Particle Characterization

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Module No. # 11

Lecture No. # 29

Nano-particle Characterization: Bottom-Up Synthesis Methods

Welcome to the twenty-ninth lecture in our particle characterization course. In the past couple of lectures, we have been looking at methods of characterizing the chemical and compositional properties of particles. Initially, we started by discussing microscope base methods, then we looked the techniques for organic materials, and then in the last class, we discussed two techniques in a little more detail, atomic force microscopy and 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.

Now, before we start discussing methods of characterizing nano-particles, I want to take a few minutes to talk about some basics of nano-technology including methods of synthesizing nano-particles, methods of dispersing them in suspensions and finally, characterization of the various properties of nano-particles and nano suspensions.

Now, the reason that is important for us to spend some time discussing the basics of nano-technology is that, nano is like do you know the proverbial elephant on the blind man. It depends on what aspects of nano-technology you deal with, you have a very different perception of what nano-technology is. So, it is very important to have a more common understanding of what constitutes nano-technology.

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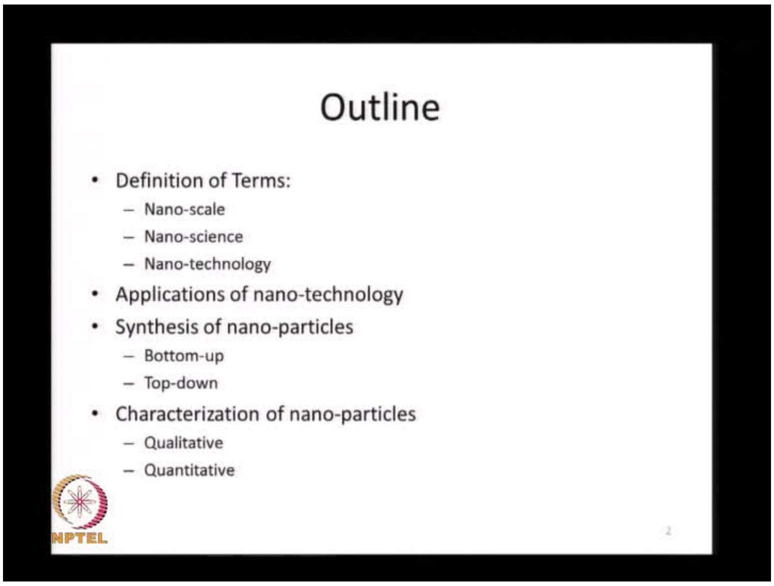

So, the outline of this module is going to be as follows. We will begin by defining some terms: what is nano-scale, what is nano-science, what is nano-technology. We will talk about some applications of nano-technology, methods of synthesizing nano-particles from the bottom-up approach and the top-down approach and finally characterization of nano-particles which we classify as qualitative methods and quantitative methods.

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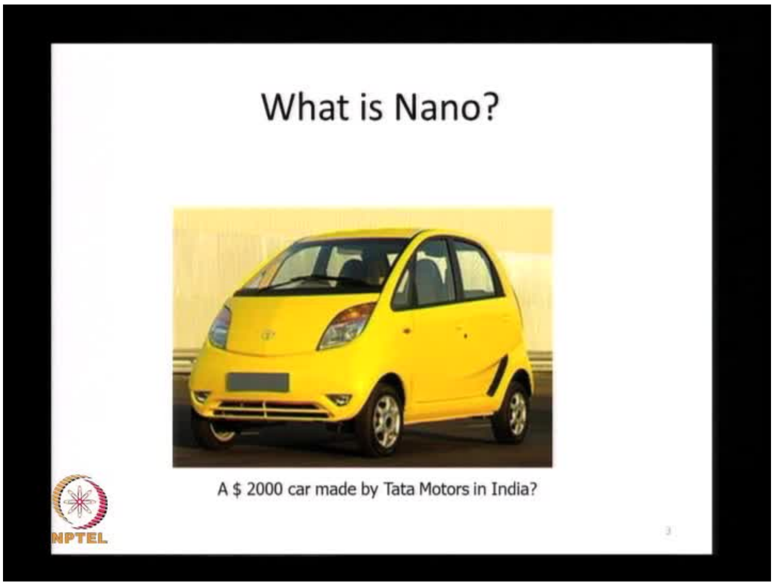

So, what is nano? You all have seen the car that is made by Tata is the nano, does it fit the term? Is it really nano-technology? It is small, but is that sufficient to qualify it as nano in the way we perceive nano. Nano gives a quantization of something that is technologically very advanced, something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

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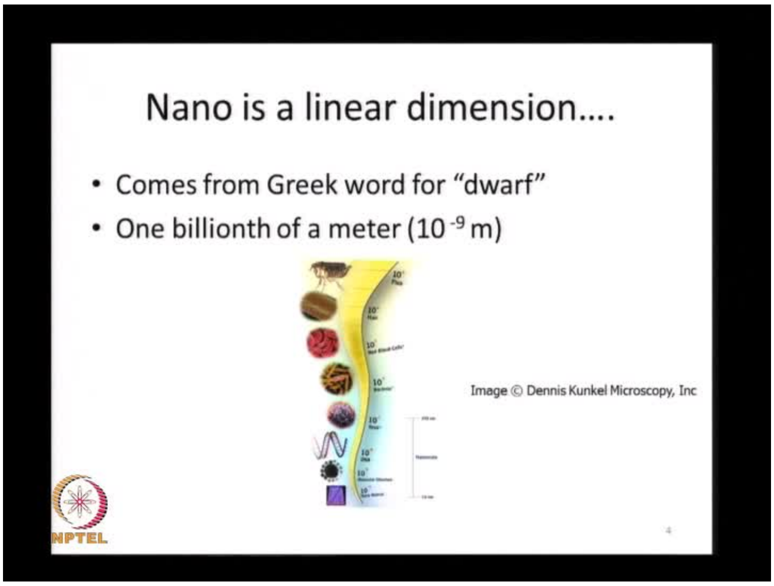

But, what is nano? It is a dimension; it is nothing more and nothing less. Nano is a linear dimension; it is actually derived from the Greek word for dwarf. So, clearly the connotation of small size is there and it is one billionth of a meter or 10 to the power minus 9 meters. Now, just to give a perspective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

The 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 nano-scale, the last three 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 nano scale.

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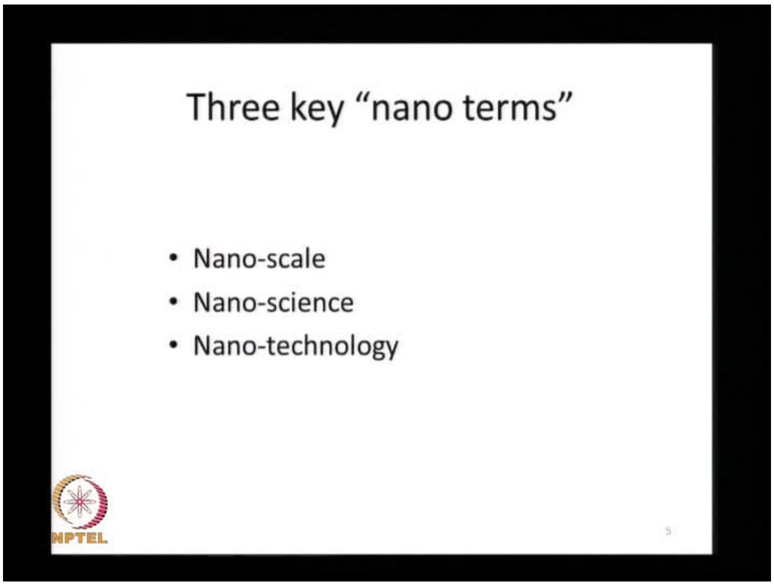

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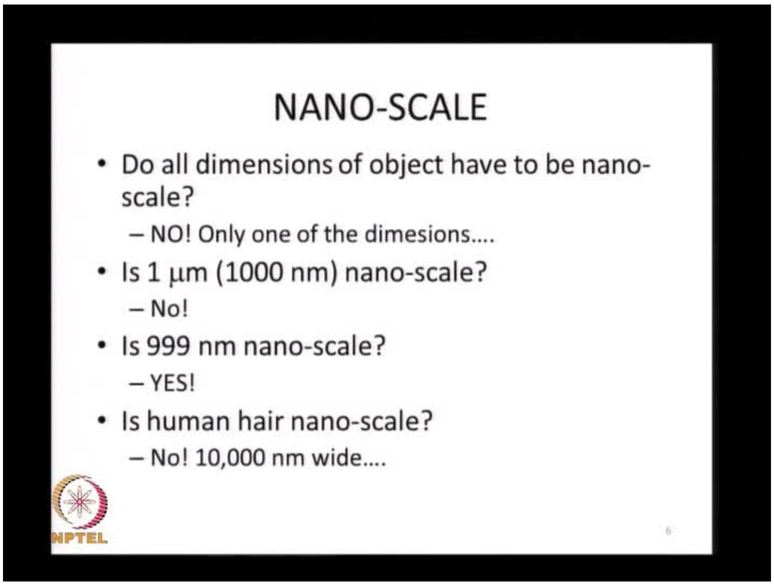

Now, there are three key nano terms; nano-scale, nano-science, and nano-technology. Let us take a few minutes to understand what these are. When we say nano-scale, do we mean that all dimensions of the object have to be in the nano range? No, not really, as long as one of the dimensions it is in the nano-scale, we can consider it to be a nano object, is 1 micron considered nano-scale? Conventionally no but, is 999 nanometers consider nano scale? According to convention, yes so, it is not a very clear definition I mean, why would you call 999 nanometers as nano-scale and then 1 nanometer more as micron scale, you just traditionally that is how particle sizes have been referred to.

