Surface Engineering of Nanomaterials

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Lecture - 40
Main Problems in Synthesis of Modified Nanomaterials

Hello. At last we have reached in our last lecture or may be the last presentations, actually which is dealing the Main Problems in Synthesis of Modified Nonmaterials.

So, what we have done till today is that we have tried to give a brief overview about the surface engineering's, what kind of problems generally we are facing, then how we are trying to modify those surfaces, then in terms of nanocomposites on nanofillers how we can make the modification of these kind of nanofillers nanomaterials. Then we are trying to enhance properties in terms of mechanical properties, maybe the thermal properties, maybe the optical properties, maybe the biomedical applications, or maybe some kind of other properties too. But still when we are using this kind of materials still we are facing certain kind of problems.

As we know that always our demand is increasing, our demand is going on so when we are trying to make today tomorrow we are trying to enhance its properties. And not only that, that our main aim or main motto is that how we can enhance the properties within a short time so that our material should be less expensive, not only that its life time will be increased, not only that it can be sustained in two different environment. So, there are several numbers of thinking actually or maybe that research we are doing that how we can optimize the process, how we can use these kinds of materials for the various applications.

But till today still we are facing certain kind of problems. So, in this particular lecture or maybe that rather we can say that in this particular last lecture just we are trying to show you that what kind of problems generally we are facing, then we are trying to modify those problems, but still we are lacking into some cases where still the research is going on and people or maybe the scientist are trying to enhance those properties or maybe that develop some new materials so that we can get better properties than today.

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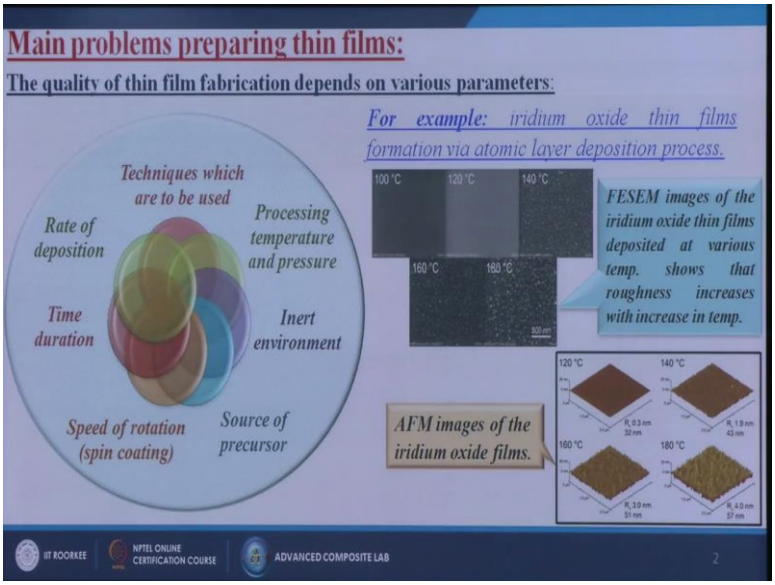

In this particular case first what the thing we are going to discuss that was the main problems generally we are facing when we are preparing some kind of thin frames. So, before going to make the thin films just for our understanding just we have to know that what kind of parameters actually it depends upon preparing the thin films. So, first is that techniques which are to be used.

So, techniques means there are n number of techniques which I have discussed throughout my lecture in brief. So, first we have to choose by which method we can make our thing films so that it can give the better properties, it can enhance its properties not only that it can stick to the surface itself or maybe it can sustain in two different environment or maybe that different temperature onto the different substrate or maybe some different conditions.

Next is that processing temperature and pressure that while making this kind of thin films; what kind of temperature I can put, what kind of pressure I can put because I will show you that at different temperature and the different pressure the material structure is totally different. So, when the material structure is totally different the material property is also totally different. Next, where I am using this kind of materials whether into the some inert environment or maybe some kind of into some gaseous environments or maybe in kind of toxic environment or maybe into the vacuum chamber itself.

So, that is also one kind of prime factor because my material should be well conversant to this particular environment, because when I am making certain kind of materials I do not know that where the material is going to be used in India or maybe whether that material is going to into some South Poles or maybe some USA or maybe some other places. That means, that material can be used into some hot environment, into some high temperature environment, into some high pressure environment or maybe I can use these kinds of materials at the top of the hill, I can use this kind of material under the sea. So, that pressure of that particular material can be changed or maybe that environmental condition of that particular material can be changed.

Then the next one is that the source of precursor; source of precursor is nothing that from what source I am making these kind of materials. So, what is the source of that particular material, whether the material can be sustained in to different environment or not, whether that material can be having the good life or not. Then the speed of rotations in terms of spin coating; that means, what is the processing conditions of that particular material, how much rotation I can put, how much pressure I can keep height, and how much temperature I can give to prepare these kinds of materials.

