Nanotechnology Science and Applications
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Lecture - 18
Experimental Approach to Study Impact of the Nanoscale on Optical Properties

Hello, in this class we will continue our discussion on looking at the Optical Properties of materials from the perspective of Nanoscale materials. In the last class, we looked at some background on what those optical properties were; and you know: what is the event that is happening inside the material that relates to the optical property that we measure. So, in this class we will look at, we will focus our discussion on some experimental aspects.

Experimental aspects which allow us to study the impact of the nanoscale on optical properties. So, we need to look at this in some detail. So, we look at how those samples are prepared, what kind of know aspects we have to keep in mind. So, we get something that we can actually study and where the results then are results that we can use to help us identify some trend or to identify some behaviour. So, that is the thing. So, we look at some points associated with the experimental approach.

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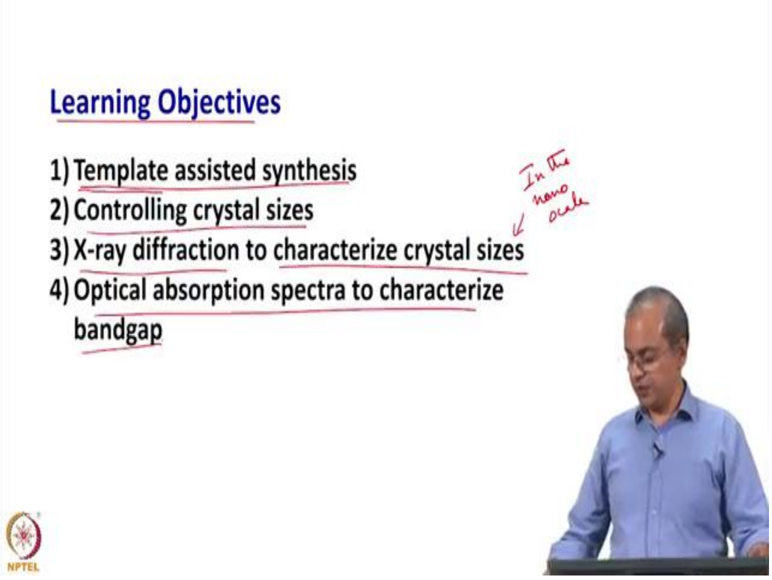

Learning Objectives

1) Template assisted synthesis
2) Controlling crystal sizes
3) X-ray diffraction to characterize crystal sizes
4) Optical absorption spectra to characterize bandgap

In the nano scale

So, the learning objectives, for our class today is, first of all, to look at Synthesis Technique that is used for nanomaterials. So, that is a very useful thing to know in general, because we are going to, you can potentially extend this to other nanomaterial systems where a similar approach can be considered. So, this is called the template-assisted synthesis of nanomaterials and it is a very interesting way of going about making nanomaterials and it has some distinct advantages, so we will look at that. We will, in particular, we will also look at how this synthesis process, this template-assisted synthesis process may help us control crystal sizes.

So, that is another aspect that we look at. We will spend a little bit of time looking at X-ray diffraction data, that is particularly looked at for characterizing crystal sizes in the nano regime; because this is actually used a number of times in many places and therefore, it is worth looking at it. We will then look at optical absorption spectra that are used to characterize the bandgap. So, both of these aspects we will look at. So, this is what we will look at in today's class.

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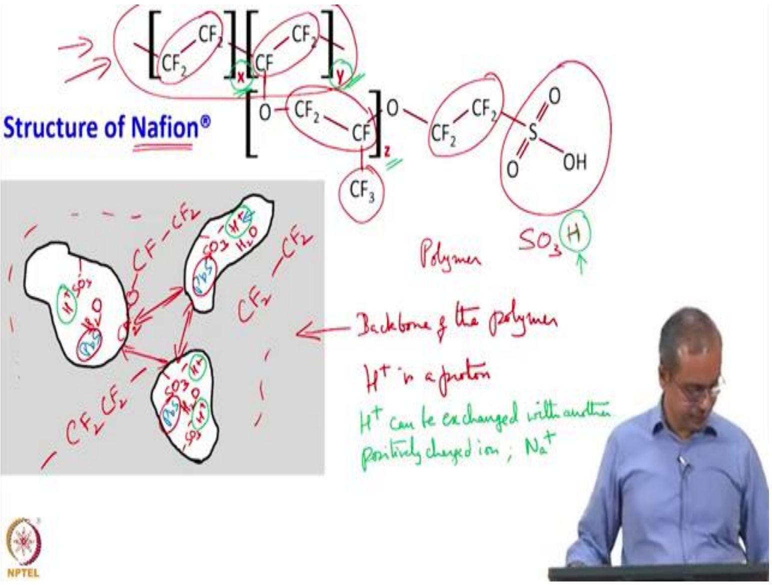

Structure of Nafion®

Polymer

SO_3H

Backbone of the polymer

H^+ is a proton

H^+ can be exchanged with another positively charged ion ; Na^+

So, to look at template-assisted synthesis, the basic idea is that you have some material, another material which is not the material of interest for you. So, that is a material, which we will use as a template. So, by that, we mean that material has in it is structure some locations where you can grow the nanomaterial. So, it acts like a host material, inside which you can grow the nanomaterial; and it gives certain interesting possibilities and certain interesting constraints within which we can do this. So, we will look at one example of such a template and in that process, we will try to generalize certain ideas.

So, that presumably you can extend this to some other template that, you can look around for and for some work that you are interested in

So, there is this polymer membrane known as Nafion, it is a material that is commercially sold by DuPont and it is used for a wide range of applications. Basically, it is a polymer and the idea is that polymer has some porosity in it certain type of pores in it and in those pores, you can grow the nanomaterial. So, let us look briefly at what is possible here with respect to its structure and the application that we can put it to.

