Chemical Engineering Principle of CVD Processes
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Module-5
Lecture 29
Basics of Nano Structured Material Synthesis: Part 1

Welcome to the 29th lecture in our particle collector (()) (0:15) course. The first couple of lectures in the past couple of lectures we have been looking at methods of characterizing the chemical and compositional properties of particles and initially we started by discussing microscope these methods than looked at techniques for organic materials and then in the last class we discussed to techniques in little more detail atomic force microscopy and the x-ray diffraction analysis and I mentioned that the importance of the analysis technique becomes increasingly evident as particle sizes decrease and when we get into the Nano size range it becomes extremely critical that we use the most appropriate method to analyze these particles.

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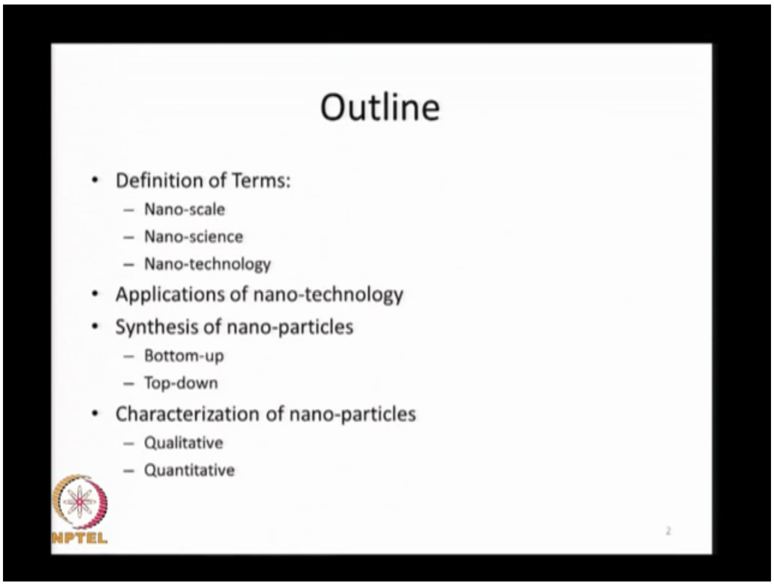

Now before we start discussing methods of characterizing nano particles I want to take few minutes to talk about some basics of nanotechnology including methods of synthesising nano particles, methods of dispersing them in suspensions and finally characterization of various properties of nano particles and nano suspensions. Now the reason that is important for us to spend some time discussing the basics of nanotechnology is that.

Nano is like the proverbial Elephant and the blind men, it depends on what aspect of nanotechnology you deal with you have a very different perception of what nanotechnology is, so it is very important to have a more common understanding of what constitutes nanotechnology. So the outline of this module is going to be as follows, we will begin by defining some terms what is nanoscale? What is nano science? What is nanotechnology?

We will talk about some applications of nanotechnology, methods of synthesising nano particles from the bottom up approach and the top-down approach and finally characterization of nano particles which we classify as qualitative methods and quantitative methods.

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So what is nano? You all have seen the car that is made by Tata, is the nano, you know does it fit the term? Is it really nanotechnology? It is small but is that sufficient to qualify as nano in the way we perceive nano, you know nano gives a connotation of something that is technologically very advance, something that is state-of-the-art, is nano representing that? I think so. I think the Nano car when it was introduced did represent the huge breakthrough in Manufacturing technology if nothing else. So I think it does fit the label of Nano very well.

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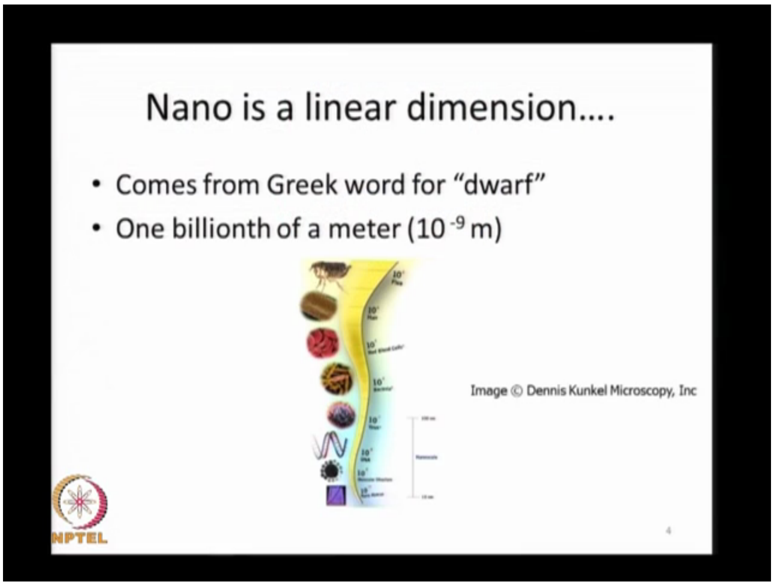

But what is nano? It is a dimension, it is nothing more and nothing less, nano is a linear dimension, it is actually derive from the Greek word for dwarf, so clearly the connotation of small size is there and it is one billionth of a meter or 10 to the power minus 9 meters. Now just to give a perspective of what that is, if you look at various objects that we encounter in life and look at the dimensions, you know common insect like a Flea is roughly 10 to the power minus 3 meters in length.

A human hair 10 to the power minus 4 meters, blood cells 10 to the power minus 5 bacteria, 10 to the power minus 6, viruses are 10 to the power minus 7, DNA is 10 to the power minus 8, molecular structures are 10 to the power minus 9 and so on. So if you look at this nanoscale the last 3 that is starting from roughly 10 to the power minus 7 to 10 to the power minus 10 is what we would refer to as the nanoscale.

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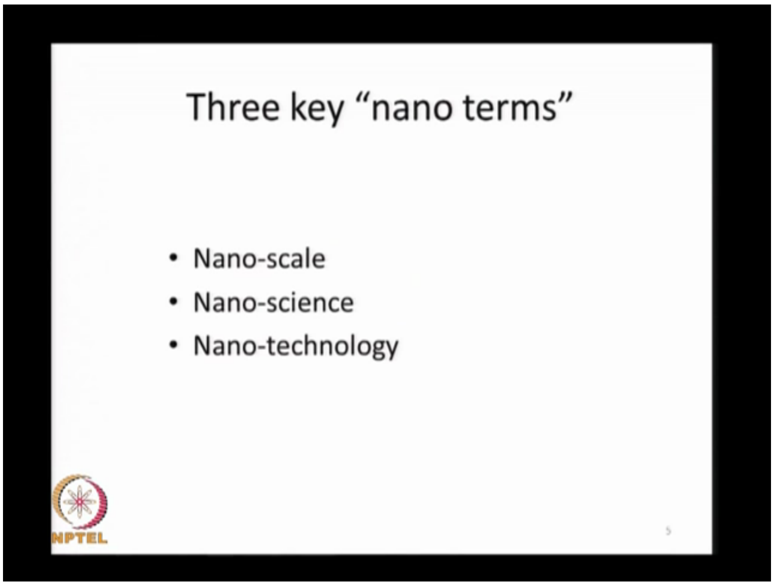

Now there are 3 key nano terms, nanoscale, nano science and nanotechnology.

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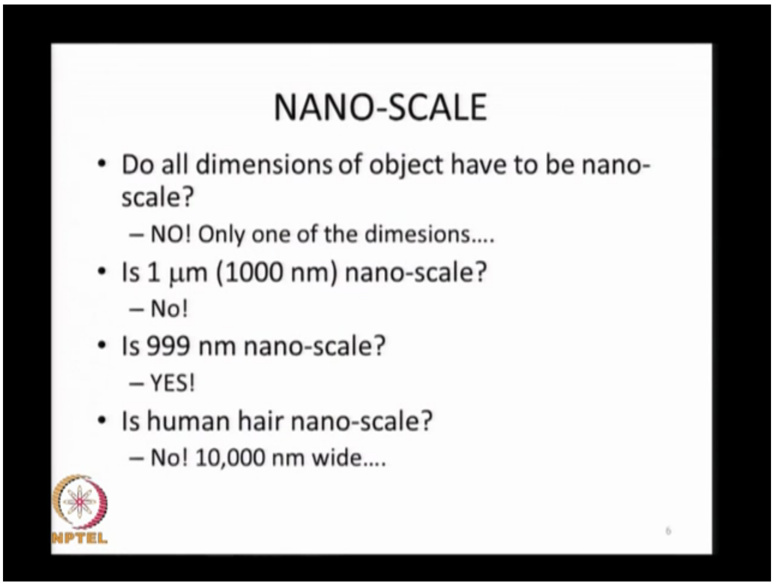

Let us take a few minutes to understand what we saw. When we see nanoscale, do we mean that all dimensions of the object have to be in the nano range, no, not really as long as one of the dimensions sits in the nanoscale we can consider it to be a nano object. Is 1 micron considered a nanoscale, conventionally? No, but is 999 nanometres according to convention, yes. So you know it is not a very clear definition I mean why would you call 999 nanometres as nanoscale and than 1 nanometre more as micron scale? It is just traditionally that is how particles sizes have been referred to and again is human hair nanoscale? No because it is actually very very long compared to the bare dimensionless.

