Chemistry and Physics of Surfaces and Interfaces
Prof. Thiruvancheril G Gopakumar
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 35
2D Molecular Materials on Surface -2

Hello everyone, welcome back to lecture number 35. So, in this lecture we will continue on the topic that we have been discussing. So, this is about two-dimensional molecular materials on surfaces. So, yesterday in the previous class what we have done was to kind of look at the first type of two-dimensional molecular material that was basically by having an aromatic linkage between the molecules in a kind of assembly, and then in this lecture I will also show you the metal doping and the influence of metal doping and the generation of two-dimensional materials and its characterization using different experimental techniques that we have basically learned during these previous lectures.

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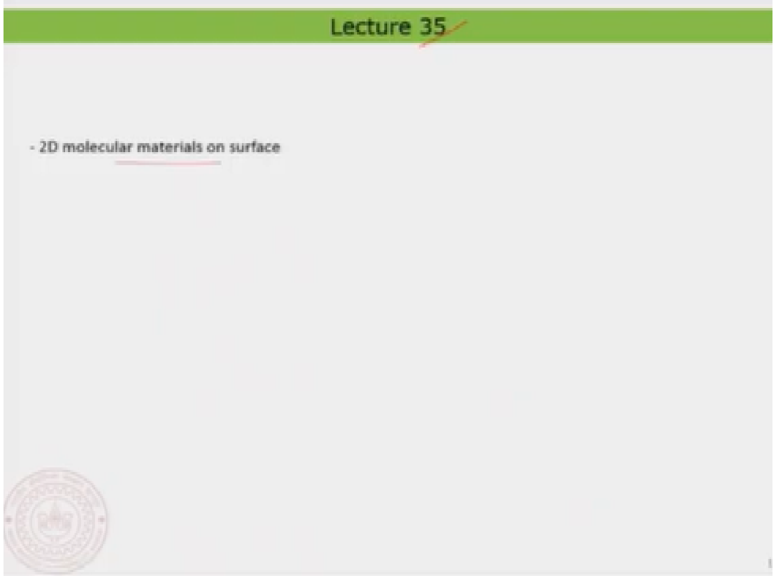

Lecture 35

- 2D molecular materials on surface

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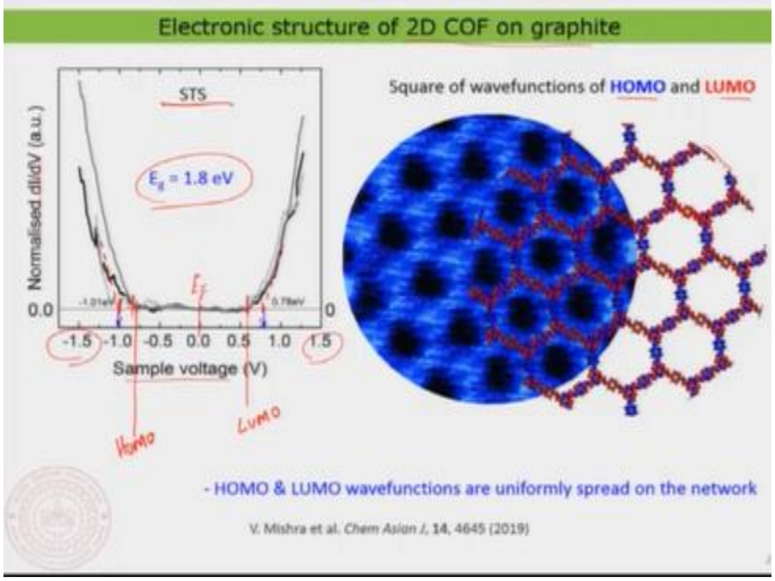

