Nanobiophotonics: Touching Our Daily Life

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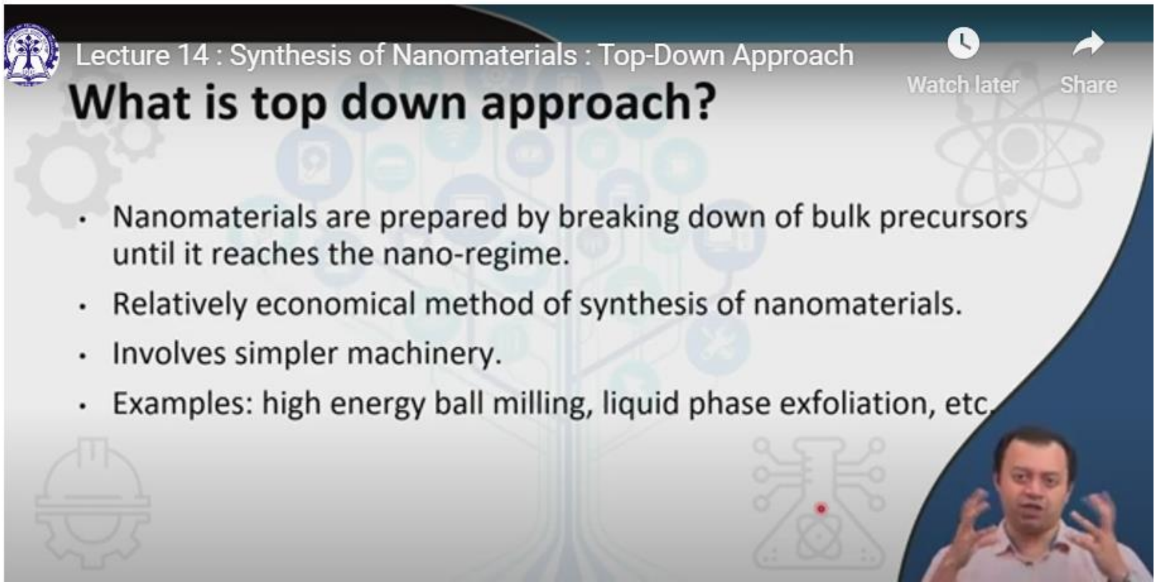
Lecture No. 14

Synthesis of Nanomaterials: Top-Down Approach

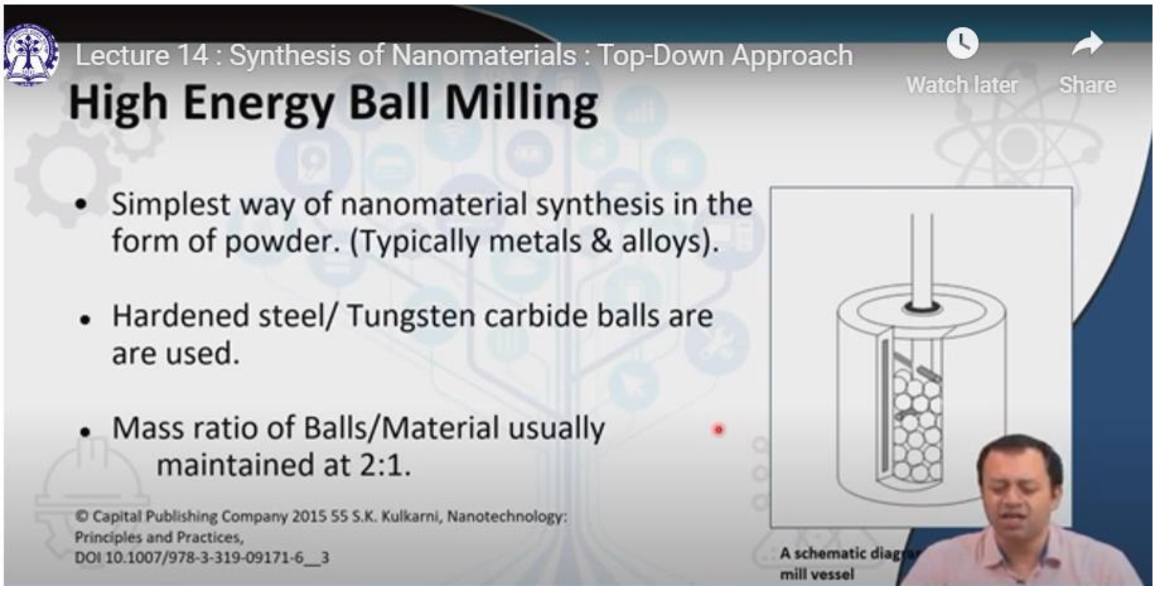
Welcome back. We are discussing the last of preliminaries, nanotechnology in photonics and today we will see if we can finish chapter number 3. In the previous 3 lectures, I have discussed about the humble atom, I have discussed about why nanotechnology is important, how nanotechnology helps and finally, I have given you an example of the bottom up approach. Bottom up approach is where you do some kind of a nanochemistry, couple of molecules not couple some more of them combined together, they form some kind of structure then you build the structure upon structure some kind like a Lego with children plays and with that you create some sort of an artificial material or you create or you tend to produce some sort of a new functionality, new properties on to this mismatch this Lego type structures that you have been able to create with various kinds of nanochemistry. The main disadvantage of such a bottom up approach is it is very costly right, only the top-notch laboratories or top most universities or academic institutions, research centers, research groups can afford such a thing. There is another approach which is possible which allows you to go through create a nanomaterial compromising on its accuracy compromising on its uniformity and that is called top down approach.