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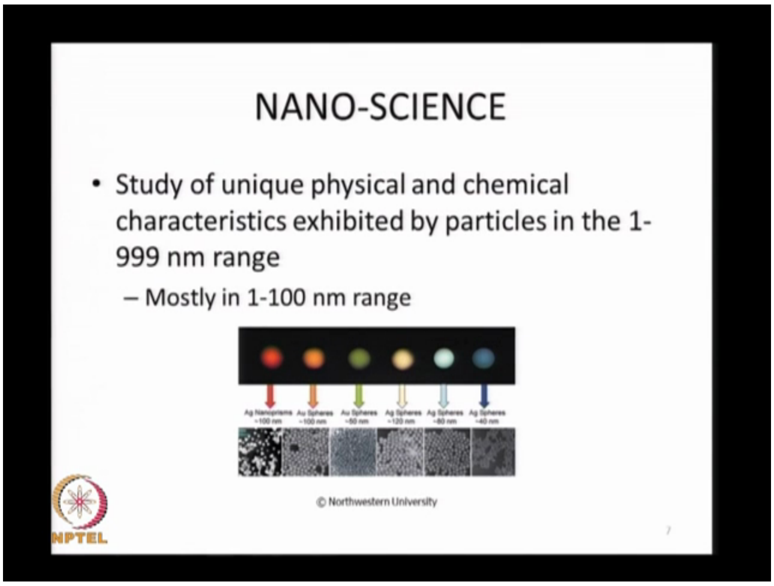

So what is nano science? Any new discovery goes through 2 stages, first you develop the signs of it then you develop its technology. Now the difference between the 2 is, science is something that you do in a lab. It is something that you do in a small scale to really understand the fundamental, physical and chemical properties of the system or material. Technology is essentially scale up.

You take something that you have developed in a laboratory and you scale it up first to a prototype scale than to actual production scale. So technology is essentially translation of science into practice but it starts with science until you develop the science you cannot develop the technology. So nano science is defined as the study of unique physical and chemical characteristics exhibited by particles and the 1 to 999 nanometres range.

Although again by tradition nano is mostly used in reference to the 1 to 100 nanometre range. Strictly speaking it ranges all the way from 1 to 999 nanometres but in practice people use 1 to 100 nanometres as a nano range and you can see some examples of nano materials here silver, gold, spheres and (()) (6:50) and so on. You can see that there are some distinct size and shape characteristics associated with nano particles as well as colour. So these are some of the unique properties of nano particles that we try to exploit in nanotechnology.

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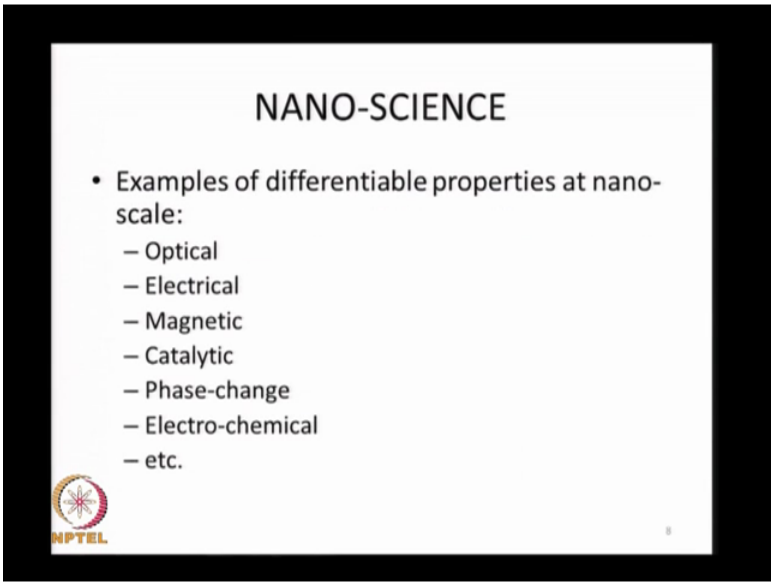

Some of the differentiable properties that you can observe at nano scale differentiable in the sense that these properties are very different at nanoscale compared to the micron scale and these are optical, electrical, magnetic, catalytic, phase change properties, electrochemical properties etc. So we will talk about some of these unique nano properties later in this module.

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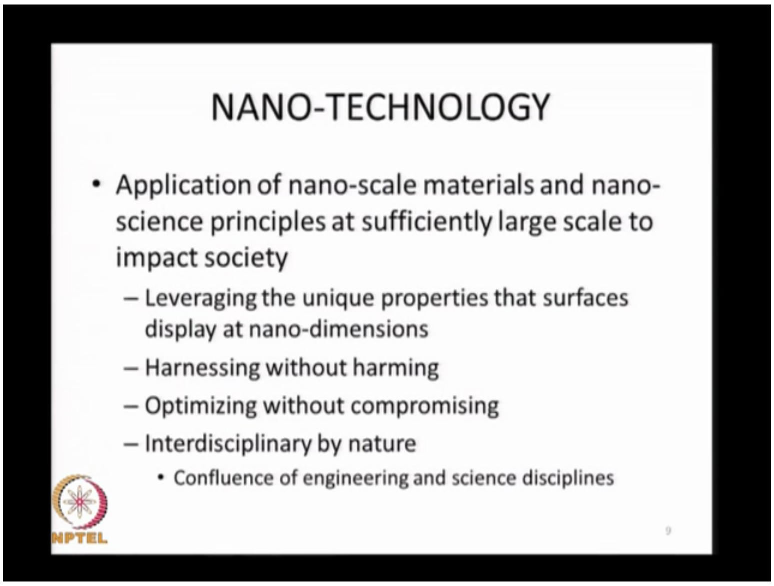

So what is nanotechnology? It is the application of nanoscale materials and nano science principles at sufficiently large scale to impact society. In other words you do not let nano just be something that people play within their laboratories, you try to make useful products with it that actually have a commercial value to the consumer at large and that is what is known as nanotechnology.

So leveraging the unique properties that surfaces display at nano dimensions, characterizing the unique properties is nano science, leveraging or making use of such properties is nanotechnology. It is to learn how to harness nanotechnology without harming the environment. Many concerns about use of nanoscale materials including their possible ecological environmental even human health aspects.

So technology when you start using nano in a large-scale you really have to start worrying about these possible consequences. So that is part of nanotechnology, optimising without compromising, as a technologist someone who is trying to do scale up through large volumes your focus should always be on optimising the process. In order to get maximum throughput at highest quality with minimum energy expenditure at minimum cost and so on.

But at the same time you want to do this without compromising the functionality of a random material you are making, you do not try to cut costs by truncating the usefulness of the nano materials. So that is again a part of nanotechnology. Now nanotechnology is very interdisciplinary by nature unlike nano science. You know, if you look at nano science that is still being primarily driven by physicist and chemist.

However if you take nanotechnology the physicist and chemist are still involved but engineers are virtually every discipline are also involved. So (()) (9:31) a confluence of various engineering and science discipline that drive nanotechnology.

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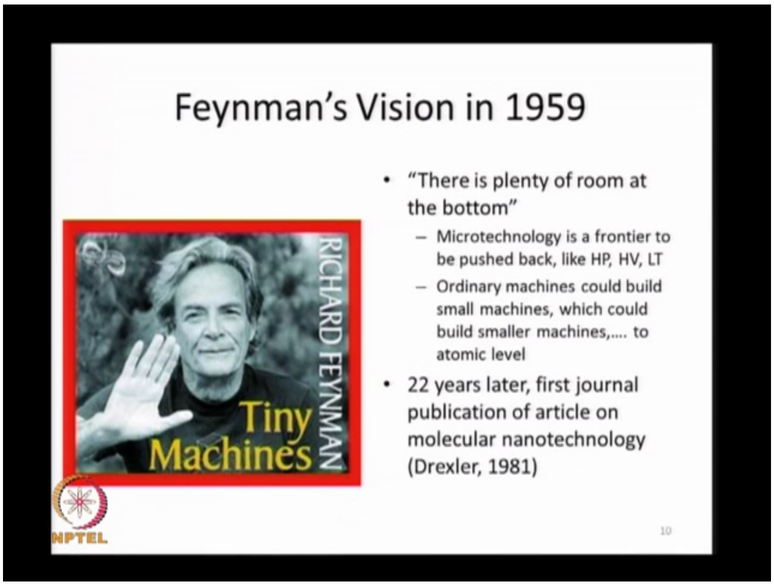

What is the history of nano? Well actually started back in 1959 when Richard Feynman stated his vision of there is plenty of room at the bottom. He said he can always keep driving technology to smaller and smaller dimensionless basically he said that microtechnology is a frontier that we need to keep pushing back just like high pressure, high vacuum, low-temperature etc. So his thinking was micro is small but we can get smaller. So let us keep pushing the boundary.

His vision was that we can make machines that build smaller machines that builds even smaller machines all the way down to atomic level and to a large extent what we have done? You know I mentioned yesterday in the last lecture that the atomic force microscope is one that can be used not only to characterize surfaces but even to manipulate surfaces. It can be used to manipulate atoms.

