Chemistry and Physics of Surfaces and Interfaces
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Lecture - 34
2D Molecular Materials on Surface -1

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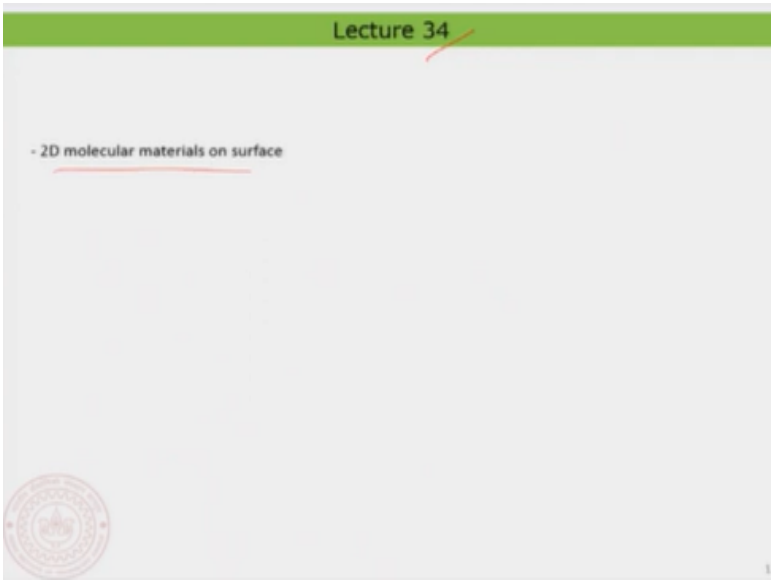

Hello everyone, welcome back to lecture number 34. So, in this lecture we will start with these two-dimensional molecular materials, why is it important and also how these materials are formed. So, this is particularly a new class of material that is coming up which is considered to be kind of an graphene equivalent material. Of course, you cannot substitute graphene because it has a very unique property but at some point, of time you would find that the graphene is not really technologically applicable due to a certain interesting aspect and that is the point where these kinds of materials are coming up, and why is it actually taught in this course is actually because this is a material that is only formed on surface. So, this is a true interface, this is one layer of a molecular material that is directly formed on top of a surface. So, that is why we are discussing this.

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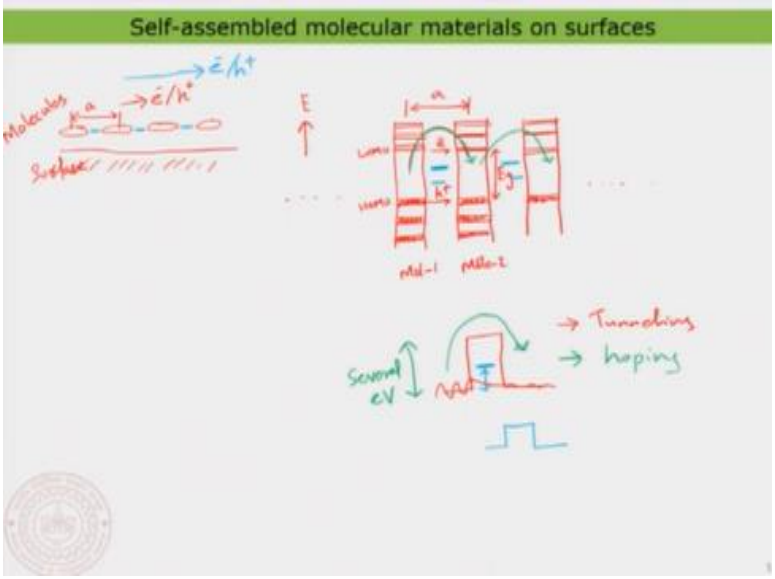