Today, we are going to discuss the top down approach in this particular lecture and it is comparatively much simpler than the bottom up approach comparatively. Remember there can be complications or simplicity in either approach depending on how intelligent, how clever, how useful you are with handling tools, but overall arguably a top down approach has certain amount of simplicity that is not available in the bottom up approach. So, welcome today we are going to discuss synthesis of nanomaterials, how to create nanomaterials, how to make nanomaterials using a relatively cheaper relatively simpler top down approach. So, what exactly is the top down approach as I said nanomaterials are prepared by breaking down the bulk precursor until it reaches the nano regime.



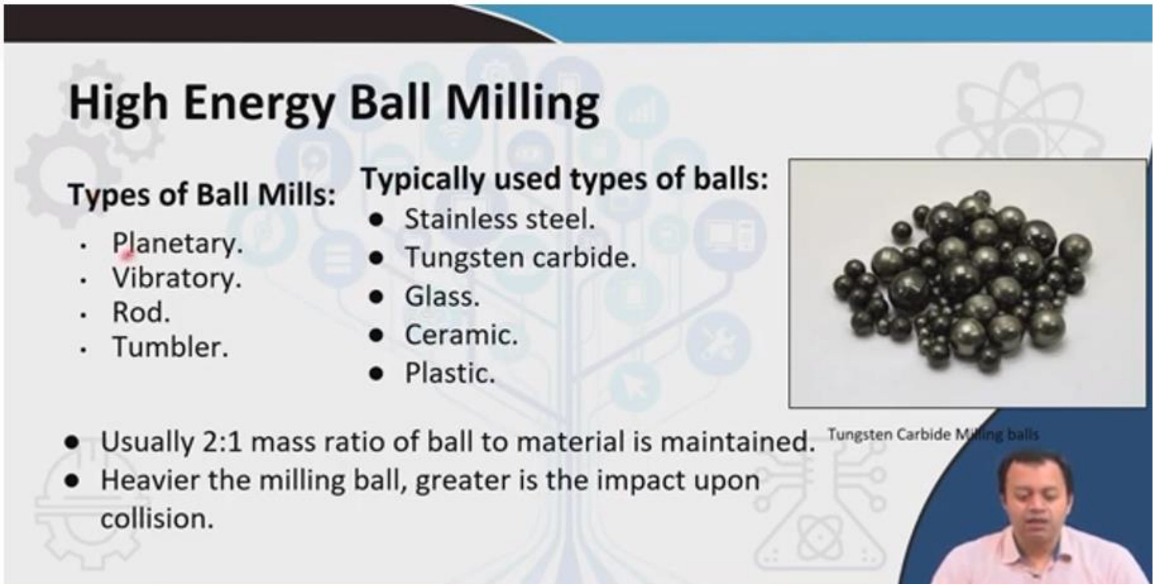
Simply you are breaking the bulk material, you are crushing the bulk material, you have taken a huge huge lump of something say for example, a silicon or some kind of a complex conjugate matter, matter a big matter a bulk matter and you are using mechanical force to an extent to break it down into constituent chunks. The more energy, the more time, the more effort you can have, you can spend the sizes of the chunks will become smaller. You go on continuing break something with a hammer simply a hammer and a chisel you take it I am giving you an analogy take a big piece of rock use a hammer and a chisel and start breaking it down for 1 day, 2-day, 5-day, 10-day, 1 year, 2 year the final final product the powderized form can be considered can be considered as a nanomaterial. Uniformity as I said the accuracy and the uniformity will be compromised the accuracy wise uniformity wise structural integrity wise you will have to you will have you will suffer. So, you cannot beat the expensive stuff you cannot beat the bottom up approach in terms of how accurate or how uniform your nanomaterials are.

Obviously this is relatively economical method very comparatively cheap I want to say very cheap because there are expensive methods as you will see and then it involves simpler machinery. The process is pretty simple it is basically breaking down a bulk substance into its constituents chunks into it constituent pieces go on doing their same process repeat over and over put a hammer onto a piece of rock and go on do that for 1 day, 2 day finally, it will break into you know it will it will convert itself into some sort of a powderized form powderized form. So, that is basically your top down approach examples high energy ball milling liquid phase exfoliation and the laser ablation method. Let us try to see what they are one by one all 3 of them for example, are kind of trying to do the exact same approach the difference between them are more or less subtle at the end of the day all 3 of them do exactly the same thing break down a bulk into its constituent chunks constituent's constituent pieces.