So essentially we have built the machine that can manipulate matter even at atomic level but there was a big gap from 1959 to 1981 nanotechnology was really not taken up seriously as a subject of investigation. Fact it was in 1981 that the first journal publication of an article on molecular nanotechnology was published by Drexler.

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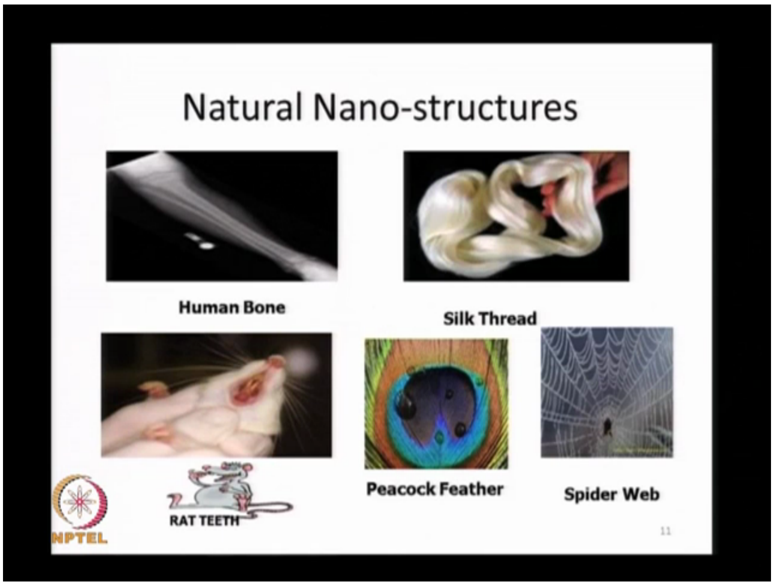

Now if you look at nature there are many many examples of nanostructures there is a human bone, silk, rat’s teeth, peacocks feather, spider web are all classic examples of structures that have nano dimensions at least in one scale.

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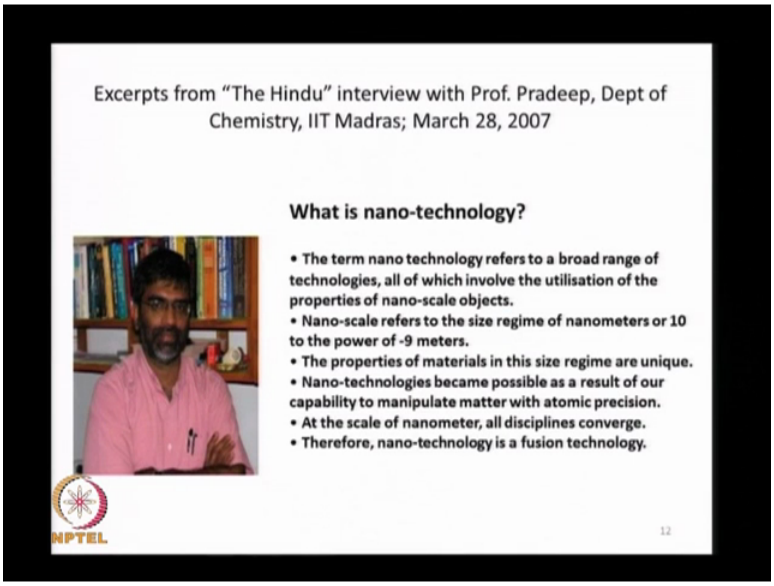

Now IIT Madras has been one of the leading research institutions in nanotechnology and Professor Pradeep in the Department of chemistry has done a lot of work in this area. This was an interview from him in the Hindu newspaper in 2007 defining nanotechnology. The term nanotechnology refers to a broad range of technologies all of which involve the utilisation of the properties of nanoscale objects, the unique properties of nanoscale objects.

It refers to the size regime of nanometres or 10 to the power minus 9 meters. The properties of materials in this size regime are unique. Nano technologies become possible as we developed capability to manage let matter with atomic precision. At the scale of nanometre or disciplines converge therefore it is a fusion technology or interdisciplinary technology.

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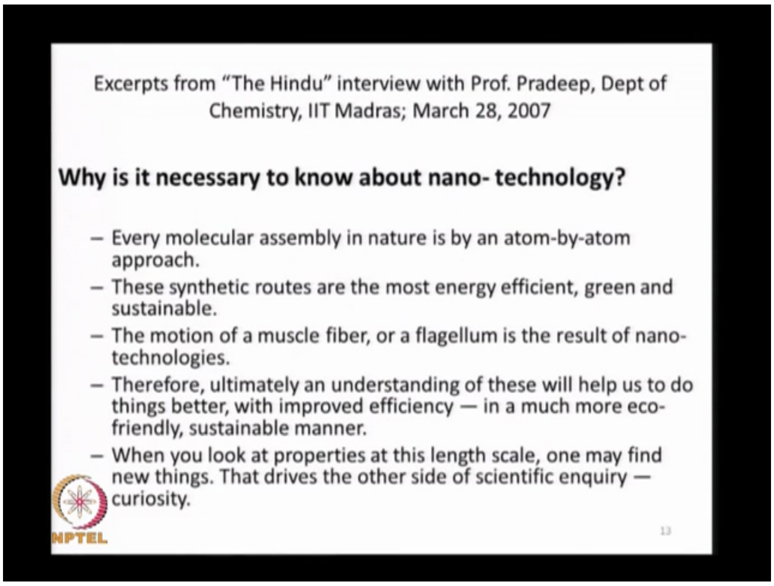

Continuing with the same interview, why is it necessary to know about nanotechnology? Because nature is nano, every molecule assembly in nature is basically is built up by an atom by atom approach. These synthetic routes are the most energy efficient, green and sustainable. The motion of a muscle fibre or a flagellum is the result of nanotechnology. You know, if you look at how the human body works it is amazing you know, it is all down to the nanoscale.

Therefore ultimately an understanding of these will help us to do things better with improved efficiency in a more eco-friendly and sustainable manner. Also when you look at properties at the nanoscale there are many many new things to find to discover. So our spirit of scientific enquiry can also build curiosity is another thing that makes nano very attractive as an area to work in.

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More recently in January 2011 there was an interview that Professor Pradeep had with The Times of India newspaper where he said from clean water to detecting ailments, nanotechnology holds the key. In fact more recently nano bio is emerged as a very very interesting discipline to work in. Interaction of nanotechnology with biology has produced some exciting results and has been used to create new materials.

This bio Nano Interface which can help solve many problems of water, food, health and environment etc. hazardous and toxic impurities like arsenic can be removed drinking water in a cheap and effective manner using nanotechnology and many of these technologies have now been commercialised and are available in the market at very reasonable prices.

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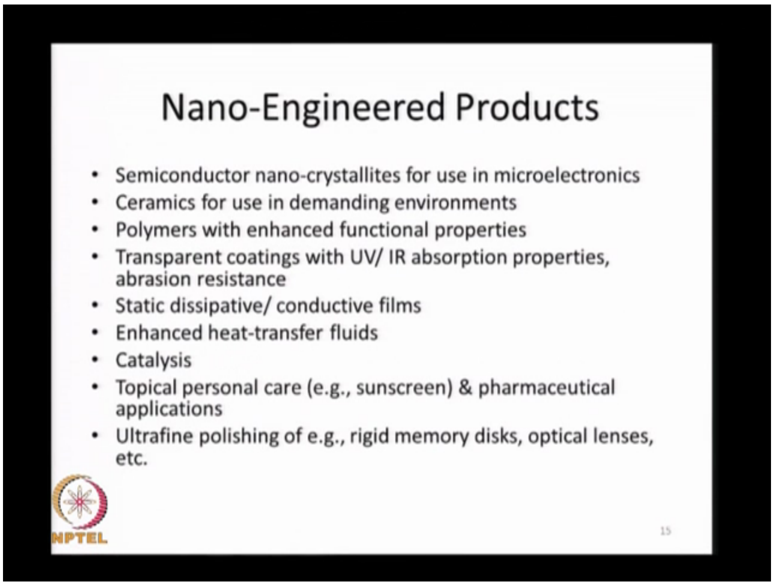

Now moving away from nano in nature, if you look at nano engineered products again there is a huge number of them. Virtually every Manufacturing industry in the world today is impacted either directly or indirectly by nanotechnology. The semiconductor industry where nano-crystallites lights are now being used in microelectronics which actually now we call nanoelectronics rather than microelectronics.

Ceramics that are made for use in highly demanding environments in terms of temperature, corrosiveness and so on. Now use nano materials for improved production. Polymers are being fabricated with enhanced functional properties primarily by making composites of them with nano materials. Transparent coatings with UV or IR absorption properties, abrasion resistance all of these are now being commercially manufactured using nano materials.

Static Dissipative films, conductive films particularly for packaging applications use nano components. Enhanced heat transfer fluids use nano fluid technology, it is something that is finding increased use and again will cover this in more detail later in this module. Catalysis, since catalyst primarily help chemical processes by means of providing extended surface area. Nano catalysts have a huge advantage over large size catalyst materials and therefore nano catalysis is an area that is just taking off. Topical personal-care and Pharma products and finally ultrafine polishing of memory disk, optical lenses etc use nano material is the polishing medium.