Now before we start looking at the two-dimensional molecular material, let me also just give you a kind of understanding about why do we need to make this material or what is it so bad about the two-dimensional molecular materials based on the self-assembly that we have seen. Because I have also showed you a lot of examples about different type of molecules, self-assembling and forming thin films. So, what is the problem with that? We could also use that as a material. So, that is something what I want to discuss with you. For that I will just use an energy diagram to explain that to you. So, now assume that you have a surface and then we basically have kind of molecule adsorbed on the surface. So, that is basically a film an ultra-thin film of a molecule. So, let us assume that I have basically just molecular adsorbates, so they are just packed nicely. So, this is kind of a schematic representation of any molecule. So, this is some kind of a let us say semiconducting organic molecules that is absorbed on the surface. So, this is the surface and these are the molecules. So, now the point is that when such a self assembly happens the molecule-molecule interaction, something that we have already talked about is very weak. So, these interactions are typically controlled by Vander Waal's interactions, hydrogen bonding interactions and so on. So, therefore the so-called electronic interactions between the molecules are very weak, well we will see that in a minute. So, I am just going to demonstrate that. So, because of this very weak interaction if I want to basically transport charges, let us say electrons or holes, h plus. Through this kind of layer, it is basically very very difficult and that is what makes this material not very promising for several transports-based applications because their transport property; a charge transport property is basically very limited compared to let us say a

silicon technology and so on. What is the reason for it? So, that is something we would like to understand. So, when you look into a molecule, so I am just like depicting a molecule using this bar here, this is a single molecule. So, like let us call it molecule one and you know that this molecule has a filled HOMO then you have HOMO minus one and so on. So, I am just shading it is to indicate that these are molecular filled levels. So, this is the filled levels and then after a certain gap I also have the molecular LUMOs or molecular unoccupied level. So, where you have the LUMO being the lowest unoccupied and then you have the LUMO plus 1, 2 and so on. So, this is typically the energy diagram of a molecule. So, this is nothing but just the MO diagram of a molecule. But now you know that when you arrange molecules together, so there is a certain spacing between the molecules. So, you can see this would be something like let us call it as 'a' that is a spacing between the molecule that is of course given by the geometry of the molecule. So, that means when you if you look into the energy diagram of the molecule. So, you will also see that that the next molecule, the molecule 2 for example is basically just looking like this. So, where again it also has the filled orbitals like this, filled molecular orbitals like this and it also has the unfilled molecular orbitals like this. So, this is the energy electron energy axis. So, this is basically the energy axis that representing the energy of the different MOs or molecular orbital. So, similarly I have here the next molecule and so on. So, this is basically continuing like this, so just let me depict here like this and it actually just continue in all the direction. So, this is basically what it is. Now the interesting thing what you see is that typically this energy gap for a typical semiconducting molecule is actually in the order of a few electron volt or in some cases it can even be like smaller like half an electron volt and so on. So, this is something which we call it as the Eg or the energy gap between the HOMO and the LOMO. But now you see that if I want to basically transport an electron from one molecule to another one, so now you see typically where they would basically going. So, if I want to move one electron from here to here or if I want to so sorry this would be like a hole if I want to transport a hole or if I want to basically transport an electron through these molecular electronic levels then you see that there is actually a distance that is associated to it. So, this is basically my a that means there is a distance. So, that means whenever an electron or a hole want to get transported through the molecule so you always have to end up in a barrier. So, that barrier is basically coming from this so called gap between HOMO and the LUMO. So, you clearly see that there is a gap, so that means if I want to transport something across this you see the only possibility for the electron is to kind of tunnel

like what we have seen in the previous case. So, that is something we can do. So, that means either this is actually a tunnelling process or the electrons need to basically just jump from one molecule to another molecule. So, let me just depict it with a slightly different colour. So, this is actually jumping of electron from one molecule to another but that jumping require to go like this. So, this is basically very high. So, this energy order is actually several electron volt and therefore at normal temperature this would not be possible. So, that means a typical way of electrons or holes just going around the molecule is either by hoping or by tunnelling. So, these are the two ways that the electrons or holes can basically just move across the molecular film and but they are all quite distance dependent. Because you know that the tunnelling is strongly distance dependent and hoping is also basically some kind of a distance different process. So, hoping is something you can almost forget at normal temperature because the typical barriers that the molecule need to come across is quite very high and therefore hoping is not even really possible. So, that is the reason why this kind of molecular film, so the self-assembled molecular films are not very much celebrated in using as an electron transport material. But of course, they find applications in organic light emitting diodes and things like that because they are good emitters for example. But in transport applications they are not very much celebrated. But therefore, people thought well we can do something else; we can try to add some new states in between. How can we do that? If you would basically, just add some new state. So, if I would basically just add a new state here or I add a new state here, what will happen that you can clearly now you see that the barrier for example has decreased. And also, you can see the hopping energy is also now decreased. Because now the hopping energy is somewhat like this and also the new barrier is basically if I would depict it here you can see now the barrier is also decrease. So, you know that tunnelling when the barrier goes down, the tunnelling is basically stronger or when you have new states also the hopping is basically more efficient, because you have low lying energy level. So, this is what is interesting. So, that means if I would do something in between the two molecules so if I would take two molecules and add something in between which can create new states that are low lying-in energy then you can effectively do something. So, you can basically add also like you know more of them not just necessarily one, you can add more of them and then these materials could make it interesting. So, I am now just using a longer arrow here for the transport of electron and hole because you see the transport property can be improved if I would add basically something called a dopant state or some kind