Not only that time durations, that how much time it is taking to make the final product, whether the reaction will be very short time, whether the reaction will be for a longer time, because I have shown in my some previous lectures also if I increasing the reaction time automatically the thickness of that coating or maybe the thickness of the thin film can be increased. So, this is also vital input parameters for making the thin films. Not only that the rate of deposition; that how fast the material is depositing or maybe how slow the material is depositing, because it depends upon so many properties that addition of that particular material how fast it is, whether the addition properties of the substrate is very high so that it can easily absorb the materials or maybe the materials can be deposited easily onto the substrate or not, or may be that how slow the deposition rate it is. So, depending upon that the thickness of that particular thing claims can be increased or may be that decreased.

So, here we have given certain examples. The examples, is for the iridium oxide thin claims formations via ALD process or may be the atomic layer deposition process. What in this particular efficient image and in this particular atomic force microscopy image just what we are trying to show that if we increase the temperature, means the

preparation temperature of that particular material so how the surface roughness of that particular material is going to be changed. So, in this particular case when I am applying the 100 degree centigrade you can see that some kind of smooth surface of this particular material, but still when I am increasing my temperature for 100 to 120 then 140 then 160 and 180, so you can see that how the material surface is totally changing.

That means, from the smooth surface we are trying to make the rough surface of this particular material. And same thing has been proved by the atom force microscopy image of this particular sample at different temperatures. So, from this particular temperature you can see at around 180 degree centigrade the surface roughness value has been gone up to 4 nanometer. That means, initially it was 0.3 nanometers, then how the temperature is affecting the surface roughness of these particular thin films.

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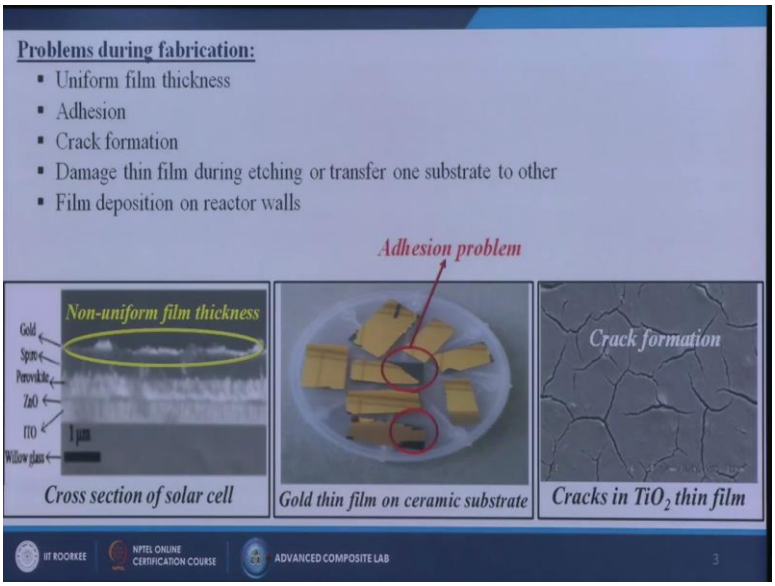

Next, there are several types of problems we can face during the fabrications: first one is that uniform film thickness that is the vital parameter because every time we are talking about the coating but coating properties also depend upon the thickness. Not only that the deposition rate of that particular material onto the substrate itself. So, first one is called a uniform thin film thickness. In this particular case we have done the cross sections of the solar cell materials. And the top of that we have done the coating by its gold, but from this particular image you can see that coating thickness has been varied in two different

zones. That means, non uniform thickness has been observed for these particular materials.

Then, we are trying to give the addition properties, because that is also the biggest and foremost parameters for any time of coating materials. Because when I am depositing our material or maybe that coating material onto the substrate itself then what is the addition properties of that particular material so that it can stick easily to the substrate itself, or maybe if the addition properties is not good simply it will come out from that substrate film. So here also the same thing, I am using certain kind of substrate, then I am doing certain kind of coating materials over there, but still the addition properties is not good so that you can see some kind of coating materials has been detached from the substrate side. So, gold thin flame on the ceramic substrate is the example for this addition problem.

Then another one is that crack formations. So, when I am doing our coating materials or maybe the coating on to the substrate then after drying when I am trying to use these kind of coated materials maybe there is some cracks or maybe that pores can be generated at that particular point. So that actually taking place that some kind of crack formation. So here, we are trying to show some kind of cracks in the titanium dioxide thin films. So, crack has been formed in that and we have seen this kind of phenomena by doing the FESEM or maybe the scanning electron microscopy images.

Next, damaged thin films during etching or transfer one substrate to another; yes because, sometimes what happened I am using or maybe I am quoting my materials onto some substrate, because whatever the actual substrate I need maybe that coating cannot be possible for that particular purpose. So, what we are trying to do? We are trying to do the coating onto some switchable substrate, then simple after coating I have to take out that coating material and I have to put onto my desired materials. So, during the transfer also this kind of problem can be occurred. Not only that the frame depositions on the reactor walls that is also a very vital parameter or may be very common problem where we are facing these kinds of problems.