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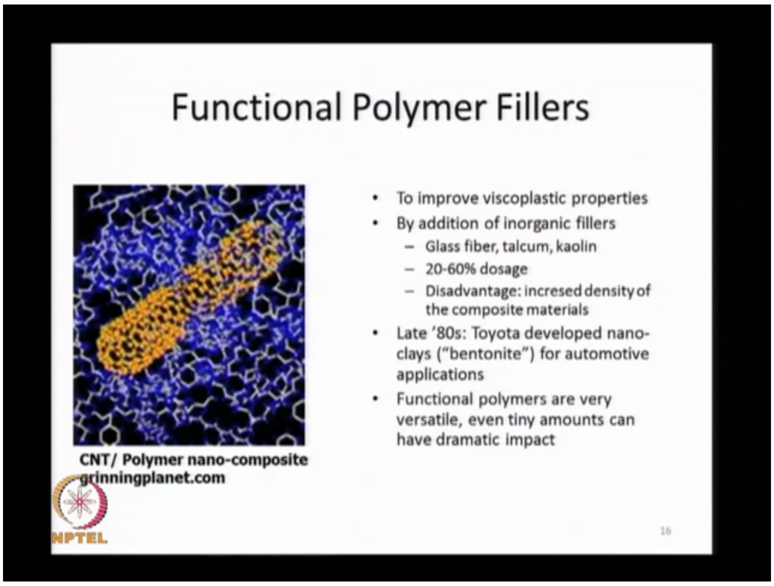

So just to go through some examples of these functional polymer fillers. Carbon nano tube is widely used as filler material but there are others as well. Primarily this is to improve the Viscoplastic properties of these polymers. The fillers are predominantly inorganic materials like glass fibre, talcum and kaolin. The dosage is 20 to 60 percent. However the disadvantage is that there is an increased density of the composite material which can lead to higher weight and when you have applications where the weight of the material is a limiting factor.

Nano composites do have a disadvantage over the pure or virgin polymer materials. One of the first uses of nano composites was the nano clay Bentonite which was used in the late eighties by Toyota for automotive applications. Functional polymers are actually very versatile even tiny amounts can have a dramatic impact. The 20 to 60 percent dosage mentioned earlier is a fairly high estimate and in fact it has been found that the nano materials, the nano fillers can start having an impact even at 2 to 5 percent by volume.

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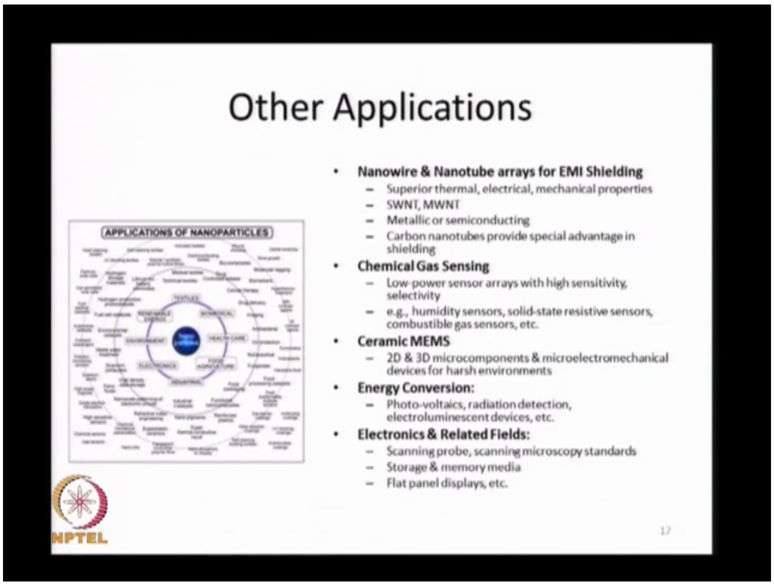

Now there are many many other applications. The applications of nano particles encompass so many different areas industrial, electronics, environment, renewable energy, textiles, biomedical, healthcare, food, agriculture etc and some of the examples are cited here nano wires and nano tube arrays can be used for EMI shielding. Extremely high sensitivity sensors can be fabricated with nano materials for detecting gas leaks, humidity and so on. Ceramic MEMS technology now uses nano materials. Many devices used for energy conversion employ nanotechnology and in the electronics and related fields nanotechnology finds wide usage as well.

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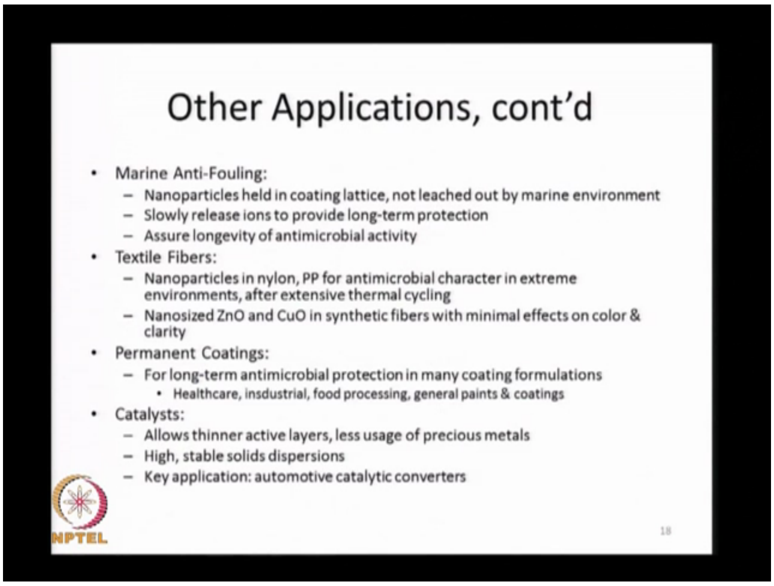

Other applications include Anti-Fouling coatings typically for marine environment. The nano particles are laid down as a layer on the surface and also incorporated into the lattice of the basic material and they actually provide long-term protection by slow-release phenomena and bacterial and anti bacterial or antimicrobial coatings are possible using nanotechnologies.

Textile fibres can be usually improved by incorporation of nano materials example nano particles incorporated in nylon and polypropylene provide antimicrobial but is in extreme environments even after extensive thermal cycling. Nano sized zinc oxide and copper oxide in synthetic fibres provide additional enhancement in properties without affecting colour or clarity.

Permanent coatings can be laid down using nano materials in many applications and again catalyst where we can use thinner layers, less usage of precious metals as possible with catalyst, very high stability solids dispersions can be used while the key application is in automotive converters where increasingly nano catalyst are starting to be employed.

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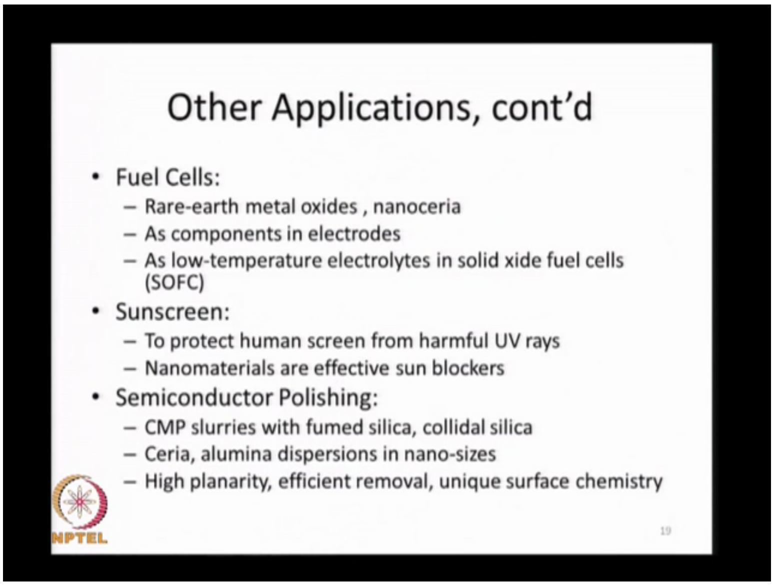

Fuel cell, sunscreen products, semiconductor polishing are all other examples where nano materials are used very effectively.

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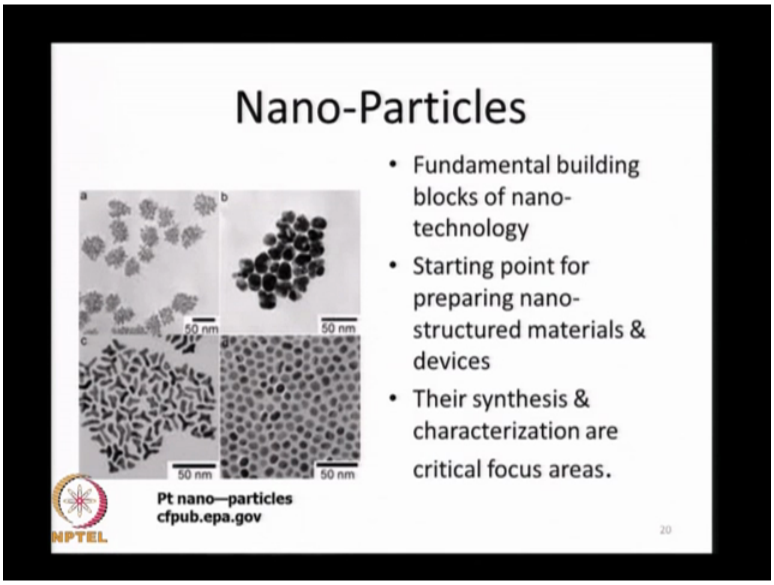

So given that we have this variety of publications that nano material are used in. We have to start with what drives these technologies and the starting points for the fundamental building blocks of nanotechnology are the nano particles. They are the starting point for preparing nano structured materials and devices and therefore their synthesis and characterization are critical focus areas.