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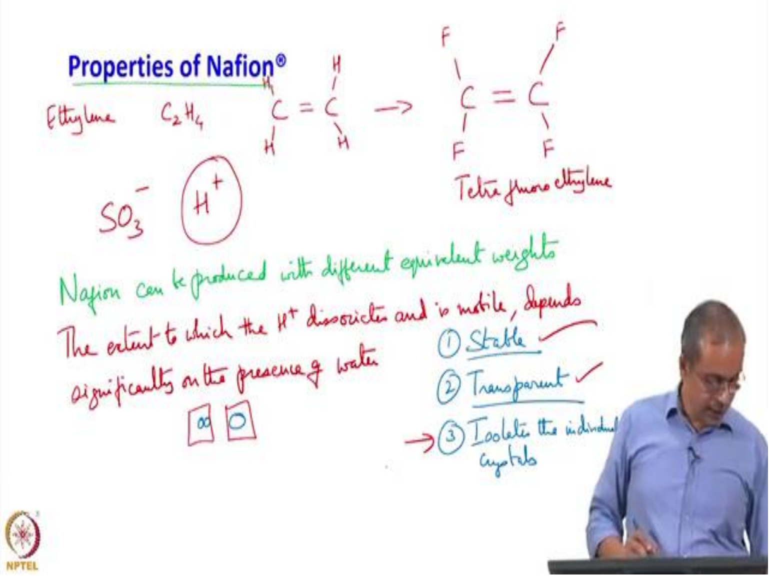

Properties of Nafion®

Ethylene C_2H_4

Tetra fluoro ethylene

SO_3^- H^+

Nafion can be produced with different equivalent weights

The extent to which the H^+ dissociates and is mobile, depends significantly on the presence of water

① Stable

② Transparent

③ Isolate the individual crystals

So, if you see, if you look at ethylene it is basically C_2H_4. So, we have C double bond C and then we have a hydrogen, we have a hydrogen and hydrogen. And we can make from this something called tetrafluoroethylene. So, we can make tetrafluoroethylene which simply means that all the four hydrogens have now been replaced by fluorine. So, you can have F. So, this is ethylene and this is tetrafluoro. So, this is tetrafluoroethylene. Now using this tetrafluoroethylene, you can make a polymer.

So, if you go back here, this structure that you see on top is a polymer; where you actually have one part of it which is considered like the backbone of the polymer and another part which is considered the side chain of the polymer. So, you can sort of think of this as the side chain. So, you can think of this as the backbone and whatever else is there you can think of it as the side chain. So, the way this works is you can see here the

CF_2 group here that is the tetrafluoroethylene and that is the primary unit that you see at various locations in this.

So, you see some variation of it one more fluorine has been removed and that is how you have got this side chain that is shown showing up here. And here also you see the CF_2 CF with one CF_3 that is present here. You see the CF_2, CF_2 here. So, you see the considerable presence of this CF_2, CF_2 group, So, this is called a polymer where it is pair fluorinated, which means all the hydrogens have been removed from a hydrocarbon and it is all those hydrogens have been replaced by fluorine.

So, now, in this polymer, in the end, you have an SO_3H group. So, this is an SO_3H group. And this is considered as an acidic group, it is very similar to H_2SO_4; H_2SO_4 sulphuric acid that kind of a group this is SO_3H. So, it typically, actually shows up as you will see here as SO_3^- H^+. So, it will dissociate like that and that H^+ will be relatively free to roam around based on the circumstances it is placed in. And therefore, the acid it provides the acidic property for that material and this SO_3^- H^+ group is this acidic group that is present there

So, this is the polymer structure. I will also point out to you, that you can see here the value x and the value y. So, this means you can change the length of the backbone, you can add more x units, I mean the x can become to a larger can go to a larger number can grow to a larger number. So, therefore, the backbone can be of different kinds, you can make different types of backbones with this general formula, and you can make longer backbone or shorter backbone etcetera with respect to the same side chain that is present.

So, therefore, when we talk of an equivalent number; an equivalent number, in this case, would be the weight of the rest of that polymer for every proton that is present. So, for every proton; so, you can see for this entire formula that is out here, you have one H that is present here. So, based on the value of the small x that you use here and the small y that you use here and the z that you use here etcetera you can come up with one particular version of this polymer, where you can then get the weight of the backbone or weight of the entire polymer all the molecules that are all the atoms that are present in that polymer for every H that is present there. So, that is then your equivalent weight.

So, therefore, you can get nafion, can be produced at different equivalent weights. So, you can produce nafion with different equivalent weights. And therefore, the extent to which it is acidic is something that you can control, so to speak. Now it is; so, this is what it is, and also it is very sensitive to water the behaviour of Nafion is very sensitive to water. So, the extent to which the H^+ dissociates and is mobile, in the sense that it can actually move along the polymer it depends on the presence of water, depends significantly on the presence of water.

This way it depends quite significantly on the presence of water. So, if you actually look at the structure, this is the polymer the formula is out here; the formula is what we have written out here this whole unit that you see here. When you actually make it as a polymer and then try to put it for some application, what you will see is that the polymer that is made out of this is typically a very clear transparent polymer.

So, it looks no different than polythene sheet that you may purchase for any other purpose. So, it just looks like a transparent plastic sheet that is basically how it looks. So, on the face of it, you will not see any dramatic difference between that and any other transparent plastic sheet that you may obtain for any other purpose. But fundamentally polymers being I mean that being the nature of those polymers, internally the chemical structure may be very different from what you may get for any of those sheets.

So, the property of this polymer is very unique in terms of what it can do. Within this polymer, so this is like a magnified schematic of a magnified view of that polymer; what you see is this is the area where the backbone exists. So, the backbone of the polymer is here. So, all these $CF_2=CF_2$ groups, for example, are all here, etcetera. So, then you get this O whatever and then you get the $CF_2=CF_2$ etcetera. So, you get this chain out here.

So, throughout you get the $CF_2=CF_2$. So, those the backbone of it for I mean uses up all of this location. And then here in this what you see here is marked as white regions, those are sort of like microcavities or micropores present inside this material; and these pores you have the SO_3^- H+ groups pointing in. So, this is what you get.

So, this is how this structure is. So, these H^+ ions seem to be located in this kind of region and water is also typically present here. So, a lot of study has gone onto these sorts of membranes to understand, what is happening there with respect to water, with respect to the proton, etcetera. So, they talk in terms of a hydronium ion which is a H_3O^+ kind of ion and that is what is supposed to move around and then. So, the H^+ associates with the H_2O and you get a more you know, I mean associated structure called H_3O^+ and that is what seems to move around. So, in the absence of water the protons do not move around. So, H^+ is a proton and it does not move, if the membrane is completely dry.