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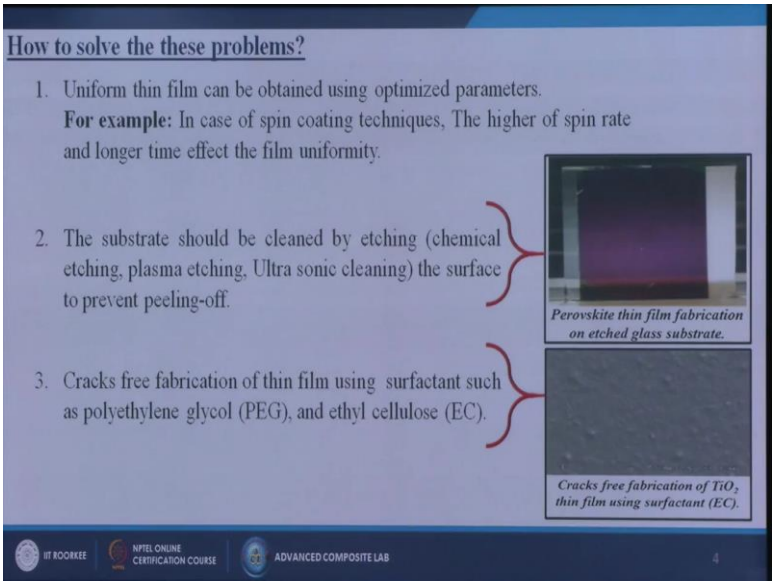

So, how to solve these problems? So still as I told already initially that still scientist or maybe the people are trying to modify these kind of problems to solve these kind of problems may be up to certain level the problem has been solved, but still a long long way to go to solve these kind of problems, because there is no end up preparing any materials so that when we are trying to make the complex materials also the problem will be complex. So, we have to think those complex problems, we have to modify these problems and when we are trying to modify these problems may be some problems can be solved, may be some will be till unsolved.

So, how to solve this problem? First is that uniform thin film can be obtained during optimized parameters; for example, in case of spin coating techniques the higher of spin rate longer time affect the film uniformity. So, this is one kind of parameters or maybe this is one kind of requirements by which we can increase the thickness or maybe that can get the uniform thickness of that particular material, but still this remedy is not same for all. Maybe I can use some kind of material tomorrow where I cannot get the same thickness over there. So, still scientist or maybe the people are trying to modify this kind of problems.

Here, the substrate should be cleaned by etching process; chemical etching, plasma etching, on with ultrasonic etching, the surface to prevent up peeling off. So, by doing the etching process we can announce the addition properties, because when I am trying

to coat our coating materials onto the substrate itself if the addition properties is not material is good so what will happen or maybe some kind of oil or maybe some water molecules are present simply the coating material will not stick with onto the substrate itself. So what we have to try to do, we have to make certain kind of rough surface over there or maybe some water molecules or oil molecules we have to take it out or maybe there is some dust particular present, so we have to remove those that dust particles so that our coating material can stick properly onto the substrate itself.

So here, we are trying to show some kind of parovskite thin film fabrications on each glass substrate. So, first we have done the etching of that particular glass, and then we have deposited this thin film onto the glass substrate itself. Here, some kind of crack free fabrications of thin clean using surfactant such as polyethylene, glycol, PEG and the ethyl cellulose here. So what we are trying to do, we are trying to use some kind of binder materials so that that coating materials will be crack free, and when it will be deposited onto the substrate itself there will not be any formation of crack or pores will be occurred.

So, here the crack free fabrications of TiO 2 thin film using the surfactant that is the ethyl cellulose. So, here from this FESEM image you can see that there is no formation of cracks or maybe that pores has been taken place.

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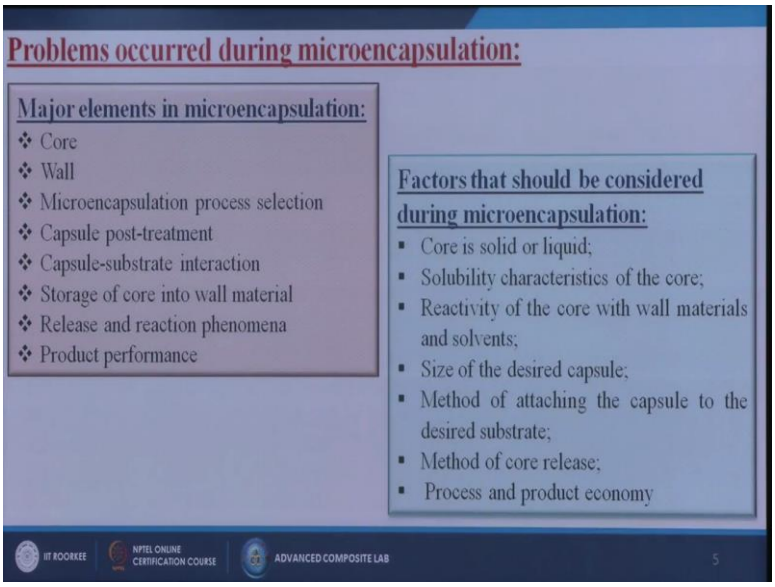

So, here while we have already discussed about the micro encapsulation also; we have discussed that how we can do the micro encapsulation, how we can do the coatings of these particular micro encapsules. So, in this particular case again we are trying to see that what the problem is generally we are facing at the time of preparation of the micro encapsulations. Before going to start first we have to know that; what are the major elements in micro encapsulation process. So, first one is called the core, then wall, then micro encapsulation process selections, capsule post treatment, capsule-substrate interactions, storage according to wall material, release and reaction phenomena, and the product performances. So, these all are the major elements in micro capsulation process.