Electronic structure of 2D COF on graphite

- HOMO & LUMO wavefunctions are uniformly spread on the network

V. Mishra et al. *Chem Asian J*, 14, 4645 (2019)

So, we have already seen the two-dimensional COF that to be prepared on the graphite surface. So, what I want to show you finally is the electronic structure of that. So, what we had looked at was the microscopic structure, so we have understood how the molecule or the atoms are arranged within the covalent organic framework, the two-dimensional covalent organic framework, and then we also had a look using X-ray photoelectron spectroscopy. We also had a look at the chemical structure and we have actually just confirmed that there is actually an imine bond formation. Now it is also important when we want to take these materials to kind of electronic applications to understand the electronic structure, because always when we talked about, we said it is important kind of control the HOMO-LUMO gap or the generating a band kind of structure and so on in material so that we can basically just use them in electronic applications. So, that is the main motto behind us. So, what we do is, we do a scanning tunnelling spectroscopy. So, this is for the same system that we have shown before. So, I basically do is I take the COF and then I place my scanning tunnelling microscopy tip and then just ramp the voltage. So, from -1.5 here to 1.5 volt, you ramp the voltage and then you take the first derivative of this. So, that is what you see here. So, it is a kind of normalized dI by dV that is what you are looking at that, the unit is unimportant in this context, and then what you see clearly is that this would be your fermi level. So, this is basically our Ef and with respect to that you can basically see around the fermi level, it is almost no density of states. So, that is quite interesting, and then after a while you can see that there is a small onset at which the density is basically increasing on the positive side that is indicating the conduction band and on the negative side you can basically see another onset here this is actually indicating the onset of the valence band. So, always keep it in mind that whenever we talked about scanning tunnelling spectroscopy or microscopy you have to define the voltage with respect to what and I told you in the class that we should always do it with respect to sample but it is not necessary that we have to do it with respect to sample, but in all the cases that we have discussed in all the cases it was basically with respect to sample. So, that means that is why I can basically say that the positive side is indicating the conduction band and the negative side is indicating the valence band if you switch the voltage, that means if you start to apply the voltage with respect to the tip then you will see it will be just the opposite. So, that is the reason why I am emphasizing that. Now, I see nicely this onset and then there is a clear increase in the density of state and if I would just do some kind of calculation, so I can basically just get some kind of a mean value of the onsets and that gives rise to something like a band gap of about 1.8 electron volt, this is quite nice. So, this looks like that whatever COF that you have prepared on the graphite is kind of a semi-conducting material and it has a clear gap around the fermi level. So, this is something quite nice because what was also our intention was actually to kind of make or modify or generate a graphene equivalent type of material which is having a band gap because if I want to use this material in electronic application, it is quite important to have a band gap and that is what you have actually just achieved in this case. So, that is nice, then what I can also just do is that I can also look like where this conduction band edge and the valence band edge, so for materials like this it is better to call it as the conduction band edge and the balance band edge, but they are also somewhat equivalent to the LUMO or HOMO of a molecule. But since we are actually forming this material from their molecule itself from precursor molecules, so it is also sometime represented that this to be like a kind of HOMO and LUMO. So, what now I am going to show you is a kind of plot of the HOMO and LUMO of the molecule. So, what I am basically just plotting here, so this is actually the network, so the hexagonal network you can see clearly and then on top of that what I have done is actually I have kind of plotted the square of the wave function corresponding to the HOMO and also the LUMO. The wave function square is nothing but the representation of the probability of finding the electron and therefore it is important that we look at the density rather than the wave function alone. So, that is the reason why we plotted it and when you do that what you see interestingly is that the HOMO and LUMO is basically just spread over the network in a uniform manner. So, that looks like the so-called pi conjugation so, when you form this imine bond you know that the precursor molecules are also aromatic. But when you form the imine bond between the two precursor molecules there is actually a true electronic conjugation or there is a pi conjugation between the precursor molecules through the imine bond. So, because of that you have a true delocalization of the pi electrons across the network structure and that is also something that you can compare here. So, this is basically our hexagon that we have resolved using the scanning tunnelling microscopy, and now you see clearly that around the entire network the electron density is actually distributed. So, this is very useful because if I want to basically call this material to be kind of an graphene equivalent material. You will have to kind of see this effect and that is what you see. So, that is about the electronic structure of this material. Now we can switch to the next type of material.