So, if you take this membrane in dry condition and you try to see if the proton is moving and there are ways in which you can measure to see if the proton is moving, you will find that the ability of the proton to move is extremely low and that that ability is we are referring to as proton conductivity. That proton conductivity of this membrane is exceptionally low if you keep it in the dry condition. At the same time if you make it wet if there is enough moisture in it if there is enough liquid water in it if boil it in water then it tends to move very well.

So, this is the nice thing about this membrane. There are some other interesting aspects of this membrane which is what makes it interesting for our application; and one of them is the fact that this H^+ that you have here, that you have here and you have here, we just have few examples of it here, this H^+ can be exchanged for some other ion ok; so, H^+ can be exchanged with another positively charged ion.

So, for example, we can replace H^+ with, for example, Na^+ so. In fact, this membrane is often sold when it is obtained you instead of sending it in the acid form, they may sell which means the H^+ ion is present; they will actually sell it to you in the sodium form where the Na^+ ion is present, and then you again boil it in an acid it will change over to the H^+ form

So, this is the kind of way in which you can manipulate this membrane. You can change the ion that it is holding by simply boiling it in excess of that ion, and then by diffusion and such phenomena that ion will go in and it will replace most of the ions that are present inside and then eventually you pick it up you essentially have it at the sodium form. So, you can actually take this membrane and fill it with different ions and any positively charged ion. So, typically any metallic ion you can fill inside this.

So, that is a advantage as well as a disadvantage depending on where you are trying to use it. So, in our application, where we are trying to create nanomaterials of some particular variety, this turns out to be an advantage because we want a different metal to be present inside this membrane. And that is what we are trying to do, and therefore, this turns out to be an advantage. There are other applications, for example, this membrane is also used in fuel cell applications; wherein those applications they want it to remain in the proton form, in the H^+ form because the H^+ is the ion that is getting conducted across the membrane for that application.

So in those applications, if you have some impurity in the form of some other ion that is coming because the liquid is water is flowing through some pipes and those pipes are metallic and some ion comes through those pipes; then those ions can actually go in here and remove the H^+ and occupy the spot of H^+. And then what happens is if you are still trying to get protonic conductivity out of that material, you will find that the protonic conductivity has decreased.

So, the feature is there that you can replace H^+ with some other ion; it really depends on these circumstances under which you are using that membrane that replacement may be good or that replacement may be bad. So, that is the point that we have to remember. In our case, we want to put some other ion in here. In fact, in our case for looking at optical properties you can put various other ions, you can put cadmium, for instance, you can put lead. So, those kinds of ions can be put. So, I am going to discuss the possibility of putting lead inside it and then doing something else with it. So, for that this is actually particularly useful.

I must also add that some of the properties of this nafion which make it convenient for our kind of application here; are that one it is stable. So, it is stable in the sense at room temperature, atmospheric conditions, etcetera; it is an extremely stable membrane, you can leave it in the room for a long period of time and it is absolutely fine. So, that is a particularly good aspect to have, if you want to create nanomaterials and use them over a period of time and it is transparent. So, particularly for optical applications, this is very useful.

So, the reason being you are now going to grow something inside it and you want to know the optical property of that material that you have grown inside it. Now if this template or the host material itself has some significant absorption of light and it is actually very dark material of some sort, then you are not going to see the property of the Nanomaterial that you have grown inside it very well, this is going to mask that property. So, if it is inherently transparent then that is something that is convenient to you.

So, these two are very useful properties to have, the fact that it is stable and the fact that it is transparent. So, between these two you get a nice situation that you can utilize this membrane particularly for studying something that is related to optical properties. And over and above that this structure where you have this set of pores that are present in that material where you can grow something. And we will see how we can manipulate that growth process and, in that process, you can actually keep those particles created. So, we will come back to that in just a moment.

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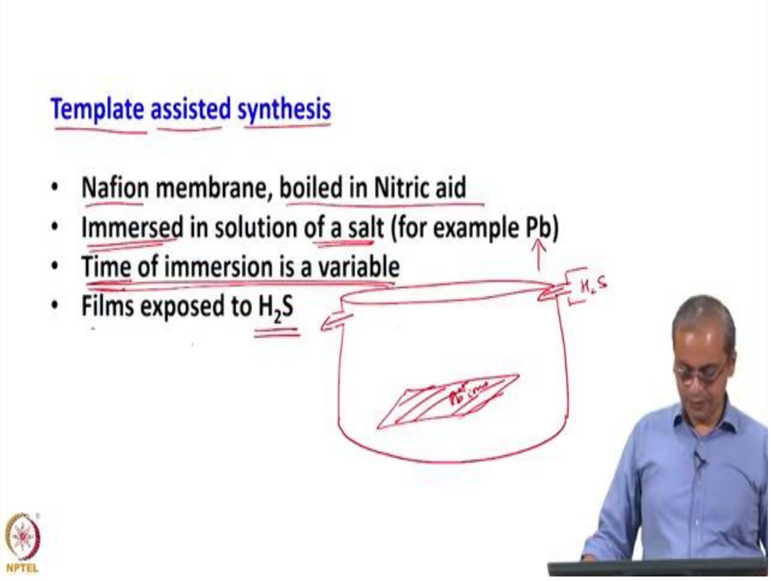

Template assisted synthesis

- Nafion membrane, boiled in Nitric aid
- Immersed in solution of a salt (for example Pb)
- Time of immersion is a variable
- Films exposed to H_2S

So, this is something about nafion, the host material. And let us now look at, how that can be used to do, what is called template assistate synthesis. So, to do this what we what is typically done is a template; in this case, we are talking of Nafion template which has this acid form etcetera to it. So, we will look at it from the perspective of what needs to be done to this particular template. So, the steps that I am discussing here, have to be generalized a bit, if you are trying some other template.

So, if you are trying some other polymer membrane to mimic this kind of procedure that I am showing you here, you have to understand clearly what is that membrane, what is present in it and what is it you would like to remove from it, what is it that you would like to add to it and then those steps will have to be modified accordingly. So, what steps I am showing you here are very specific to the Nafion membrane being used to host some lead-based sort. So, that is very specific here. So, you have to be ready to look at variations of it.

