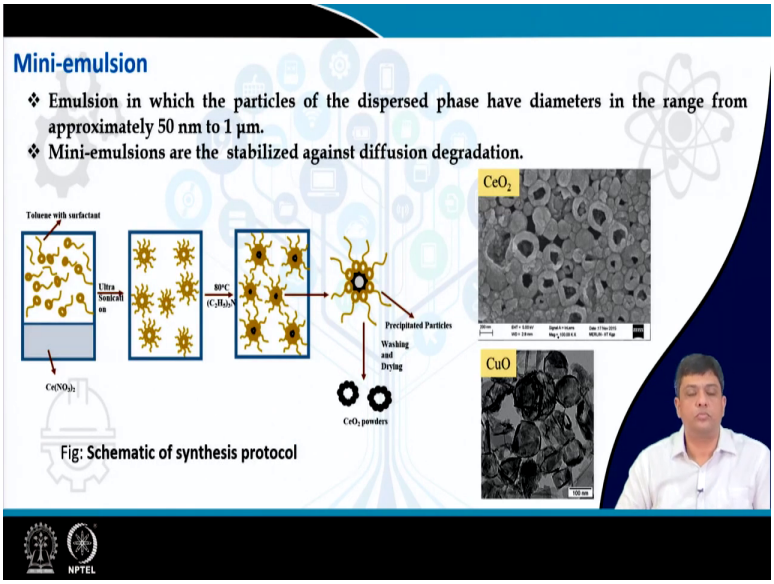

Then there are techniques which are called us emulsion based techniques. So, what you do, you use an emulsion which has a continuous phase and the dispersed phase. And you have the interface between the continuous phase and the dispersed phase and then the reaction takes place at this interface and as you allow the reactions to continue, if you allow it to continue to long period then it you will get solid structures and if you allow it for shorter period of time, then you can even get hollow structures.

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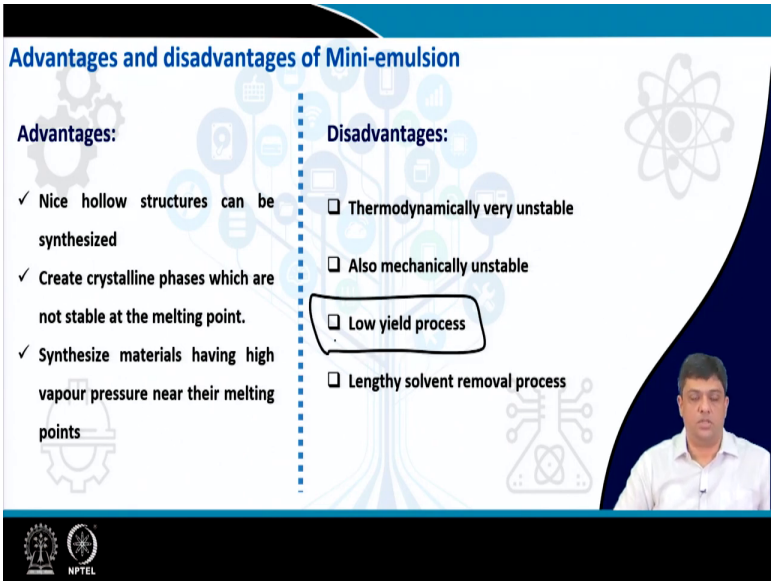

So, these are emulsion based techniques with their own advantages and disadvantages. The main disadvantage of these technique is that it is a low yield process, but the advantage is you can get hierarchical and very novel nano structures using these techniques.

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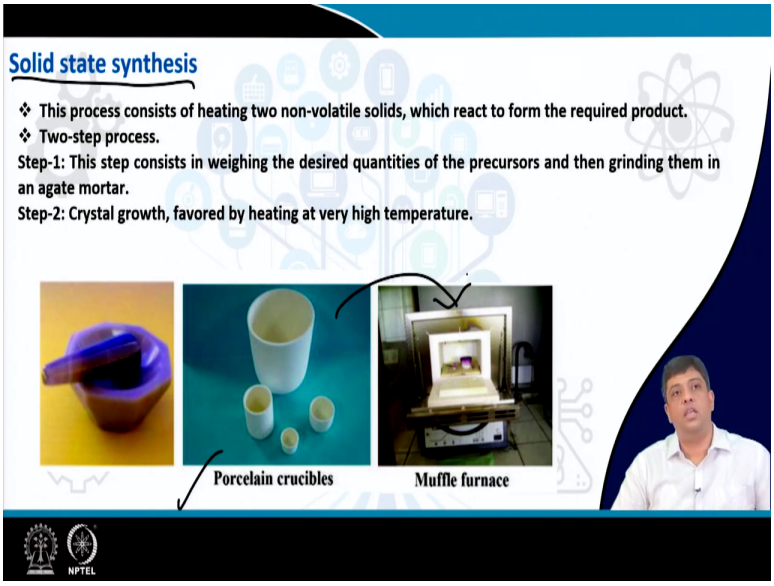

