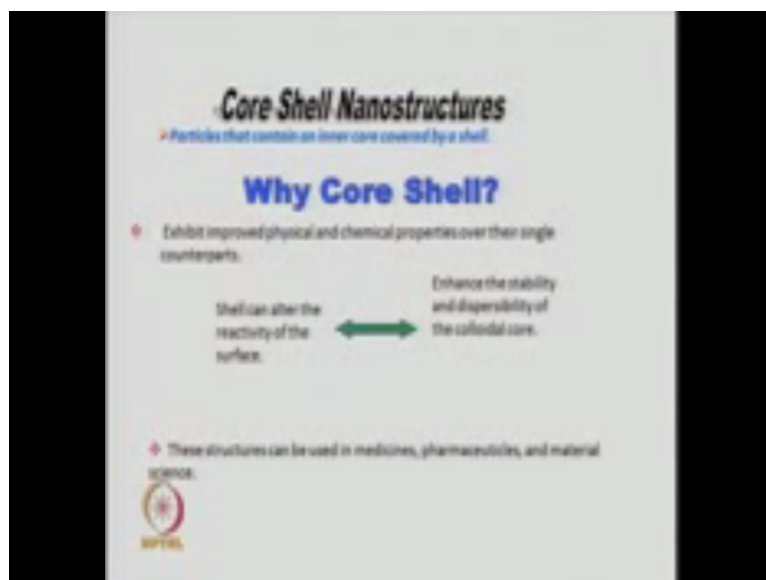


Nano structured Materials-Synthesis, Properties, Self Assembly and Applications
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Module - 3
Lecture - 24
Core Shell Nanostructures – I

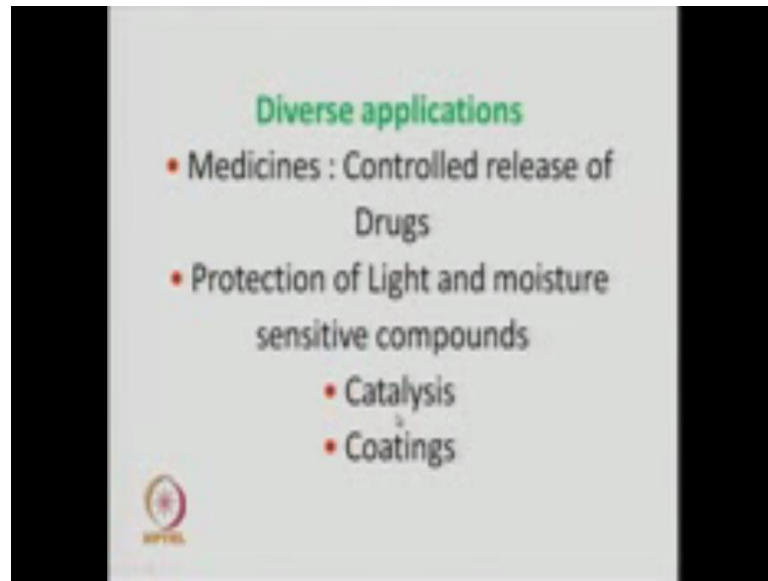
Welcome to this course on nanostructured materials synthesis, properties, self assembly and applications Today, we are in the model 3 lecture 10. And we begin a series of 3 lectures on core shell nanostructures. Today is the first lecture on this 3 part lecture series of core shell nanostructures and that belongs to the module 3, lecture number 10.

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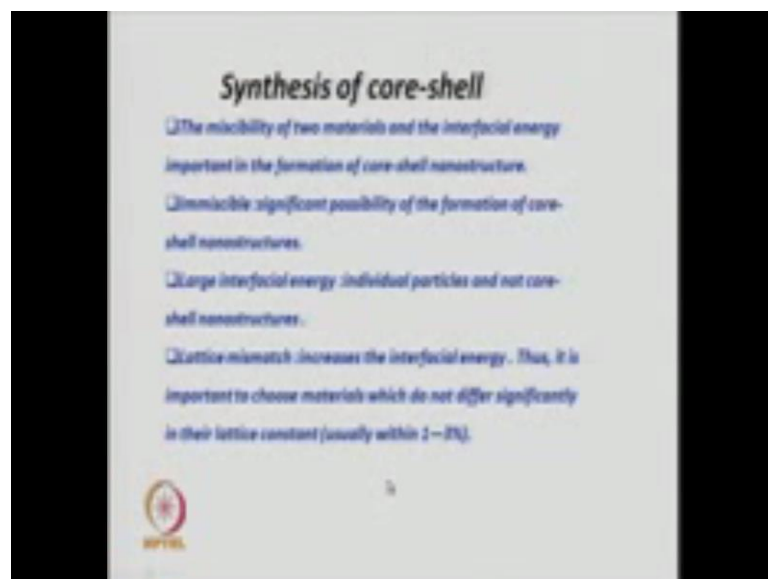
Now what are core shell nanostructures? These are particles that contain an inner core covered by a shell. Now, so the inner core can be of one material and the shell can be of a different material. So, why core shell nanostructures are important? They are important, because they gave improved physical and chemical properties over their single counterparts. For example if you have a core of a material a and a shell of material b. Then the core shell of a and b can give you improved reactivity on the surface can enhance the stability and dispersibility of the colloidal core. And they can be used in many, many applications. So, what are these applications?