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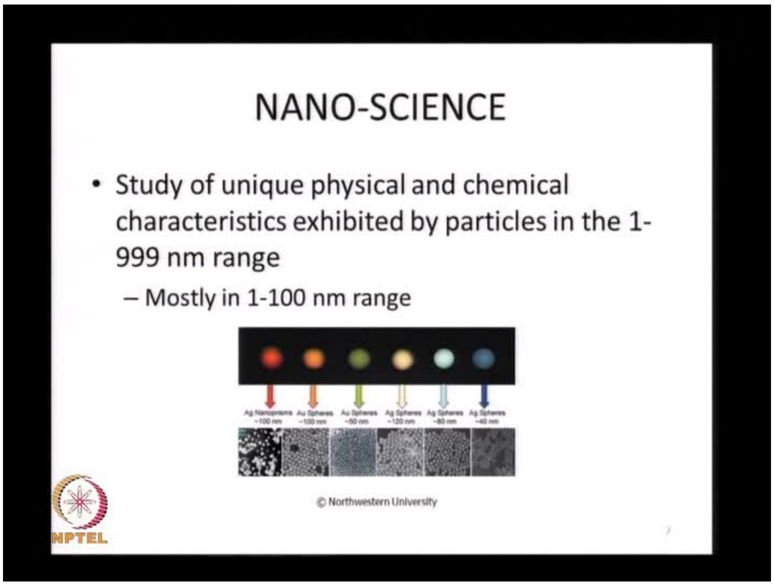

And again, is a human hair nano-scale? No, because it is actually very long compared to the nano dimensions. So, what is nano-science? Any new discovery goes through two stages; first you develop the science of it, then you develop its technology. The difference between the two is science is something 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 scalar, you take something that you have developed in a laboratory and you scale it up first to a prototype scale, then to actual production scale. So, technology is essentially translation of science into practice, but it starts with the 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 in the 1 to 999 nanometer range. Although again by tradition, nano is mostly used in reference to the 1 to 100 nanometer range. Strictly speaking, it ranges all the way from 1 to 999 nanometers, but in practice people use 1 to 100 nanometers as a nano range. And you can see some examples of nano materials here (Refer Slide Time: 06:42); silver, gold, spheres, and prisms and so on. You can see that, there are some distinct size and shape characteristics associated with nano-particles as well as color. So, these are some of the unique properties of nano-particles that we try to exploit in nano-technology.

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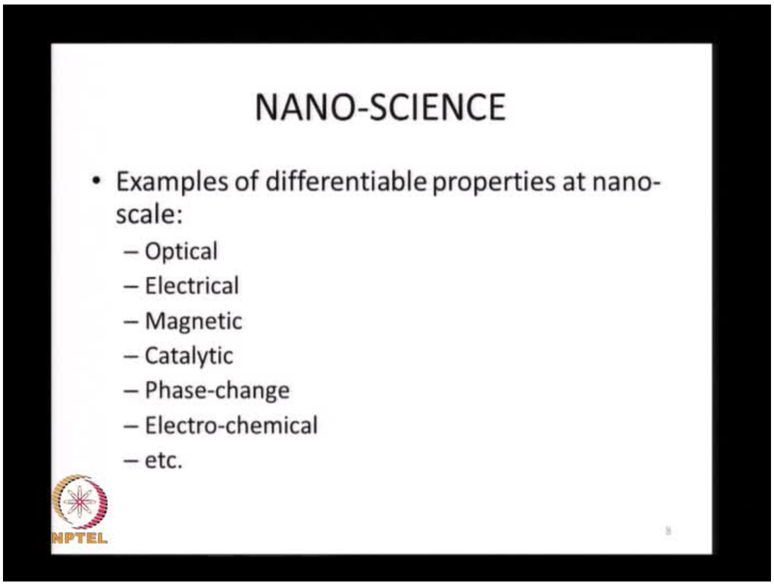

Some of the differentiable properties that you can observe at nano-scale, differentiable in the sense that, these properties are very different at nano-scale compared to the micron scale; and these are optical, electrical, magnetic, catalytic, phase-change properties, electro-chemical properties etcetera.

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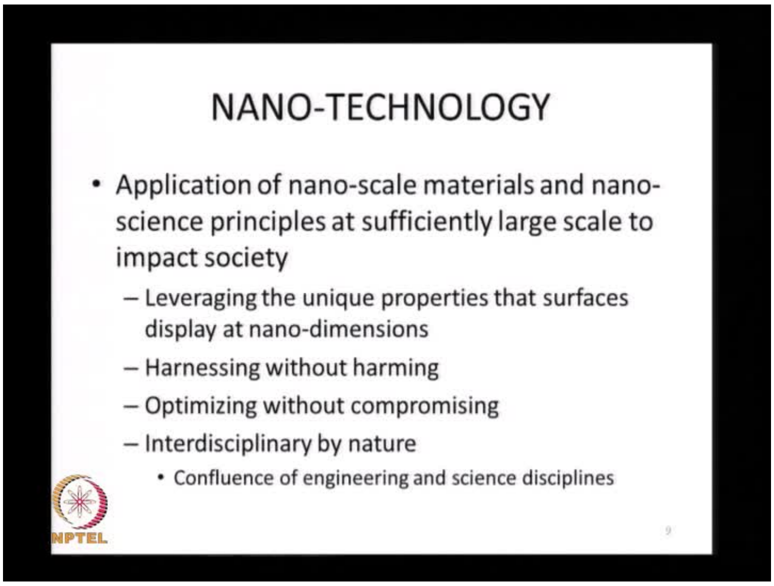

So, we will talk about some of these unique nano properties later in this module. So, what is nano-technology? It is the application of nano-scale materials and nano-science principles at sufficiently large scale to impact society. In other words, you don't let nano just be something that people play within their laboratory; 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 nano-technology.

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 nano-technology. It is to learn how to harness nano-technology without forming the environment; there are many concerned about use of nano-scale materials including their possible ecological, environmental, even human health aspects.

So, technology when you start using nano in large scale, you really have to start worrying about the possible consequences so, that is part of nano-technology. Optimizing without compromising, as a technologist, someone who is trying to do scalar to large volumes, your focus should always be on optimizing 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 the nano material you are making; you do not try to cut cost by truncating the usefulness of nano material. So, that is again a part of nano-technology. Now, nano-technology is very interdisciplinary by nature unlike nano-science; if you look at nano-science, it is still being primarily driven by physicist and chemist; however, if you take nano-technology the physicist and chemist are still involved, but engineers are virtually every discipline are also involved.