If you start a synthesis protocol and you are new into this area, then the one of the first technique which you will be using is the solid-state technique. So, what you will do you will have two non-volatile solid you will mix them together in a in a mortar pestle, put it in a crucible and take that crucible inside a furnace and heat it at very high temperatures and because if this temperature increases there will be reaction and you will get the final product.

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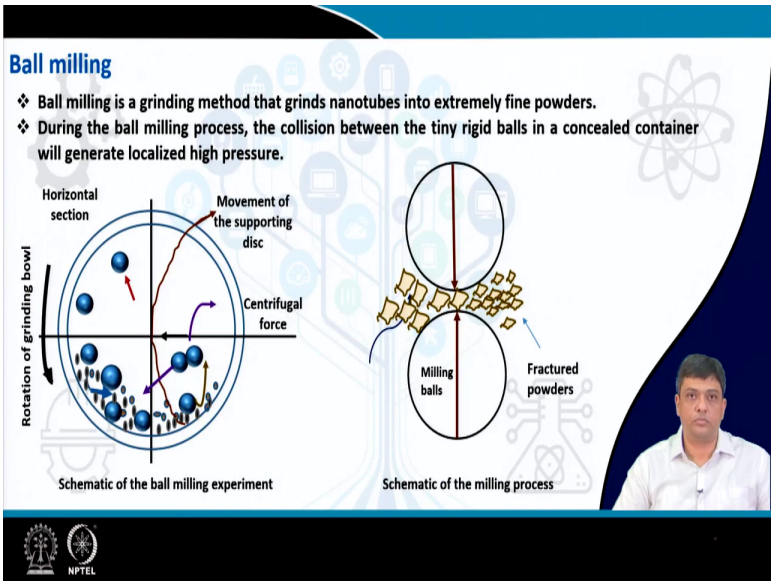

The next technique which you will use is most probably the ball milling technique, here you have a job where you have the balls inside. So, you can have very high grade steel or hard zirconium jars or if you are using softer materials like polymers, then you can have the jars made up of aluminium or so. And then what you do because of the collision between these balls which are inside the jars, then you crush the bigger size particles to smaller sized particles.

And then you have a laminar flow in between these two balls and as they move over each other, you transfer this energy to the larger size particles and as they absorb this energy they are made to crash to a smaller size process. And the thing is that you need to ensure that you are having a mixing media. So, if you use only solid materials then they will sediment at the bottom. So, you need to have a liquid material, which is the mixing media which does not react with the particles which are made to stir together and then you can under this whole process of wall milling.

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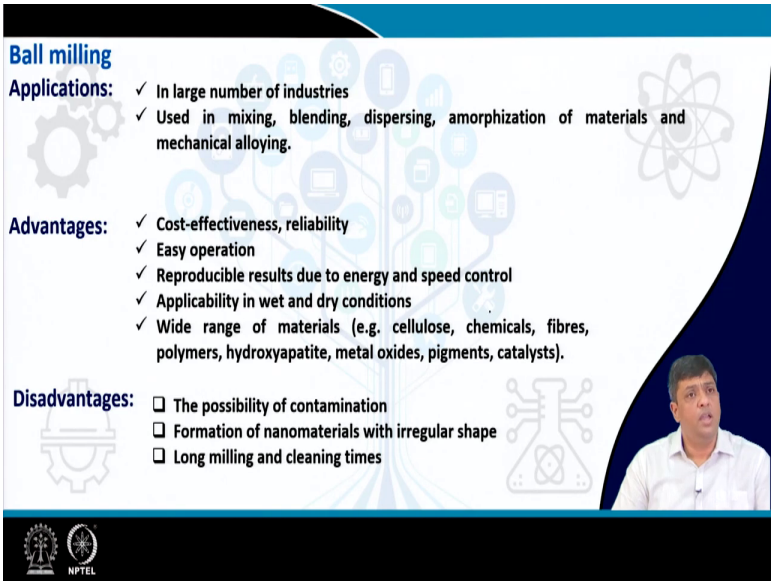

It is extensively used in large number of industries, it is quite simple, cost effective can lead to high yield processes, but the problem is that if you do not clean the jars properly after each cycle, then even have contamination issues, you can have in homogeneous distribution in particles size as well as particle shapes. And sometimes if you use the cornea-based jars or balls, then they are very expensive also.

