Nanobio Technology Enabled Point-of-Care Devices
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Lecture - 19
Strategy for Electrochemical Detection and Tuning of Electrocatalytic Activities (Continued)

Dear students, so, let us show you the Strategies of Electrochemical Tuning again. Last class I taught you like Fenton's reagent the new method. Let us come with all proper explanations and with proper data and the surface images.

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So, mainly we will cover again the activities with some new treatment method and the with proper explanations.

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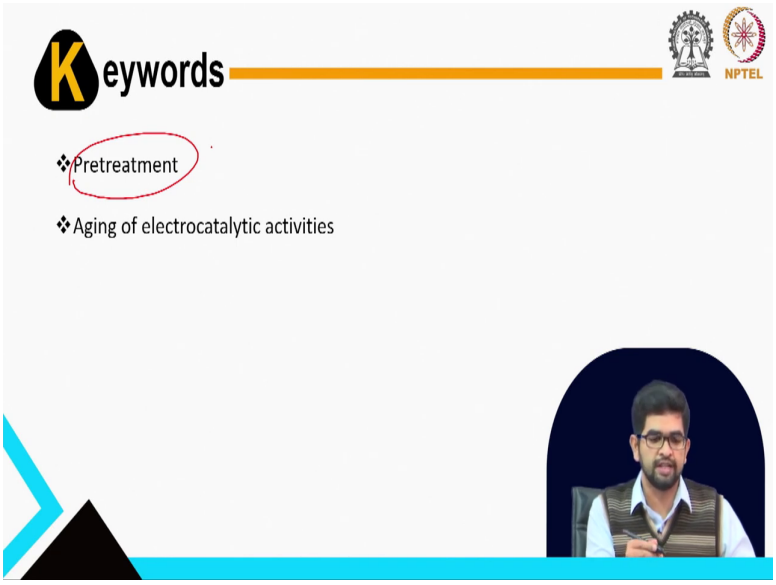

So, you can search this all the classes this main keywords. So, you may get more informations like kind of research going on currently worldwide like people also involve like tuning the effect of electrocatalytic effect with some different different treatment. You also can think about who are doing your like future who want for like PhD or higher study please think about some new method.

You please that is why you should search in Google like or even if you search I all in all the slides you can see I already mentioned different different references I already put. You please go through all the references and please go also some more example of this study that is already reported by different group. So, you please check it.

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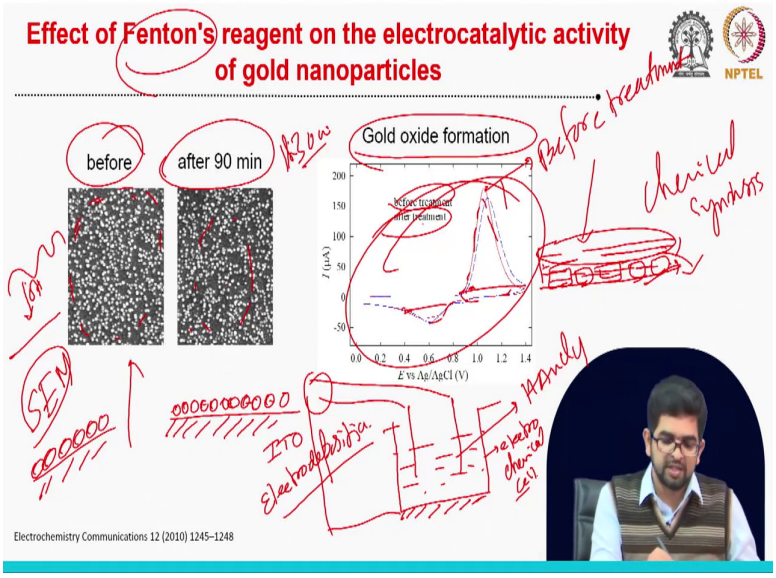

See here today I am going to show you some data like just before treatment and after the Fenton treatments. So, I taught you this Fenton treatment can be done on gold electrode, gold disc electrode that is solid surface like pure gold. Now, I am going to show you these treatment also can be similarly can be applicable on nanoparticles also.