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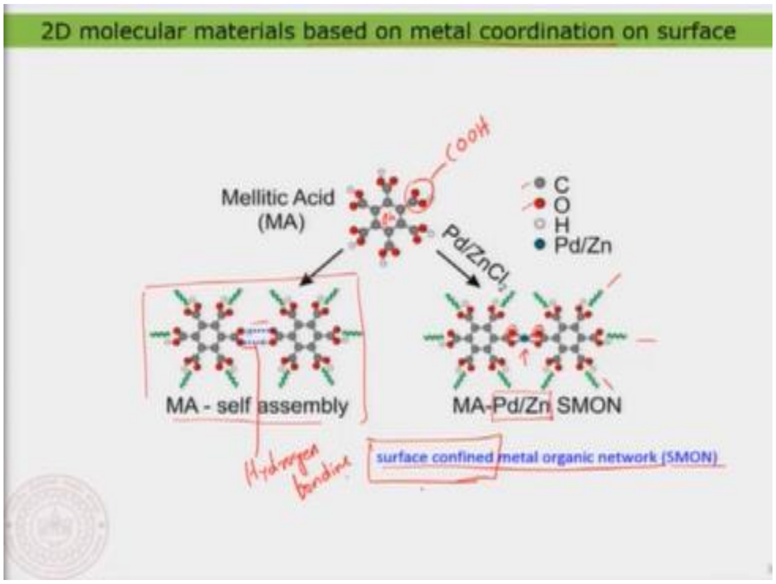

2D molecular materials based on metal coordination on surface

surface confined metal organic network (SMON)

So, that is basically is the two-dimensional materials where we are going to do some kind of a metal coordination or metal doping within the self-assembly. So, this is another method that we have actually discussed in the previous class with that we can basically create some kind of a state which will help actually in improving the transport properties of this molecular self-assembly. So, the molecule that I am just using so again it is a typical example. So, there are enormous possibilities left out are there in the world of molecule that you can choose and I have actually just chosen mellitic acid which is actually again a benzene ring and then you have like carbon, oxygen so you have basically here the COOH group. So, that is actually the acid function group and the reason why we choose is something you will understand, because the oxygen atoms are the one, we are going to use as the atoms which would actually coordinate with the metal. So, that is for therefore the COOH groups are important. Now we choose a molecule where you have the phenyl group and then all the carbon atoms are actually like connected to a COOH group. Now if you would put this molecule on surface, you would naturally imagine, because you have the COOH group, so you remember we talked about that the COOH group is actually capable of forming a kind of dimeric hydrogen bonding, and because of that you can basically see that this molecule can kind of form a nice molecular self assembly through this kind of hydrogen bonding. So, the blue indicator here is actually nothing but the hydrogen bonding between the molecules. So, you can basically form that nicely and they would propagate in all the two-dimensional 2D direction, because you can see there are many many COOH groups available within the molecule. So, they can actually propagate the assembly in the two dimension and then it actually can form a nice well-ordered self assembly, so, that is all right. Now what we want to do is we do not want to actually just have a simple molecular self assembly. Because we know that the electronic connection or the so called true electronic coupling between the molecules are very weak because of that there is a huge barrier for the electrons to hop or the holes to hop from one molecule to the other molecule. So, therefore what we want to do is we want to basically connect this molecule using metal atoms. So, this is where it is. So, we are we are now in this particular example I am going to do is actually I am going to connect this mellitic acid molecules using palladium and zinc just to see the capabilities and also to see the differences when you dop with two metal. So, what I do is I connect now this. Now you see that the oxygen atoms are nicely getting connected to the palladium and then I can basically propagate this connection in the two dimension and basically, I can generate some kind of a nice network of molecule connected through a metal atom. So, this kind of network is generally known as a surface confined metal organic network or commonly known as SMON. The reason is very simple. In this particular case you might have actually just heard about metal organic framework. So, this is clearly different from that, well the principle is the same but here you need to have a surface because the surface is now going to act as a template in order to facilitate the growth only in the two directions. Because you would imagine that the coordination is not just limited to always grow in two dimension if you actually do this kind of synthesis in in gas phase or in solution phase. So, there you can actually have coordination in any direction between two adjacent molecules therefore you would actually just end up in making a three-dimensional crystal. So, that is not what we want, we want to clearly have a layer type of material. Because we want to generate a 2D material to use in thin film applications. So, therefore the surface is very important and that is the reason why it is called as a surface confined metal organic network. So, that is commonly known as SMON for example. Now let us see how we can do that and then we try to understand it more clearly.