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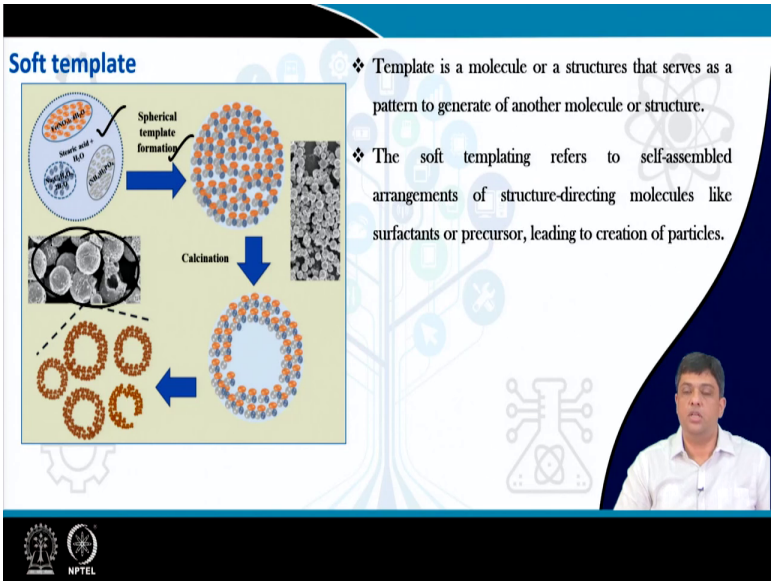

The other technique is the soft, soft template. So, you use a template to obtain the final material by removal of the template.

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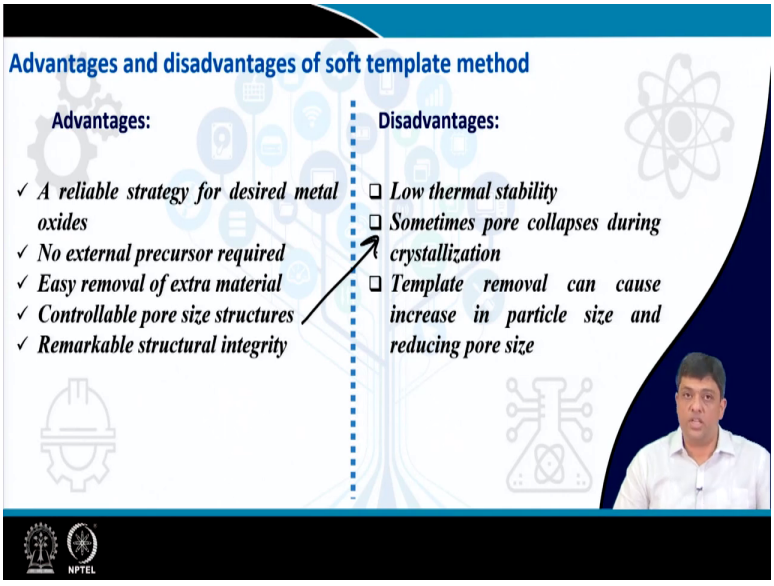

It has the advantage of reliability; you do not need external precursors. Easy removal of extra material that is a template can be removed, you can control the pore size by controlling the rate at which you are removing the template. But there are advantages which lead to disadvantage, here we said controlled pore size structure, but you can clearly see that sometimes because you

have induced a porous structure or a pore inside this structure, then this pore can collapse during crystallization or cycling process of a device and that leads to the underperformance of the material and the device characteristics start to change.