So, because you may think like bulk electrode and nanomaterial how they are behaving, right because they are activations not all not the similar right how they are behaving during the electrocatalytic activation so, electrocatalytic treatment or FA. So, that they all are not same right bulk electrolysis some on effect and nanomaterial has something else.

So, let us use this Fenton's reagent that EDTA hydrogen peroxide and ferrous sulphate this mixture when we apply for the gold in nanoparticle. So, what we can do? So, we can modify

this nanomaterial on some electrode. So, suppose you have you have ITO indium tin oxide electrode, indium tin oxide coated electrode. There you modified gold nanoparticle.

How you modified gold nanoparticle on indium tin oxide? You can apply any gold nanoparticle modification method that I have already taught you. You can use the electrodeposition method. Electrodeposition like how you can deposit gold nanoparticle? I just summarizing like you can take your like your ITO electrode is there.

And, this is a electrochemical cell electrochemical cell here you can use a gold salt solution right which gold salt like chloroauric acid HAuCl 4 and here you can put one reference electrode and one counter electrode. So, you your working electrode should be connected with potentiostat, reference electrode and counter electrode they can they should connected with a potentiostat.

Then you can apply some negative potential or maybe with some potential scan you can do then you can deposit the gold nanoparticle on the ITO electrode surface or maybe you can synthesize chemically chemical synthesis you can follow like ascorbic acid reductions or you can follow citrate method or sodium borohydride reductions method and then those nanoparticle you can deposit on the ITO on the ITO surface you can deposit all the nanoparticle that you are chemically synthesized.

Now, this you can take a petri dish. You know the petri dish. You can take a petri dish there you can put all a small small chip that is gold nanoparticle coated, right. Now, draw your Fenton's reagent right up to this much they should be fully dipped with the Fenton's reagent your Fenton's reagent content ferrous sulphate EDTA and hydrogen peroxide mixture that I taught you already in the last class which chemical ratio you should follow.

Then one important phenomena you please remember last time when I told you when we use the gold disc electrode after the Fenton treatment the surface become very smooth, right. The surface roughness when you check the atomic force micrograph image before treatment after treatment surface become surface roughness change actually. Before treatment is very rough

there you can remember the hill and valley type surface, but after Fenton treatment you saw surface become almost smooth.

Here you can see when you did before treatment this is the SEM image scanning electron microscope image. You can see this all the gold nanoparticle on the surface and after 90 minute means one and half hour almost 1 hour 30 minute we treated with Fenton's reagent and we show the number of nanoparticles and almost the similar, it means nanoparticle actually behaving different then gold the disc electrode.

Disc electrode case it surface almost it become knock out surface hill and valley type surface which becomes smoother. But nanomaterial case you can see something like similar, then we checked actually the gold oxide means is there a number of nanomaterial nanoparticle is similar or not, if nanoparticle surface become changed or not that also we checked gold oxide formation CV.

See before treatment and after treatment see this this red one this is the before treatment before treatment with Fenton's reagent. You see this is the cyclic voltammogram oxidations peak and reductions peak. So, by this we can actually measure if we integrate this surface area you can actually measure the surface actual your active surface area you can measure if you integrate this surface this area.

Now, the oxidations or the reductions: you can see after treatment it is also almost similar not much change it means your actual surface area not was not change much.