of an electronic state between these levels. So, that is what we would do basically in the two-dimensional material. So, I would just show you how to do that.

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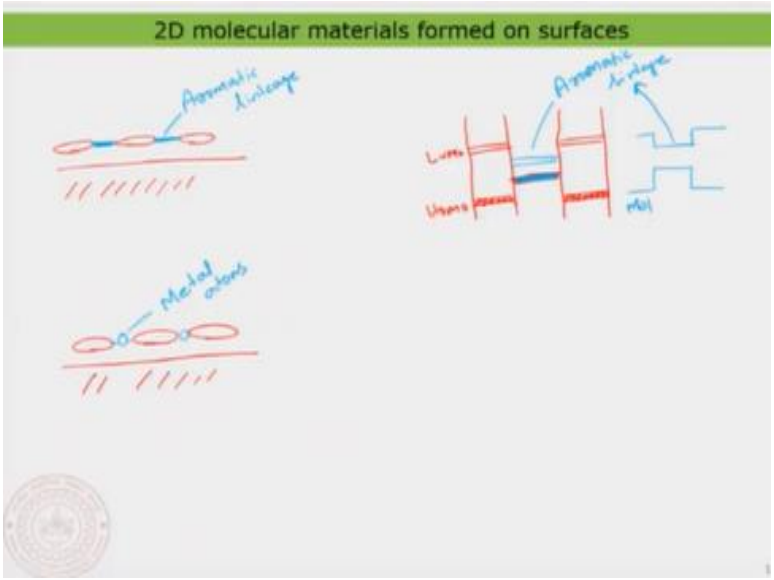

We can basically do that by two methodologies, one, again take the molecule, so we have again the surface, so we can take the surface, take the molecule again and then you can basically just add something like an aromatic linkage. So, we can do that by adding an aromatic linkage. So, just make here a connection like aromatic linkage. So, you will see that in the example or I can do something else I can also just do a slightly different technique. So, I can just take again the surface are the molecules here and then I can actually just do a connection by adding metal atoms here. So, that is also kind of a connection. So, this would be something like metal atoms. So, I can add metal atoms so that is something known as doping. So, I can add metal atom or I can add aromatic linkage then I can basically improve the electronic structure. So, how does it look like? So, if I would again draw my MO diagram of the molecule. So, this is basically the HOMO and this is the LUMO, so I have two molecules just for a representation and then I can basically if I would do an aromatic linkage what I would even do is I would basically just add a band that is in between. So, I can even add bands like this so this is again a filled band sorry for that. So, we can add a filled band here and an unfilled band of an aromatic linkage so, this is actually an aromatic linkage. So, now you clearly see that the barriers have actually just reduced. So, you effectively see now the new barrier is just looking more or less like this. So, this is just the barrier for the electron, sorry for the hole and for the electrons this is basically the barrier that

comes from this. So, this is how the new diagram is looking, so this is basically the molecule and this is the aromatic linkage. So, that is the interesting thing, or you can basically just take again the metal atom and the metal atom is also going to add some kind of states that are in between and they will also basically be doing something similar. But that can also add, they can also come in between the most states of the molecule and then they could actually just act or they could help in improving the transport. So, effectively what we have done is that by adding an aromatic linkage or by adding a metal atom in between the molecular self-assembly. We are now kind of going to improve the transport properties of the 2D material, and that is also why this entire thing is actually called as a 2D molecular material, this is a new class of material this is slightly different than the molecular assembly itself. So, now we will look into the example and will try to understand that in greater detail. So, you will also see in this example that we are not only just looking at this particular example. We will also just take this example in understanding the entire chemical, electronic and also the microscopic structure using all the techniques that we have actually just learned. So, that is the idea.