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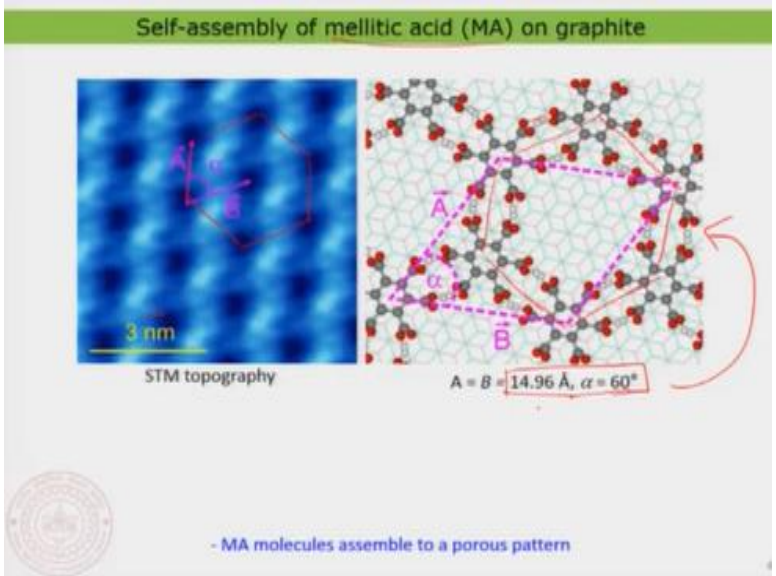

Self-assembly of mellitic acid (MA) on graphite

STM topography

A = B = 14.96 Å, α = 60°

- MA molecules assemble to a porous pattern

Now let me just show you the self assembly first of the mellitic acid. So, just we can do it in a systematic way. So, the mellitic acid molecule of course as expected, they can actually just undergo this hydrogen bonding between the molecules and they can actually form a nice network structure. So, it actually forms a porous network structure. The porosity is actually due to the fact that this hydrogen so there is actually a strong hydrogen bonding between the adjacent molecules as I have just depicted here. So, they can basically just kind of get connected through hydrogen bonding. And two COOH groups of each molecule is basically getting connected to two COOH group of adjacent molecule. So, that means you form a dimer along this direction and then you form a dimer along this direction and then nicely you can see you form a perfect hexagon between through the molecular interaction. So, that is exactly what you are also seeing here in the experiment. So, you can basically see that kind of hexagon is something that I can basically form. So, I can also just connect these black spots instead. So, you see nicely they are getting connected like that. So, you firm a perfect hexagon. Now the thing is so you can also just measure now using STM, because you have the scale of the STM. So, this is basically it and using the scale you can also characterize what is the distance between the molecule and that is something we have written here. It is about 14.9 angstroms and also you can measure the angle between the molecules, and by measuring these experimental parameters you finally come up with this kind of model because you also have the notion that these molecules are supposed to form actually a strong hydrogen bonded network. So, therefore you would basically expect something like this kind of a bonding and therefore by inputting these parameters like the angle between the molecular lattice and also, the distance between the molecular lattice points, you can basically just come up with the structure. So, this is how you kind of characterize it. So, we will also just look at some assignments when you read this lecture. So, then you can also try to solve by yourself some examples that I will be sharing. So, this is how you solve the STM image here. So, this is of course an STM image made in the ambient condition so not in ultra high vacuum. But then once you measure that you need to do some kind of averaging for example and this is actually kind of an averaged image, so to get the quality for example. Now what we want to do is we want to basically mix the mellitic acid and the metal atom. So, for that what we generally do is you take a solution of the mellitic acid and the solution of the corresponding salt of a metal and then you mix them and make a nice solution of it, and then you basically pour onto the surface of your interest. Then you can also gently anneal the surface in order to just remove all the solvents that you are using in the preparation. And then once you do that then you can clearly make the metal coordinated mellitic acid network.