What are the factors that should be considered during the micro encapsulations? First one is that core is solid or maybe the liquid; solubility characteristics of the core; reactivity of the core with wall materials and solvents; size of the desired capsules; method of attaching the capsules to the desired substrate; method of core release; process and product economy. So, first we have to make certain kind of coating materials or maybe the core materials on top of the core we have to do certain kind of coating material, then the whole materials I have to put into some thin films or maybe some into some functional groups so that it can be attached with the substrate itself. So, these all are the factors that could be considered during preparations of the micro encapsulations.

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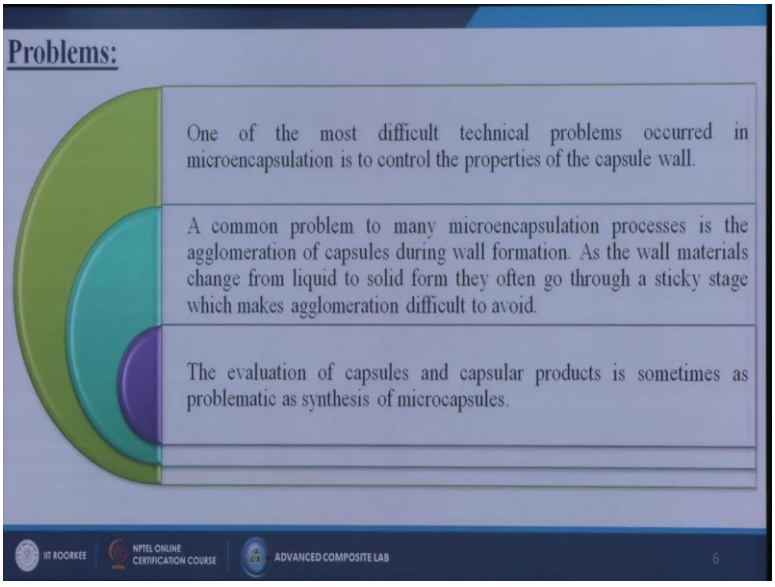

But while I am taking these kinds of parameters maybe I can face certain kind of problems, what are the problems generally I can face? The number one is; one of the most different technical problems occurred in micro encapsulation is to control the properties of the capsule wall. So, that is the vital problem generally we are facing now. A common problem to many micro encapsulation process is the agglomeration of capsules during wall formations. As the wall materials change from liquid to solid form they often go through a sticky stage which makes the agglomeration difficult to avoid.

So, these microcapsules and size is very very small into the nanometer range. And what we are trying to do the coating material first initially it will be liquid then it will form the solid, so while it is transformed from liquid to solid always there will be stickiness in between that; so there will be agglomeration in between the capsules. So, that is also one vital problem generally we are facing.

Next the evaluation of capsules and capsular products is sometimes as problematic as synthesis of the microcapsules. This is also one vital problem over there.

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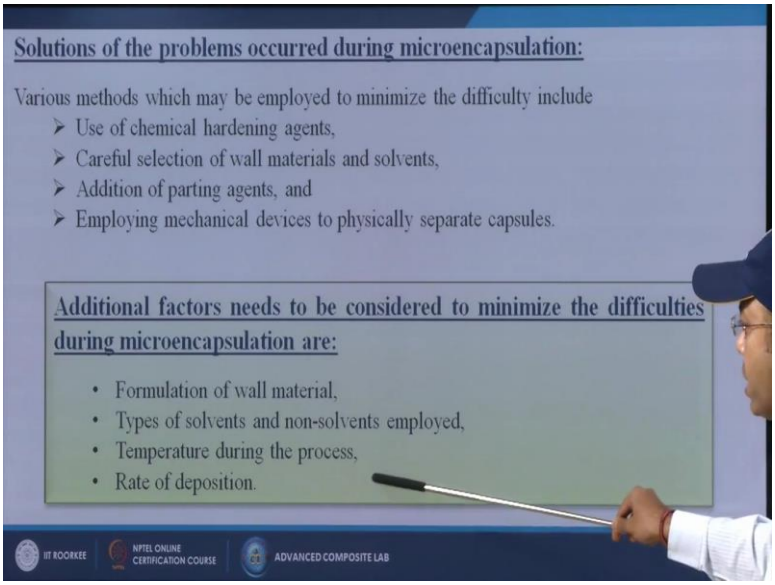

So, what are the solutions of these problems, how we can solve these kind of problems while doing the micro encapsulation. So, first there are various methods which can be used or maybe the minimize that the difficulties. Again I am telling you we are trying to minimize these difficulties; we are not deleting all the difficulties over there, because still

there are lots of difficulties lots of problems people are maybe the scientists are still trying to modify these kind of problems or maybe to solve these kind of problems.