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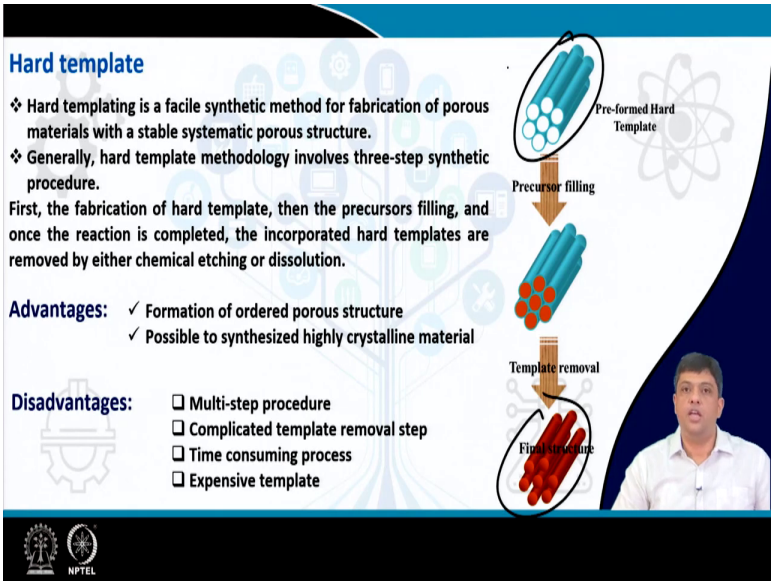

Similarly, to soft template you have the heart template process, similar concept you have the templates which can be removed and then you can obtain the final structure. So, template which are finally removed.

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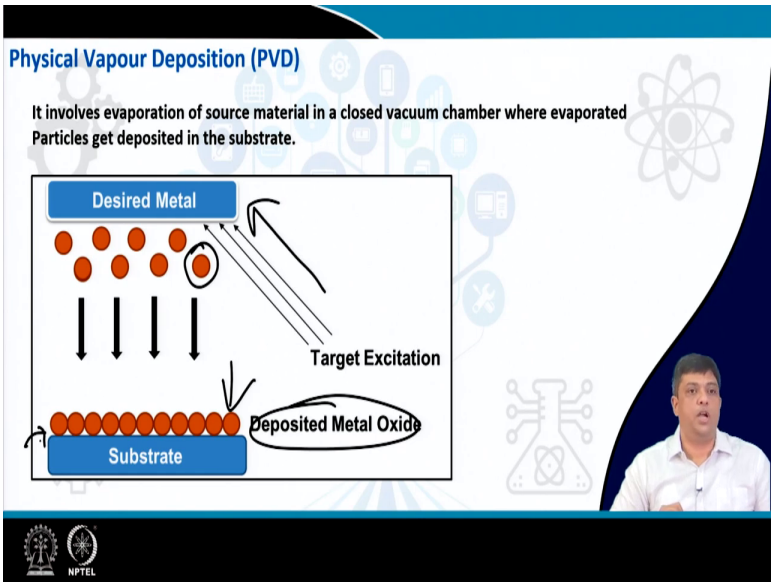

And similarly, to CVD, you also have physical vapor deposition techniques, which can lead to the deposition of nano structures on a substrate if you induce high energy beams on the design material, which gets ablated or are made to remove come out from the design material, then those materials will get deposited on the substrate in a pattern or a regular assembly or assembled order.

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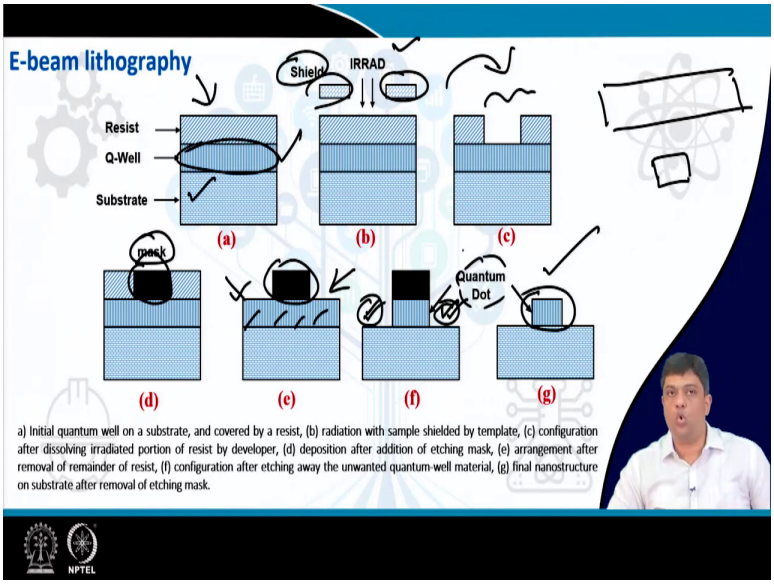

One of the most common technique used for top down process is the lithographic lithography you can have optical lithography, you can have electron beam lithography, or you can have iron

beam lithography. It is a very simple process, but it actually involves a lot of instrumentation and also chemical processes. And hence, the cost of this process goes up quite significantly. How does it work, you have a substrate, you have a structure on which you want to obtain the nano structure?