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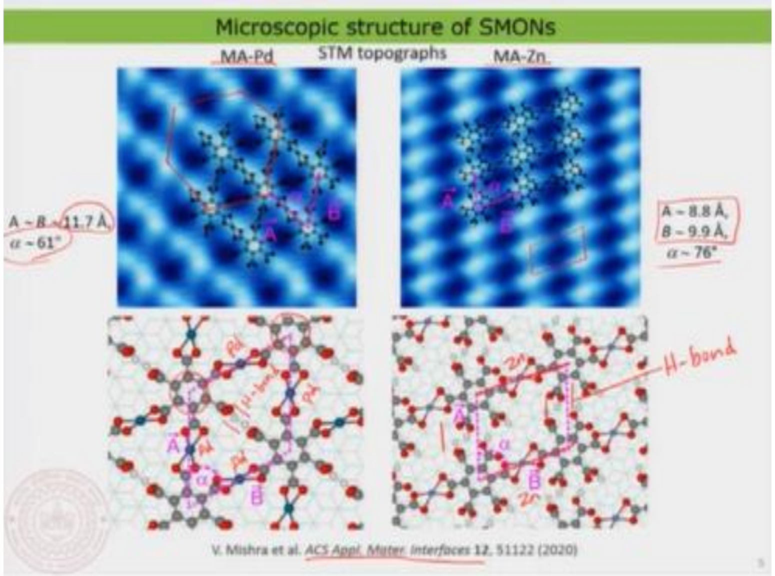

Microscopic structure of SMONs

STM topographs

V. Mishra et al. *ACS Appl. Mater. Interfaces* **12**, 51122 (2020)

So, that is something I want to show you now. So, first let us do that of the mellitic acid and palladium. So, here I use palladium chloride as the salt I simply take the two mellitic acid and the salt. So, you mix them and then you pour that solution, a dilute solution of that onto the surface, that means your graphite surface in this case, and then you have to gently anneal and then finally everything is formed. So, now you see that in the STM image you clearly see a different type of pattern but still the pattern is actually looking like a hexagonal pattern. So, you can clearly see that if you draw a line across all these things so you would finally just make a hexagonal pattern. So, the pattern that you have also seen before was actually hexagon. So, therefore it is important that you measure the distance between the molecules. So, of course we have the scale of the STM image so you can measure that. Once I measure you see the distance between the adjacent molecules in this coming out to be about 11.7 angstrom which is definitely much much smaller than what you have actually just seen in the mellitic acid assembly. So, then it is clear that there is some kind of a metal coordination between the molecules and only then you can actually bring the molecules closer. So, that is why we thought about it and then by just doing a lot of iteration. You can also just measure the angle that is why I told you it is a hexagonal type of network, and then you can basically come up with the model and there you see this is actually the mellitic acid core and the adjacent molecule, and you can see the molecules are now connected along this direction and where you have a palladium atom coordinating to it. You also see that along this direction you have a palladium and also here you have a palladium and also here you have a palladium but there are two free carboxylic groups left and they are interacting through hydrogen bonding again. So, H bond is written that is indicating that these two particular carboxyl groups are basically interacting through hydrogen bonding. So, that is the thing. So, that means there are about two palladium atom per unit cell. That is the thing and then you can also correlate this structure there are also like theoretical calculations you can do to understand it more correctly. So, we have also done it. So, you may actually just look in this literature to get a bit more of insight about the project. So, what eventually you see that you can basically coordinate the metal, the molecule with the metal atom. So, this is quite nice good. So, now we want to do the other molecule. So, what we have done is actually we have now doped actually the mellitic acid with the zinc metal. So, when you do with a zinc, we again do the same preparation. So, we have taken the zinc chloride so what you see clearly in the STM image is that the unit cell is quite different here. So, this looks like kind of an elongated oblique than the one you have seen in the previous so that was basically kind of a hexagon. But here you see something like an elongated oblique. So, this is quite different. So, that already tells you that the molecular interaction and the coordination is going to be very very different. So, how do you then again make sure of it, so you can definitely look at the lattice parameters. So, this is basically A and B you basically see and also the angle between the lattice parameters something you can measure. And then by using these parameters you can clearly see that along one of the direction or you can actually come up with a scheme of molecule coordinating with metal in this fashion where the interesting thing is that the two adjacent molecules are coordinating through zinc along this direction and also along this direction but they are the identical direction but along this direction you basically see this is kind of a hydrogen bonding again and also here it is basically hydrogen bonding, so not through metal. So, that means the number of zinc atoms per unit cell in this case is just one, because in the palladium it was basically two. So, that is quite notable. So, which means that what we are actually just looking at is a completely different kind of structure between the two different molecules. So, that is nice. So, now we have actually just understood the microscopic structures using scanning tunnelling microscopy.