So, we take Nafion membrane and it is typically first of all boiled in nitric acid, this is done to ensure that if there is any other impurity in it, it is all removed. So, by chance by during the synthesis process, if there is still some sodium present in it or some other salt has penetrated in it, etcetera; we can make sure that it is no different than washing some other sample before you start using it, washing some vessel, etcetera. We basically boil it in nitric acid, to remove any residue that may be present from some prior step, prior handling of this membrane and so, you can feel reasonably confident that what you have is clean Nafion membrane.

This Nafion membrane is then immersed in a solution of a salt. So, for example, if you want lead ions to get into it, you have to immerse it in a solution that has lead ions, so some lead salt. So, for example, I think lead acetate trihydrate can be tried, it is a salt. So, that salt has you have to put it in some solution form and then this membrane has to be put into that solution and that allows these lead ions to start diffusing into the membrane.

And in this process, we also have to control the time of immersion. So, that is a variable that we have at our disposal the time of immersion; and this is important it seems like a simple way of handling the situation, but it is in fact, the correct way of handling the situation. And in any of our studies we want the simplest process possible to get our job done. The time is a very important factor here because the process by which the lead ion is getting inside the membrane is simply a diffusional process.

So, diffusion is occurring and the lead ion is going inside the membrane. So, that diffusional process is totally time-dependent, you wait long enough more material will diffuse; for the same concentration gradient if you wait long enough more material will diffuse and of course, as the material diffuses the concentration gradient keeps decreasing. So, the rate at which it is entering the material will steadily go down. So, those kinetics are there, there is diffusion kinetics that we have to be conscious about, but the main parameter that we can control there is the time.

You can also change the temperature and increase the diffusion rate if that is something that is important to you. In this case we are not necessarily looking at that we are simply doing it at room temperature, you can control the amount of immersion time and that controls the amount of lead salt that has gotten into it. Now once the lead salt is in, we have to expose the films to H_2S. So, once the lead salt is in, you then do some little bit of cleaning of the film and then you keep it in a in some kind of container.

So, this is your film and then you have some kind of a container and you can flow H_2S. So, you have H_2S flowing overnight which exposes this membrane. So, this is your membrane and it contains lead salt. So, that is present here lead salt and then it has been immersed in that salt. So, the lead ion is present there. So, they are present there and then you send this H_2S and you get PbS.

So, Pb^{2+} ions are present here and then you get PbS salt that is being formed with the membrane. So, now, you have lead salt that has been formed in this membrane. And what we have to see here, is that if you go back to the structure it means now that you have the lead salt here. So, in this region in this where you have this H^+. So, now, the H^+ got replaced by Pb^{2+} and then you basically have Pbs here. So, that is how you get lead sulphide in this material.

And based on the time of immersion, the amount of lead sulphide that has gotten into these pores changes and naturally the longer you wait you get more lead inside the material. And this is a factor that we can use to control the amount of lead in the membrane and therefore, the crystal size of the lead sulphide that is formed. So, you can get and it turns out that if you do this over several minutes, you do from 5 minutes, 10 minutes, 15 minutes know half an hour or 45 minutes of immersion that kind of thing.

Some timeframe in the range of say 1 minute to a 1 hour in that range, if you do a series of experiments you find that you can get lead ions and lead crystals, lead sulphide crystals of relatively uniform size scale; wherein the size scale is in the nanometer range and therefore, we can get nanocrystalline lead sulphide. Now, one of the things that we should understand why this is a very interesting technique to use this templated assisted technique, from the perspective of nanomaterial synthesis in general and also the nanomaterial synthesis from the perspective of optical properties; is that, if you go here as I said it is very stable and it is very transparent.

So, the lead sulphide that stays inside it, is now providing the optical property the membrane itself is not providing anything it is relatively clear. And importantly it helps isolate the individual crystals; the individual crystals are isolated. So, they are all sitting isolated. So, therefore, one major concern with respect to nanomaterials work in any nanomaterial work is that because you have got this nanocrystal in size, it is extremely small crystal size, therefore; the surface area is large.

So, per gram the surface area is very large, the specific surface area is large; therefore, those particles are actually very reactive. So, if you have two tiny particles, they are more likely to coalesce to form a larger particle. So, two tiny particles will coalesce to form a larger particle, because when they do so, the total surface area comes down and that is energetically favourable.

So, this is the direction in which they will move. So, anytime you work with nanomaterials, if you want any long-term application with that nanomaterial. And most of the time, that is the case you want a product which is going to last several years. So, for those several years, if you are looking at some property that was possible because that material was formed in the nanoscale; then for those several years that material should remain in the nanoscale.

If you keep them this kind of close proximity, this type of close proximity they will coalesce and form this very quickly. So, maybe one month down the road, the material will no longer be here nanomaterial. So, you sell a product and it is doing something very unique because it has nanomaterials in it. One month down the road the particles have coalesced they are no longer nanomaterials and therefore, that property is no longer there in that part and therefore, your product will not function.

So, therefore, you are left with this absurd situation that you cannot have a warranty period which is reasonably long, your warranty period will have to be less than a month; because after at one-month time your product will anyway not work. So, this is the problem. So, you want to stabilize individual nanocrystalline particles, it is a very important aspect of any nanotechnology that you develop; individual nanoparticles have to be stabilized. The template-assisted synthesis, so I am sorry this you have to remove isolates, the template-assisted synthesis does this for us very naturally, because you can see here that the lead sulphide that is here is physically separated.

From the lead sulphide that is here is physically separated from the lead sulphide that is here and so on. So, they are all physically separated. So, they actually do not get in touch with each other. So, in fact, when you create nanomaterial like this, you can actually keep that nanomaterial stable for months, maybe even years you can have it completely stable; it is not in a position to go through the polymer and contact the next nanoparticle in the adjacent pore and then do a sintering process, so to speak. So, it cannot coalesce. So, therefore, this template-assisted synthesis actually is a very nice process and, in any circumstance, that you can use it this seems like a very nice process to adopt.

Maybe the only drawback that I can think of is that because fundamentally it is a polymer it restricts your temperature range of operation that is number one. And number 2 it also means that this is like a sort of a dilute presence of the nanoparticle; because you're going to have mostly polymer here and there you were to have the nanoparticle. So, if you want a very high concentration of nanoparticles, then this may not be very useful for you in those circumstances.