In order to be able to control the quality as well as quantity of nano materials you first have to be able to measure them and that is where characterization comes in. Unless you can measure the properties of these nano particles you cannot optimise them for any specific application and you cannot even control the process very well. So synthesis and characterization goes hand-in-hand and so what you will do in this module is first talk about synthesis method and then we will switch over to talking about characterization techniques.

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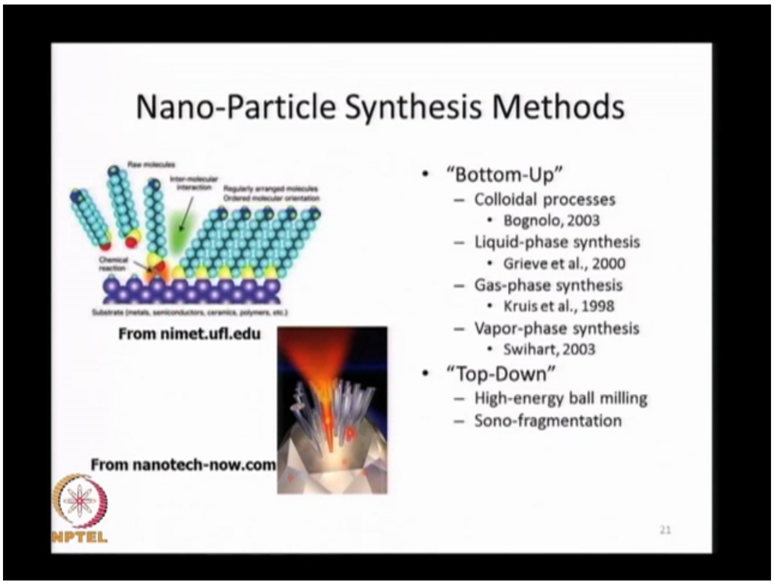

So what are the 2 basic types of synthesis methods? Bottom up and top-down the difference between the 2 is that in the bottom up approach essentially you take atoms or molecules and you tie them together to make nano materials. So it is essentially an assembly process very much like what is done in nature. In the sense that what you are doing is taking these atoms or molecules causing them to interact both physically and chemically.

So by bringing these molecules together we can take advantage of the cohesive technologies to bind them together but you can also take advantage of the enhanced reactivity to make them react in a certain fashion, so that the output that you get is regularly arranged molecules in ordered molecule orientation. So this is a nano material that you can synthesise by using the bottom up approach and there are various methods of doing these colloidal processes, liquid phase synthesis, gas phase synthesis and vapor phase synthesis and we will talk about this in more detail later on.

And then you have the top-down approach where you begin with particles that are larger in size for example micron sized particles and you basically fragment them to produce finer particles. So high-energy ball milling and Sono fragmentation are examples of top-down techniques that are used to synthesise nano particles.

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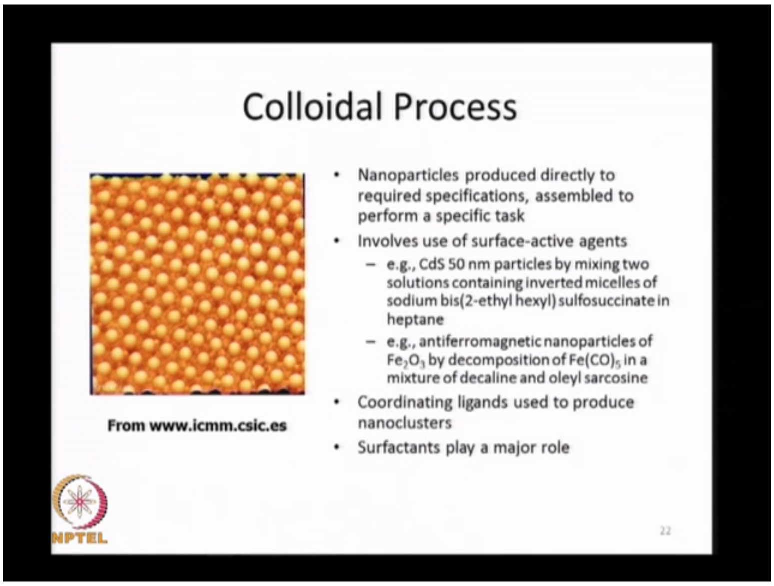

Let's about some of the bottom up approaches first what is a colloidal process? Now in this process essentially you build up the nano material an atom at a time. So you take the specifications that have been laid down for properties of the nano material and you take nano particles and assemble them in a certain way to be able to meet the specifications in order to be able to form a specific task.

So this requires essentially surface active agents, surfactants, coordinating ligands to produce these clusters. So in order to get these nano particles to bind together and make a nano material with specified properties you have to be able to do manipulations at atomic level. So it is a more complex process compared to for example the top-down approach but the advantage is that you have very very precise control over the physical structure as well as the chemical properties of the resulting nano material.

Some of the examples are 50 nanometre particles of cadmium sulphide that is produced by mixing 2 solutions containing micelles of sodium sulfosuccinate in Heptane. Another example is anti-ferromagnetic nano particles of Fe2O3 that are produced by decomposing FeCO5 in a mixture of Decalin and Oleoyl Sarcosine these are examples of nano particles or nano materials that are obtained by taking 2 reactants reagents and mixing them together at molecule scale to produce a nano dimensional material.

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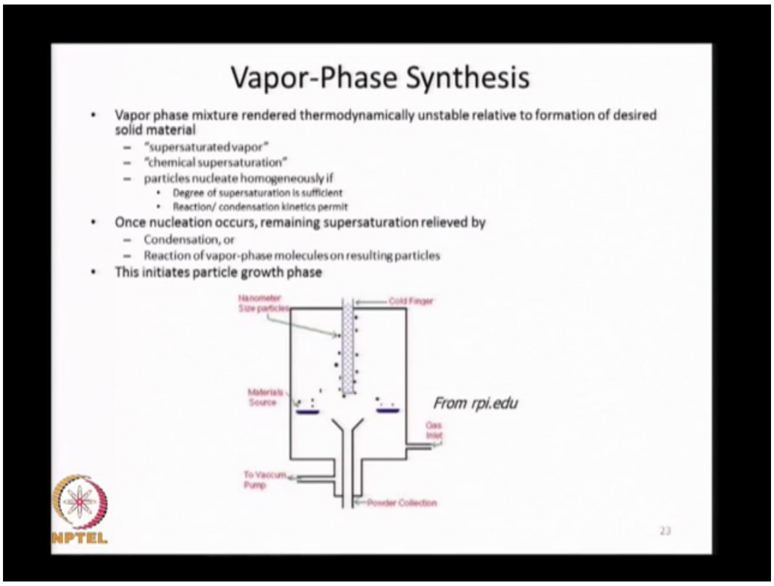

Vapor phase synthesis on the other hand is one that you essentially saturate the vapor phase with the nano material that you are trying to synthesise and then you actually make it thermodynamically unstable and leading to the formation of the desired material.

So the way that you make your saturated vapor phase unstable is essentially by providing sudden cooling. In the example that is shown here this is done by essentially inserting something called a cold finger into this mixture which immediately results in the formation of these nano sized particles from the vapor that is present. So what you do is, you essentially take a saturated vapor or a super saturated vapor and you provide an impetus for nucleation.

Now this can happen either homogeneously or heterogeneously. Homogeneous nucleation happens when you have a sufficiently high degree of super saturation and the kinetics favor the formation of the nano material. So the reaction as well as condensation kinetics should be such that particles can nucleate homogeneously.

Heterogeneous nucleation on the other hand has a much lower energy barrier; it is much easier to get particles to nucleate on a heterogeneous surface. So, for example if you insert this cold finger as it is called which is essentially a cool surface then particles will immediately nucleate preferentially around the circumference of this object at you have inserted. Once nucleation occurs you can relieve the remaining super saturation by condensation or reaction of the vapor phase molecules on the resulting particles.

So the nuclei that are formed start growing by these 2 mechanisms, condensation of the vapor that is still left in the gas phase onto these nucleated particles as well as reaction between the vapor phase molecules and the resulting particles. So this is what initiates the particle growth phase. If you recall that (()) (26:45) model particle size this equation that we have sketched in one of the earlier lectures the nucleation process has to be followed by a growth process in order for the cluster sizes to keep increasing.