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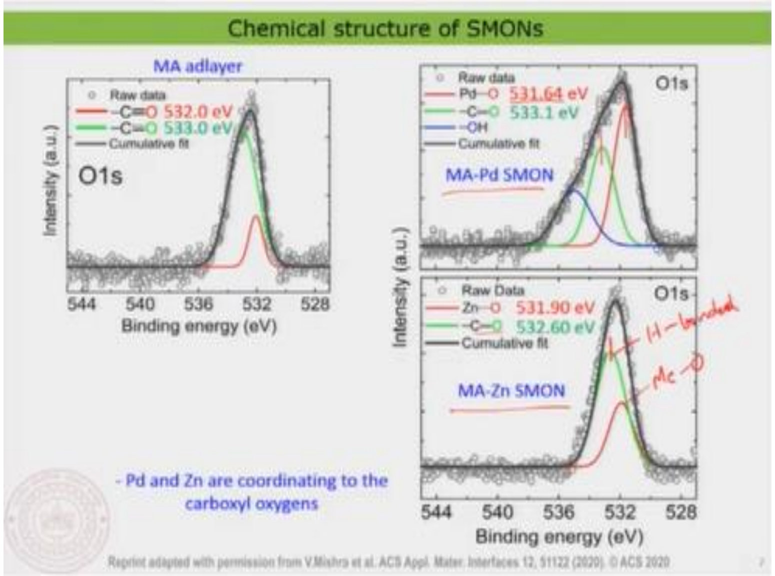