But if you just want a film which has those nanoparticles and then can be used for any other application you can do that. And this film is also mechanically stable, so once you have made it in this form, you can fold it and put it in some application and you can roll it up for some other application, you can put it out stretch it out flat in some other application. So, lot of physical no confirmation to different physical shapes, you can actually accomplish once it is in film form.

So, many positives to this template-assisted synthesis, very important technique for nanomaterial synthesis for use in nanotechnology and this is the general what I have shown you here is the general process with one particular example of how you would go about doing that.

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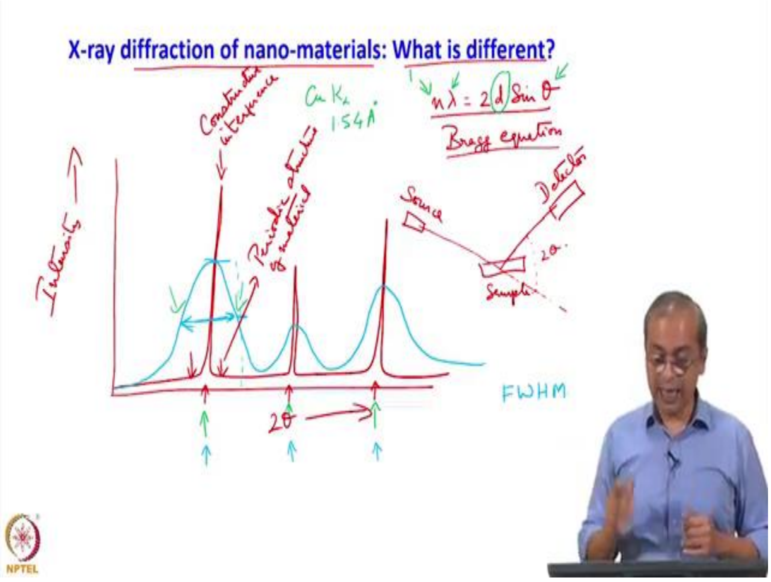
X-ray diffraction of nano-materials: What is different?

So, now, we have made this nanoparticle, we would like to do some characterization of it say. So, one of the easiest techniques that is accessible to us in any material science department, the metallurgical engineering department is the X-ray diffraction technique. And the primary equation we use there is

$$n\lambda=2d\sin\theta$$

this is the Bragg equation. And many different types of analysis that you can do with X-rays, can be done with pretty much this equation. So, you can do a fair bit of analysis using this equation, there are other equations that we that can be used, but this is the primary equation.

Now typically, so we would like to, first of all, understand this is something that you already know, the Bragg equation is something that you may have come across in many different circumstances. But what is interesting to us is that when you look at the diffraction from a nanomaterial there is a difference, when compared to the diffraction of the same material in the non-nano scale in the macro scale, so to speak. So, we would like to understand what is this difference and where is this difference coming from.

So, if you look at the typical data. So, you will have intensity in some arbitrary units headed that direction and this is 2θ the angle at which your detector is. So, you have a sample, you have a source of X-rays and you have a detector. So, you have this angle and this is your 2θ. So, that is your 2θ θ angle that we are looking at. So, now, the what we need to do is typically we have data that looks like this, something like this. So, there are sharp peaks in this data, at specific values of 2θ. So, at specific values of 2θ, you have very sharp peaks and they are actually vertical peaks, I have just hand-drawn them, so they maybe look at an angle, but typically they are just straight vertical peaks.

And so, for every value of 2θ that you get, you can, therefore, plug that value of 2θ here as the θ half of that as the θ here. So, sinθ is known. So, once sinθ and λ which is the frequency of the X-ray your using monochromatic X-ray that you are using for this experiment, which would be one fixed value usually it is copper k alpha; copper k alpha radiation. And then that is typically about 1.54 angstroms is the wavelength that is used. And so, once that wavelength is fixed and n is the order of the reflection. So, typically it is usually 1.

So, once that is fixed, n is fixed, λ is fixed, θ is fixed you can get your value of d. So, the d spacing corresponding to each of these locations can be determined. And that gives you the d spacing of different crystal planes which are present inside that material and then you can get the crystal structure of the material. So, this is typically what we do with X-ray diffraction. Now when you go to the nanomaterial scale, what you see which is different is the fact that these peaks they still appear at the same position, but they are no longer sharp peaks you actually get very broad peaks.

So, you get something like this, some I am just drawing a schematic here you get broad peaks here. So, this is a width, this is called full width at half maximum. So, full width at half maximum. So, this is the maximum of the peak, you take half of that maximum and you take the full width here and half maximum. So, this full width at half maximum is a significant value when you go to nanomaterials. So, this is what is different ok

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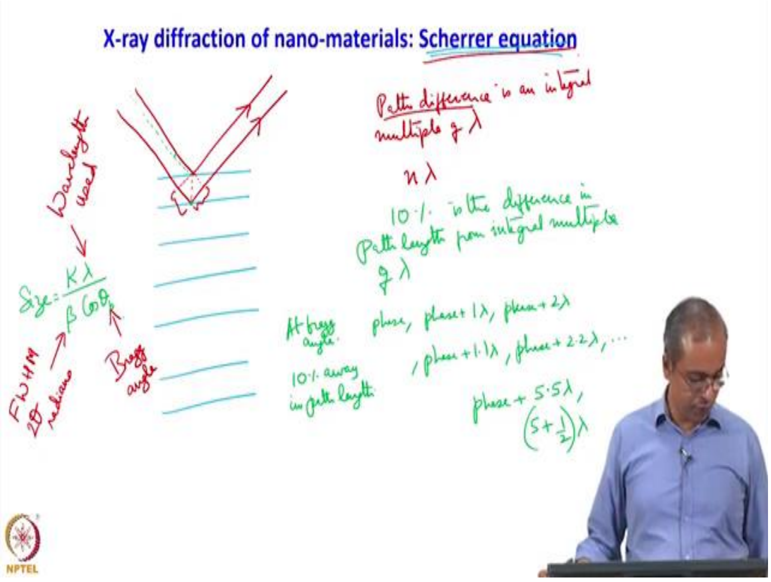
X-ray diffraction of nano-materials: Scherrer equation

$\text{Size} = \frac{K\lambda}{\beta \cos\theta_B}$

Path difference is an integral multiple of λ

$n\lambda$

10% is the difference in Path length from integral multiple of λ

At bragg angle: phase, phase + 1λ, phase + 2λ

10% away in path length: , phase + 1.1λ, phase + 2.2λ, …

phase + 5.5λ, $\left(5+\frac{1}{2}\right)\lambda$

So, that is how the data would look like which we just saw. So, the data would look like that, with this full width at half maximum; being a significant value for a particular peak, I am just showing you for a particular peak this is 2θ and this is intensity. So, this is what we will look, it will look like. So, this leads us to something called a Scherrer equation, but to understand that Scherrer equation let us go back to this plot here. To understand why is it that when the crystal structure is large, you get a sharp peak and why is it when the crystal structure sorry when the crystal size is large you get a sharp peak when the crystal size is small you get a broad peak.