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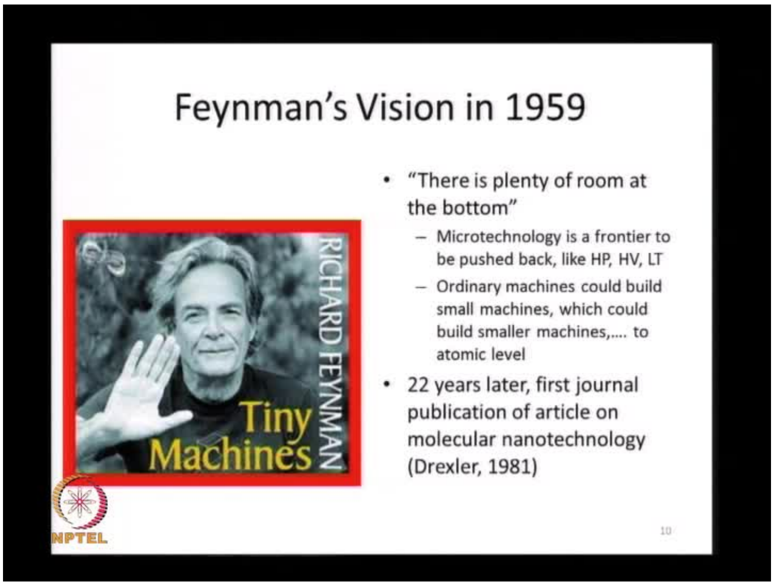

So, it is really a confluence of various engineering and science disciplines that in drive nano-technology. What is a history of nano? We will actually started in back in 1959 when Richard Feynman stated his vision of there being plenty of room at the bottom, he said you can always keep driving technology to smaller and smaller dimensions. He basically said that, micro technology is actually a frontier that we need to keep pushing back just like high pressure, high vacuum, low temperature etcetera.

So, his thinking was micro is small, but we can get smaller. So, let us keep pushing the boundary, his vision was that we could make machines that build smaller machines that build even smaller machines all the way down to atomic level. And to large extent that is what we have done, 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 a machine that can manipulate matter even at atomic level, but there was a big gap from 1959 to 1981 nano-technology was really not taken up seriously as a subject of investigation. In fact, it was in 1981 that the first journal publication of an article on molecular nano-technology was published by Drexler.

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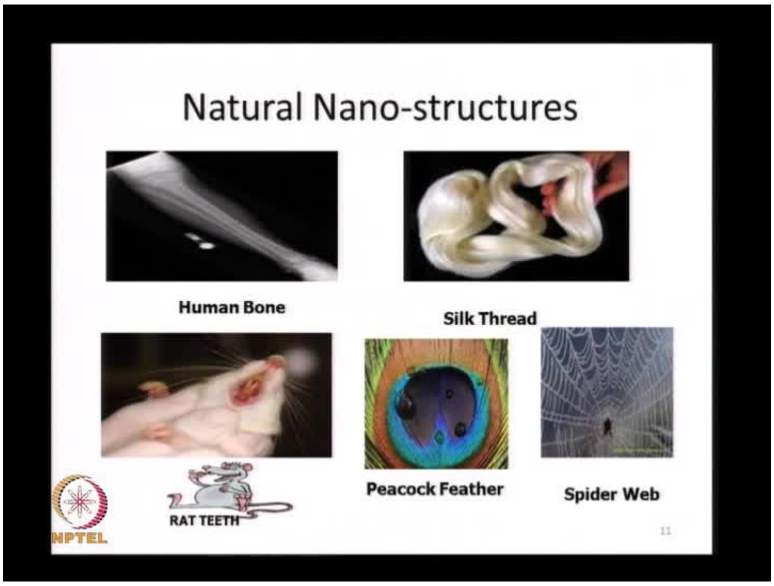

Now, if you look at nature, there are many examples of nano structures. There is a human bone, silk, rat's teeth, peacock feather, spider web are all classic examples of structures that have nano dimensions at least in one scale.

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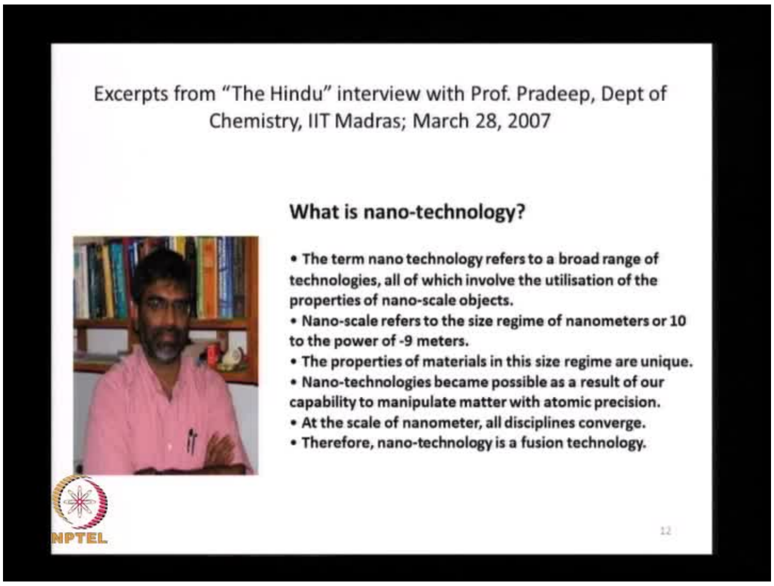

Now, IIT Madras has been one of the leading research institutions in nano-technology and Professor Pradeep in the department of Chemistry has done a lot of work in this area. This was an interview from him in the Hindu newspaper in 2007 (Refer Slide Time: 11:43). Now, defining nano-technology, the term nano-technology refers to a broad range of technologies all of which involve the utilization of the properties of nano-scale objects, the unique properties of nano-scale objects. It refers to the size regime of nanometers are 10 to the power minus 9 meters; the properties of the materials in the size regime are unique.

Nano-technology is become possible as we develop capability to manipulate matter with atomic precision at the scale of nanometer, all discipline converges; therefore, it is a fusion technology or interdisciplinary technology.

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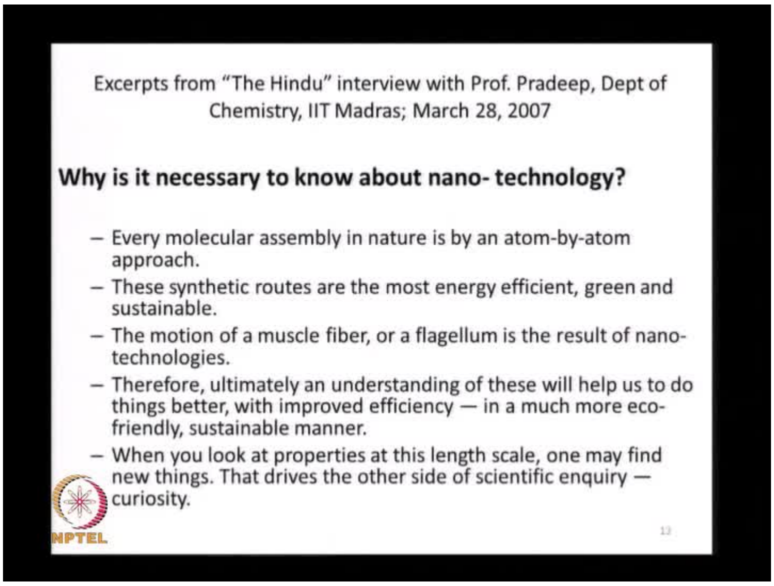

Continuing with the same interview, why is it necessary to know about nano-technology? Because nature is nano, every molecular assembly in nature is basically built up by an atom-by-atom approach. The synthetics roots are the most energy efficient, green and sustainable. The motion of a muscle fiber or a flagellum is a result of nano-technologies. If you look at how the human body works, it is amazing; it is all down to the nano-scale.

Therefore, ultimately an understanding of these will help us do things better with improved efficiency in a more eco-friendly and sustainable manner. Also when you look at properties, at the nano-scale there are many new things to find, to discover.

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So, our spirit of scientific enquiry is also kindle or curiosity is another thing that makes nano very attractive as an area to work in. 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 aliments, nano-technology holds the key.

In fact, more recently nano bio has emerged as a very interesting discipline to work in. The interaction of nano-technology with biology has produced some exiting results and has been used to create new materials. This is a bio-nano interface, which can help of may solve many problems water, food, health, environment etcetera.

Hazardous and toxic impurities like arsenic can be removed from drinking water in a cheap and effective manner using nano-technology and many of these technologies have now been commercialized and are available in the market at very reasonable prices.