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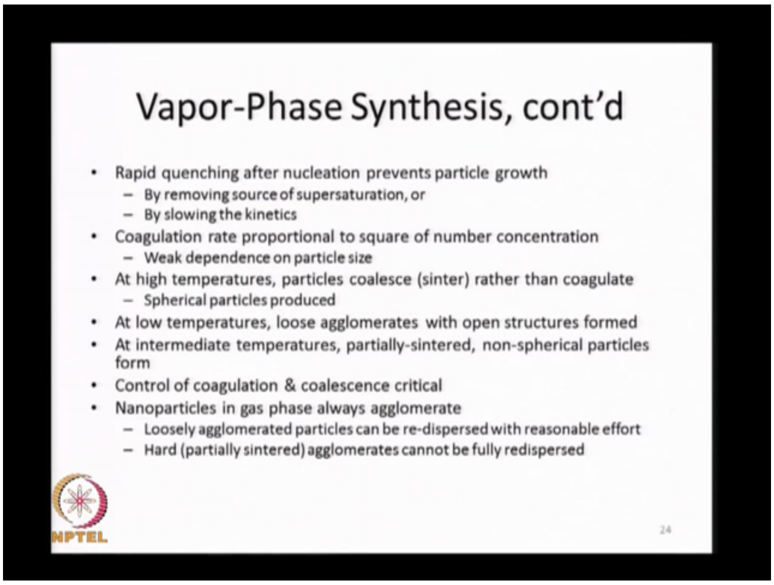

Now sometimes you do not want the growth, you want the nuclei to remain as nuclear, you want the dimensions to remain essentially a few nanometres in size rather than going to tens of hundreds of nanometres need to do is quench the growth, so do not allow the particle growth to happen. Now how do you do that? You have to remove the source of super saturation; you have to immediately shut off the flow of the vapor in order to eliminate the source you have to slow the kinetics of the growth phase.

Now the coagulation rate is proportional to square of number concentration, so the more concentrated the vapor phase is the greater will be the rate at which these nuclei coagulate. So a simple way to reduce coagulation or growth kinetics is to reduce the concentration of the reactive vapor in the gas phase. Coagulation rate is interestingly enough only weakly dependent on particle size when we are doing vapor phase synthesis of nano materials.

As temperatures increase coagulation is replaced by coalesce for sintering. The primary difference between coagulation and coalesce a coalition happens you form loose agglomerates with open structures. At intermediate temperatures you get partially sintered agglomerates which are non-spherical in form. At high-temperature the coalesce dominates you form spherical particles. So control of coalition and coalescence is critical, you can control not only the size of the nano clusters but even the shape of the nano clusters. So the point is coagulation is a low-temperature process and it results in the formation of (()) (28:56-58) amorphous type of clusters.

As you keep increasing the temperature you get more and more crystalline material and if got extremely high temperatures you read coalesced sintered crystalline particles. So depending on what you are looking for, can essentially control the temperature to achieve the structure as well as the size that you are looking for.

Now nano particles in the gas phase always have a tendency to agglomerates as we have discussed extensively in previous lectures. Loosely agglomerated particles can be re-dispersed with some effort but when agglomerates are sintered or partially sintered it becomes very difficult to re-disperse them. So for example if you have particles that are loosely adhered into clusters you can essentially use mixing, agitation or even sonication to break them apart into individual particles and nuclei but at high-temperatures when they have sintered together you cannot use any physical means to really break the cluster apart into its individual components.

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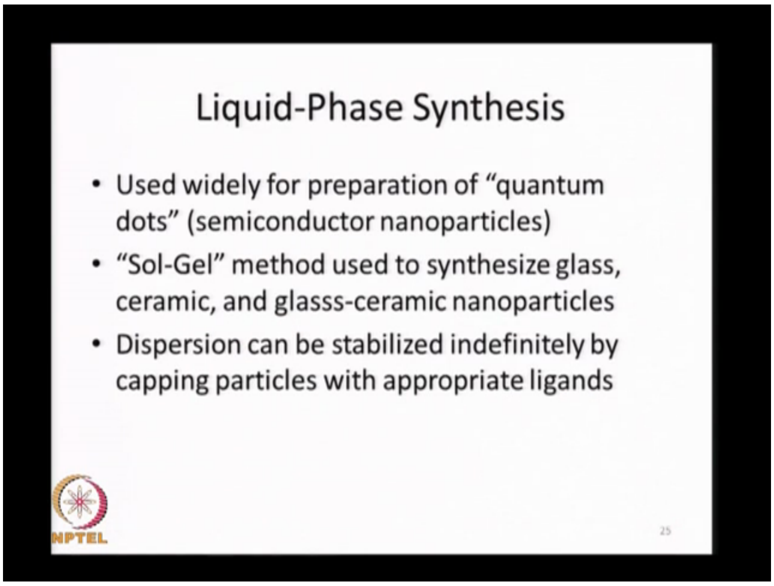

Now liquid phase synthesis is a slightly different technique, the most common example of it is the Sol-Gel method. It is used for preparation of quantum dots which are semiconductor nano particles. The method can also be used to synthesise glass, ceramic is a glass ceramic nano particles. Dispersion can be stabilised here by capping the particles with appropriate ligands.

The difficulty in the Sol gel method is that it is actually a combination of bottom up and top-down. You essentially make a powder of the material using a bottom up approach but then you have to grind it down to the nano dimensions by using a top-down approach and as you do that dispersion can become an issue, the agglomeration can be a problem which can be avoided by essentially preventing the particles from attaching to each other by capping them.

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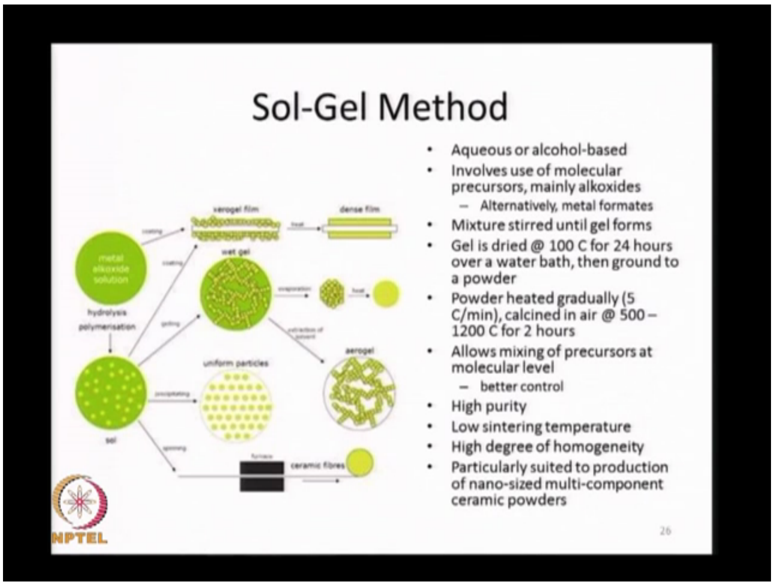

So here is the schematic of the Sol gel method. The Sol gel method can be aqueous or alcohol-based. It involves use of molecular precursors primarily Alkoxides or metal formates are used. The idea here is to take a mixture of the constituents; liquid-based constituents stir them until you form a gel. It should have a consistency of a gel. The gel is then dried at 100 degrees centigrade for 24 hours over a water bath and then grown to a powder and that is where the top-down process comes in.

This powder is then heated gradually at 5 degrees centigrade per minute then calcined in air at 500 degrees to 1200 degrees centigrade for 2 hours. Now the advantage of this is that the mixing is occurring at the molecular level, so that is the bottom up approach but then the size control is achieved by a top-down approach. So to some extent it combines the best of both worlds.

You could very high purity materials using this technique, low sintering temperature, essentially this process can be run without resorting to high temperatures which introduces all the problems associated with sintering. The degree of homogeneity you can achieve is quite high is particularly suited to production of nano sized multi component ceramic powders. The reason for that is twofold multicomponent because you can take many different precursors in liquid form makes them to form a gel and then grind them down.

Ceramic is particularly advantages because this top-down approach of grinding to achieve a final size works particularly well for materials that are hard and brittle and ceramics satisfies both requirements they are hard as well as brittle, so it makes very easy to grind them down to certain size.

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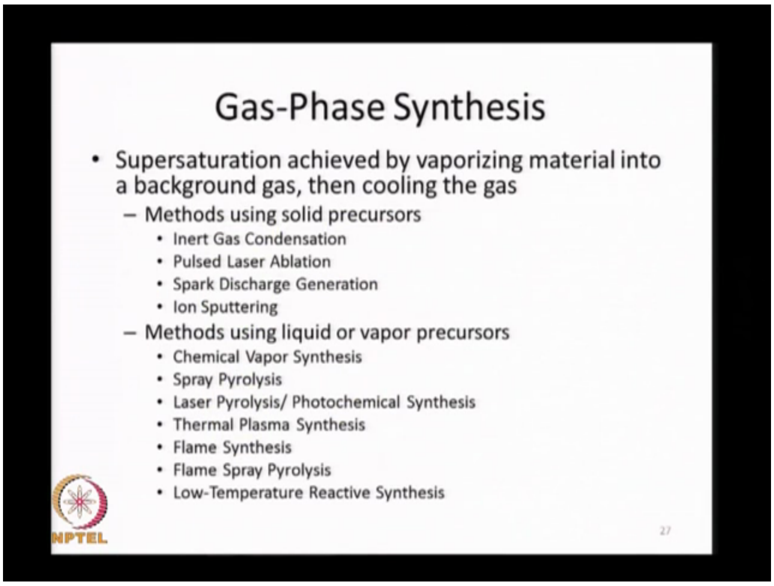

Now gas phase synthesis is actually very similar to what we have termed earlier as vapor phase synthesis, the difference here is you have a background gas into which you are vaporising material and the super saturation here is achieved by vaporising a material into a background gas and then providing appropriate cooling of the gas to achieve the super saturation.