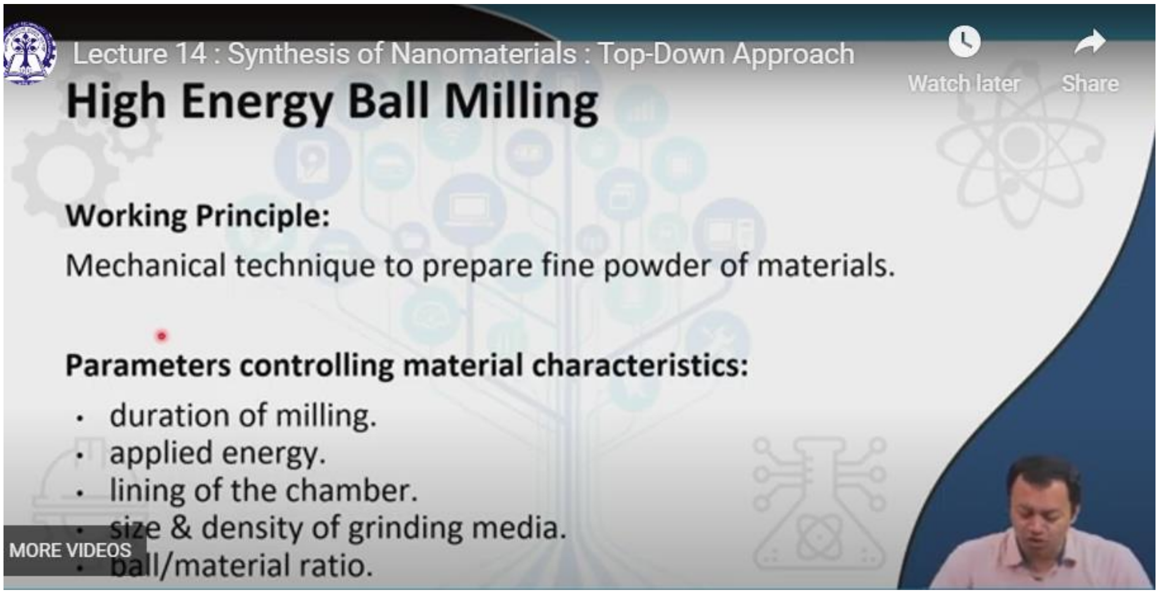


So, in the first case it is high energy ball milling it is by far the simplest way nanomaterial synthesis is done typically metals and alloys are you know created into their nanostructure ah constituent nanostructure using high energy ball milling you put hardened steel or tungsten carbide balls the balls have to be very very strong you put your sample in between them you put your sample and using these balls apply some mechanical force into this.

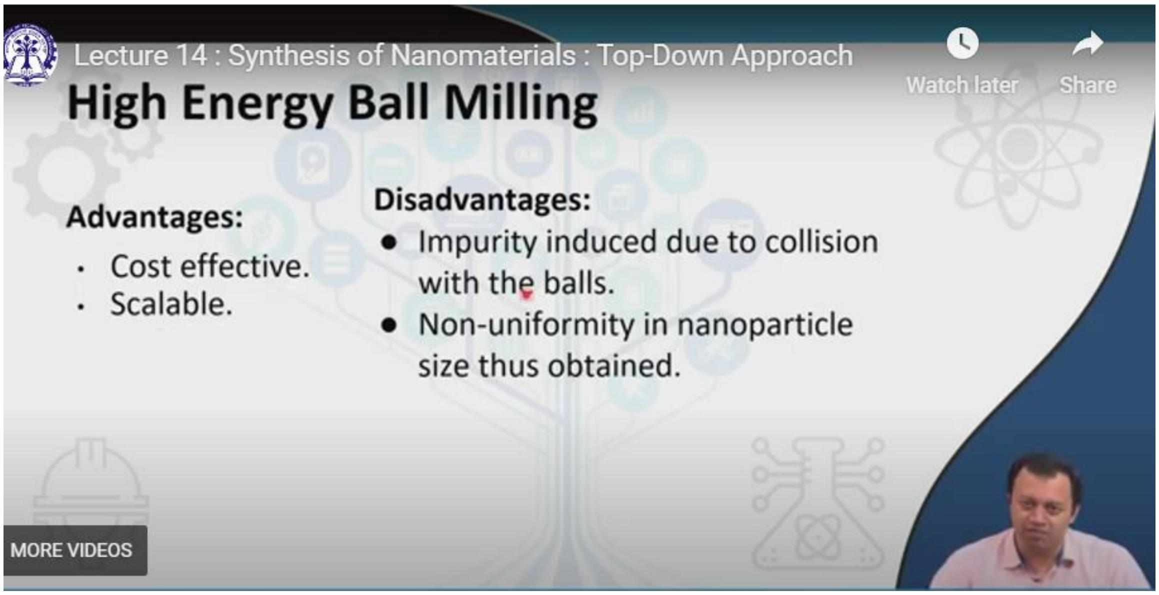
So, called mortar pestle you must have seen we use it in our kitchen where big pieces of spices cardamom ah all those all those spices etcetera I am forgetting the English name of most of the spices right now ah those things are crushed you also have mortar pestle or you have those things in which you know our mothers my mother used to put 3 or 4 different ah spices like cardamom and ah clove and the bark the cinnamon yeah right cinnamon barks etcetera and then break it down this is a high energy highly sophisticated version of that this is like a mortar pestle you need to have hardened steel or carbide balls you need to have something that is strong itself because you will be pounding you will be crushing your sample ah for a longer period of time. So, what you are crushing with has to sustain it cannot break down or it cannot convert itself into nano material itself and the mass ratio of those those those hardened tungsten balls with respect to your sample is 2 is to 1. So, less amount of sample more amount of this hardened balls they are put inside of a closed chamber and then you keep on pounding you keep on giving mechanical force and thereby your your your your material breaks apart simply mechanical force simply hammering it simply using some kind of a hammer chisel mechanical processes in order to break it down right.