So here, first one is called the use of chemical hardening agents. So, by using the chemical hardening agents we can modify or maybe solve this kind of problems; careful selection of wall materials and the solvent so that they should not stick together, so that agglomeration problem can be removed; addition of parting agents so that there will not be any stickiness in between the coating materials so that the particle will not stick together; employing mechanical devices to physically separate the capsules. So, after drying we have to use certain kind of steerer so that easily this particle can be separated together.

There are some kind of additional factors also that needs to be considered to minimize the difficulties during micro encapsulation are: formulation of wall material, types of solvents and non solvents employed, temperature during the process, and the rate of the depositions. So, these are the additional factors or may be the additional things what we have to take care while preparing these kinds of micro encapsulations.

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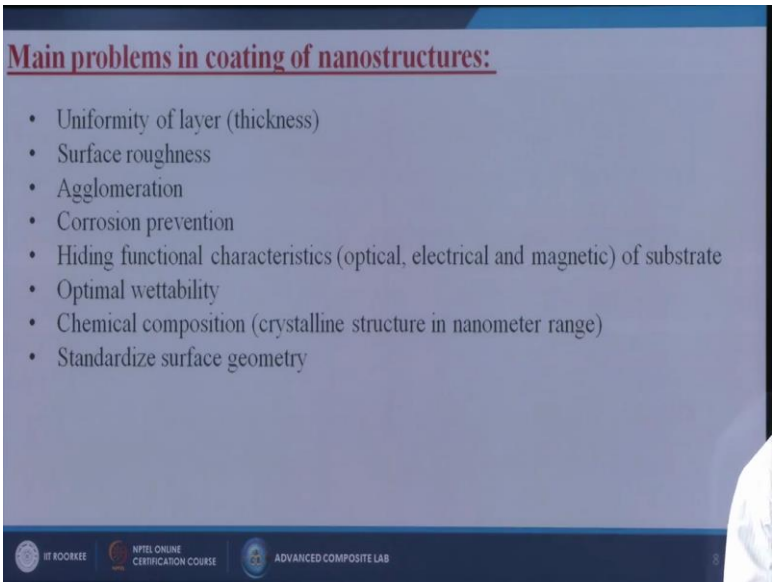

Next we are trying to discuss what are the main problems generally we are facing that when we are doing some coating of the nanostructures or may be on to the substrate itself. So first is that the uniformity of layer thickness that is the vital one, because

sometimes we not get some kind of homogeneous layer over there sometimes we can get the heterogeneous layer, maybe sometimes there I can see some kind of pores or many cracks on to the systems, maybe some reach point at that particular point so that rough surface roughness is very very bad. Sometimes I can get certain kind of agglomerations of the nanoparticles onto the substrate itself, some kind of I can get certain kind of corrosion prevention at that particular point maybe I have made certain kind of materials which is not the corrosion resistance easily that materials can react with the environment that absorb the water molecule from the environment itself so that its corrosion can be taken place.

Also some kind of hiding the functional characteristics like optical, electrical and magnetic to the substrate itself; yes of course, because when I am trying to use the coating materials onto the substrate simply it will hide the substrate properties, because it will coat all over around so whatever the substrate properties actually that substrate is having so it will diminish those properties; only we will get that what the coating material properties is having. Then some kind of optimal wettability or problem can be occurred some kind of chemical compositions, like crystalline structure in the nanometer range that can be a biggest problem at that particular point. And another one is the last one is called the standardized surface geometry, that different shapes and size when you are making that keeping the dimension throughout the coating process is very very difficult for this kind of nanocoatings.

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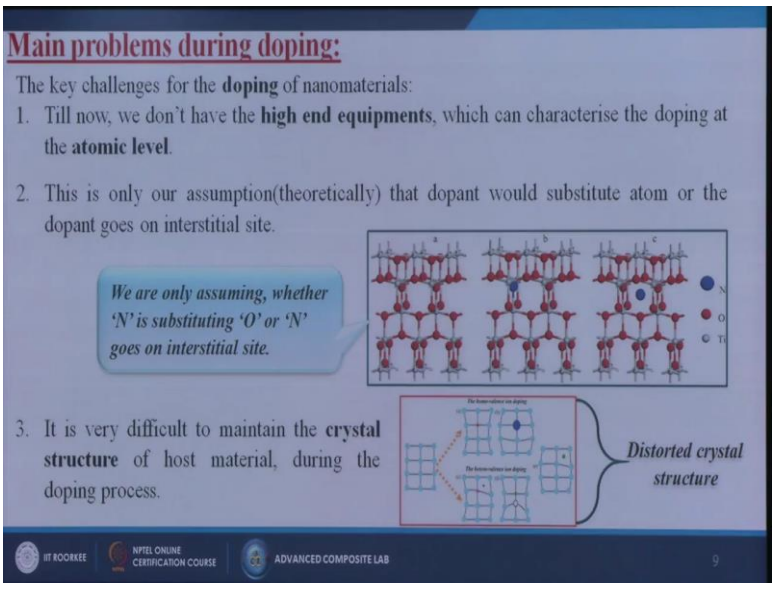

So, also what the problems actually we are facing when we are doing the doping of that particular material. So, first the key challenge for doping nanomaterials is that; till now we do not have the high end equipments which can characterize the doping at the atomic level, yes of course whatever the doping we are doing simple by getting the XPS image or maybe the FTIR or maybe the XRD we are trying to prove that doping is taking place. But how the doping is taking place, where the doping material is actually going, how it is attaching with the substrate materials it is very very difficult to detect. Not only that while doing the doping whether the doping has been done or not, how much percentage of doping has been done that characterization also is very very difficult.