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There are diverse application in medicines for example, in controlled release of drugs. And drug as drug delivery agents they can protect materials from light and moisture sensitive compounds. So, if you have a moisture sensitive compound you can make it as the core. And you can cover a shell which will prevent reaction of the atmospheric oxygen or moisture on the course. So, you can stabilize the core material then you can use them as catalysts as coatings several applications are there for core shell nanostructures.

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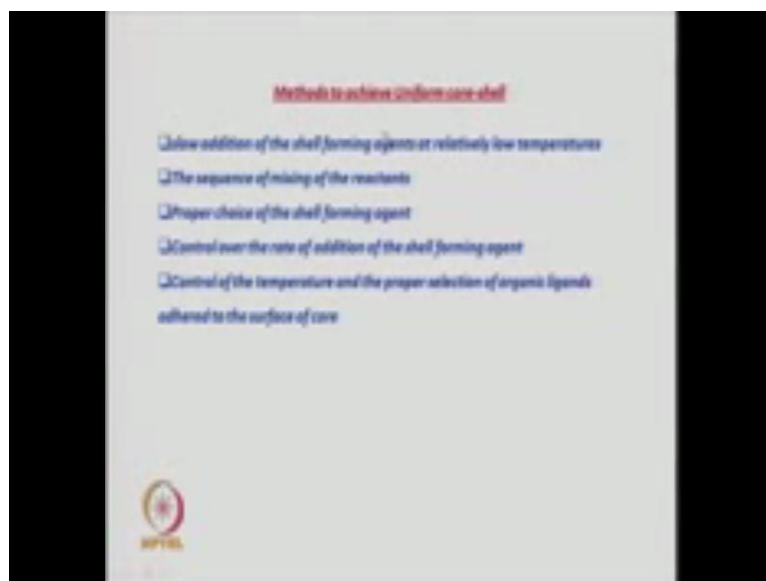


Now, the synthesis of a core shell nanostructure can be followed on basic principles which are the miscibility of two materials and their interfacial energy. That is very important when you design core shell nanostructure, if there is a significant possibility of the formation of core shell nanostructures are there. However if they are miscible then they may form a solid solution so this interfacial energy is important. Now you if you have a large interfacial energy then you get individual particles.

So, you have a and b and you want to make a core of a and shell of b if the interfacial energy between the a and b material is very high. Then chances are that you will not get a core shell material but, you will end up with 2 materials 1 a and 1 b and such a material will then be called a composite material it will not be called a core shell material. So, large interfacial energy is not good for core shell nanostructures then if you consider lattice mismatch that effects to basically the lattice parameter of 2 materials a and b.

If the lattice parameter that is their unit cell parameters are widely different then that will increase the interfacial energy. And thus you have to choose materials which do not differ significantly in their lattice parameters or lattice constant and should be within 1, 2, 3 percent. So, if you have large changes in lattice mismatch large lattice mismatch then that will increase the interfacial energy. And that in turn will make it difficult for you to make a shell on top of the core. And you will in turn end up with 2 different types of particles which is a mixture and then it is called a composite.