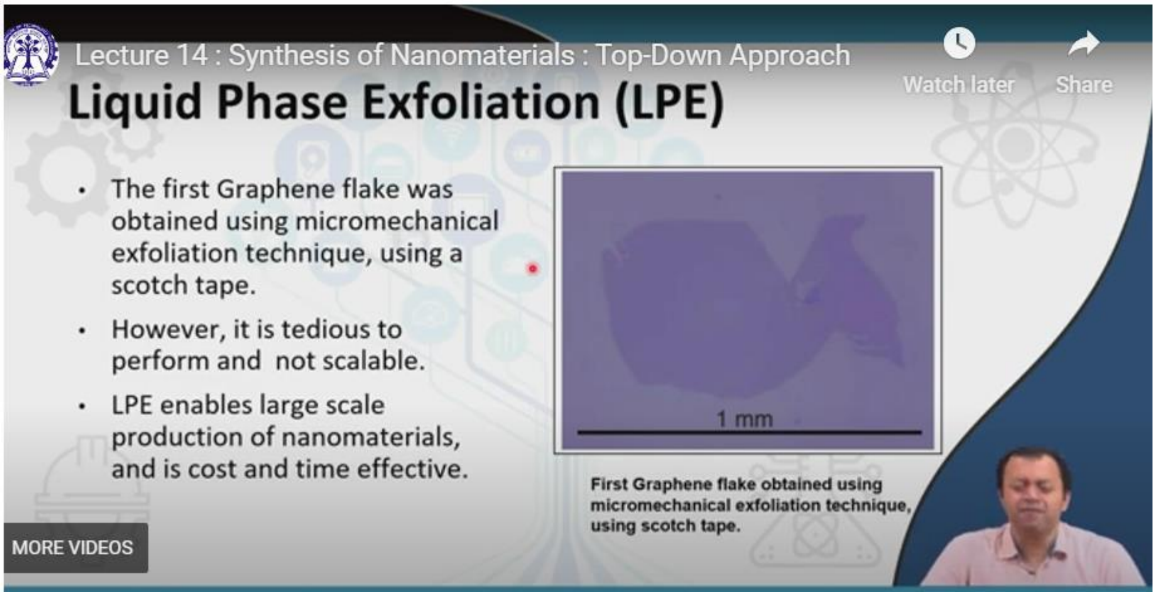
There are several types of ah these hardened balls that could be used stainless steel tungsten carbide glass and ceramic hardened glass remember you have also have bulletproof glasses and the motion that you will use rotary motion vibratory motion tumbling motion determines the above all speed the relative uniformity relative accuracy of the materials that you are breaking down right you do not need to always do it like that you need to ah tumble the system you need to rotate it you need to shake it ah you need to put some sort of a vibration in between all of those things are ah created and it is a simplest possible way to break something and create it into powder remember in the beginning I said something about the 3D nano materials. So, these are something that create a 3D nano materials most often than not none of the particle sizes have ah either the length breadth of height within nanometer scale range within less than 100 nanometer, but it is a start it is a beginning you start with it then you add some more a different material you crush material A you crush material B combine them together try to do some kind of a nano chemistry in between and then they can combine and they create some kind of a third material material C.



So, this technique is viable this technique believe you me is used more often than you think not everybody or every research institute university of college can afford to have highly sophisticated clean rooms and photolithography machines and molecular beam epitaxy, but it should not deprive them of ah working in the field of nanotechnology. Moral of the story anyone with just a chisel and mortar can start working with nano materials as a nanotechnology you create nano powder powderized form of different bulk materials and then try to create chemistry of material A with material B and then try to see what could be done. As I said the working principle is simply mechanical technique to prepare fine powder of material the parameter that controls the material characteristics are simply how long you have been doing this how long you have ah pounded it how long you have ah produced the force how much energy each pound have been utilized ah obviously, the chamber how the lining of the chamber how compact the machine the material is being hold holding the size and density of the grinding media how much amount of those hardened steel balls you have put and obviously,



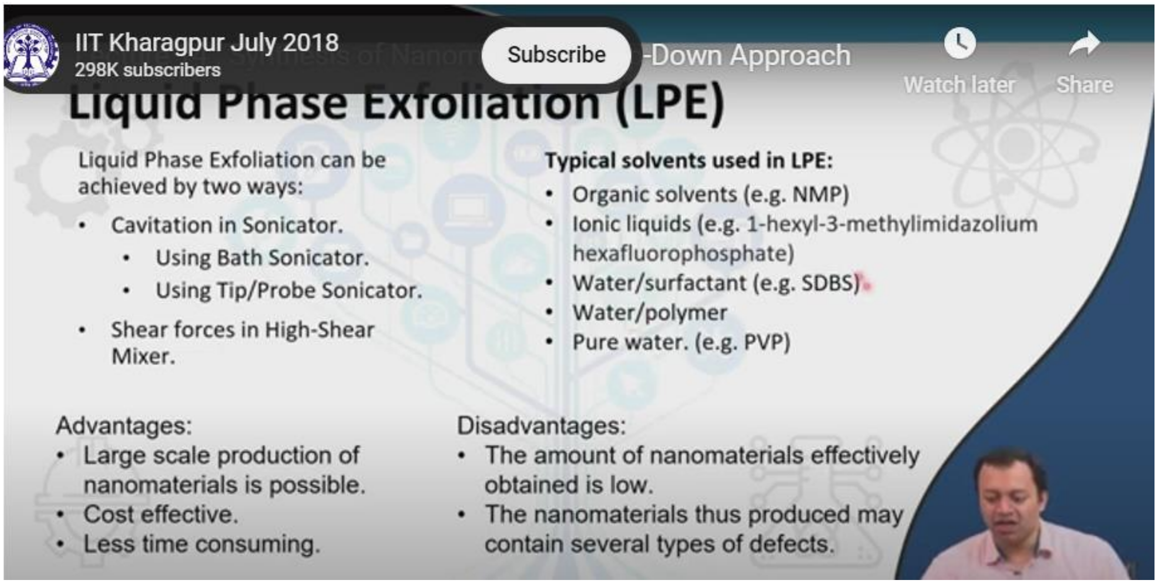
the ball to material ratio the material has to be less amount 2 is to 1 ratio that the ah advantages are obviously, cheap all you need is a mortar pestle and it is very very scalable if you have 10 mortar pestles at a time and you have either electrical pounds or you have a human being who is willing to do that. So, 10 mortar pestles can produce 10 different type of nano materials at parallel and then you can mix and match them and create some kind of an artificial material. The disadvantage are obviously, non uniformity ah and lots and lots of impurities lots and lots of impurities some amount of collision from the balls materials from the ball starts ah going inside it then lining of the chamber then the pound that you have used that is going to affect if you are putting it in a non sterilized and non clean room environment then dust particles any other impurity can fall in and the result is obviously, non uniform ah, but still it is cost effective it is ultra cheap and you can create if you have enough time money and energy kilos of nano materials kilos of powders start breaking start take a bulk material and then ah simply pound it into powder and store that powder and start selling it if you if you want to be profitable.So, high energy ball milling simply utilizes mechanical force to break a bulk material powderize a bulk material



then comes liquid phase exfoliation as I said it will be quite similar ah how many of you have heard of graphene you might have heard, but how many of you actually know. So, graphene is a single layer of graphite what do I mean single layer. So, graphite material is so called Van der Waal material in which the carbon the carbon atoms are arranged mostly in hexagonal structure. So, it is a layered like structure 6 carbon atoms 6 carbon atoms 6 carbon atoms form a sheet a sheet like a piece of paper a sheet like simply a piece of paper. So, there is one sheet there is another sheet just below there is another sheet just below and so on and so forth up till infinite.