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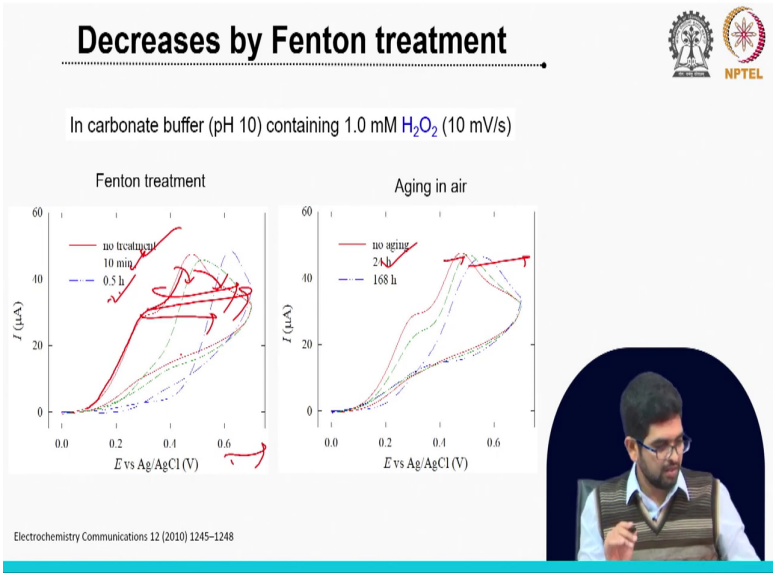

Now, come to the interesting phenomena that I am going to tell you if you measure their electrocatalytic activity. So, we checked hydrogen per oxide oxidations peak or even you can try like some other substrates also like glucose forming acid you can see when treatment no treatment the hydrogen per oxide peak is something like this, but after 10 minute treatment or after 30 minute treatment see peak actually shifted towards right.

What the meaning of this if it shifted towards right? It means your surface deactivated right it shifted towards right more potential shifted, it means your surface deactivated. So, although your nanomaterial coated your surface, your active area almost similar after treatment of Fenton for 10 minute or half an hour even we tried for the one and half hour treatment, but activity actually decreasing it was not shown by gold disc electrode.

In that case, your gold disc electrode case what we have seen surface becomes smoother and activity also decreased, but in this case active decrease, but surface almost similar. But you can say sir, because of aging also surface can be deactivated can be changed where it can shift towards the right side right because aging also can effective phenomena after half an hour this is also half an hour you are storing basically.

Yes, we checked almost 24 hours we checked there is not that much deactivation or even we checked almost 1 week also not the advanced deactivation, but Fenton treatment just for 10 minute or half an hour is deactivated too fast hm. So, this is kind of treatment like one treatment can deactivate the surface rapidly.

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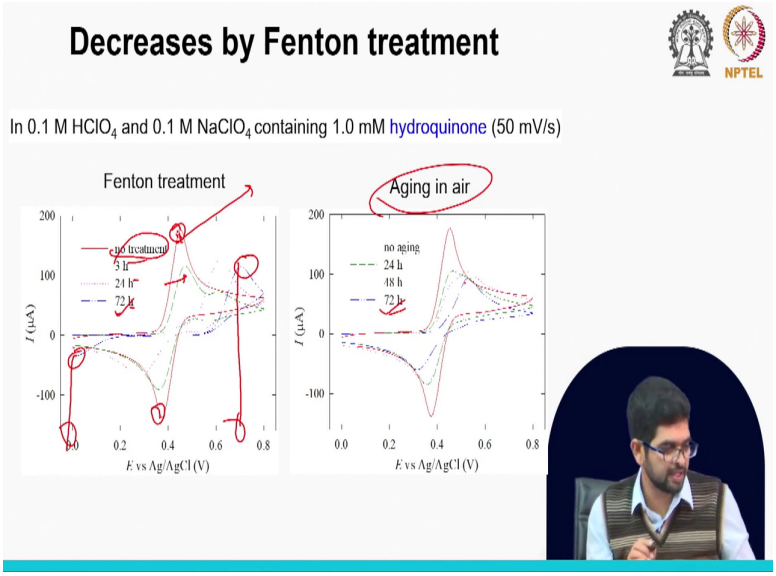

So, we check this one also for hydroquinone oxidation reductions not only hydrogen peroxide we check the hydroquinone. You see just no treatment when there was no Fenton. You see

this very oxidations peak and reductions peak they are very close right they are almost this is called almost reversible or semi reversible, almost reversible this surface because you can see that you have very close the they are very low because their oxidation peak reduction is very close.