So, what do you do, you have a photoresist on top of it. Photoresist it changes its characteristic, basically resistance when there is not radiation falling on it. So, in the second step, you cover the area where you don't want the radiation to fall and then from the window in between the shield, the radiation falls on the photoresist. In the third step, the area which was exposed by the radiation is then treated and photoresist is dissolved so it gets dissolved.

In the next step, what you do you cover the removed area, the area of the photoresist which was removed using a mask. Now, you remove the extra photoresist. So, what is remaining, the mask and the structure on which you want to grow the nano structures then you can etch out so, you have a mask which will prevent any kind of damage to the structure underneath it and then you can actually process etch the extra material which is there.

So, you have now removed the extra material which was initially on the right and the left side of the structure which is covered with mask and finally, you remove the mask and what you get is the structure which you wanted. So, you had the material available and from large size material, you have gone to a small size material for example, in this case you can call it a quantum dot.

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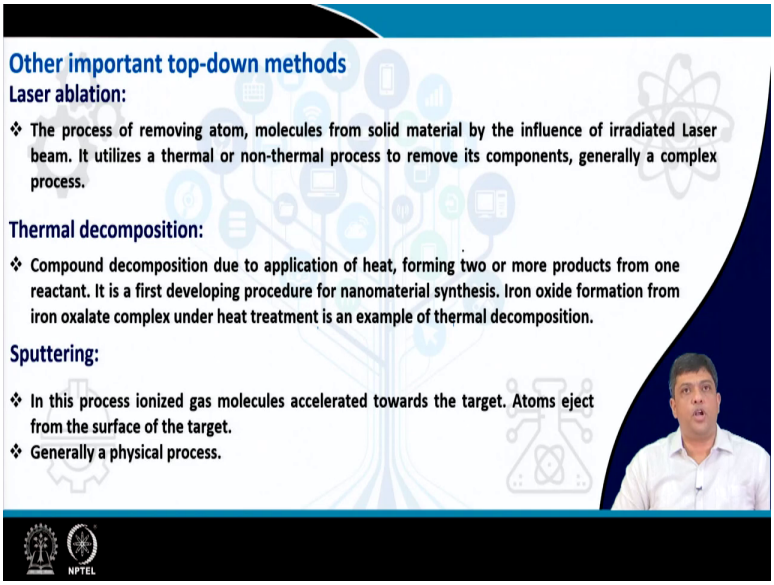

Other important top down methods are laser emulation, thermal decomposition and sputtering.

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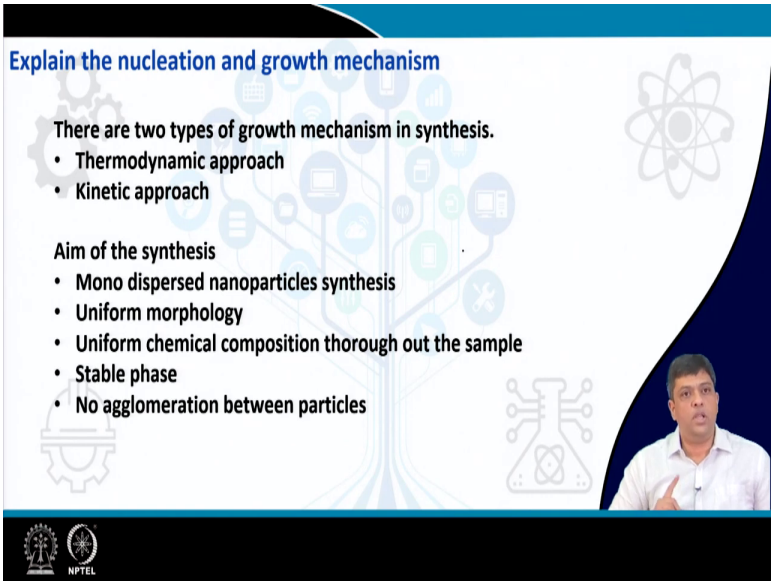

But all these processes actually are controlled by the growth and the associated process by which the system minimizes the energy.