So, these are the problems or may be the key challenge when we are doing the doping of those particular materials. Not only that this is only our assumption of theoretically that dopant would substitute atom or the dopant goes on interstitial side. Yes, is totally theoretical base, we are having some kind of softwares by which simply we are proving that doping is like lithium doping is on to the interstitial side or maybe the boron doping on to the substitutional side, but there is no experimental validation over there. So, simply what we are trying to do, simple from the FESEM image or maybe the XRD analysis or maybe the Raman spectra we are trying to sort that that dopant material is present onto the substrate, but it will never give you that where the doping material is actually staying.

So, here we are doing some kind of assuming that whether the nitrogen doping cell is substituting oxygen or nitrogen goes on interstitial size; yes of course. So, in this particular case when we are doing the doping of this particular material sometimes we are thinking that the doping is going on to the substitution site or maybe sometimes it is on to the interstitial side, but we do not have any exact chemical characterization by which we can prove that whether the doping is interstitial or maybe the substitutional.

Also sometimes it is very difficult to maintain the crystal structure of the host material during the doping process. Yes of course, because it is very very difficult to know the particular doping characteristics where the atoms is staying. So, after doping it is very very difficult to get the final crystal structure of that material. If it is substitutional the crystal structure will be changed, if it is interstitial the crystal structure will be changed, but overall material dimension will remain same. So, that is why the distorted crystal structure can be formed by which we can get some kind of dope materials with advanced

properties, but still the crystal structure of that particular material a getting is very very difficult.

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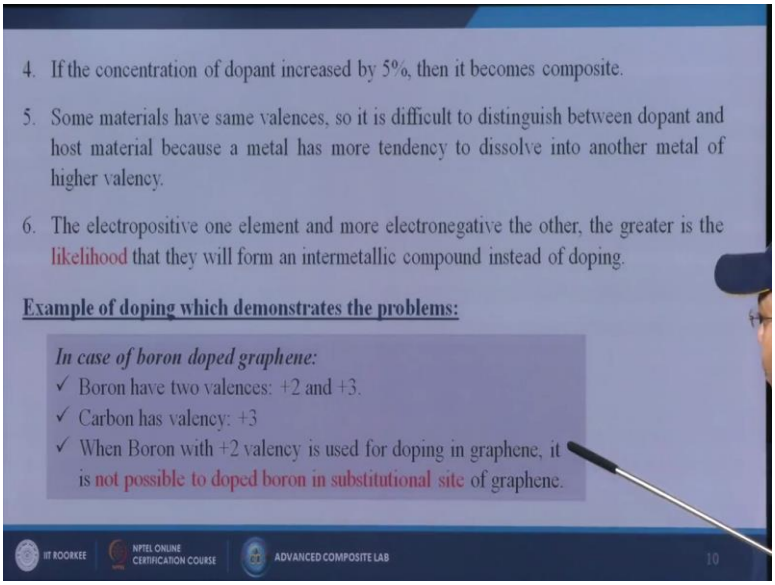

If the concentration of dopant increased by 5 percent then it becomes a composite; that is also a vital parameter, but throughout the chemical reactions or maybe that chemical process or maybe that at the time of doping maintaining this particular percentage is also very very difficult. Not only that, when I am adding the 1 percent dopant, 2 percent dopant also it is very very difficult to prove whether these 1 percent depend or 2 percent dopant is still it is presence inside the substrate system or not; or maybe while washing we are losing some kind of dopant materials. So, these are the different problems what we are facing.

Also this is also one kind of assumption that some materials have same balances, so it is difficult to distinguish between the dopant and host material because metal has more tendency to dissolve into another metal of higher valency. Yes of course, because when we are trying to do the doping, suppose I am telling that a material is dropping onto the b material then it depends upon the valency of these two materials a and b. So, which valency will be higher that material will goes into the second one, but in that particular case if that valency of a and b will remain same then it is very very difficult that whether a is going inside b or b is going inside a. So, in that case that is also a biggest problem that when the valency is equal for both the materials like dopant, or maybe the substrate.

The electropositive one element and more electronegative the other the greater is the likelihood that they will form an inter-metallic compound instead of doping. This is also one kind of assumptions, because whatever the things actually we are doing doping has been started very very; maybe few months or few years back. So, this is the new topic to us still there are lots of things that we have to see, we have to know, we have to research because we are having very limited knowledge on the doping itself. So, many people are working. So, in that particular case whatever the results actually we are getting all on the assumption based, but we do not have any particular characterization tool by which we can prove that which material is doping unto which or maybe after doing how the materials is look like or maybe the how the material will behave.