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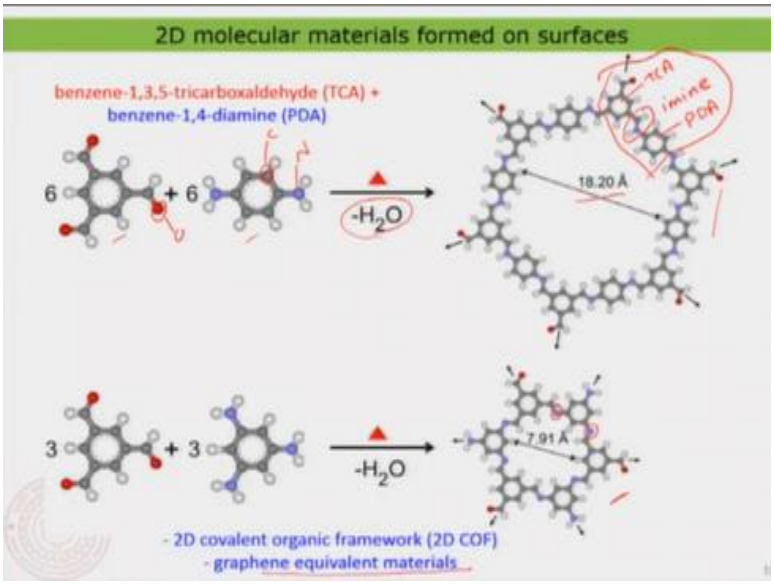

Now let us do this; how do we do that? So, like I want to basically now do prepare this two-dimensional molecular material on surface. But before that let me just ask you a very simple chemical chemistry question. So, this is actually an aldehyde molecule so that is what you see here and then I have here an amine molecule. So, this is nothing but nitrogen and this is carbon and this is oxygen. So, this is just for your guidance and this one these two molecules when you

react them when you let them react you know that a water molecule would eliminate and then you would form something like an imine bond that is something that you have studied in simple chemistry textbooks and this chemistry is very well known and this is known as a Schiff based chemical reaction. That is something which is very widely used in chemistry to form new carbon-nitrogen bond. So, that is what exactly happens because you eliminate a water molecule. But now what we want to do is we want to take again the same type of chemistry. But now I am going to do the chemistry on surface. What would happen? That is an interesting question because when the chemistry happens inside solution or in gas phase these two molecules can interact in any way. So, although I have basically just shown the projection where the two molecules are interacting like that. But in the chemistry world or in the world of a chemical reaction that would happen in a pot in a solution or inside gas, let us say they would basically just interact in any kind of orientation. So, that means it is not necessary that they will always just come like this what I have shown in the scheme. But if you, do it on surface, we can basically just do a chemistry and we can form something like this. Why is that possible? It is possible because here all the movement of the molecule in the third dimension is basically restricted. So, imagine that I have my surface, the two molecules are on the surface. Now the molecule need to basically just move like that and I can restrict all the movement of the molecule like in the third dimension and then by confining the chemical reaction in a certain plane you can actually let the molecule to react like this, and then you would form a kind of planar imine, monomer or an oligomer and those oligomers would basically just form something like this kind of a nice network structure. Since the symmetry of the aldehyde is 3-fold and that of the imine is 2-fold eventually what you are going to get you can see here this is actually the imine bond. So, this is the imine bond that you have formed and you can see this is basically the TCM, I am calling it as TCA, and this is the PDA that is the aldehyde and you can see nicely that they would form in a planar fashion and they form a nice planar oligomer. So, those oligomers so this would be an oligomer, this would be a unit and that unit can get connected to another unit and then they can basically propagate because of the symmetry of the aldehyde and the amine, you can basically make this kind of a nice hexagonal network, this is beautiful. So, now you are basically doing the chemistry on the surface and you have a greater control on the chemistry and you can basically form a kind of material which is like this. This would not be possible if you do this chemistry in solution. Because then you would be basically just forming a monomer of these two