Now, the force by which the carbon atoms are in plane in plane is very strong, but the force by which the carbon sheets are vertically stacked are very weak Van der Waal forces this is covalently bonded this is Van der Waal bonded Van der Waal is simply fluctuation of electrons that allows it. So, you have stack right like playing cards you know playing cards considered you have made a stack of a playing card large stack of playing card or large stack of papers just one on top of another the paper in this direction is strong you will need some effort to tear it, but if you have stacked your playing cards or stacked paper like this you can simply blow from your mouth some wind and it will go away. Liquid fluid liquid phase exfoliation tries to do something example liquid phase exfoliation has been done in non-Van der Waal material as well, but the fact of matter remains that if you have some kind of a structure like that for example, graphite it is possible to produce enough mechanical energy. So, that these sheets which are very loosely bound to slide off and then you just take one paper one playing card one sheet of that carbon atom and utilize it that carbon atom that sheet of carbon atom has a finite length and finite breadth, but the thickness is just one atom thick and that is your graphene. The very first method in which graphene was made from graphite was using a scotch tape method the cool name for it is micro mechanical exfoliation that is the term what they did they put a cellotape just a cellotape on top of a graphene layer and just peeled it after doing the peel enough time you have peeled certain certain amount of graphite flake will come up into this into this ah cellotape of your scotch tape of yours you then again press it again take it up this this flake will further divided into few pieces keep on doing this keep on doing this bring in another plate stick it and take it out after you know fifth or sixth or tenth attempt you can create your single layer graphene that was the easiest way and the very first way in which graphene was made a scotch tape method in which a single layer of ah graphene was made try it yourself you can do it all you need is a sharpened pencil the nib of pencil contains graphite you need to have a good enough cellotape a scotch tape there are enough videos in the social media internet which teaches you how to it is very very easy and then put it under a microscope and you will see some kind of an image like this which is having a finite length finite breadth what is the thickness, but the thickness is simply one nanometer and you can actually see it under a microscope you can even see it if it is big enough using naked eye it has a purplish color it is not black as as graphite generally is.

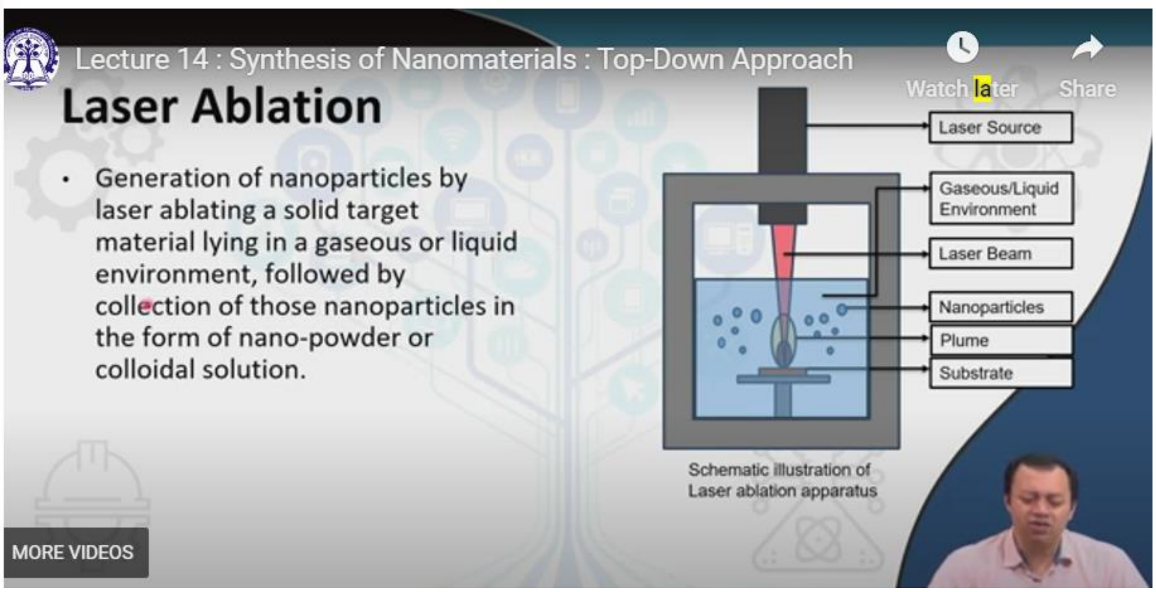
So the point being here is if you want to make large amount of such you know two dimensional material graphite material two dimensional because it has a length and breadth 2D the height is in nanometer scale, but if you want to make a large area if you want to make you know 10000 of this you cannot always use scotch tape you cannot always you know start breaking it up. So, we use liquid phase ah exfoliation to create large scale production of nanomaterials right large-scale production of nanomaterials what it does well you need a sonicator it is a vibrator right. So, it is a bath sonicator or a tip probe sonicator where you put your sample in some kind of a solvent, solvent is the liquid thing organic solvent ionic liquid water ah anything pure water surfactant I have used acetone I have used isopropyl alcohol put some amount of graphite material etcetera put it in some sort of a sonicator. Sonicator of those things you might have seen in hospitals or ah even pharmacist even chemistry lab has this. So, it is like a box like thing and you switch it on and it vibrates with ah sonic sound.