Chemical structure of SMONs

- Pd and Zn are coordinating to the carboxyl oxygens

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So, now the question that you would ask is are they basically really coordinating or do you have the clear understanding about the coordination between the two molecules. So, that you can understand if you look at the chemical structure. So, how do we do so we basically just run an XPS measurement so X-ray photoelectron spectroscopy. So, let us do that first for the MA adlayer. So, you clearly see here this is the mellitic acid adlayer. So, the interesting thing what I want to mention here so you have here the carbon and you have the double bond O, you have the OH group and then when it actually just coordinate to make a hydrogen bonding between the other molecule. So, you have something like this. So, this is basically the two carboxylic groups that are actually coordinating, actually just kind of making hydrogen bonding. So, what you would have expected basically for carboxylic group is actually just an equal abundance of an OH group that is coming from the alcohol group and also the oxygen coming from the C double bond O group. So, that should have been basically an equal contribution. But what you see here in the experiment is that this red peak that is corresponding to the C double bond O and the green peak is actually corresponding to again a C double bond O but it is not really like a C double bond O, it is kind of a partial C double bond O. So, that is why I have indicated with this dashed line. This is showing that what is really happening is that when the hydrogen is coordinating with the two molecules, so what eventually happens is that you have some kind of a weak interaction between. So, just I think I have just made a small mistake here, so let me just correct it. So, I have here OH then I have O here and then I have here again OH. So, now when it actually make a connection like this. So, what you are going to get is actually some kind of a partial double bond for both the oxygen atoms. So, that eventually means both the oxygen atom is actually kind of becoming similar if you have a strong hydrogen bonding, and that is the reason why by majority that is a green peak the majority is basically kind of indicating a kind of hydrogen bonded carboxylic group, so that is an indication. So, now we can do this for the two other palladium and the zinc SMONs. So, then what you see clearly is that in this case that the relative ratio of the hydrogen bonded and also the next one which is corresponding to the oxygen connecting to the palladium is actually just changing. So, particularly noticed that for the palladium case, the hydrogen bonded oxygen is basically just decreasing and the one with the metal bonded one is actually increasing, and that is also what you expect because you remember you actually just seen in the microscopic structure that you have two palladium atoms per unit cell. But in the case of zinc, you clearly know that you have more hydrogen bonding because you have only one palladium per unit cell. So, that means the four other groups of a given molecule is basically just having still the hydrogen bonding or the carbonyl group here. So, that is the reason why you have basically here in the case of zinc, you see that the hydrogen bonded so that is the one here, the hydrogen bonded carboxylic oxygen is actually higher in percentage and the metal one, so this is actually the metal oxygen and this is the hydrogen bonded here. So, that is basically higher than that of the metal oxygen. So, this is actually giving you a hint that we have actually clearly formed some kind of a metal oxygen bond inside.

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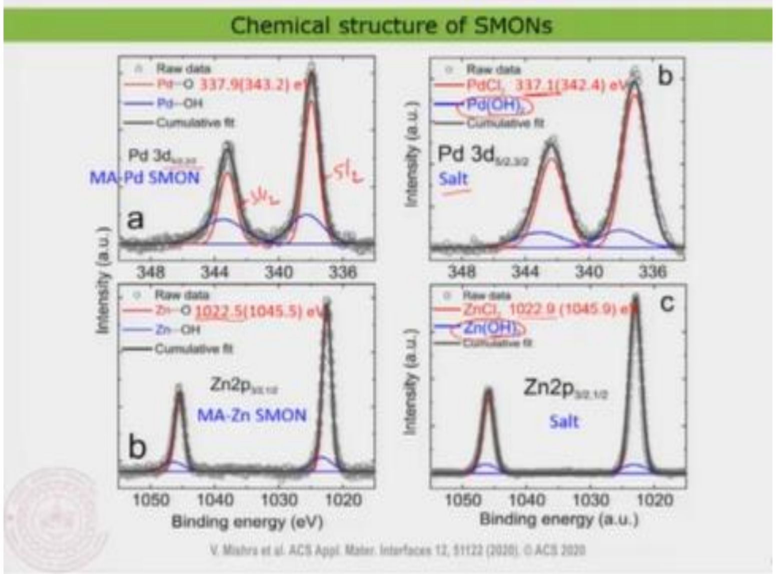

Chemical structure of SMONs

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We can also look at the metal itself. So, this is actually the palladium. So, you remember that we talked about for palladium you have actually two spin split states that is actually the 5/2 and the 3/2. So, this is basically the 5/2 and this is the 3/2. So, as expected the 5/2 is basically much more intense than the 3/2 and then you also see that the corresponding peak position is actually not matching with that of the salt. So, we have actually just done a control experiment that is actually for the salt, and the salt is actually just having a slightly lower binding energy when the metal is coordinating to oxygen, since that bond is actually stronger you see clearly that there is actually an upward shift of the binding energy. So, that means this is actually clearly an indication that we have now coordinated the metal to the oxygen. Now I can also do the same thing with zinc. So, this same observation you see that for zinc when it is coordinated to the oxygen. So, basically there is a shift in the binding energy compared to that of the salt, you see clearly there is a shift. So, now you see for both molecule of both metal and oxygen there is a different direction for the shift, that is actually indicating the strength of the metal oxygen bonding. So, this is quite important. So, by comparing these kind of things you can basically understand that the palladium oxygen case is kind of a very dense packed or more strongly bound case than that of the zinc. So, that is also something we know because in the palladium case we have two atoms, two palladium atoms per unit cell. This blue peak is something you can ignore right now because they are actually coming from some impurity that is present in the experiment that is actually coming from a hydroxide group so, that you can somehow omit in this case study.