molecules and that is it. The reaction may propagate, so you may form polymer but it is not necessary that you would form in this nice hexagonal fashion. Now I want to show you also a slight another example and to show you the possibilities here. See now instead of taking this two-fold imine, I have actually just taken a three-fold imine where I am having actually three functional, three amino groups inside. And now you see that if you make the stoichiometry correct, I can do again a chemistry at the surface and I am going to again make actually another hexagonal network. But the network structure is actually just a bit smaller than in the other case. So, here the distance between the edges of the frame is about 18.2 angstrom and here it is about 7.9 angstrom. So, this is quite interesting that means what you are ideally doing is by selecting the right precursor, you are kind of again making a sheet, a two-dimensional sheet of carbon and nitrogen. That is nothing but the graphene or that is nothing but the dopped graphene. So, you can see here I have a graphene like structure and I have actually inside dopant atoms. This is something if you would ask a graphene chemist that is what they are doing daily to dope nitrogen atoms or oxygen atoms within the graphene adlayer in order to basically just facilitate the so called band gap engineering. So, typically graphene is known to be a material that is having zero band gap zero band gap is not very useful for making any electronic device. So, what you need is basically to open up the band gap and therefore they can actually become more useful. So, graphene what people do is they do dope nitrogen atoms or oxygen atoms or maybe even other type of elements in order to basically just modify the electronic property, and now you see here by doing a chemistry on surface I have made something like graphene equivalent material, purely two-dimensional material. The two-dimensional nature comes all due to the fact that I have done this experiment on the surface. So, this is the interesting aspect about it. Now I want to show you the real experiment and the outcome of the experiment.

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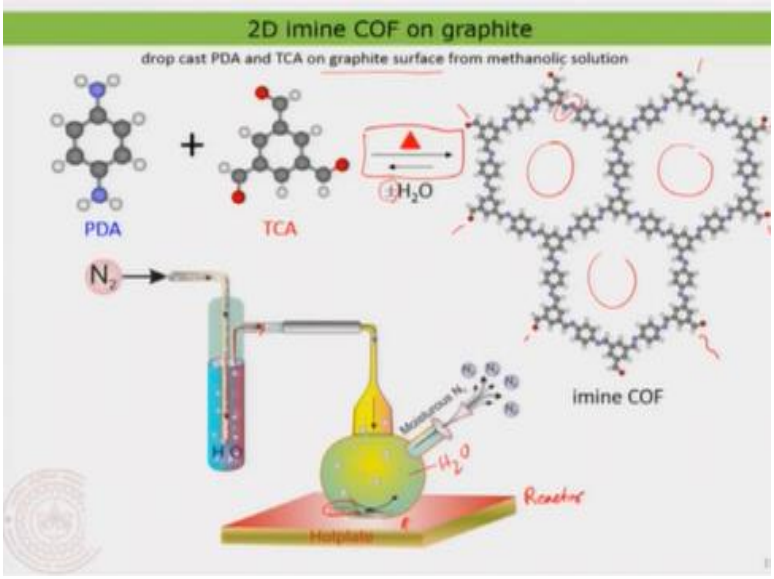

So, let us have a look at the molecules again. So, this is the chemistry I have already told you. I am now going to let them react and then I am going to make basically a network. So, you can see here they are actually forming a network and then I can continue it in all the two directions and then I can basically just make a nice network of this molecule. But now there is something interesting that you have to also practically, although theoretically we have predicted this. Practically, it is not necessary that I will always come up with hexagon. Of course, a pentagon is possible or a heptagon is possible, a slight variation in the symmetry is still allowed. Of course, you would not make a square so this would not be possible because there is a huge frustration in the bond that you form. So, therefore it is not allowed. But a pentagon or a heptagon is actually allowed, because you do not actually just change a lot with these bonds if you would be only just making a pentagon or hexagon or a heptagon. Therefore, when you make these kinds of layers on the surface, it is likely that sometime you end up in defects which we call it as a pentagon or a heptagon. So, to do the correction what you actually do, you can see here I have added a plus and minus that means you do this chemistry not just in a dry atmosphere, you basically do this in some kind of a moisture atmosphere which meaning that you do this chemistry at an equilibrium condition. Why do you want to do in an equilibrium condition? Because in case I have made a pentagon and I can basically open up that bond again, because by adding water molecule into the network structure and basically coming back to the precursors again. So, I can keep on correcting and that correction will help me basically in propagating the two-dimensional structure to a larger area. Otherwise, what happens is like I would always get a small small domain of the 2D