So, we need to understand that, so that we can utilize this equation in a very effective manner. So, the way we need to look at it is that when you look at this nλ equals 2dsinθ equation it basically tells us that the path difference between a way that. So, if you have a series of planes here and then you have an X-ray that is bouncing off the top of the topmost plane and then you have another X-ray which bounces off the second plane diffracts off the second plane and so on.

Then this path difference, this extra path difference that is travelled by the ray that goes to the wave that goes to the second plane is an integral multiple of λ. So, that is what it is the path difference is an integral multiple of λ, which means it is some integer n times λ that is what it means integral multiple of λ. And as long as the path difference is an integral multiple of λ, then the wave that is coming off the top surface and the wave that is coming off the bottom surface are exactly in phase because one λ the difference between them is exactly one λ. So, as this is climbing that will also be climbing, as it is coming down it will also come down. So, they have continued to go that way and they add to each other and so, you have constructive interference. So, the reason we see a peak in X-ray diffraction is because there is constructive interference.

Now it is very interesting to see that you get this peak here because of constructive interference. And that is due to the periodic structure of the material. What is interesting is that this the fact that you get zero intensity here immediately after the peak and immediately before the peak, you are getting zero intensity; that zero intensity or near zero intensity is also due to the periodic structure of the material. So, normally we only think of the peak as being present there because of the periodic structure of the material.

We sort of do not talk much about the background, but what we need to understand is that just as the peak is a direct result of the periodic structure of the material, the background which reaches 0, also reaches 0 because of the periodic structure of the material. Why is that the case, it is quite simply this. So, if you have many such planes. So, now, you are 10% off of this Bragg angle. So, that is what we mean by saying is slightly before the Bragg angle or slightly after the Bragg angle. So, 10% off of the Bragg angle, 10% off. So, it is 10% away from the Bragg angle; then the reflection from the second plane is 10% difference in path length.

So, 10% away in Bragg angle. It may not be exactly because you will do sinθ in this equation, but the reflection from the top plane and 10% is the difference in path length from multiple of λ, from an integral multiple of λ. What do we mean by that; it means that previously when it was an exactly Bragg condition if you have the first wave, wave from the first topmost plane comes out with one phase; the second plane is that phase+1 λ; third plane is phase+2 λ, etcetera like that it goes.

Now what I am saying is if it is point it is 10% off, from the second plane you are actually getting whatever is that phase of the first reflection+ 1.1 λ, and from the second plane you are getting phase+2.2 λ like this you are getting. Now if you continue this process by the fifth plane you will have. So, this is plane 0, this is 1, this is in 2 and so on. So, by the time you reach the fifth plane, I am sorry this is yeah. So, this is in phase at Bragg angle.

So, this is 10% away in path length. So, if you continue this process by the time you reach the fifth plane, you are at phase+5.5 λ. So, in other words, the fifth plane has a reflection that is half a wavelength out of phase some integral multiple 5+ ½ λ, So, 5+ 1/2λ is what is the difference in path length from the fifth plane relative to the first plane.

So, therefore, the reflection from the fifth plane is half a wavelength exactly the 5 will add up, but the half will put it out of phase; it will be exactly half a wavelength out of phase with respect to the reflection from the first plane and so, it will cancel the reflection from the first plane. Similarly, the sixth plane will cancel the reflection from the second plane, the seventh plane will cancel the reflection from the third plane like that it will continue; and therefore, all the reflections will cancel each other out and your intensity drops to 0

So, that is the idea of the X-ray diffraction pattern and that is the reason that I say that the extent to which it is showing constructive interference due to the perfect, what shall I say constructive interference of the path lengths being this integral multiple of λ. The same phenomenon actually creates destructive interference when you are even marginally away from the Bragg angle.

Now given this situation why is it different for nanomaterials? In nanomaterial’s the point is that the number of the crystal size is extremely small. So, therefore, you have only a limited number of planes. So, for example, you go to a Bragg angle where the second plane is 1% out of phase from the first plane; it means you need to go to 50 planes before you find a wave that is coming that is half a wavelength out of phase with respect to the first plane.

So, you have to go to 50 planes down before you find that; but supposing the crystal size is less than 50 planes, it means then in that sample the fiftieth plane does not exist. Therefore, that half a wavelength out of phase at 1% away from the correct path length does not exist; that half a wavelength out of phase does not happen and so, destructive interference does not happen.

So, the smaller you get in size the less the destructive interference is that occurs when you go away from Bragg angle because those planes are not there in that sample, you have removed those planes, you have kept that number of planes less. That is why you can go to regions away from the Bragg angle and still have fair bit of intensity. So, this is why the X-ray diffraction pattern of nanocrystalline materials looks different from the X-ray diffraction pattern of macrocrystalline materials, where you have huge number of planes 1000 of planes. So, even the slight tiniest bit you go off of Bragg angle there will be some plane which will enable destructive interference and that plane will be present in that sample.

So, this is what we see and this leads us to this Scherrer equation, which basically says that the crystal size. So, size equals some factor say Kλ. So, this θ_b is your Bragg angle, the same Bragg angle that we talked about; beta is the full width at half maximum in 2θ radians. So, you have to put the correct units, you have to put it in 2θ and in radians, you have to put and λ is the wavelength. So, this is the Scherrer equation, this is used very extensively in nanocrystalline studies because it helps you understand the crystal size.