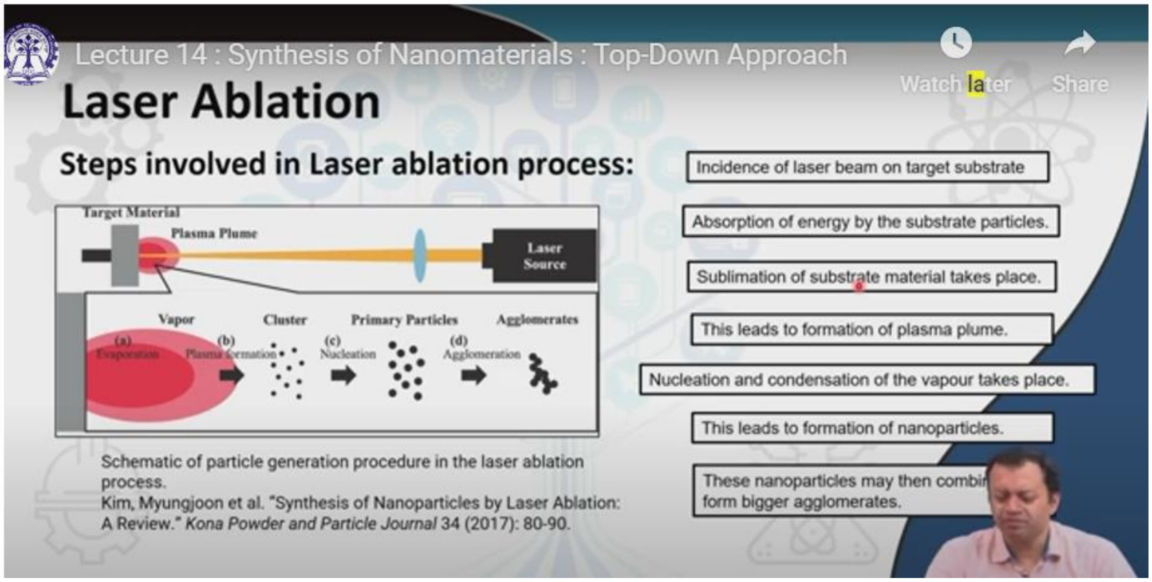
So, it is making this high pitching sound and the thing simply ah vibrates at a particular heart at a particular frequency. There is also tip type tip sonicators available they vibrates ah you have a beaker in which liquid material is present IPA isopropyl alcohol acetone water you have put your material you put your sample which you want to ah sonicate which you want to break there is a tip like structure that keeps on churning in chemistry laboratory it is very easy that keeps on churning that will go on churning for like 1 hour 2 hour 24 hours 38 36 hours etcetera. And with that shear force with either this vibration using the bath sonicator or the churning of the tip or probe sonicator ah your material will be broken down into smaller and smaller pieces as I showed you in the previous case even one atom thin materials right. Especially if you have layered structure like that they are stacked right and you have put it and then you are probing it churning it or you are simply ah vibrating it using a sonicator it simply breaks down into individual sheets then you can ah filter them out and thereby you can get ah individual sheets or couple of sheets accuracy is ah under question, but you can have that ah have some kind of a nanomaterial and it is very very cost effective I have a bath sonicator in my laboratory which cost me ah 4 to 5000 Indian rupees which will be less than 20 25 dollar US right. And all you need an electrical connection a beaker some amount of solvent like water or acetone or ah isopropyl alcohol big chunk of graphite that is also cheap you just put it and switch it on for 24 hours 48 hours and finally, it will settle down which you filter out and if you are lucky you will find some pieces which are big enough, but very very thin.

Again I keep on repeating this accuracy how much of that you will get or the the the uniform shape size is is something that you will have to compromise on. Large scale production is possible you produce you keep 10 different bath sonicators put a beaker with 1 litre of liquid solvent and 1 gram of that ah material which you want to break down into and switch it on if you have electrical connections that is it cost effective. Comparatively less time consuming now there is a debate regarding whether this is less time consuming than the previous one in both cases I have seen 24 hours is required, but maybe it is my material ah I want you to look into this. The disadvantage of the method is the amount of nano materials effectively obtained is low because even after breaking down these individual sheets they tend to coagulate. So, at the end of the day what has broken down and settled at the bottom of the beaker have simply started merging together.