So, they are very much reversible, but when you go for the treatment 3 hour, 24 hour, 7 72 hours like we increase now slowly we are increasing the time of the treatment, you see the peak shifted see almost is quite shifted long right here we have see the oxidations peak after a longer incubations with Fenton's reagent. But, if you see for aging in year there also certain aging effects so, almost 72 hours.

So, almost 72 hours aging also can effect because as I told if you store for longer time, but aging can decrease the activations very slow, but Fenton's can decrease the activity rapidly very fast. So, that you could you should remember.

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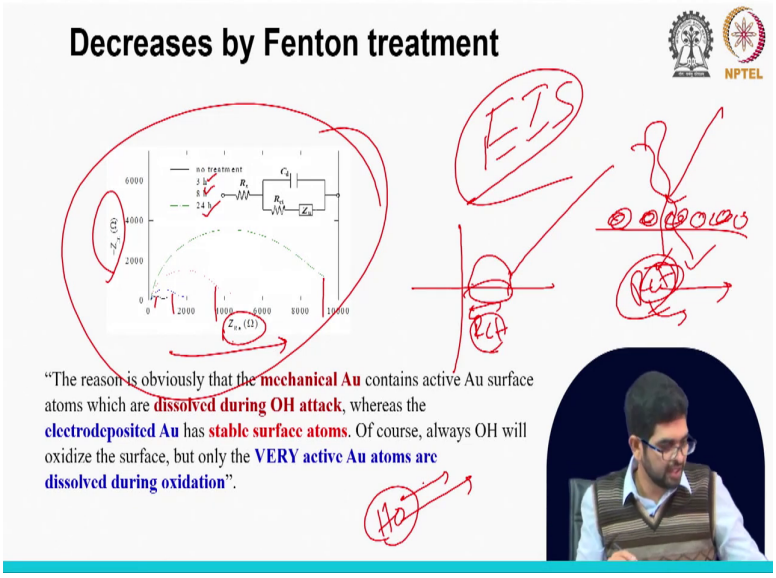

So, this decreased activity also we measure with the help of impedance spectroscopy the EIS, Electrochemical Impedance Spectroscopy. I think you remember last time I taught you like if this is the x-axis we are measuring the impedance of real value and y-axis we are measuring the imaginary value. So, and you can remember I think, right. So, like this impedance this semicircle this R this is the R ct charge transfer resistance. So, based on this value we can measure the electron transfer rate.

So, after the Fenton's treatment you can measure the electron transfer rate also on the gold electrode surface. So, you have the gold nanoparticle on the surface just gold after the synthesis and you can then immediately you can measure the electron transfer rate on the surface after the Fenton treatment you wash the surface then again measure the electron transfer rate R ct value.

So, although there is no protein molecules on the surface still you may get the decrease of the R ct value means R ct value will increase I mean decrease of the electron transfer rate. So, if R ct value increase means electron transfer rate decrease if see no treatment very small R ct this much then 3 hour 8 hour 24 hour we are increasing the treatment say R ct value see R ct value how the R ct value increases.

So, it means you although you have the same nano material gold nanoparticle and because of the Fenton treat treatment your charge transfer resistance actually decreasing, right. So, this impedance value actually predicting and giving you this information to you. Now, see the reason this is very obvious we can explain it why Fenton treatment for the gold disc electrode case something depend and gold nanoparticle case is something different.

Why? This is we call the gold surface it has the very active site, right. So, mechanically the when we polish the gold electrode it has some active site of gold. So, that active site of gold can be dissolved during the hydroxyl radical attack. So, these hydroxyl radical can attack on the gold active site, specially the disc electrode case it can be dissolved easily. That is why you are getting the smoother surface ok.

So, during the Fenton treatment, your gold surface atom which is dissolved in the hydroxyl attack for disc electrode that dissolve dissolution is not effective for the gold nanoparticle case; because this is very stable surface atom gold nanoparticles surface atom is very very stable. This hydroxyl radical attack is cannot be very much effective to dissolve that surface.