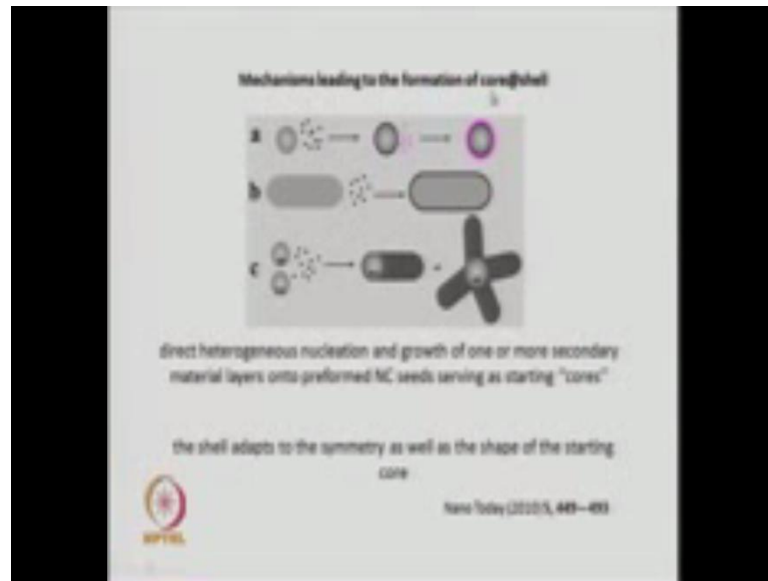
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Now how do you achieve uniform core shell structures if you slowly add the shell forming agent at relative low temperatures that is important. Then the sequence of mixing up the reagent how if you want to make a on top of b or b on top of a the sequence of mixing of the reagents which are related to a and b are important the proper choice of shell forming agent is important. For example, if you want to make a shell of silica then you have to take appropriate reagent, which contains silicon for example, some alkoxy silanes like ethoxy silane, ethoxy silane they will be use for making the shell. So, appropriate reagents have to be taken between be related to the shell forming agent.

Then the edition of the-shell forming agent is important for making a proper shell and the control of the temperature and the selection of an organically ligands which adhered to the surface of the core. So, these are some of the key parameters which one has to take into consideration when one is planning to form a uniform core shell structure. So, there is thermodynamics and there is kinetics both involved and making a stable core shell structure. And of course, by changing parameters you can sometimes get meta stable phases. And you can stabilize those which normal thermodynamics will not allow you to make them stable especially, because your making the synthesis in the nano dimensions.

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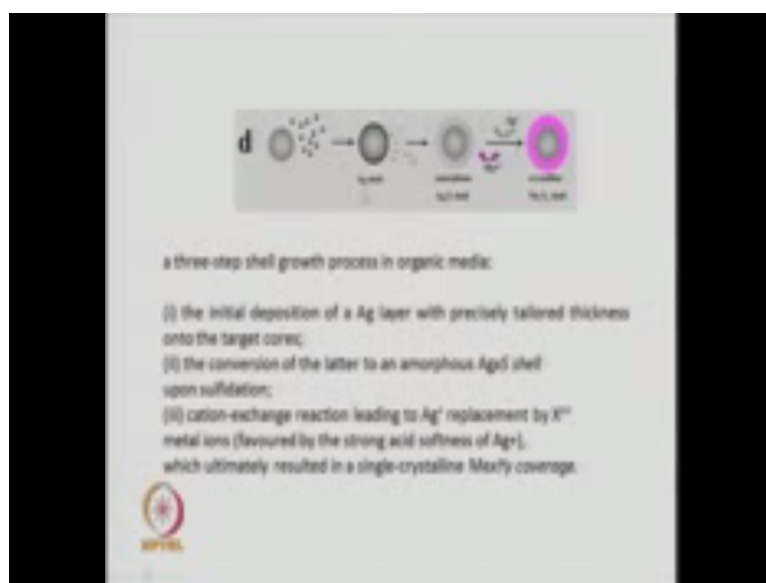


Now, some other mechanism which lead to the formation of core shell structures typically core shell structure is represented like core with this symbol which is at. And shell that means whatever suppose you are making a is the core so you a write a at b where shell is b. Now, the there can be several different mechanisms by which you can form core and shell. So, here for example, you have a particle which is going to be your core material and then you want to make a shell of some other material. So, if this material and this material come close and they start agglomerating rating on the surface right you can make a shell like that. So you can do what is called heterogeneous nucleation and growth. So, you have this a reaction showing you direct heterogeneous nucleation and growth.

And it can form a seed then on top of that you can make share like this so fast you can have one layer which can be kind a capping layer and it forms one black layer on top. And then you have a material which can be put on top of that capping layer. So, here you have the core and then the capping layer and then that shell however you can directly make a shell on top of a core. If you have a rod like particle you can get rod like core shell structures then you can also have. Suppose you have this is the example of zinc sulfide if you have a zinc sulfide or in the woods sight structure or zinc sulfide in the zinc blend structure depending on the 2 structures is the different.