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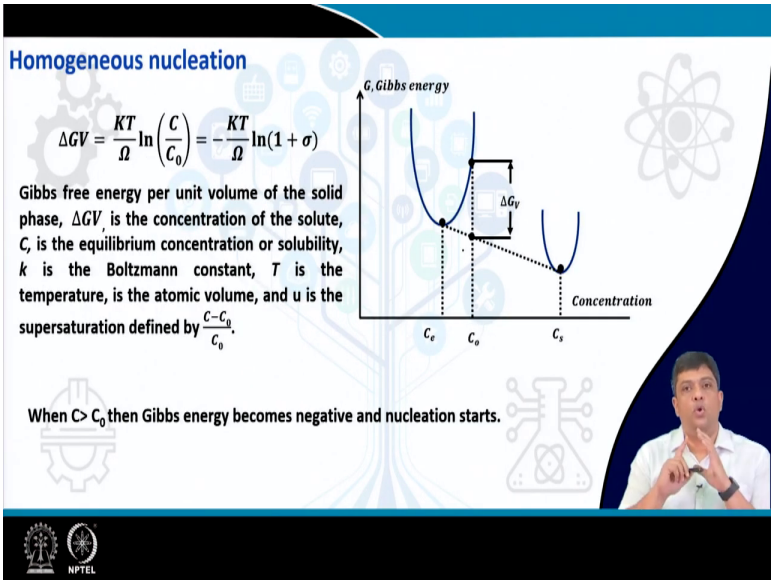

So, in homogeneous growth mechanism which is basically nucleation followed by growth mechanism what is done, you have the Gibbs free energy which tries to minimize its energy. So, you start with the material and then you have to go to the final condition such that you can minimize the energy. So, what do you do, you take these reactants go to a supersaturated

condition, when you reach the supersaturated condition then you induce the condition of nucleation and followed by growth process. So, you need to go to a supersaturation condition where the nucleation starts and then the growth process takes place.

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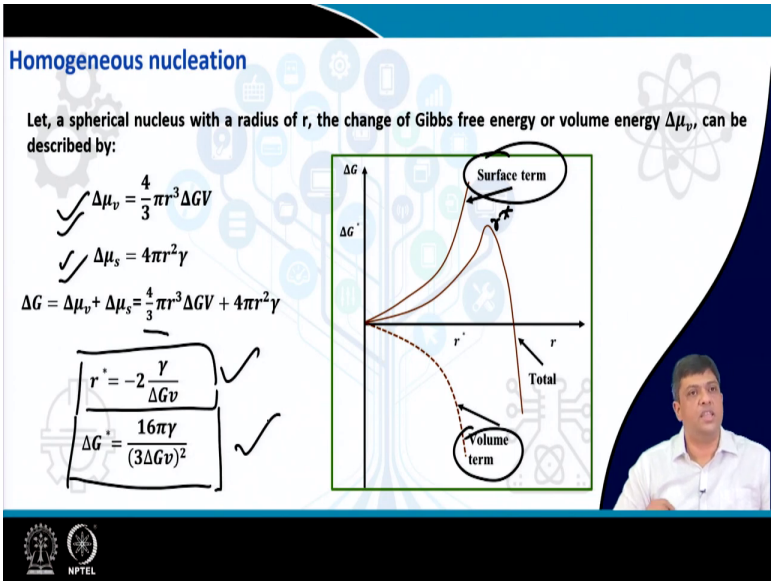

This is the whole process of what is happening you have two terms the surface energy term and the volume energy term, one of them increases as the square the other increases as the cube. So, initially the squared term dominates. So, the surface energy term dominates beyond a certain time but cubed term dominates and the volume energy term starts to dominate. So, the change in the Gibbs free energy can be written as 4 by 3pi r cubed delta Gv plus 4 pi r square comma.

And the critical radius r star with where the system will see nucleation is given by the differentiation process and you will get r star where the energy is getting minimized is equal to minus 2 gamma by delta Gv and therefore, you can get the change in the Gibbs free energy associated this r star as 16 pi gamma by three delta G v whole square. So, you know at what radius the growth mechanism will take place and what will be the change of Gibbs free energy and this is called the homogeneous nucleation induced growth mechanism.