That is why if you go back the nanoparticle is same image if you see almost the similar and you are getting this oxidation reductions peak of C V almost similar because it is not dissolving. But, disc electrode case before it was like this surface and after hydroxyl radical attack you can see the surface become almost smooth. So, nanoparticle surface actually is very stable, that is why this is one probable reason.

So, of course, the hydroxyl radical actually is not dissolving electrodeposited gold has the very stable atom surface. So, very active gold atoms are dissolved during the oxidations for a case of gold disc electrode ok.

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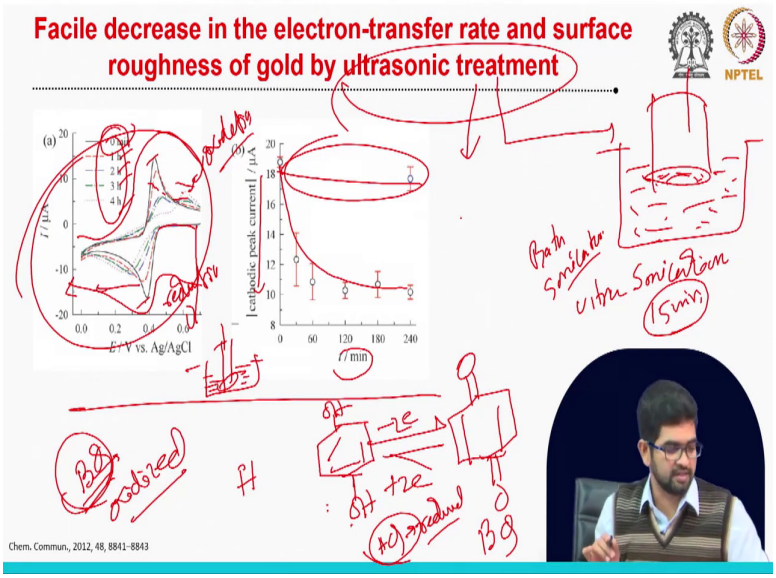

Now, the similar Fenton treatment I want to correlate with another treatment. See in this slide I want to teach you again Fenton similar kind of Fenton treatment, but this is ultrasonic treatment. See another interesting treatment come now.

You know generally after polishings of the gold electrode surface I mentioned like if you have the gold disc electrode, then we are polishing first the gold disc electrode with alumina slurry then you washing with the di water then we are taking this gold disc electrode in a water bath.

Then we are sonicating right sonication, ultrasonication we are sonicating this surface in a bath sonicator. We are using a bath sonicator then we are sonicating in for 15 minute, but sometime you may go for the quite longer sonications, but that effect now I am going to tell you.

So, if you go for a quite longer sonication sometime, it may impact on your gold electro catalytic activity. How? So, you may ask sir why you are showing there is a correlation with Fenton's? Yes, there is a relations with Fenton's reagent and if you go for the longer ultrasonic treatment for this gold electrode surface just after polishing after this mechanical polishing.

See, here I am showing some cyclic voltammogram of the hydroquinone benzoquinone couple. Here actually I started from right side the cyclic voltammogram it means I started from benzoquinone. It is a starting point. So, if you start with the benzoquinone because it is the already oxidized species, right. So, you can remember like hydroquinone you know the structure of the hydroquinone, right. This is the OH, OH this is hydroquinone and this one benzoquinone, right and they can reversibly they can transfer on each other.

So, if it release one if it release the 2 electron and if you give the 2 electron, again then it can be reduced back to again hydroquinone and this is benzoquinone. So, when you start with the benzoquinone because it is already oxidized species, right, it is already oxidized and hydroquinone it is the reduced form. So, if it is already reduced for you cannot further reduce if you start from the right side of this cyclic voltammogram. So, if you start from the right side then you have to use the benzoquinone.