These gas phase synthesis method can be further classified based on the form in which the precursors come in. The precursor or the material that is vaporized can be in solid form or it can be in liquid or even vapor perform. The methods that use solid precursors of material is then get vaporized include in a gas condensation, pulsed laser ablation, spark discharge generation, ion sputtering.

And methods that use liquid or vapor precursors are chemical vapor synthesis, spray pyrolysis, laser pyrolysis, photochemical synthesis, thermal plasma synthesis, flame synthesis, flame spray pyrolysis, low-temperature reactive synthesis etc.

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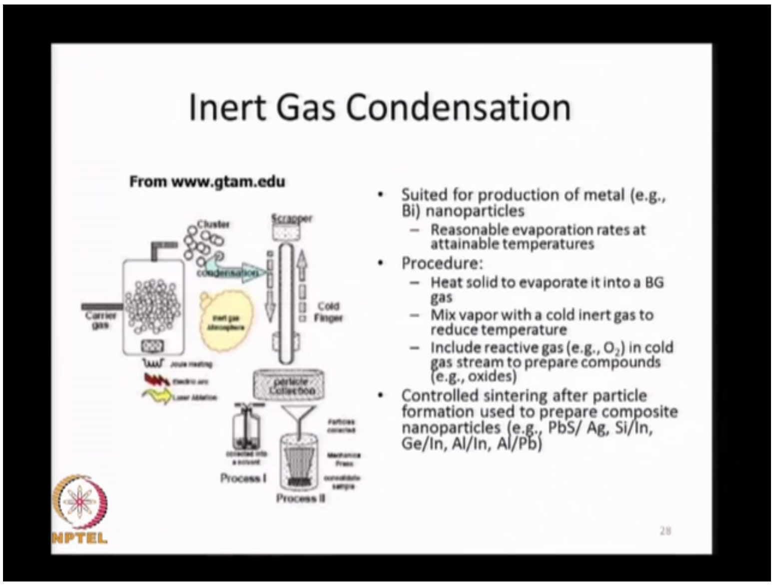

Let us look at a few examples of these. This is a schematic of an inert gas transition process which is particularly suited for production of metal nano particles. Now these metals have reasonable evaporation rates at attainable temperatures. So as we saw in the previous slide the first step is to take a precursor and convert it to the vapor form. So in this case the precursor is solid metal.

Now to convert it to a, perform simply by heating is not something you can do for all metals obviously. So only certain metals lend themselves to this method of vaporization. So here the procedure is to heat the solid and evaporate it into a background gas mixture vapor with a cold inert gas to reduce temperature and then essentially you introduce reactive gases in the cold gas stream to prepare compounds if you like.

For example if you are trying to make a nano oxide you can do that by introducing a stream of reactive gas into the cold gas stream. If you are only try to make nano sized metal than simply hitting the solid into a background gas and then cooling it is sufficient to produce a super saturation which can then be relieved with homogeneously or heterogeneously to produce the nucleates.

You can also do control sintering after particle formation to prepare composite nano particles, various examples are given here, so this essentially has 2 stage process where you first do a low-temperature process to make nano particles that have essentially a loose structure and then you do a high-temperature sintering to provide a more specified composition and structure by introducing multiple precursors into the reacting mixture.

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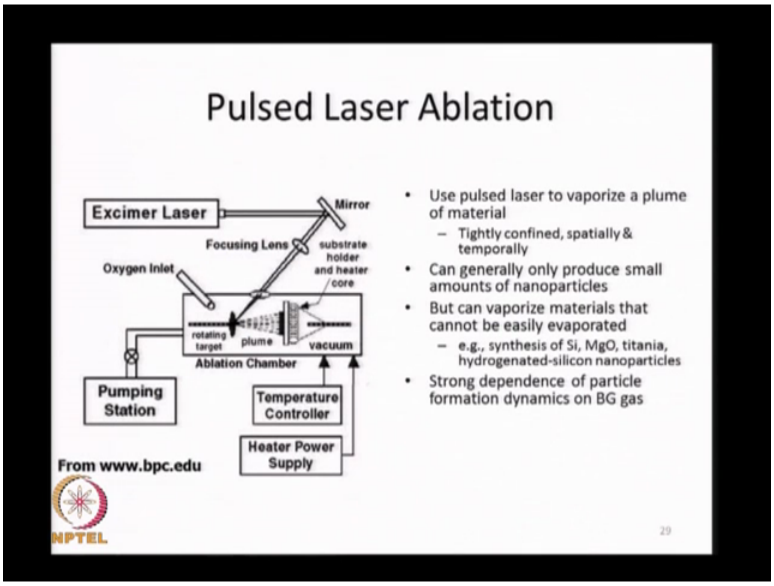

Pulse laser ablation is another way to vaporized material. So for metals that cannot be vaporized simply by heating, you hit the metal surface with high-energy laser and it vaporizes essentially a plume of material. Some of the advantages of this technique is can be very localised, you can hit certain geometry on the surface and vaporized material only in that area.

So it is tightly confined more spatially and temporally, what you mean by that is, you can confine your vaporization to a small zone of the metal and also you can do it for a fixed amount of time and you only have to just turn the laser off and that stops the vaporization process. So you have achieved both spatial control as well as time control using this process. The drawback of this method is because of the way it works it can only produce small amount of nano particles, it is not a bulk production process.

But the advantage of course is that it can vaporise metals that cannot be easily vaporized just by heating the metal for example silicon, magnesium oxide, titania these are materials that have fairly low pressure and they have to be heated to extremely high temperature in order to get them to vaporize and for such materials this laser ablation process works very well and there is a strong dependence of particle formation dynamics on the background gas.

So simply by changing the nature of the background gas you can affect the kinetics with which particles are formed. You can again control the size, shape as well as the chemical composition of the nano particles by changing of the nature of the background gas for example by changing from an inert gas to let say air you can actually produce oxidised nano particles.

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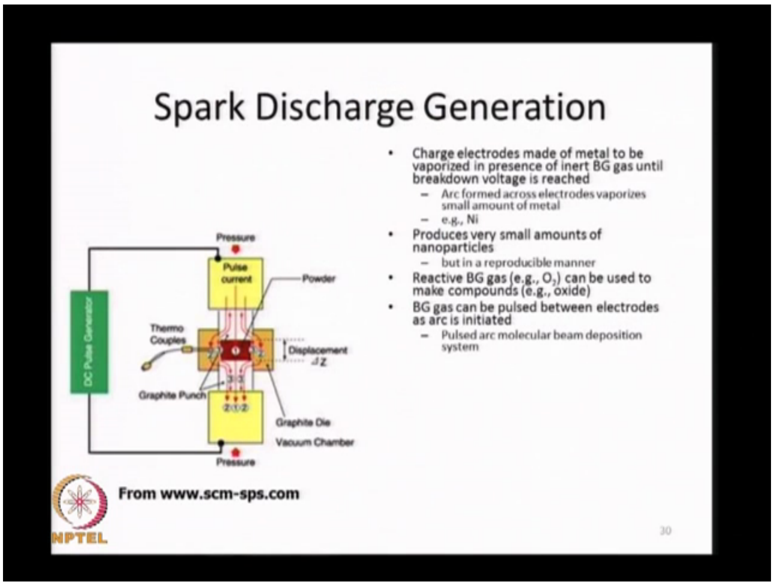

Spark discharge generation is another technique to take solid metal and vaporized it. So here you essentially make electrodes of the particular metal to be vaporized and you charge them in the presence of an inert background gas until you reach the breakdown voltage. Above that voltage and arc forms across these metal electrodes and vaporizes a small amount of the material which can then be used to make nano particles of that material example is nickel.

Again the drawback is it produces very very small amounts of nano particles and the advantage is it is a very controlled repeatable and reproducible process and just like in the pulse laser ablation technique while using a reactive background gas you can make compounds, by using oxygen you can make oxides and so on. The background gas itself can be pulsed between the electrodes as the arc is initiated and this is called a pulse arc molecular beam deposition system.