network. So, for that what we do is we do all this chemistry so of course you see the surface is basically graphite surface so that is what is indicated here, this is a synthetic graphite. So, what we do is we take both the molecule, take a mixture of one is to one or one is to two as per your requirement and deposit that molecular substrate or molecules or the precursor molecules on the surface and then you let them inside a kind of reactor. So, what you are seeing here is a reactor, this is actually a small reactor in which this is actually the reaction chamber. So, where you have the heating is actually happening in the reaction chamber. But while you are heating you are also just sending water molecules inside. So, by just taking dry nitrogen so you basically just let it pass through a water container and then this water molecule is basically passed through this and then finally it reached the reaction chamber. So, that means every time the reaction happens inside a water atmosphere. So, this is basically water inside, small humidity is maintained and then if you maintain that nicely then you can clearly form the nice beautiful adlayer on the surface.

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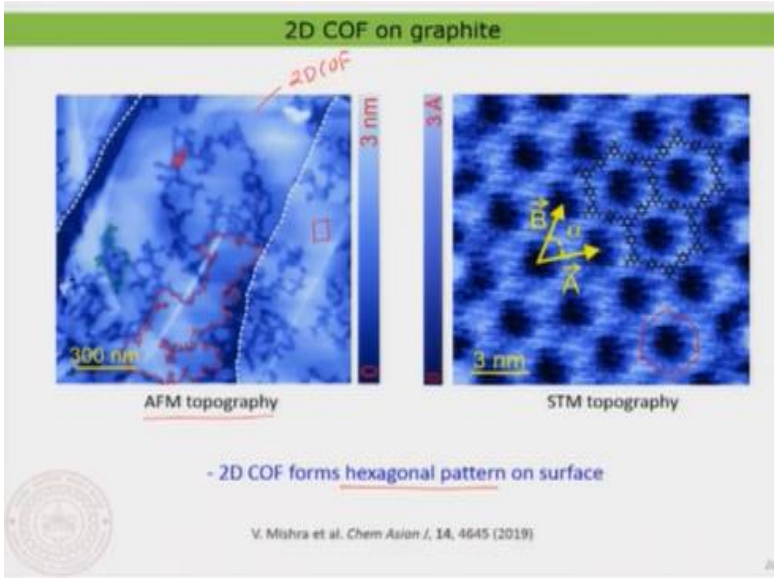

So, now I just want to show you how it looks like in an air from topography. So, this is an atomic force microscopic topography, you see the blue light blue this part is nothing but the 2D curve. So, that is what is marked with this red line here and that is actually the smooth two-dimensional layer which is actually forming on the surface. And then the other region, these regions which are marked here which are actually some kind of an unreacted or like non uniform two-dimensional COF layer. But nonetheless you can see in this image you clearly form a very large

uniform layer of the two-dimensional COF. So, that is the interesting thing. So, of course you can now apply a scanning tunnelling microscopy because I want to see what is inside. So, you can just take a small part here, apply a scanning tunnelling microscopy or image scanning tunnelling microscopy and now you see that beautiful hexagonal pattern of the of the COF as expected. So, like now you can see I have also just embedded on top of it, the chemical structure on top of it and now it is actually fitting very nicely and you see that it forms a hexagonal pattern as expected on the surface. So, therefore just keep it in mind to get this the water is very important here, the water atmosphere is very important, the temperature is also very important and the surface is also very important. So, this can only be formed on a to on a surface so that is the important thing.