The shell will form in a different manner for example, if you take wood sight type zinc sulfide and you are trying to make shell on top of it. Then you normally get this kind of a rod shaped structure when you take zinc blend typically you get this kind of tetra powers. So, the shell adapts to the symmetry as well as the shape of the starting core so that is what is shown here. So, here the core is an isotropic and the shale which forms on top is also an isotropic here the symmetry of zinc blend. And wood sight is taken into consideration when the shell forms so on wood sight you get an isotropic structure. Whereas, on a zinc blend you get a tetra powered like a structure because of the tetrahedral symmetry. So, the symmetry is important and the shell adapts to the symmetry.

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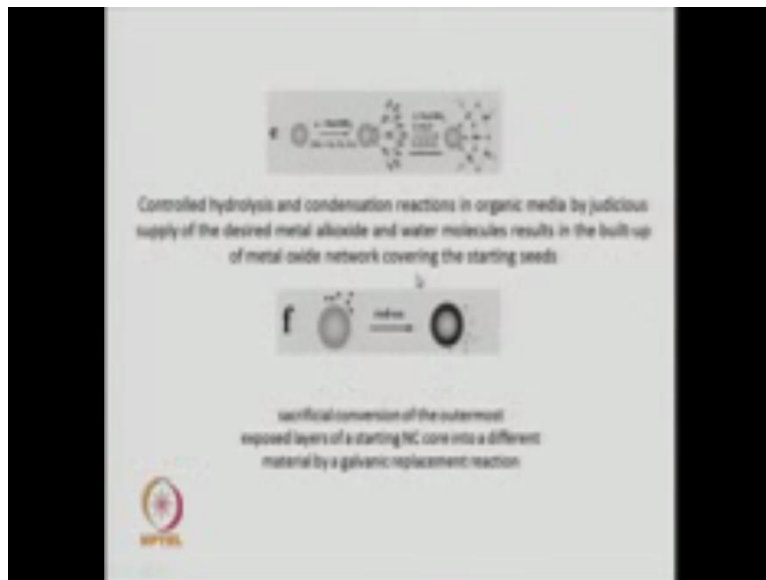


Now, you can also have a 3 step shell growth process example in an organic media here you are making a silver shell on a particle. So, you are adding some silver nitrate and then you are making the shell on top which is initially amorphous and you add some other alkylating agents. So, you do some cation exchange on top of that and you can remove the silver and you will get this shell which is a favored by the strong acids softness of silver plus.

So then you can get this kind of a coverage on top of the core. So, you can have 3 step shell growth process inorganic media the way it has been explained using first or silver shell which forms then an amorphous silver sulfide or shell on sulfidation. And then you

can remove the silver ion and you can exchange the cation with silver. And then you get a different shell amid this sulfide on top of it. So, this kind of 3 step shell growth process is possible in organic medium.

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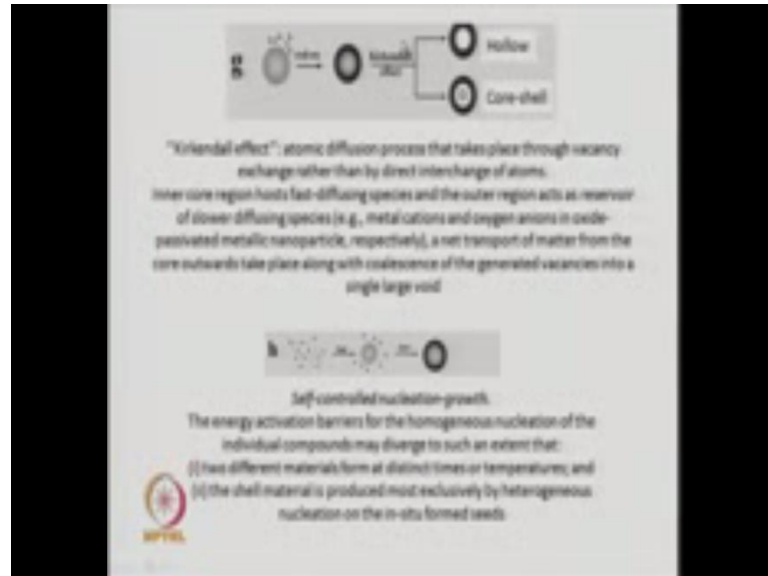


Now, this is another process by which you can get core shell structure so it is a controlled hydrolysis and condensation reaction in organic medium. So, you supply a metal alkoxide it can be silicon alkoxide or titanium zirconium and you have a core particle. And then you build this kind of a structure on top of that core. And then you have hydrolysis and then condensation and then you get this kind of shell form on top of it. So, this is one mechanism you can also have a sacrificial mechanism where you start with the particle. And then you some of these expose layers of the starting core are removed and these particles come on top of the inner core. So, the core diameter you see here it gets reduced in the core shell structure.