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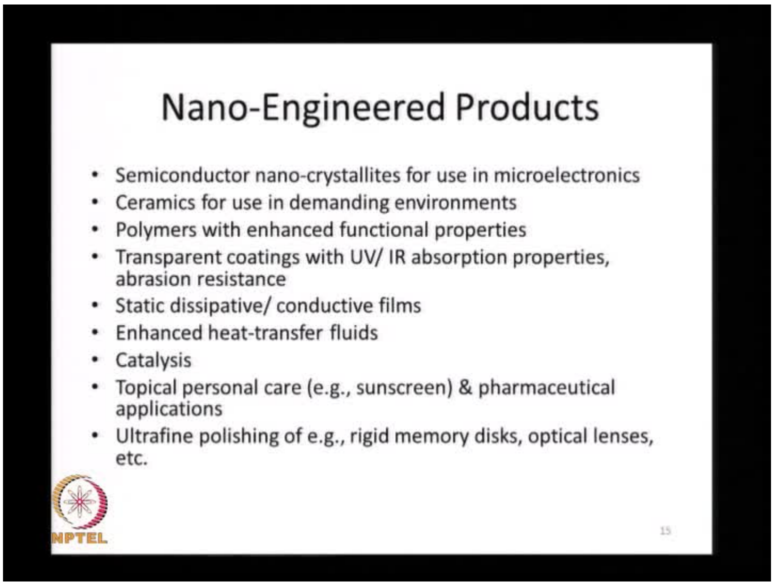

Now, moving away from nano in nature, if you look total nano engineered products again, there is a huge number of them virtually every manufacturing industry in the world today is impacted either directly or indirectly by nano-technology.

The semiconductor industry where nano-crystallites are now being used in microelectronics, which should actually now we call nano electronics 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 protection.

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 deceptive films, conductive films particularly for packaging applications use nano components. Enhanced heat transfer fluids use nano, nano fluid technology something that is finding increased use and again, we 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 catalyst have a huge advantage over larger sized catalyst materials and therefore, nano catalysis is an area that just taking off. Topical personal care and pharmacy products and finally, ultrafine polishing of memory disks, optical lenses etcetera use nano material as the polishing medium.

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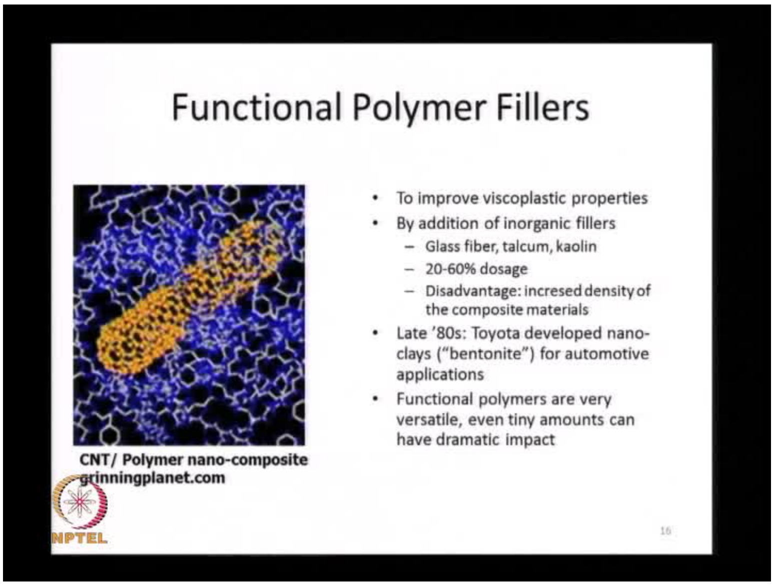

So, just to go through some examples of this functional polymer fillers, carbon nano tube is widely used as a filler material, but there are others as well. Primarily this is to improve the visco-plastic properties of these polymers.

The fillers are predominantly inorganic materials like glass fiber, talcum, kaolin the dosage is 20 to 60 percent; however, the disadvantage is that, there is an increased density of the composite materials, 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 users of nano composites was the nano clay bentonite, which was used in the late 1980s by Toyota for automotive applications. Functional polymers are actually very versatile, even tiny amounts can have the dramatic impact; the 20 to 60 percent dosage mentioned earlier are fairly high estimate. In fact, it is been found that nano materials, nano fillers can start having an impact even at 2 to 5 percent by volume.

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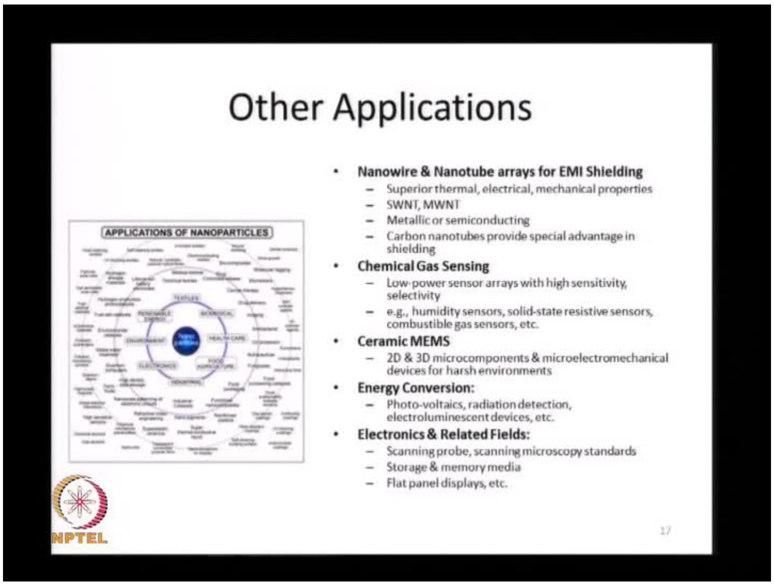

Now, there are many other applications, the applications of nano particles encounters so many different areas industrial, electronics, environment, renewable energy, textiles, biomedical, health care, food, agriculture etcetera. And some of the examples are sited here nano wires and nanotube arrays can 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 employee nano-technology and in the electronics and related fields nano-technology find wide usage as well.

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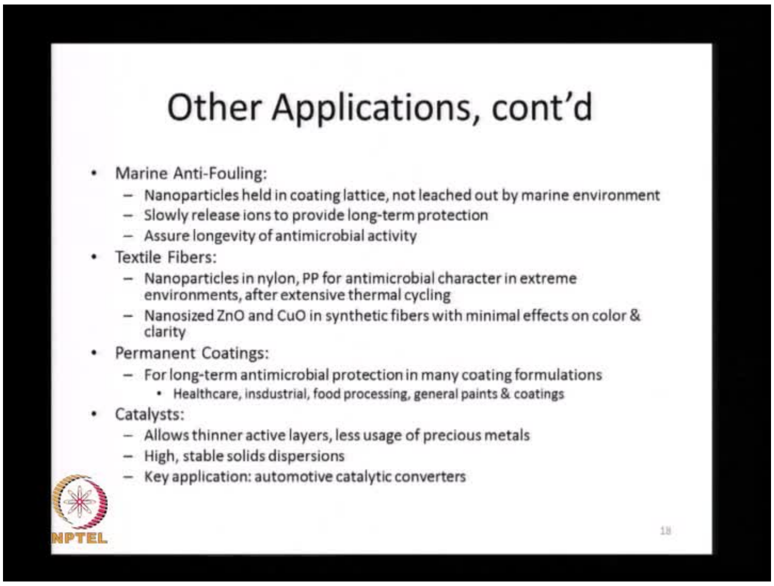

Other applications include anti-fouling coatings, particularly for marine environments the nano-particles are laid down as a layer on the surface and also incorporated into the lattice of the basic material and they actually provide long term protection by slow release phenomena. Bacterial and anti-bacterial or anti-microbial coatings are possible using nano technologies, textile fibers can be hugely improved by incorporation of nano materials for example, nano-particles incorporated in nylon and polypropylene provide antimicrobial properties in extreme environments, even after extensive thermal cycling.

Nano sized zinc oxide and copper oxides in synthetic fibers provide additional enhancements and properties without affecting color 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 is possible with catalyst, very high stability solid dispersions can be used. One of the key applications is automotive convertors, where increasingly nano catalysts are starting to be employed.

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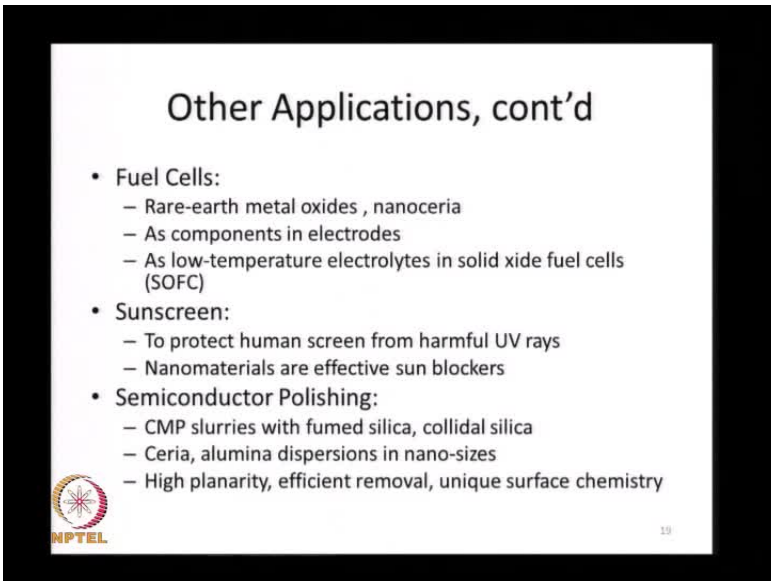

Fuel cells, sunscreen products, semiconductor polishing are all other examples of where nano materials are used very effectively.