Not only that, here also we have given certain example of doping which denotes the problem in case of boron doped graphene boron have to valence is plus 2 and the plus 3, carbon as balancing is the passed plus 3. When born with plus valence is used for doping in graphene it is not possible to drop boron in substitutional side of grapheme. Yes of course, because the valency of this particular boron is less than the valency of this particular carbon. So, in these particular case what is happening that we are knowing that one valency will be higher than the another one then the doping can be possible, but if in that particular case the boron valency is lesser than a carbon that is why the doping will be not possible. But still we do not have any characterization that by which we can prove this one, this is also one kind of vital assumptions while we are doing the doping.

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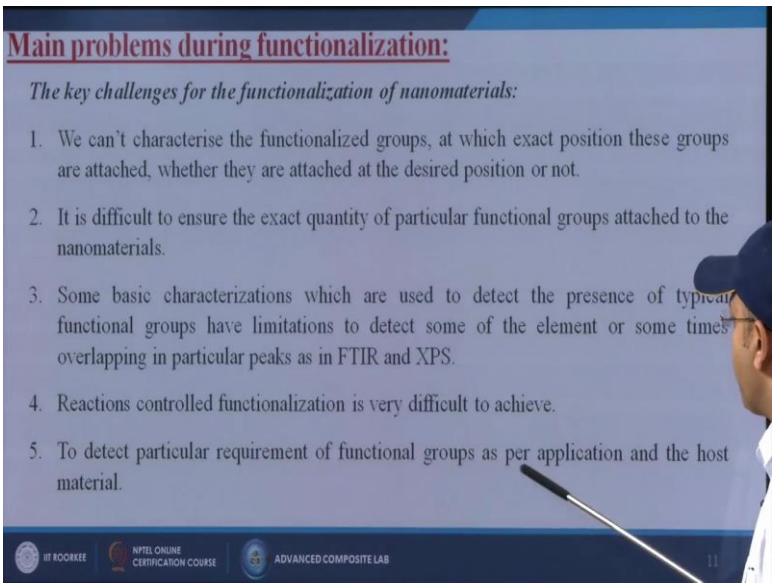

Then we can see certain kind of problems during the functionalization of these nanomaterials. So, the key challenges is that first is that we cannot characterize the functionalized groups at which exact position these groups are attached, whether they are attached at the desired positions or not. Of course, when you are trying to do the functionalization we are trying to wrapping the polymers onto the nanofillers or maybe that carbon nanotube. So, while some lectures on the transference process we have told that either that material will attach at the end point of this particular nanofiller or maybe on to the some defect sides. But still that is also one kind of assumptions, because we do not have any kind of characterization tools that whether the material is only attached on that defect size or maybe the add ends or maybe not other places.

Then it is difficult to ensure the exact quantity of particular functional groups attached to the nanomaterials. Some basic characterizations which are used to detect the presence of typical functional groups have limitations to detect some of the element or sometimes overlapping in particular peaks as in FTIR and XPS, Of course, because when we are attaching some kind of materials that is below the carbon it is very difficult to detect those materials inside the systems itself. Suppose, I am doing some kind of lithium when it is very difficult to detect that the whether the lithium has been attached to the substrate or not or maybe the lithium is present to the systems or not, because about the carbon groups then only it is possible to detect these kind of materials through some kind of characterization. So that is a lack of this kind of characterization techniques.

Not only that, some reactions control functionalization is very very difficult to achieve. To detect particular requirement of functional groups as per applications and the host materials. Not only that, when I am doing this kind of functionalizations I am doing some kind of chemical reactions whether that exact particular group has been attached to that filler or not it is very very difficult to detect. So, simple by doing several characterizations we can assume that this kind of materials has been attached to the system, but it is not fully confirmed.

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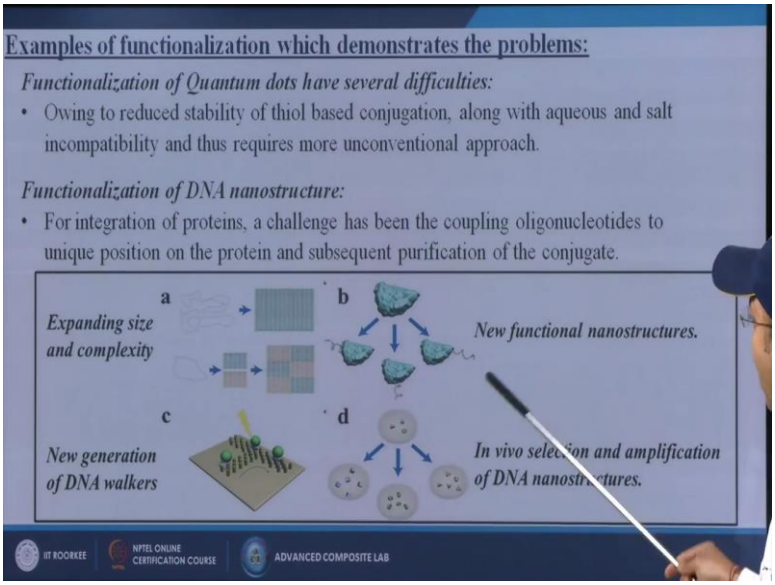

Next we are trying to give certain kind of examples of functionalization which demonstrates the problems. Functionalization of quantum dots have several difficulties going to reduced stability of thiol based conjugations along with aqueous and salt incompatibility and does request more unconventional approach. And also we can do the function of DNA nanostructures for integration of proteins a challenge has been the coupling of oligonucleotides to unique position on the protein and subsequent purification of the conjugate.