So, first benzoquinone means first reduction. So, this is the reduction scan and then again oxidation scan. But, if you start from the hydroquinone then you have to start first oxidation right because it is already reduced form. So, then you have to start from the left then to right, first oxidations and then reduction if you start from the hydroquinone, ok.

So, that is the electro chemistry just I am reminding you basic time to time I also remind you so that you can correlate with your data with your basic concept. See, so, we started the benzoquinone. So, just after 0 minute means just after mechanical polishing see you can see the very high sharp of reductions peak and oxidations peak and they are very close. It means your surface is highly electrocatalytically active that is why.

Now, 1 hour, 2 hour, 3 hour, 4 hour means quite longer ultrasonications I am doing, then you may face the deactivations of the sensor your surface. So, generally people are not doing the longer incubation this with sonications. But if you go for this what is the effect generally people are not check this effect also.

You can see generally after 0 to a 4 hour if you stored just in the water in water bath if you take a water bath and store your gold disc electrode, just in water after polishing you can see in this calibration curve there is not that much electrocatalytic activity change. So, current almost similar.

But if you go for the sonications see is shifted your oxidations peak shifted towards right and reductions peak shifted towards left it means electrocatalytic activity is decreasing see like this way. So, with time your current also peak and peak also they are also changing and catalytic activity decreasing. So, this means during the ultrasonication something going on. What is this? What is the factor? Let us try to learn.

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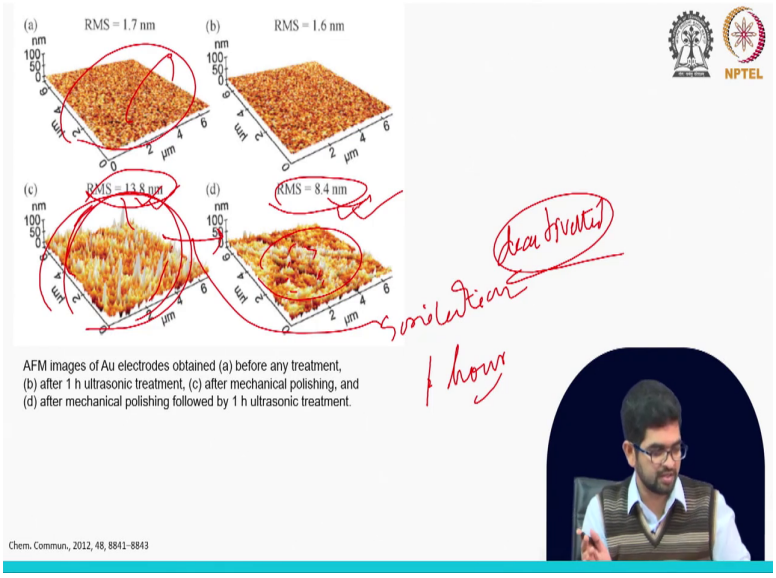

So, first we investigated the surface roughness. As I told you in the Fenton treatment that before the Fenton reagent treatment the surface become very see very rough after the mechanical polishing you can see the surface roughness 13.8 and then after the sonications when the sonicate sonication for like 1 hour if you go for the 1 hour sonication you see surface becomes smoother and roughness become 8.4. So, it was 13.8 now become 8.4 nanometre.

So, it means that again the active surface again knock out and it become smoother and deactivated, right deactivated surface. You can see if your surface is not polished means your surface is not that much rough, then it is difficult to check the roughness change. So, at least your surface should have the hill and valley types rough surface then only you can see the roughness change during this ultrasonication, this ultrasonic treatment.

That is why we choose the surface after the mechanical polishing the surface roughness become 13.8 nanometre and it become now 8.4 nanometre just up to sonications.