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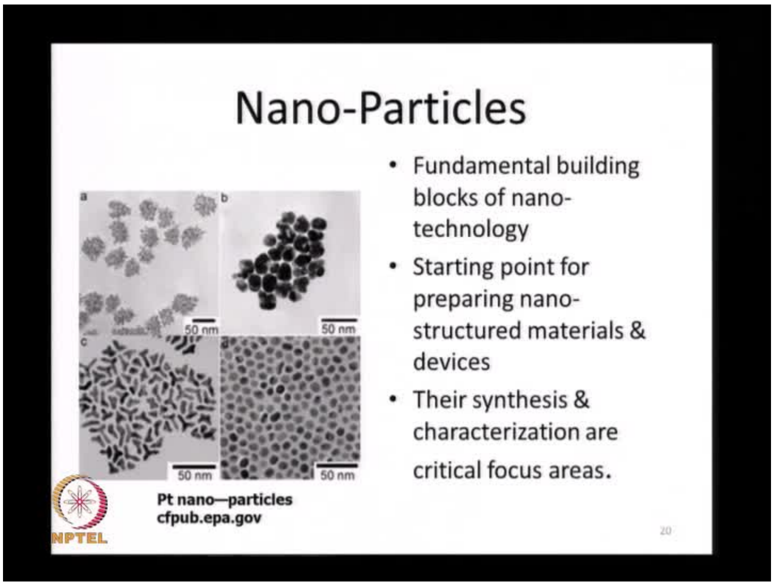

So given that, we have this variety of applications that nano materials are used in. We have to start with, what drives these technologies and the starting point or the fundamental building blocks of nano-technology or the nano-particles.

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 the quantity of nano materials, you first have to be able to measure them and that is what characterization comes in, unless you can measure the properties of these nano-particles, you cannot optimize them for any specific application and you cannot even control the process very well.

So, synthesis and characterization go hand in hand and so what we will do in this module is, first talk about synthesis methods and then, we will switch over to talking about characterization techniques.

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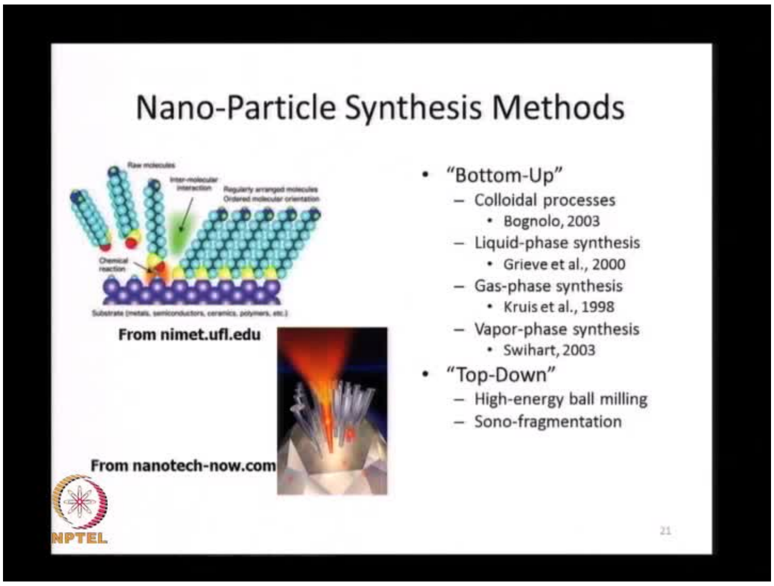

So, what are the two basic types of synthesis methods? Bottom-up and top-down, the difference between the two is that, in the bottom-up approach essentially you take atoms or molecules and you tie them together to make nano materials.

So, it is essentially and 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, you can take advantage of their cohesive properties to bind them together, but you can also take advantage of their enhanced reactivity to make them, react in a certain fashion. So, that, the output that you get is regularly arranged molecules in ordered molecular orientation. So, this is the nano material that you can synthesis by using the bottom up approach and there are various methods of doing this colloidal process; liquid phase synthesis, gas phase synthesis and vapour 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 synthesis nano-particles.

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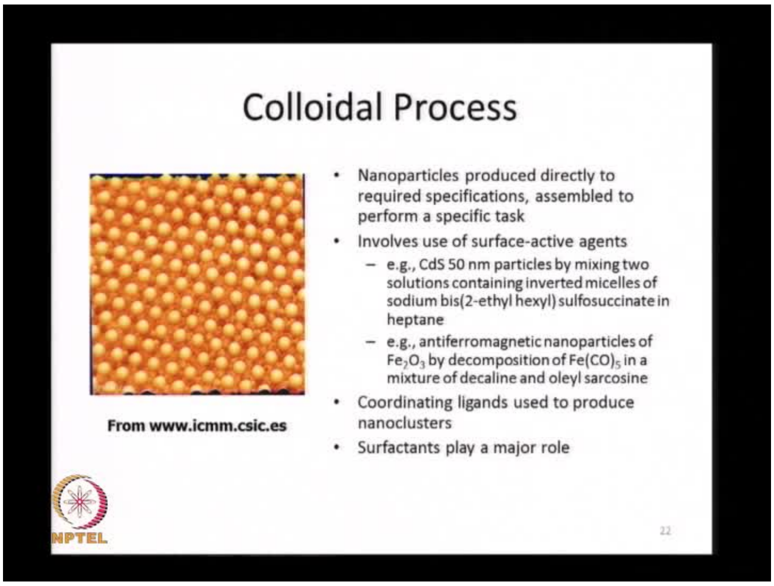

Let’s talk about some of the bottom-up approaches, first what is a colloidal process? In this process, essentially you build up the nano material and atom at a time. So, you take the specifications that have been laid down for properties of the nano material and you take nano-particles and assemble them in a certain way to be able to meet these specifications, in order to be able to perform 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 precise control over the physical structure as well as the chemical properties of the resulting nano material.

Some of the examples are 50 nanometer particle are cadmium sulphide that is produced by mixing two solutions containing micelles of sodium sulfosuccinate in heptanes. Another example is antiferromagnetic nano-particles of F e 2 O 3 that are produced by decomposing F e C O 5 in a mixture of decaline and oleyl sacrosine.

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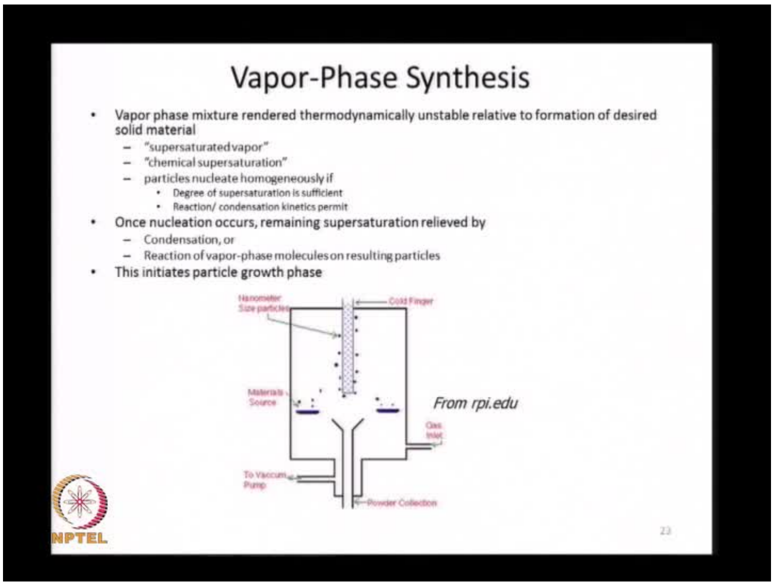

These are examples of nano-particles or nano materials that are obtained by taking two reagents and mixing them together at molecular scale to produce a nano dimensional material. Vapour phase synthesis on the other hand is one, where you essentially saturate the vapour phase with the nano material that you are trying to synthesize and then, you actually make it thermodynamically unstable and with leading to the formation of the desired material.