The same thing I am telling once again that when I am doing the functionalization of this particular material I do not know whether that particular material is going to the particular site or not or maybe the function is taking place by this particular material or not. So here, in this particular case we are showing that when we are expanding the size and complexity that how the new functional nanostructure is forming. Then new generation of DNA walkers, so here in this particular case we are getting some in vivo selections and amplifications of DNA nanostructures.

So, still I am trying to add some kind of molecules on with functionalize onto this DNA structure, but still I do not know that whether this material is going to the particular side or maybe the particular positions or not.

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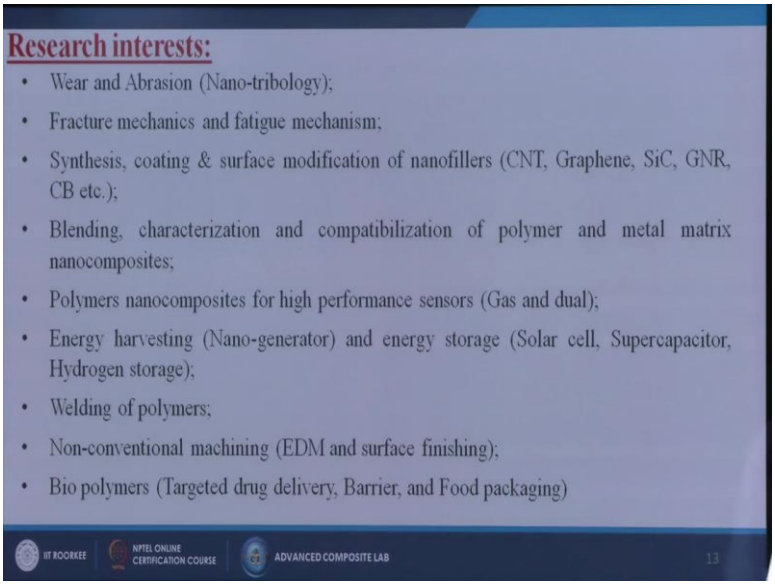

Then at the end of things that we are trying to say about the surface engineering's and these applications; now in a brief just I am trying to tell you that in my lab what we are trying to do or may be on which topic we are doing work on may be what is our research interest. Generally, we are working on the wear and abrasions of these particular materials which is coming under the nanotechnology. Then we are doing some kind of fracture mechanics and fatigue mechanisms of some metal or maybe some polymer materials. Then main thing actually what we are doing we are trying to do some kind of synthesis coating and surface modifications of some kind of nanofillers like carbon nanotubes, grapheme, silicon carbide, then graphene nanoribbons, carbon black, then carbon dots. So, there are various materials we are preparing in our lab, then we are trying to modify these materials, then we are trying to use these kinds of materials for various applications.

Then we are using this kind of blending characterization and compatibilizations or polymer and metal matrix nanocomposites. Basically, these kinds of materials generally you are using for the aerospace applications, automobile applications, or maybe some kind of other implants. Not only that, polymer nanocomposites for high performance sensor actually we are trying to do, we are trying to use these kinds of sensor materials for toxic gas detections. Not only that, nowadays we are trying to use this kinds of can sensors for that dual gas applications where there will be a mixing of gases and we are trying to recognize those toxic gases over there. Then we are using these kind of

materials generally we have prepared in some kind of nanogenerator, so by pressing these materials we can generate the electronic maybe the electrical energy or maybe we are working under some energy storage applications like the peroxide solar cells, some kind of flowable super capacitor and the hydrogen storage systems.

And here, we have done one work on the welding of polymers also because you know the welding of polymer is very very difficult, because we cannot put the direct heat to that particular polymer system then it will melt. So, here we are trying to use some kind of vibration of welding techniques by which we can weld different polymers together. Then we are using some kind of non conventional machining process in terms of electro deposition machining, and the surface finishing process some kind of advanced surface finishing process. And we are also working on the biopolymers say for the targeted drug delivery sub barrier applications and some kind of food packaging techniques. Not only that, nowadays we are trying to make certain kind of magnesium alloys which can be used for the orthopedic implant.

So, here this is my whole team, we are working in the advanced composite lab of IIT, Roorkee. This is myself, here these two are the main backbone of this particular lecture or maybe that whole lecture. So, one is mister Vinay Panwar and another one is Miss Keerti Rathi, those who are working as a TA 1; teaching assistant 1 and teaching assistant 2. And these all are my group members including these two namely; Subhash Singh, Souvik Bag, Jitendra, Pushpendra, Nidhi, then Navjot, Farhan, Tushar and Manmeet, by whom that we have made this kind of lecture in front of you.

Thank you.