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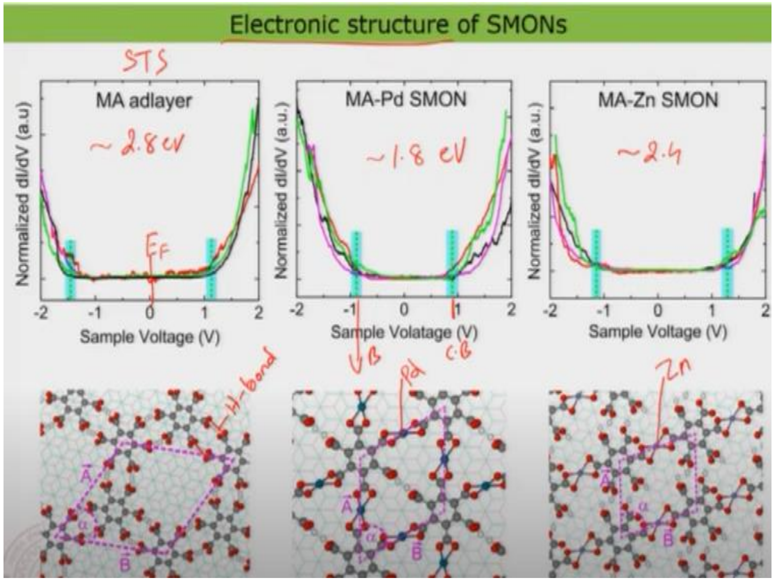

Electronic structure of SMONs

Now what I also want to finally show you is the electronic structure. So, we have now solved the microscopic structure, the chemical structure and now I just want to do the electronic structure. And now look at the electronic structure, how do you measure I would again measure the scanning tunnelling spectroscopy here. So, again 0 represent the fermi level, so this is the fermi level and you clearly see that the band gap of a normal mellitic acid self-assembled layer is about 2.8 electron volt, and in the case of palladium that is about 1.8, this is approximate value you can read out more properly or in this case it is about 2.4 approximately. So, you can clearly see that as soon as you coordinate the molecule with a metal, so there is a huge reduction in the band gap. So, that is exactly what we were hoping in the beginning when we discussed about the molecular self-assembly where you have a large barrier for the electrons and holes to get transported through but you clearly see both the conduction band and the valence band edges are kind of shifting towards the fermi energy which is indicating that these materials are actually much more suitable for transport properties or even transport based application or electronic application than a simple melodic acid assembly. So, that is also something to do with the microscopic structure as I have told you that here there is like weak hydrogen bonding here. So, that is not a true electronic coupling between the molecule but as soon as you have metal coordination here, metal here zinc, you see clearly the band is actually just reducing that is showing that as soon as you coordinate the molecules with metal atoms and also depending on the type of metal. So, palladium is quite important, because palladium has actually kind of a planar geometry for the coordination. Therefore, the interaction between the molecule is much stronger and that is also the reason why palladium is actually the best in our case and we have also tested a few more examples and in out of that palladium is seemingly the best. So, what I want to show you here is basically that we can now characterize the electronic structure. So, what you have seen in these two examples that we have taken two cases and systematically analyse their microscopic structure using STM and AFM. You will also see the AFM in the next class anyways, and then we have looked at the chemicals structure using X-ray photoelectron spectroscopy and the electronic structure using scanning tunnelling microscopy. So, it is always the combination that you have to use to completely characterize and understand their applicability, but in also I wanted to show you this particular example, because these are two-dimensional material which is truly created on surface. Otherwise, these materials would not be possible. With this I would like to conclude this lecture and then I see you in the next lecture with atomic force microscopy as a tool for other microscopic applications. Thank you very much.