So, the way that you make a saturated vapour 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 reserves in the formation of these nano sized particles from the vapour that is present.

So, what you do is, you essentially take a saturated vapour or a super saturated vapour and you provide imputers 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 nanomaterial. 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 cooled surface, and then particles will immediately nucleate differentially around the circumference of this object that you have inserted.

Once nucleation occurs, you can relief the remaining super saturation by condensation or reaction of the vapour phase molecules on the resulting particles. So, the nuclei that are formed start growing by these two mechanisms; condensation of the vapour that is still left in the gas phase on to this nucleated particles, as well as reaction between the vapour phase molecules and the resulting particles. This is what initiates the particle growth phase. If you recall the tri model particle size distribution 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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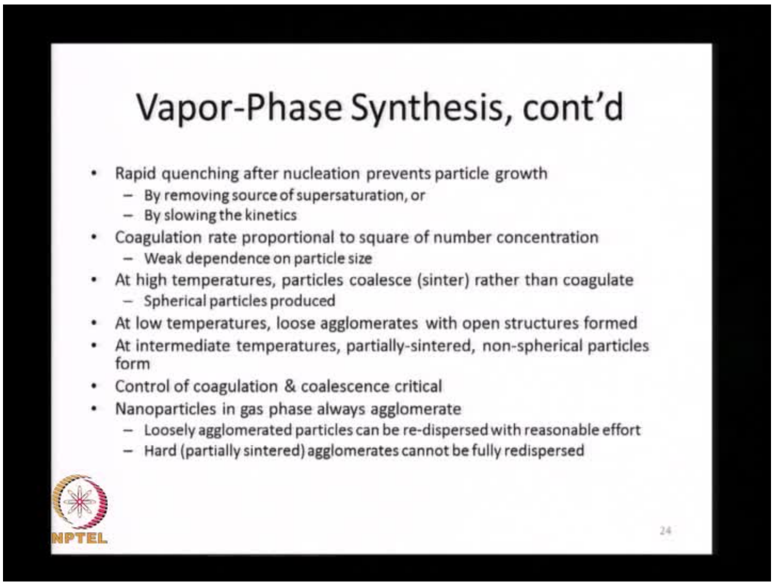

Now, sometimes you do not want the growth, you want the nuclei to remain as nuclei, you want the dimensions to remain essentially a few nanometers in size rather than growing to tens of hundreds of nanometers, then what we need to do is quench the growth. So, do not allow the particle growth to happen. 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 vapour in order to eliminate the source or 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 vapour 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 vapour in the gas phase. Coagulation rate is interestingly enough, only weekly dependent on particle size, when we are doing vapour phase synthesis of nano materials.

As temperatures increase coagulation is replaced by coalesce or sintering. The primary difference between coagulation and coalescence is that, at low temperatures where coagulation happens, you form loose agglomerates with open structures. At intermediate temperatures, you get partially sintered agglomerates which are non-spherical in form at high temperatures, where coalescence dominates you form spherical particles.

So, control of coagulation and coalescence in 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 flakey, porous, amorphous type of clusters. As you keep increasing the temperature, you get a more and more crystalline material and at extremely high temperatures, you get coolest sintered crystalline particles.

So, depending on what you are looking for, you 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 agglomerate as we have discussed extensively in previous lectures, loosely agglomerated particles can be redispersed with some effort.

But, when agglomerates are sintered or partially sintered, it becomes very difficult to redisperses some. So for example, if you have particles that are loosely adhered in to clusters, we 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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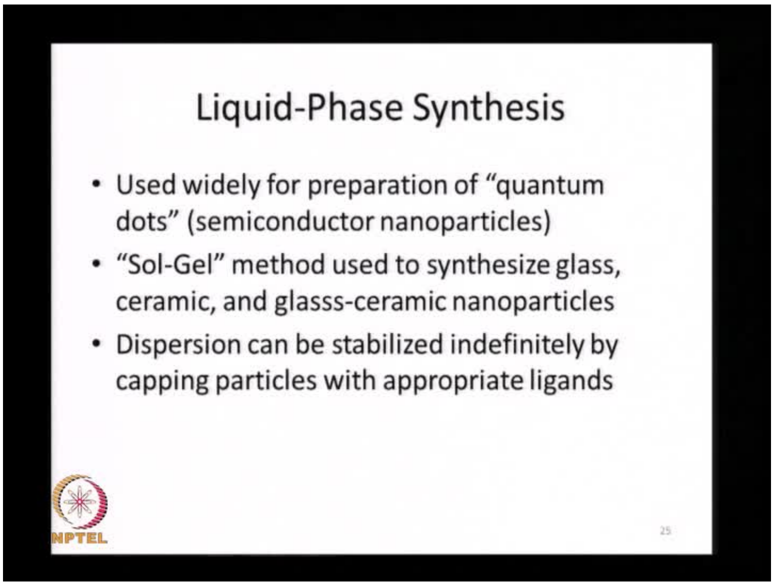

Now, liquid phase synthesis is a slightly different technique. The most common example of it is the Sol-Gel method; it is used for preparation of quantum dots which are semiconductor nano-particles. The method can also be used to synthesis glass, ceramic as well as glass ceramic nano-particles.

Dispersion can be stabilized 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.

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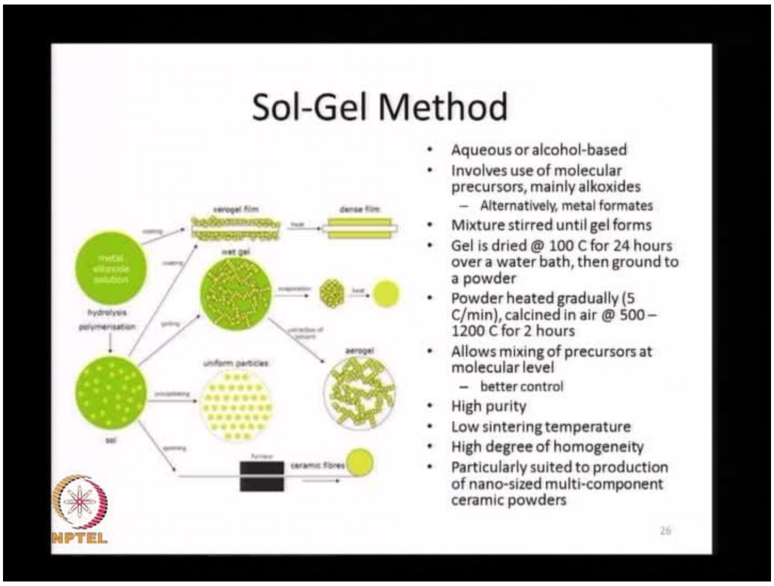

And as you do that, dispersion can become an issue, re-agglomeration can be a problem which can be avoided by essentially preventing the particles from attaching to each other by capping them. So, here is a schematic of the sol-gel method.

The sol-gel method can be aqueous or alcohol based, it involves use of molecular precursors, primarily alkoxide or metal formates are used. The idea here is to take a mixture of the constituents, liquid phase constituents stir them until you form a gel, and it should have the consistency of a gel. The gel is then dried at 100 centigrade, for 24 hours, over a water bath and then ground to a powder.

And that is why the top down process comes in. This powder is heated gradually at 5 degree centigrade per minute then, calcined in air at 500 degrees to 1200 degree centigrade for 2 hours. Now, the advantage of this is that, the mixing is occurring at 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 wells, you get very high purity materials using this technique.

Low sintering temperature it 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. It is particularly suited to the production of nano sized multi-component ceramic powders.

The reason for that is twofold multi-component because you can take many different precursors in liquid form, mix them to form a gel and then grind them down; ceramic is particularly advantage is because this top-down approach of grinding to achieve a final size works particularly well for materials that are hard and brittle and ceramics satisfy both requirements, they are hard as well as brittle. So, it makes it very easy to grind them down to a certain size.