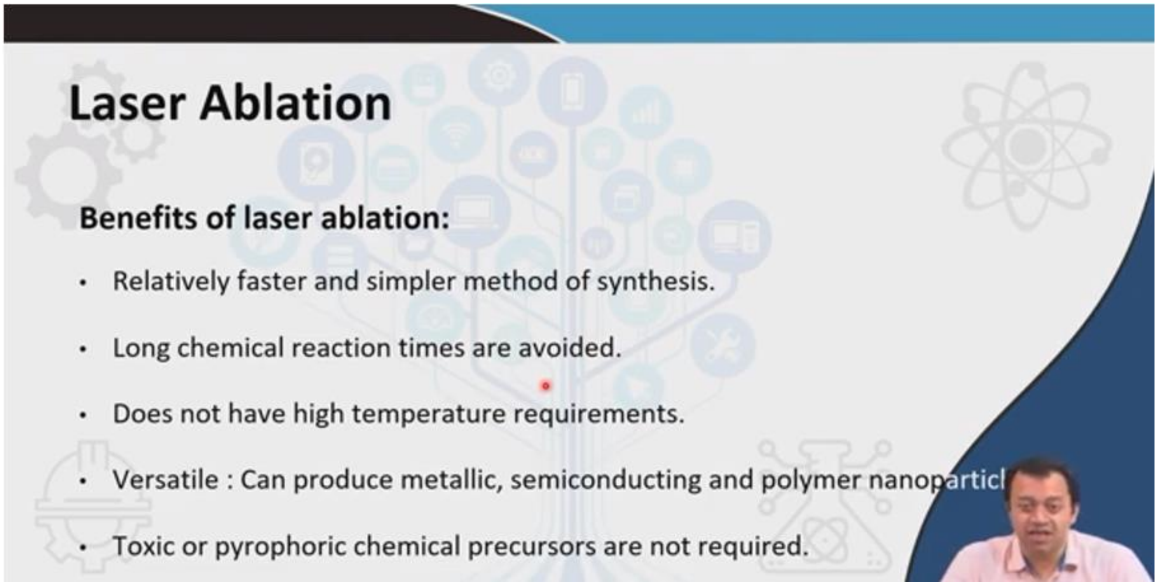
So, you have big clunks that you need to redo and redo and keep on doing it and of course, the nano material thus produced has huge huge amount of defects several types of defects they have broken each sheet is breaking down it is falling into another and churning and then there is tearing shear forces from both sides you are producing a substantial amount of energy. So, this might break most definitely, but can you guarantee that there will be no problem in this direction it is very strong scovalent bond, but you keep on giving more and more energy to it sooner or later some sort of ah shear stress is going to break the entire thing right.



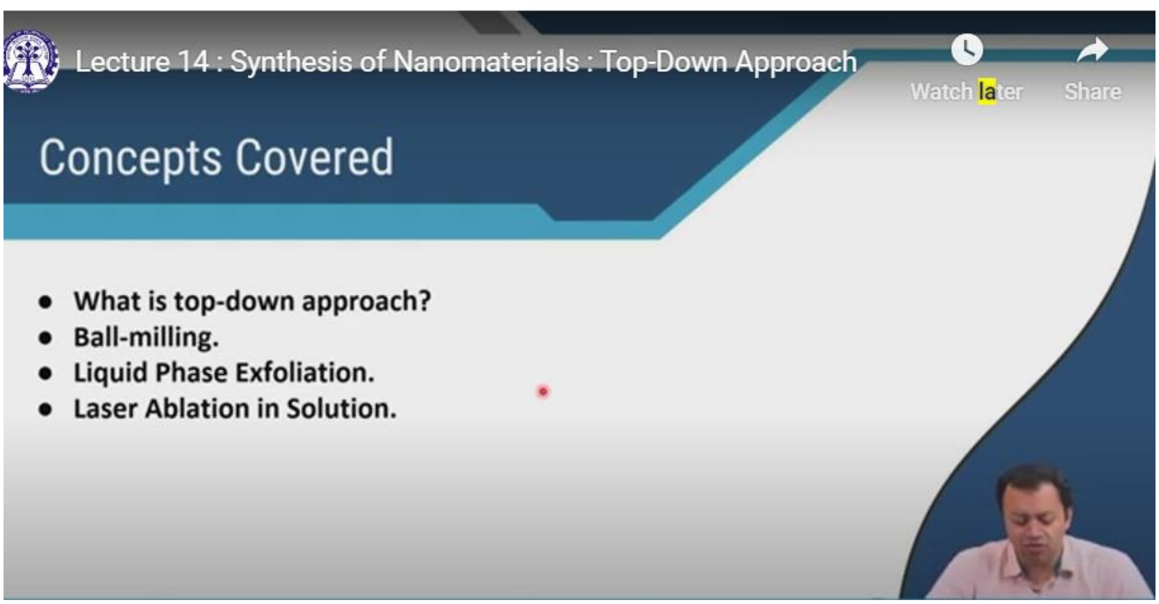
The final one I want to discuss is laser ablation this is bit more sophisticated bit more accurate it is generation of nano particle by laser ablation by keeping a solid target material lying in a gaseous or liquid environment for which you are heating with a laser. So, you it is exactly the same like last type you had a beaker liquid material and keep on churning for like 2 days 3 days here instead of churning you heat the material with a laser light a high power laser hits the material in the liquid the material absorbs ah the light energy breaks down the broken part the clunks the pieces they are simply collected in the liquid media and then you filter it out yeah followed by collection of those nano particles in the form of nano powder or colloidal solution. So, you have a laser source this is a fixed chamber to prevent impurity from coming this is the laser beam you have the liquid and this is the material that you want to break down into the laser is constantly heating it and the laser light is being absorbed by the constant molecules they are absorbed they break it down and the chunks are collected.