That is because part of the expose layers have been removed during this reaction which maybe a redox type of reaction. And ultimately that core diameter is smaller than the starting nanoparticle and the shell is of course, formed why the new material which you have started. And this can be done by a galvanic replacement reaction in a shell. And you can see these particles which going out is actually belonging to the core material. So the some of the particles of are removed from the core material and the incoming material is

deposited on that inner core. Ultimately giving you a smaller core sized compared to the starting material so this is called a sacrificial conversion of the core material.

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Now, there are other methods or mechanisms by which you can get core shell nanostructures for example, these are very famous method. And the effect is called the kirkendall effect where you have a core and you form a shell on top using this kind of a redox reaction or a sacrificial reaction. And then in you have the kirkendall effect where it is a atomic diffusion process which takes place through vacancy exchange without having a direct interchange of atoms. So, there is a vacancy exchange was this core shell is formed. Then you basically there are fast diffusing species in the inner core and the outer region acts as reservoir of slow diffusing species example metal cations and oxygen anions in oxide passivated metallic nanoparticles.

So, what you can get using kirkendall effect is you can get a hollow structure or you can get a core shell kind of structure like this. So in this kirkendall effect your basically take taking the process is through vacancy exchange rather than direct interchange of atoms. And there is a net transport a matter from the core outwards along with covalence's of the vacancies into a large void. So, this vacancies they start moving and the vacancies all a kind of covalence together to form this gap between the core and the shell. And you have that matter transport is towards the outward. So, net transport of matter from core to

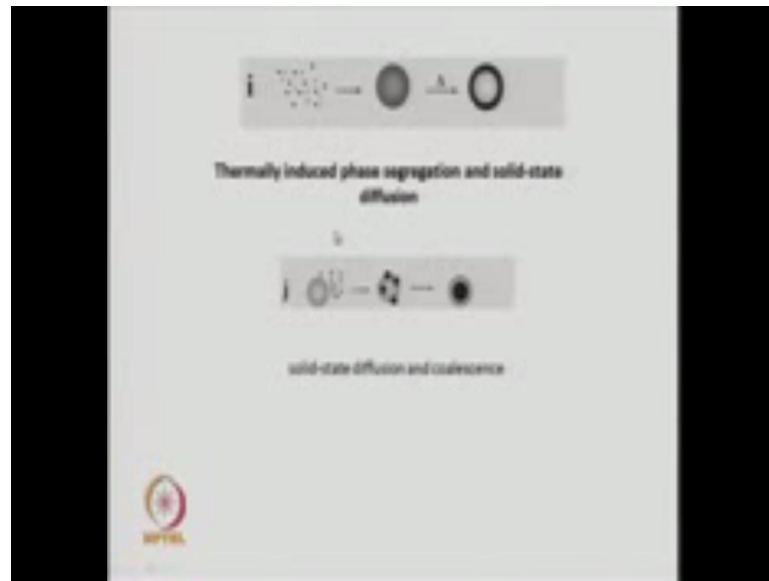
the outward direction takes place in this Kirkendall effect now you can also have a self controlled nucleation group.

So, the energy activation barriers for the homogeneous nucleation of individual compounds may diverge such that 2 different materials form at distant distinct times or temperatures. So, initially you may have one particle and so that forms the core which is the first reaction from system of 2 types of species one. You can see is light grey the other one is the dark one and what happens is the lighter ones aggregate faster. And you get a core particle and then the darker ones aggregate slowly so they form on top of the light to grey core and so they form the shell. So, this is a self controlled nucleation and growth mechanism and it has 2 different materials which form at 2 different times or temperatures.

And the shell material is produced exclusively by heterogeneous nucleation on the in situ formed seeds. So, this is the seed the light grey particle which is formed in situ from the small light grey particles this acts as the seed for the formation of the shell for which is denoted by these dark small spots. And so you ultimately get this dark shell on top of the light grey sphere. So, this is by self controlled nucleation growth mechanism that you can make a core shell structure. So, there are many, many ways by which as you see you have already several methods forming core shell structures from seeds using heterogeneous nucleation and growth mechanism.