There are some limits to the Scherrer equation you cannot use it for extremely small crystal sizes. So, it starts becoming more and more approximate, but you can still see trends using it, you can at least say that the crystal size has become smaller, the crystal size has become larger etcetera. So, there are some limits to it, but within those limits you can actually use this Scherrer equation; it is extensively used for nanomaterial studies, it is also used in the study of nanomaterials from the perspective of optical properties.

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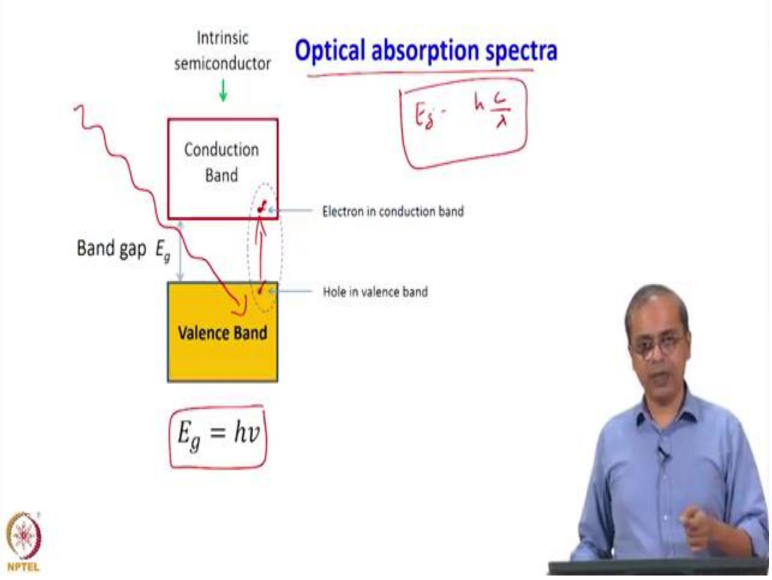

Optical absorption spectra

$$E_g = h\frac{c}{\lambda}$$

$$\boxed{E_g = h\nu}$$

So, having looked at the X-ray diffraction process from the perspective of characterizing nanomaterials, we will also look at Optical absorption spectra. So, that will be the second technique that we will look at briefly in this class and then use it in a subsequent class for the optical property analysis.

So, the way this is done is, as we saw you have some incoming radiation and that enables this transition from here to here. So, that these transitions become possible. So, now, as we said here, we have a threshold value

$$Eg=h\upsilon$$

$$Eg=hc/\lambda$$

So, something like this. So, generally what is going to happen is for a range of wavelengths, you are not going to if you start with very large wavelength which is very small frequency, and there is a certain bandgap.

That large wavelength will not enable any absorption most of it to just go transmitter, transmitter, transmitter it will not interact with the material. And then when you cross this, so if you are looking for absorption in that material you will not see any absorption, it will not absorb any radiation. When you cross this threshold of Eg as given by this equation here, and you got a wavelength lower than this; suddenly you will see that a significant amount of radiation is getting absorbed.

So, this is the absorption process and if the wavelength at which, a wavelength of the frequency at which this absorption begins to increase dramatically, that gives you a value from which you can calculate the bandgap of that material. So, the optical absorption spectrum is a very useful piece of information to have when you want to understand the optical property of that material ok

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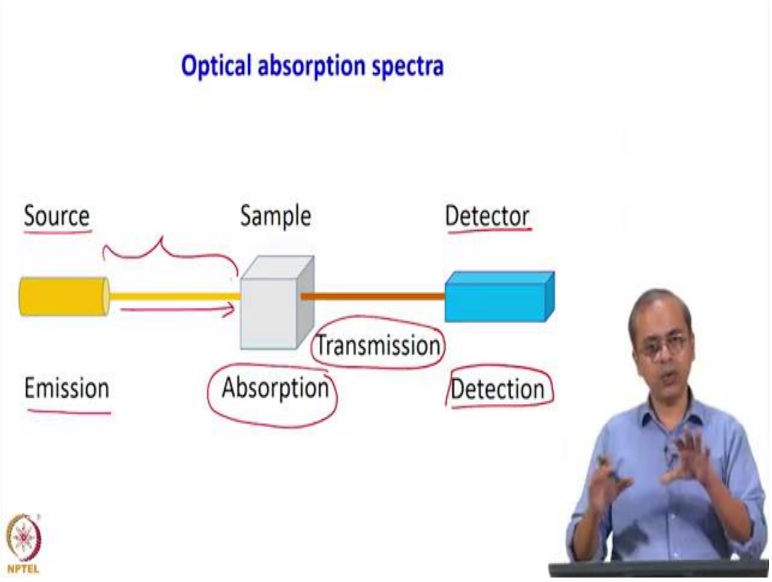

Optical absorption spectra

And, experimentally the process looks very similar to what you see here; there is a source, this source is such that you can actually send out a series of known frequencies from the source one after the other you can send. So, you can pick the frequency you can set a range of frequencies and it will generate frequencies of that range. So, there is some emission occurring from that source. So, that emission then goes towards the sample and in the sample some absorption takes place. So, some of the wavelengths that are coming to that sample are getting absorbed and the rest are getting transmitted, the remaining part is getting transmitted.

Then you have a detector and that detector is detecting it. So, you do the detection process here. So, what you detect is what got transmitted from the sample. So, if you look at the original data that came from the source and you remove what got transmitted from it, the rest of it got absorbed by the sample. Now, there is some things that you have to be careful about here because there is a path here in that process and that path can actually impact the absorption process as well. So, normally what is done in this kind of an absorption spectrum study, is that they first run a dummy sample where the characteristics are known or it is supposed to be relatively transparent in that frequency range.

So, you get the base spectrum from that sample which also will have any, any variation that the source has; even though the source is supposed to give you exactly the same intensity at all the frequencies, it may or may not give exactly the same intensity at all those frequencies. So, you cannot at least assume that about the source. So, just to correct for it, you put a known sample and you get the data off from that known sample for the entire frequency range.

And if you get the data for that known sample for the entire frequency range and if it is supposed to be mostly transparent to that range; then you have the data that corresponds to any variation from the source and any variation due to the path, between the source and the sample and the detector. Having got this information, you now remove this standard sample and you put your sample into it, you run the same scan.