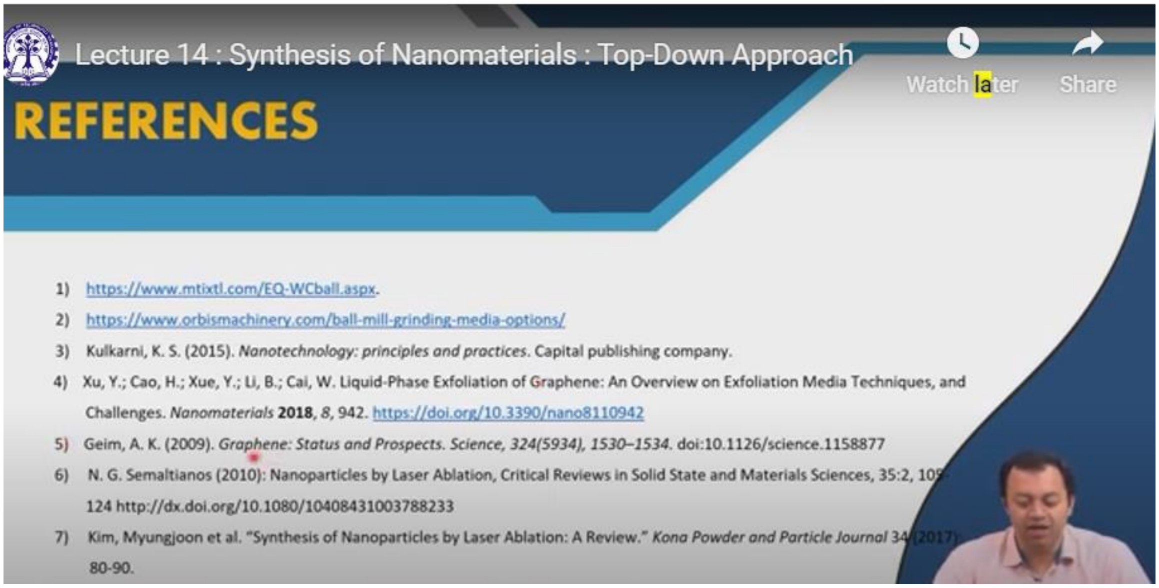
So, it is again more or less pretty simple if you go through this incidence of laser beam on target substrate absorption of energy by the substrate particle then the sublimation sublimation is when a solid convert into vapour without going through the liquid process this leads to formation of plasma fume plasma plume and you have you know small cluster they again combine for stability reason and they create this final product is this agglomerate and that can be utilized as a nano material. These nano particles may combine and form slightly bigger agglomerates you will break it down into smaller particles for smaller particles and then the small particles will combine together then this smaller particle will combine together to form a slightly bigger slightly bigger than this target material slightly bigger agglomerate conglomerate or however you want to say it and that is basically it that is how we do laser ablation at the end of the day a bulk material is hammered is broken down into its smaller constituents you can either simply hammer it down or you can turn it vibrate it down or you can shine laser light on it the laser will be absorbed and it will be broken down.



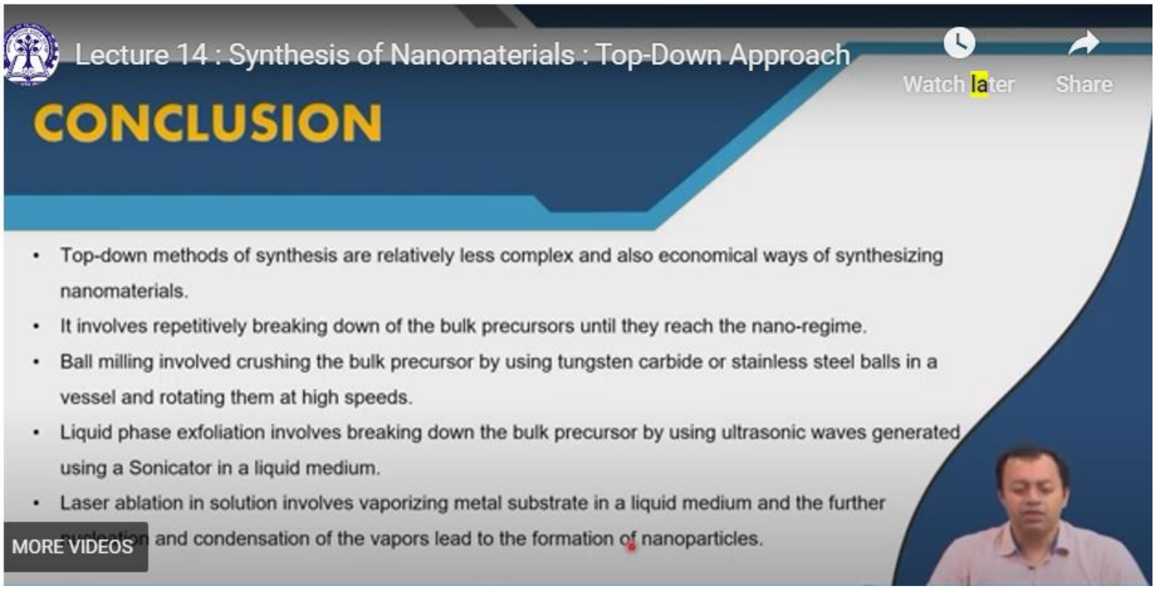
So, the benefits the comparative benefits of laser ablation are simply that they are relatively faster and simpler method you switch on the laser and that is it long chemical reaction times are avoided do not have high temperature requirements its light being getting absorbed a versatile it can work on metallic semiconducting and polymer nano particle as long as your laser is being absorbed by your material that you want to break down that is basically no type of chemical reactions precursors are required, but you technically do not require chemical precursors in the previous two cases as well. So, yeah that is one other advantage it is all mechanical rather than chemical at the very first stage the chemistry comes at later when you have got nano particles and then you are combining them together. So, overall we come to the end of this session I think I have given you enough information on the cheap way to create nano materials these are by far the simplest and the cheapest way, but the accuracy the uniformity the purity of the material has to be questioned.



So, if you are actually making a integrated circuit that is going to power your new computer perhaps these methods are not suitable, but then again IC design takes a huge several different steps maybe you can sneak in couple of these methods into couple of steps it depends. Usually the more sophisticated output you are trying to get the more sophisticated input technique you have to utilize that is the general rule everywhere no exception in nanotechnology.



So, these are my references kindly go through especially these chapter number 5 reference number 5 where the the guy who got the Nobel Prize in physics for creation of graphene talks about the status and prospects though it is an old paper, but still it is fantastically reading at least if you are a beginner in nanotechnology know want to know about graphene then I cannot recommend reference number 5 enough please go through it. List of them are also there if you are interested in laser ablation how laser ablation does there are bit more sophistication to that go through this paper.



So, these are the final conclusions that I have and I will see you in the next class. Thank you very much.