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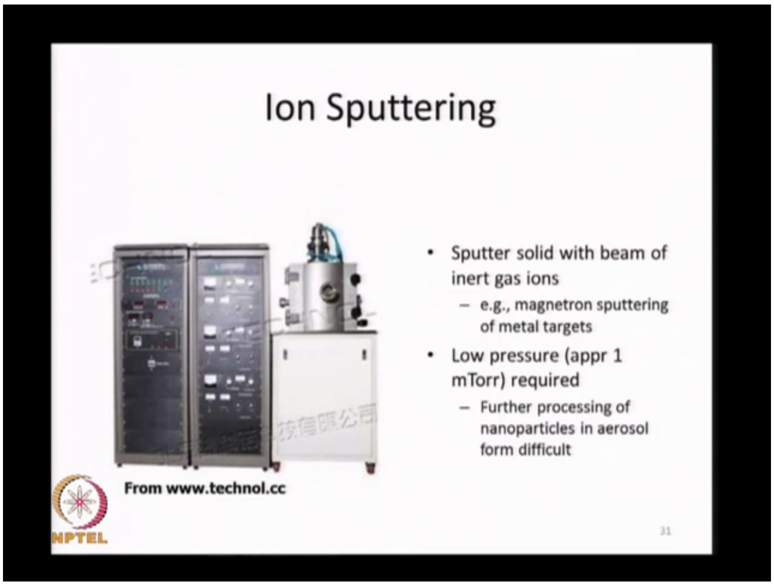

Ion sputtering is another commonly used technology where in this case you are essentially impacting the solid surface with high-energy ions so this process is called sputtering. Sputtering refers to heating the solid surface with a beam gas ions, again this can be inert reactive as the application demands.

Magnetron sputtering is a name that is commonly given to equipment that is used for this process of sputtering of metal targets to produce metal vapor. It requires low pressure approximately 1,000,000 and one of the drawbacks to this method is that further processing of nano particles in an aerosol form can be difficult because of particularly the low-pressure environment that is demanded in ion sputtering techniques.

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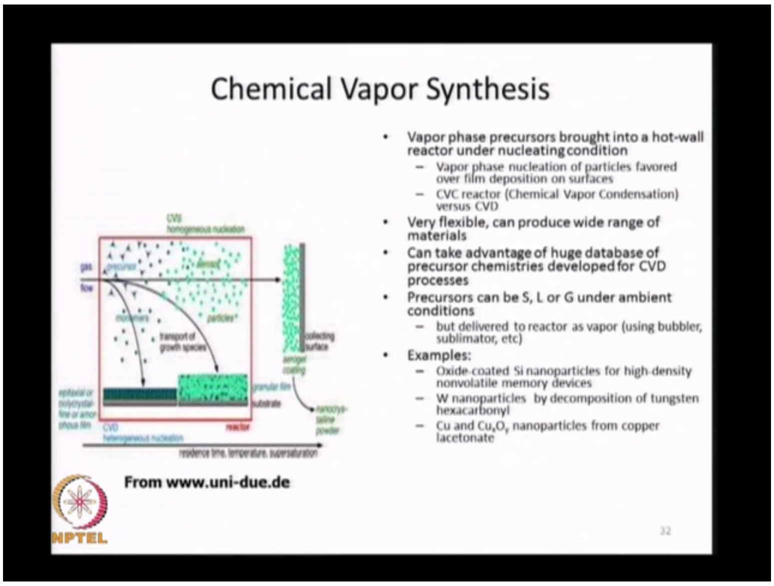

Chemical vapor synthesis is probably the most widely used method to make nano particles in the bottom up approach. Here you take vapor phase precursors and you bring them into a hot wall reactor under nucleating conditions. So essentially this is a reactor in which there is a target surface but even though walls of the chamber are heated to high temperatures because of this the entire reactor is in a condition where it promotes nucleation. So vapor phase nucleation of particles in this case is favored over film deposition on surfaces.

For those of you are familiar with chemical vapor deposition this is the exact opposite of that, in a CVD reactor you try to design the reactor conditions such that the nucleation only occurs heterogeneously on the target surface on which you are trying to put on a film. In a CVC reactor that is chemical vapor condensation reactor that is used to synthesise nano particles, the reactor is designed very differently.

All the walls of the chamber are also kept at elevated temperatures and the gas itself is kept under conditions such that homogeneous nucleation becomes possible this minimises heterogeneous nucleation on the target surface. The advantage of this technique is it is very flexible can produce a wide range of materials you are only limited by what vapor phase precursors you can make. So anything that can be made into a vapor phase form and introduced into the reactor can be made to react and produce product that is in the nano size range.

From the viewpoint of analyzing and characterizing such reactors there is a huge database of precursor's chemistries that has been developed by the CVD industries. Chemical vapor deposition has been used for long time to make thin films for various applications. So the CVD industry is very mature and it has a huge database on various chemically reactive components and the associated products.

So in chemical vapor synthesis you can take advantage of this pre-built library of data. The precursors can be solid, liquid or gas under ambient conditions but they must be delivered to the reactor in vapor form. It is critical that we do not allow solid liquid reactants to enter a CDS or CDC reactor. The reactants have to enter in vapor form but how you convert the solid liquid precursors to this vapor form is entirely up to you.

You can use bubblers, sublimators etc. some examples of nano materials that are manufactured using a chemical vapor synthesis reactor are oxide coated silicon nano particles, tungsten nano particles by decomposing of a tungsten compound (()) (43:17) also from a copper compound.

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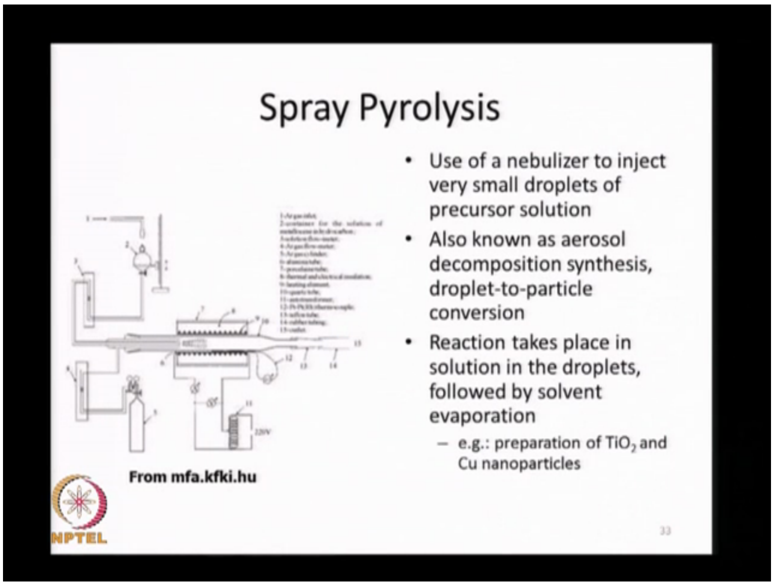

The next technique is spray pyrolysis. In spray pyrolysis essentially we take very small droplets of the precursor using a nebuliser and you inject it into an evaporative environment this technique is also known aerosol composition synthesis. It involves a direct conversion from droplet to particle. The reaction here takes place in solution in the droplets these very very fine sprays the droplets are again highly reactive because of their small sizes.

So they react and then you evaporate the solvent that we have used to make these fine droplets and you get the compound that you are looking for. Titanium oxide and copper nano particles are examples of materials that are conventionally manufactured using this spray pyrolysis technique.

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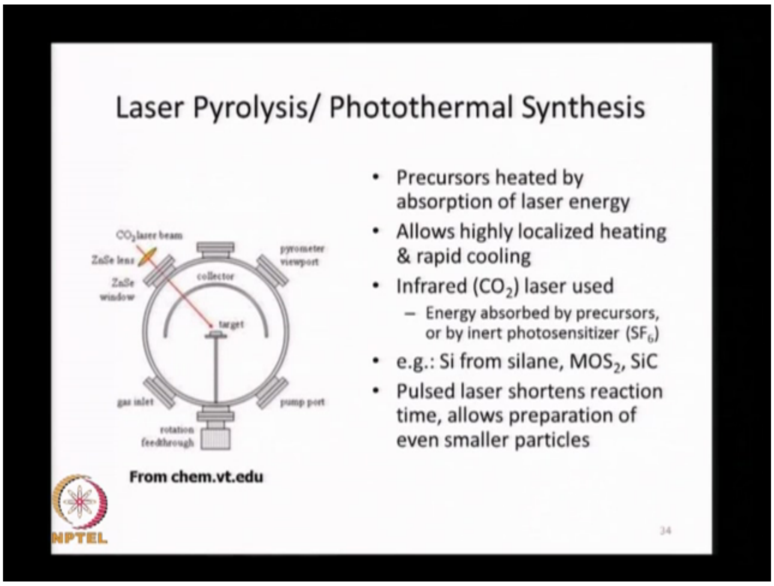

A related technique is laser pyrolysis or photo thermal synthesis. Here the precursors are heated by absorption of laser energy and this technique allows highly localised heating and rapid cooling. So quenching becomes easy when you are using this technique, you do not have to allow growth to occur beyond a point where you want to stop it. Infrared Laser, CO2 laser can be used which reduces the expense of the operation.

Sub examples of materials that are it of using this technique are silicon from Silane, MOS2 and silicon Carbide. Using the laser shortens the reaction time and allows preparation of even smaller particles. So the laser pyrolysis method is again widely used to make small quantities of nano materials.

We will stop this lecture at this point and we will consider more examples of bottom up synthesis in the next lecture and then we will continue our discussion by looking at methods of top-down synthesis of nano particles. Any questions? See you at the next lecture then.