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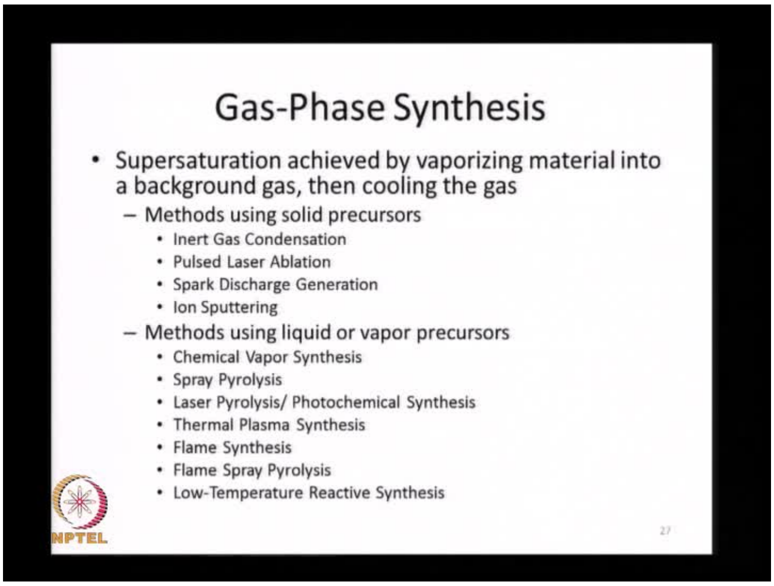

Now, gas phase synthesis is actually very similar to what we are termed earlier as vapor phase synthesis. The difference here is, you have a background gas into which your vaporizing material and the super saturation here is achieved by vaporizing a material into a background gas and then providing appropriate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

These gas phase synthesis methods 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 liquid or even vapour form. The methods that use solid precursors of material, which then get vaporized include inert gas condensation, pulsed laser ablation, spark discharge generation, ion sputtering and methods that use liquid or vapour precursors or chemical vapour synthesis, spray pyrolysis, laser pyrolysis, photochemical synthesis, thermal plasma synthesis, flame synthesis, flame spray pyrolysis, low temperature reactive synthesis etcetera.

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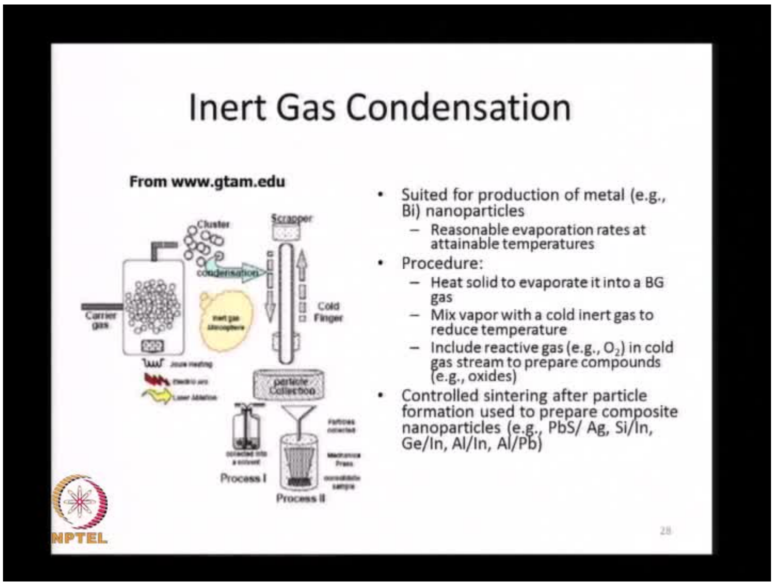

We will just look at a few examples of these; this is schematic of an inert gas condensation process, which is particularly suited for production of metal nano-particles. Now these metals have reasonable evaporation rates at attainable temperatures. So, as we saw in the previous slide, the first step is to take the precursor and convert it to vapour form. So, in this case the precursor is solid metal; now to convert it to vapor form simply by heating, it 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, mix the vapour with the coal inert gas to reduce the temperature.

And then essentially, you introduce reactive gases in the coal 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 coal gas stream; if you are only trying to make nano sized metal, then simply heating the solid into a background gas and then cooing it is sufficient to produce the super saturation, which can then be relived either homogeneously or heterogeneously to produce the nucleates.

We can also do controlled sintering after particle formation to prepare composite nano-particles, various examples are given here. So, this essentially has two stage processes 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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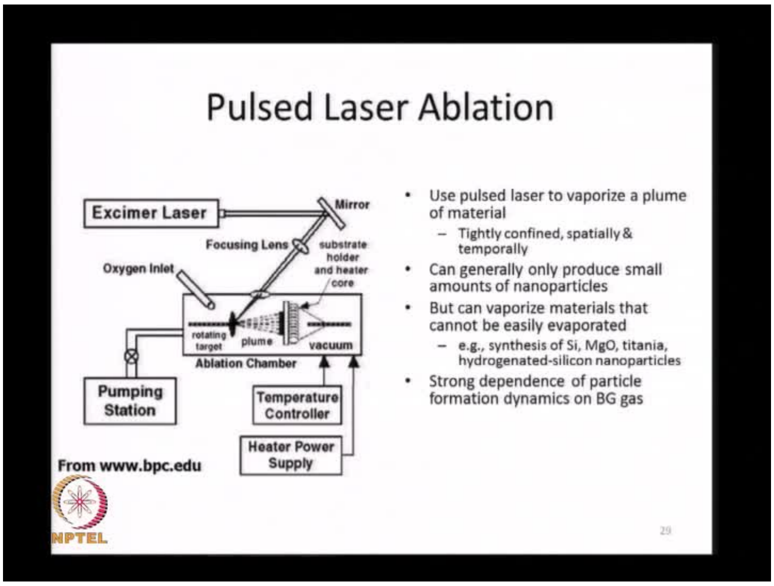

Pulsed laser ablation is another way to vaporize material. So, for metals that cannot be vaporizing simply by heating, you hit the metal surface with high energy laser and it vaporizes essentially a plume of material. Some of the advantage of this technique is, it can be very localized, you can hit certain geometries on the surface and vaporize the material only in that area. So, it is tightly confined both spatially and temporarily.

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 all you have to turn the laser off and that stops the vaporization process. So, you achieve both spatial control as well as time control using this process.

The drawback to this method is because of the way it works, it can only produce small amounts of nano-particles. It is not a bulk production process, but the advantage of course is that, it can vaporize metals that cannot be easily vaporized just by heating the metal. For example, silicon, magnesium oxide, titanium these are materials that have fairly low vapour pressure and they have to be heated to extremely high temperatures 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 and as well as chemical composition of the nano-particles by changing the nature of the background gas. For example, by changing from an inert gas to let us say air, you can actually produce oxidized nano-particles.

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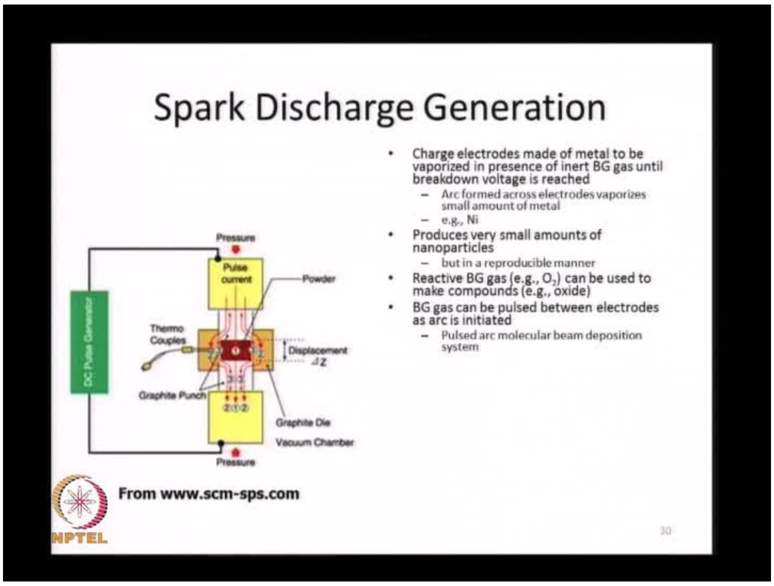

Spark discharge generation is another technique to take solid metal and vaporize it. So, here you essentially make electrodes of the particular metal to be vaporized and you charge them in the presence of an inert background gas, until you reach a breakdown voltage. Above that voltage an arc forms across 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 small amounts of a nano particles and the advantage is, it is a very controlled repeatable and reproducible process and just like in the pulse laser ablation technique by using a reactive background gas, you can make compounds by using oxygen, and 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 the pulsed arc molecular beam deposition system.