So, now, you get the characteristics of the sample, it will also have the characteristics of the source, it will also have characteristics of the path before and after the sample and so, all of that composite data is now available to you. From this data, you subtract the original data of the standard sample; once you subtract that out, you have removed the contribution of the source, you have removed the contribution of the path before the sample the path after the sample all of those have been corrected; and so, what data you get you can reasonably say, that it belongs to the sample.

And so, this is the way we do optical absorption spectra. And by carrying out the optical absorption spectrum studies, we get a like I said for a fair bit of frequencies you will not see some absorption; and then pass some threshold you start seeing some absorption, from this data we are able to calculate and extract out the bandgap of that sample. So, this is a very important technique to use for studying optical properties of materials in general and certainly of nanomaterials. And here again the template-assisted synthesis is very useful because you are able to get those particles in a clear polymer sample, which you can keep in this system and therefore, the polymer itself will not colour the data in a dramatic manner.

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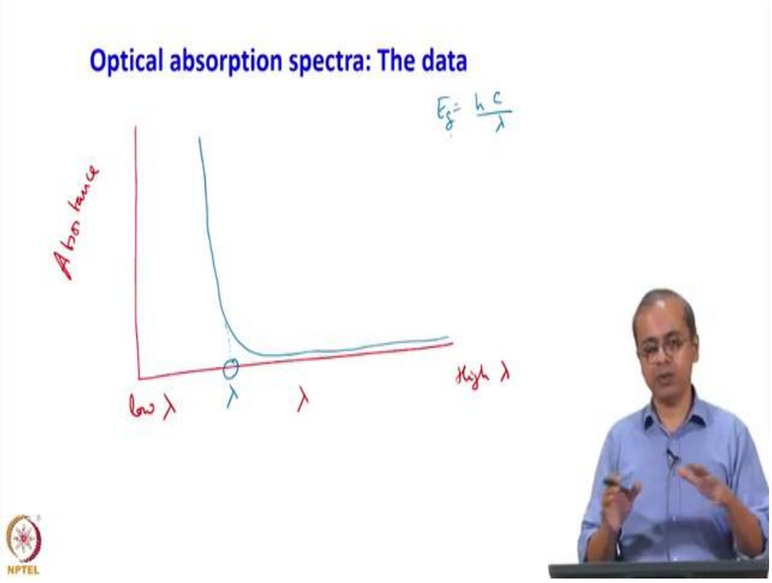
Optical absorption spectra: The data

So, the data will look roughly like this. So, you will have to say λ here and you will have absorbance. So, this is high wavelength, this is low wavelength. And so, what you will see is, you will see as you come from high wavelength which means low energy, you will simply basically see data that looks like that, I just put it here. So, you see data that looks like that. So, no absorption is happening as you keep on lowering the frequency and then suddenly at some point you will start seeing an increase.

So, this absorption that you see here, so some knee is there for this curve. So, from with respect to this wavelength here you can relate that to the $E=hc/\lambda$ and then from this you can sort of; there are some other factors to look at. But basically, this is the idea here, that you have now started seeing of wavelength, below which the absorption is very significant. So, that wavelength is going to be very close to that threshold wavelength at which you have the bandgap. So, that is the idea here and that is how we use this spectrum here

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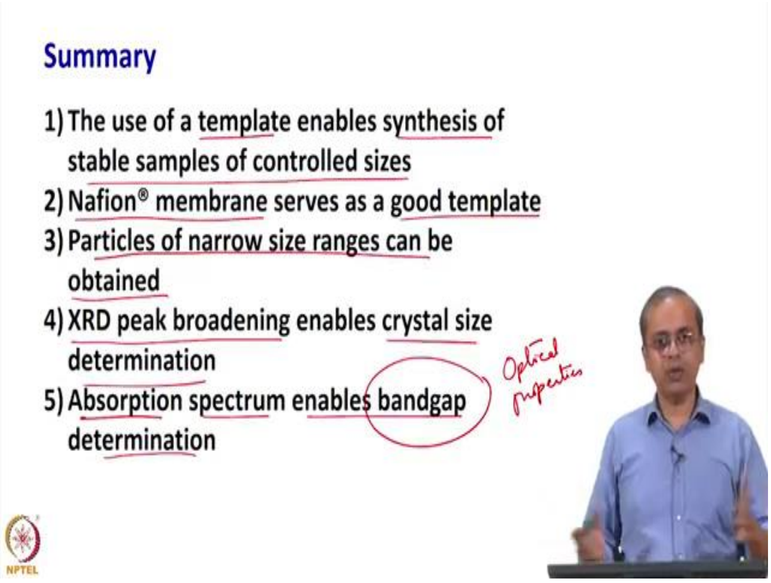

Summary

1) The use of a template enables synthesis of stable samples of controlled sizes
2) Nafion® membrane serves as a good template
3) Particles of narrow size ranges can be obtained
4) XRD peak broadening enables crystal size determination
5) Absorption spectrum enables bandgap determination

Optical properties

So, in summary, we have seen the use of a template enable synthesis of stable samples of controlled sizes as I said based on the extent of immersion you can get different sizes. So, template-assisted synthesis is a very valuable technique to have for nanomaterials for particularly for optical properties even for many other applications. It helps you get particles, that are stable because they are kept separate from each other; it helps you control the size of those particles; it helps you extend the life of the particles; main constraints being that there is a template which is going to remain with the particles and there is the fact that, I mean that template could burn or that template could get damaged in any other format.

And also, that it creates a very dilute presence of those particles, you do not have a very large number of particles that you can handle. The Nafion membrane is one of the membranes that can be used as a template and it does serve as a good template, you can think of other membranes which could possibly be used that way. Particles of narrow size ranges can be obtained; this also is something that is very useful based on the time of immersion.

We saw a lot about X-ray peak broadening and this enables crystal size determination and effectively the particle size determination of those nanoparticles, there is some variation between a crystal size in a particle size we will look at that later. And finally, the absorption spectrum enables us to obtain bandgap information which is very useful from the perspective of optical properties; and in a sense is the primary characteristic that we are interested in to help us, say something about the optical properties.

So, this is something about the experimental activities that you would have to do, related to looking at optical properties of nanomaterial’s and what differences you can see. We will look some more into this with respect to what kind of data we will get and what that implies in our next class.

Thank you.