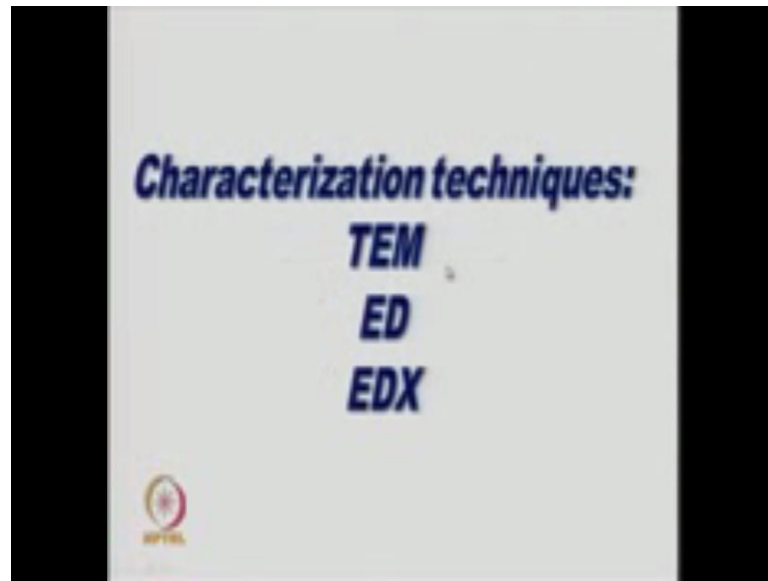
Then a 3 step shell growth mechanism then controlled hydrolysis and condensation reaction sacrificial conversion of the outermost layer of the core. Then the Kirkendall effect giving you movement of particles are matter from the inside towards the outside leading to this vacancy coalescence. And ultimately leading to this hollow core shell structure it may be completely hollow if this continues. And this is an intermediate structure this is the final structure where all the matter has moved from the core to the shell then you have self control nucleation and growth.

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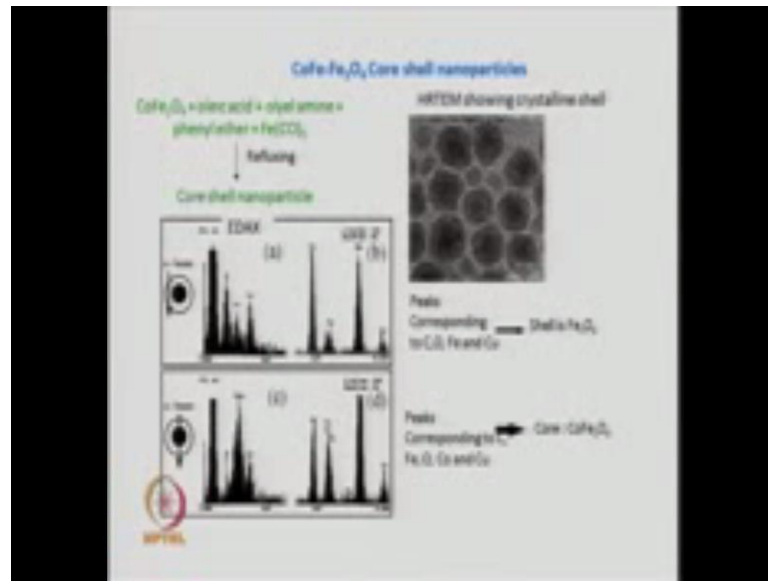
You can also have thermally induced phase segregation and solid-state diffusion. So, you have 2 types of particles here and then it forms a composite particle. And then as you heat them this composite particle as you heat them the phase segregates the dark ones and the white ones segregate to form 2 completely distinct entities one forms the core the other forms the shell. So, this is thermally induced phase segregation and solid state diffusion here what happens is you have a core particle and there is another particle and initially they adsorb on the surface. So, you have these small particles becoming larger they are coalescing on the surface and ultimately you can form a core shell type of structure.

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So, several mechanisms of making core shell structure now, we come to a very important thing that how do you look at this core shell structures. Finally, once you make the core shell structures you have to show that they are core shells. So, how do you look at them and that is very important in this kind of science or technology where once you have made this nanostructures how do you exactly identify the core and the shell. The basic technique, which is used to characterize these core shell structures is by electron. And in electron microscopy you use basically the T E M which is the transmission electron microscope. And then in the transmission electron microscope you can do several things you can a image the nanostructures or you can do electron diffraction. And find out the crystal structure of your nanocrystals. And you can also find out the composition of your nanocrystals by looking at what we call the energy dispersive x ray analysis. So, all these things can be done using a transmission electron microscope.