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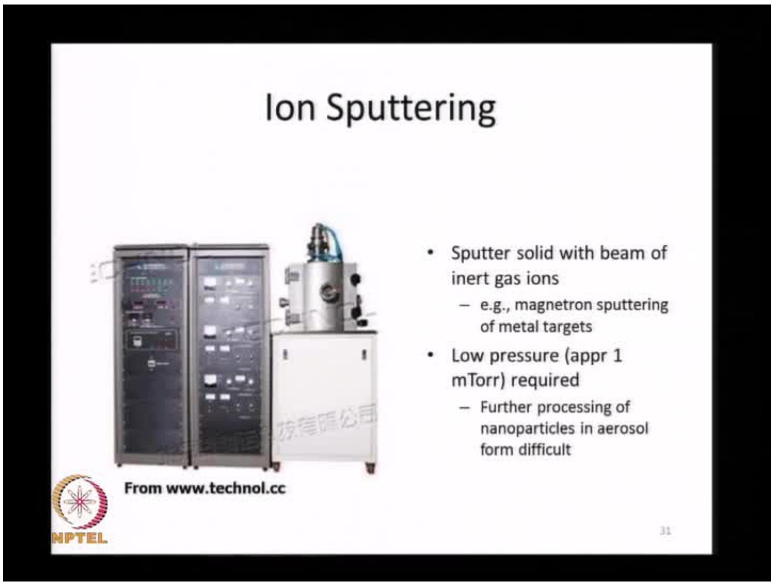

Ion sputtering is another commonly used technology where in this case, you are essentially impacting the solid surface with high energy ions. So, this process is called sputtering.

Sputtering is refers to hitting the solid surface with the beam of gas ions, again this can be inert or reactive as the application demands. Magnetron sputtering is the 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 millitorr and one of the drawbacks to this method is that, further processing of nano-particles in aerosol form can be difficult because of particularly the low pressure environment that is demanded in Ion sputtering techniques.

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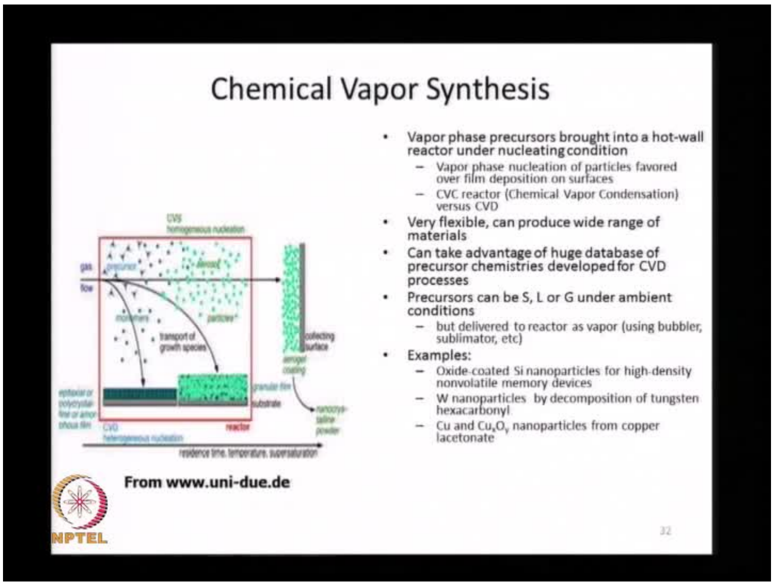

Chemical vapour synthesis is probably the most widely used method to make nano-particles in the bottom-up approach. Here, you take vapour phase precursors and you bring them into a hot wall reactor under nucleating conditions. So, essentially this is a reactor in which there is a target surface, but 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, vapour phase nucleation of particles in this case is favored over film deposition on surfaces; for those of few are familiar with chemical vapour 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 down the film.

In a CVC reactor, there is a Chemical Vapour Condensation reactor that is used to synthesis nano-particles. The reactor is designed is very differently, all the walls of the chamber are also kept at elevated temperatures. So, that and the gas itself is kept under conditions such that, homogeneous nucleation becomes possible; this minimizes 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 vapour phase precursors you can make.

So, anything that can be made into a vapour phase form and introduce into a reactor can be made to react and produce product that is in the nano size range. From the view point of analyzing and characterizing such reactors, there is a huge database of precursor chemistries that has been developed by the CVD industry, chemical vapour deposition has been used for a long time to make thin fumes for various applications.

So, the CVD industry is very matured and it has a huge database on various chemical reactive components and the associated products. So, in chemical vapour 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 vapour, to the reactor in vapour form. It is critical that you do not allow solid or liquid reactants to enter a C V gas or CVC reactor.

The reactance has to enter in vapour form, but how you convert the solid or liquid precursors to this vapour form is entirely up to you. You can use bubblers, sublimators etcetera, some of examples of nano materials that are used that are manufactured using are chemical vapour synthesis reactor or oxide coated silicon nano-particles, tungsten nano-particles by decomposing of a tungsten compound, C u and C u x o y nano-particles also from a copper compound.

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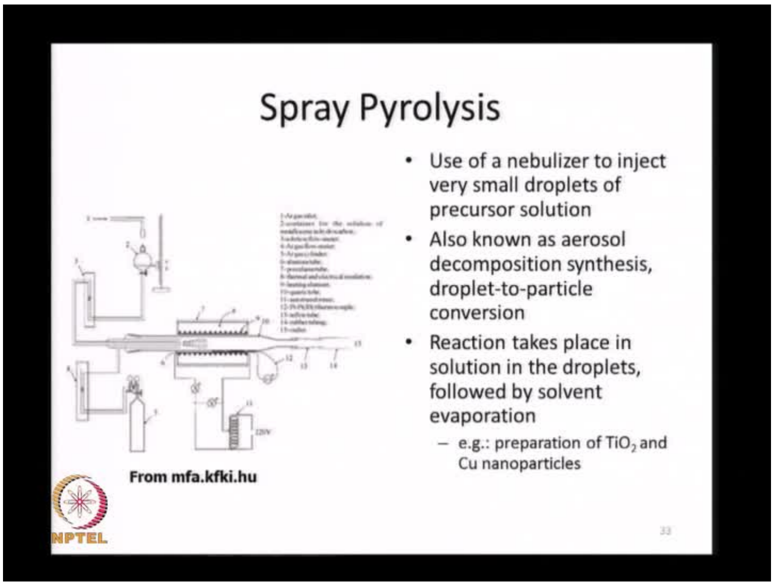

The next technique is spray pyrolysis; in spray pyrolysis, essentially we make very small droplets of the precursor using a nebulizer and you inject it into an evaporative environment. This technique is also known as aerosol decomposition synthesis and it involves a direct conversion from droplet to particle. The reaction here takes place in solution in the droplets, these very fine sprays or droplets or again highly reactive because of their small sizes. So, they react and then you evaporate the solvent that you 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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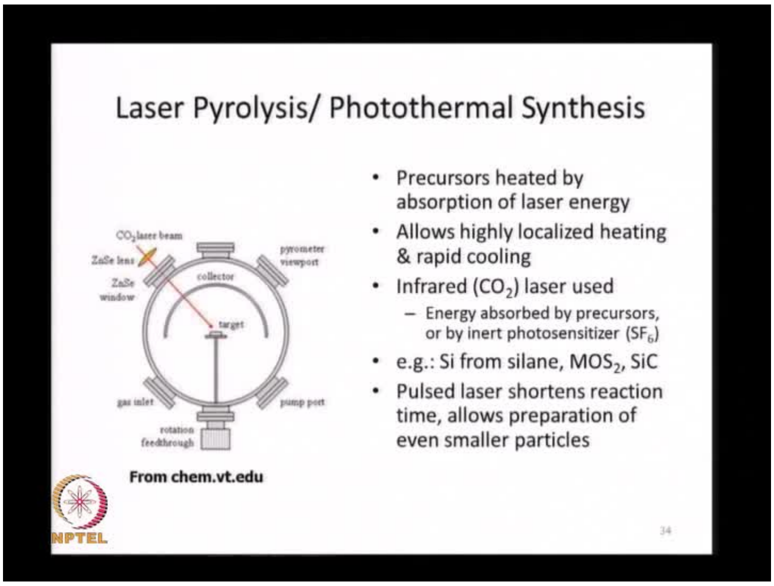

A related technique is laser pyrolysis or photothermal synthesis. Here the precursors are heated by absorption of laser energy and this technique allows highly localized heating and rapid cooling. So, quenching becomes easy when you are using this technique. You do not have to allow growth to occur beyond a point where you want to stop it. Infrared laser, C O 2 laser can be used which reduces the expense of the operation.

Some examples of materials that are made using this technique are silicon from saline, M O S 2, silicon carbide. Pulsed 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.