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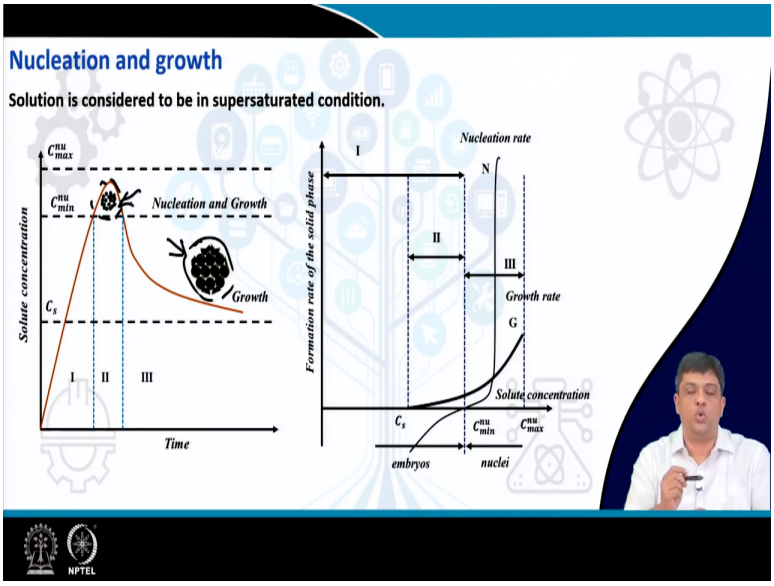

And you will see that the growth mechanism is such that initially if you do not reach to the r star condition, then the growth will not take place and particles the solution will see no change, but it is only after that the particle has actually nucleated and you see growth mechanism that the process will be changed. If you give enough time after nucleation and growth process, that is you have started seeing particle but then also you continue the process and allow the particles to come together then you will see a much larger sized particle.

And this is quite mostly the Oswald ripening type of process, where bigger size particles grow at the expense of smaller sized particles. So, what you see this your size particles growing at the expense of smaller sized particles, because they are made to come together.

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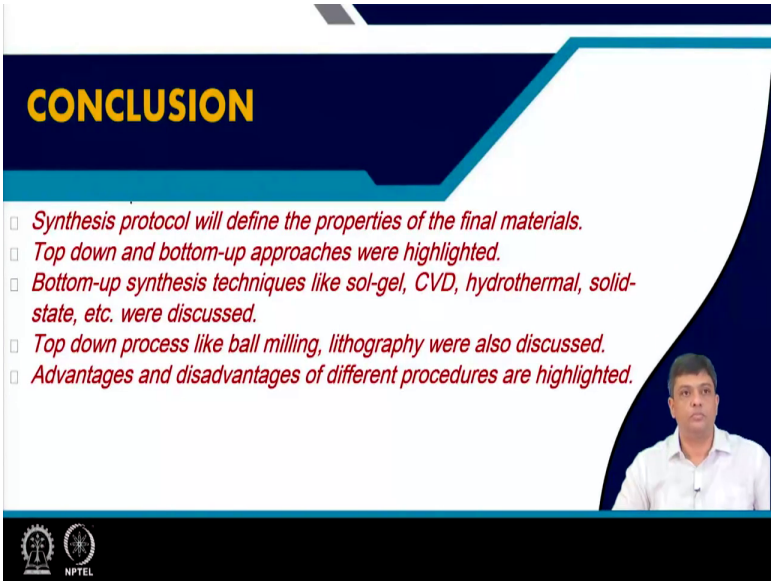

So, I hope it is clear to you that if you want to get the materials with the desired morphology, desired shape and you want to have them at nanosized then you must choose the synthesis protocol carefully you can choose either from top down or bottom up approaches or depending upon the technique which is available to you, but by changing the temperature, the pressure or any other thermodynamic parameter, you can actually get different kinds of particles.

And particles with different shapes and sizes or the pore structures and they will have different physiochemical properties. And then depending upon those properties, you can choose their use in any of the devices which we have discussed till now.

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These are the major references where you can get more details from regarding the things which were discussed today. And in the next class, we will talk to you about the synthesis of carbon nano structures or metal oxide based nano structures. And then finally, in the last lecture of this week, we will talk to you about nano catalysts. Thank you very much.