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So this is an example of core shell structure where you have cobalt iron alloy as the core particle and you have iron oxide which is the shell. So, this is the high resolution transmission electron micrograph which is showing the crystalline shell around a core. So, the core is at the center which is made of cobalt and iron and the shell is made up of iron oxide Fe₃O₄. And how do you make these particles is that you start with cobalt ferrite CoFe₂O₄ and use oleic acid and oleyl amine and then phenyl ether and iron carbonyl. If you reflux it you end up with a core shell nanoparticles of this kind this is what you see in the image and if you see the scale here this is 10 nanometers.

And so this particle diameter, the core shell diameter is around 10 nanometers and if you look very carefully then the core is here and this diameter of the core is around 4 to 5 nanometers. So, what you can say from this transmission electron micrograph is there the core has a diameter of around 5 nanometers 4 to 5 nanometers. And the shell thickness is around 2 to 3 nanometers and what is in the core and what is in the shell. If you want to find out then what you do electron microscopy bypassing the electron beam through the shell. And also through the center of the particle when you pass the electron beam from the shell then you get a spectrum.

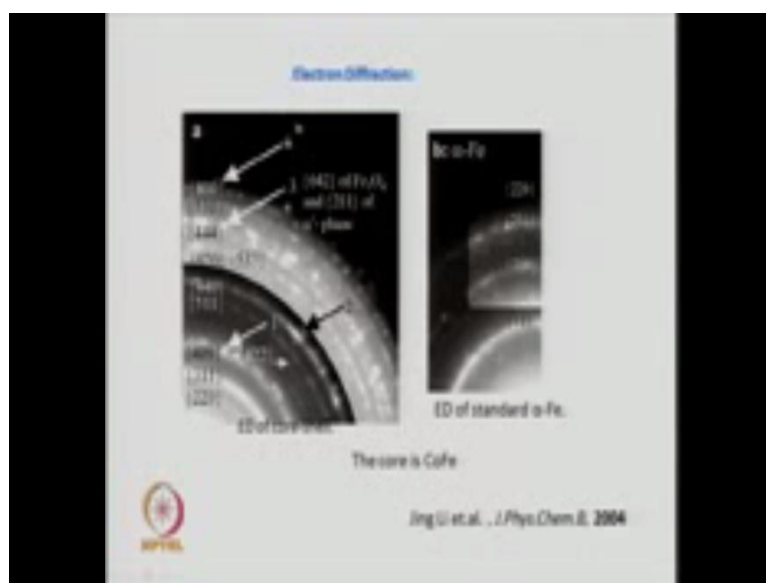
And you analyze the spectrum this is the energy dispersive x ray analysis and when you do you can identify these peaks as belonging to various metals. So, what you see here is you can see copper iron oxygen carbon now copper is coming because we have used to

copper grid to mount your sample. So, the copper does not belong to this material but, you're getting this copper line because it is mounted on a grid for holding your sample and that grid is made of copper. So, you can ignore this copper peak what you have to see is the other peaks so iron is there oxygen is there and some carbon. So, carbon and oxygen normally can come as either oxide and carbide or most of the time carbon come as an impurity. So, what you can say is that the electron beam when it passes from the shell it can see carbon oxygen iron and copper out of that carbon is an impurity and copper comes from that t e m grid.

So the material is made of oxygen and iron and hence the shell is Fe_3O_4 which is what you wanted to make. So, you can confirm that the shell is a Fe_3O_4 now when you do the same experiment with the electron beam going through the center of the core shell structure. And if you analyze the spectrum you will see that the peaks correspond now to carbon iron oxygen cobalt and copper. So, carbon and copper we ignore because carbon is an impurity and copper is from the TEM grid. So, what you find is that your iron oxygen and cobalt.