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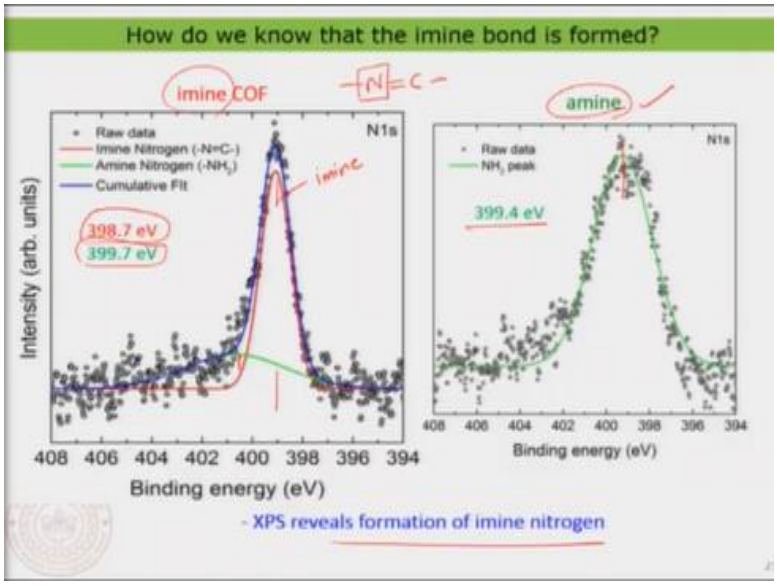

So, now the question is how do I confirm that this imine is actually formed. So, that is of course a question. Well, I have the technique which we have learned which is nothing but the X-ray photoelectron spectroscopy, I basically do the X-ray photoelectron spectroscopy, and what definitely is changing in the system is the new bond formation which is the imine bond formation. So, that is what you are forming. So, you are forming an imine bond that means you are forming an N double bond, N-C bond is what is formed. So, that means I can basically look at the nitrogen one of resonance, because that was not present previously and that forms then I should be able to detect that. So, what I do is I take the pure imine just the precursor molecule and I do an XPS measurement. You can see here everything is nicely fitted with just one

resonance that is actually about 399.4 electron volt, and that is corresponding to the typical amine type of nitrogen, that is something known in the literature. You can also just see it because here I know that I have taken basically the pure imine in this case. But now when I do the same experiment, the XPS experiments on my COF, what I do see is that I have actually a new resonance that is basically a 298.7 that means one electron volt lower. So, this is the major peak you can see, it is a nice sharp major peak, and then I also have a peak at 399.7 that is the one here which is actually somewhat close to the amine peak. So, that looks like the there is a small amount of free amines are still left, because you also remember that we have seen that there are some area which is still not very well ordered. So, probably there are still some free amine left. But nonetheless the major peak is basically coming from the imine. So, this is the imine peak and that is actually now looking at a slightly higher energy about one electron volt higher than that of the amine. So, why is it actually at a higher binding energy? So, that shows that the new nitrogen that is formed that means the imine nitrogen is kind of a more reduced state than in the amine. So, that is very clear because when you take the amine it is basically connected to nitrogen connected to two hydrogen and one carbon in the PDA molecule. So, that nitrogen is actually much more oxidized. But the moment when nitrogen is actually forming some kind of an aromatic linkage then that nitrogen is obviously a more reduced state and that reduced state is a reason why you clearly see that there is actually a downward shift of the binding energy. So, that clearly tells me that I have actually just formed an imine bond. So, this is quite an important characterization in this because just by looking at the microscopy alone. Of course, you were convinced because I could actually fit the imine COF with the expected microscopic structure. So, therefore it is quite interesting and quite convincing. But on top of it if I have actually an XPS measurement then you clearly see that I can actually consolidatively say that I have clearly formed the imine nitrogen. So, that is a direct indication of the chemical structure of the COF that I have formed. So, by now you can see the combination of the microscopy and the chemical analysis would basically give me a clear indication about the total chemical and microscopic structure of the two-dimensional material that I have formed. So, then of course there are a tremendous possibility this is also like a topic nowadays quite hot in surface science where people do prepare this aromatic linkage based a two-dimensional material that is becoming very popular known as the covalent organic framework, the two-dimensional covalent organic framework and that is actually gaining a lot of popularities nowadays. So, that is also the reason

why I thought of introducing it to you. So, as example but there are enormous possibilities are there in this type of material. With this I would like to conclude and in the next lecture we will be looking at the metal doped two-dimensional molecular material and in greater detail on that type of material and thank you very much for your attention.