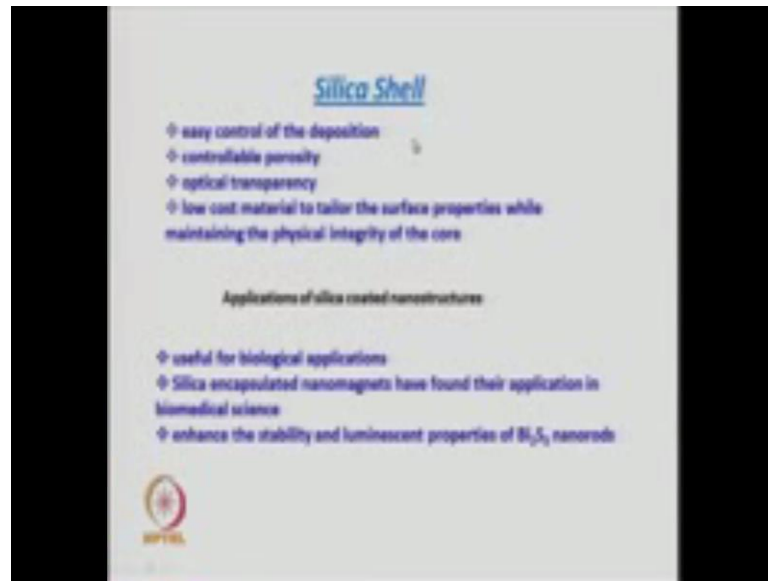
So, when the beam goes through the center you can say that cobalt is certainly at the center and iron is also possibly in the center. But iron and oxygen are certainly in the shell because that you already found out. So, from the EDX what you can say is that the core is made certainly of cobalt but, it can also have some iron. And it can also have some oxygen because that distinction you cannot make just by using this EDX analysis. You have to do some other methodology what you have to do is called dept analysis that means you have to remove the surface. And then study and then you can actually identify the real composition of the core.

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Now, you can also do electron diffraction and from electron diffraction of the core shell structure you get a particular spots. And these spots can be identified with read the Fe₃O₄ structure and also belonging to the alpha phase of iron which can be you due to the core which is made up of cobalt iron. So using electron diffraction and by assigning these reflection each spot is from a plane in the lattice crystal lattice. And when you can assign the planes of both the core and the shell you can say that both these are present in the solid. So, using electron diffraction you can assign both the structures which you see in the core and in the shell. Now, let us do some examples of core shell structures and you can choose many, many thousands of examples of core shell structures which have been synthesized over the last 10 15 years. And we will choose some selective examples to give you a feeling on the type of core shell structures that people are discussing today.

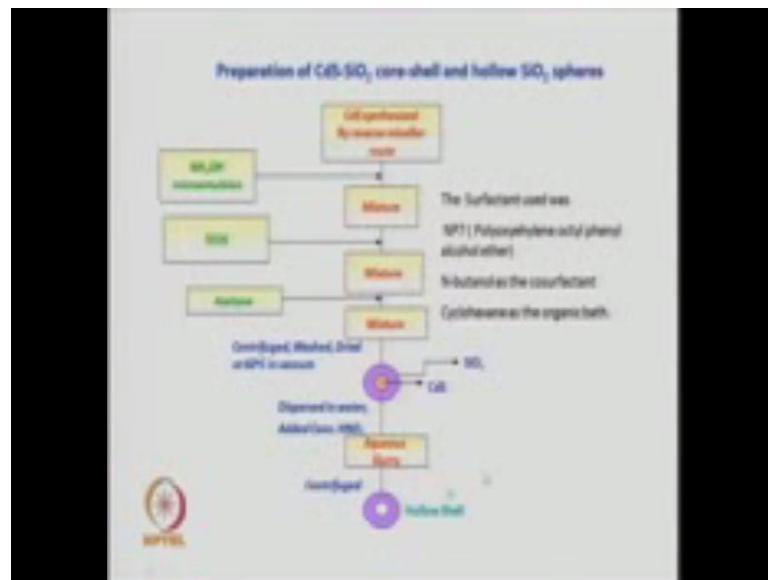
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So, first one of the most important shell making substances is silica SiO_2 , why people choose is because of easy control of deposition of the silica shell you then can control the porosity of the shell silica is optically transparent. So, whatever you put in the core if it an optical material it you can harness the optical properties of the core when you have a silica shell silica is also cheap. So, it is a low cost material to tailor the surface properties while maintaining the integrity and the stability of the core where are silica nanostructures applicable.

So, there are lot of applications of silica coated nanostructures they are used for biological applications they silica encapsulated nanomagnets have found applications as in biomedical science. And they can enhance the stability and luminescent properties of this bisulfide nanorods. These are few of the worst number of applications that you can expect from a core shell nanostructure, which has a silica shell on top of some particle. That particle can be a metal particle it can be a semiconducting particle or it can be an insulating particle. So, there are many, many examples on which silica has been coated to act as a shell.

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Now, this is a typical procedure.