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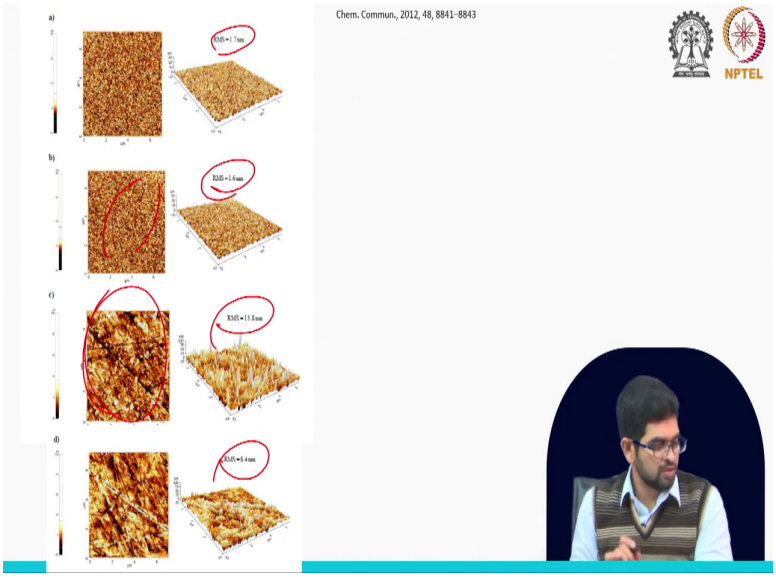

So, here is the whole images you see when your surface not polished just before polished 1.7 nanometre and, in that case, just sonications 1.6 nanometre not that much change and this is the surface just after polishing this is the AFM Atomic Force Micrograph images 13.8 nanometre and then after sonications it become 8.4 nanometre. So, we can clearly see the changes.

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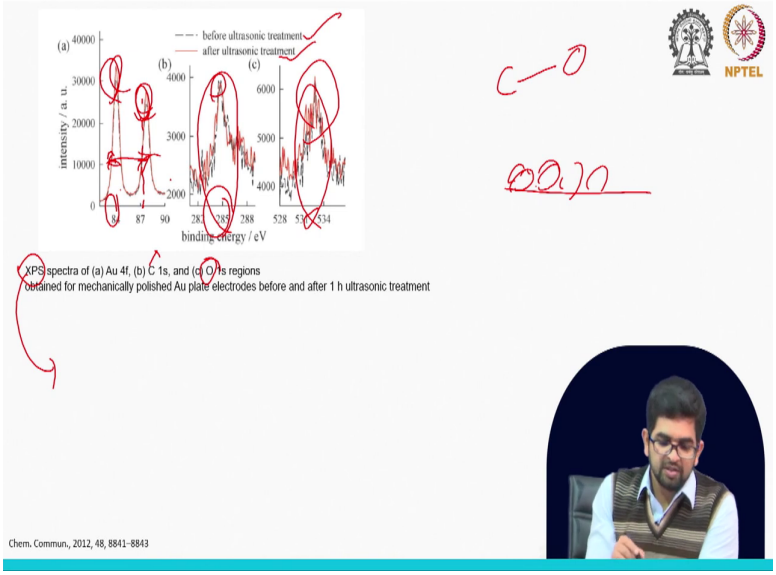

Now, so, I will come the final conclusion why the electro activity changes means step by steps I am coming I am showing you like the changes happen. So, XPS, X-ray Photoelectron Spectroscopy also we can we can measure the surface. So, why we need the x-ray photoelectron spectroscopy XPS can help you to measure the contaminations of your surface means if there is any carbon contamination or not if there is something X present or not during the sonications there is possibility of the surface contamination maybe you can think, right.

And, it can blog the active surface area the surface contamination that is why maybe you can get the deactivations. So, then you that is why you have to prove the surface like contaminations factor like if there is any carbon present or not. See let us come first the carbon base things.

So, you can see the carbon peak around 285 this area you can see the carbon peak before sonication after sonication almost similar it means there is not that much carbon based contamination. So, we can eliminate easily the contamination effect for this deactivation and we check the you can check the oxygen also oxygen region. So, I mean if there is to be defined like organic material it may a carbon oxygen also may present, right. So, oxygen peak also you can check in this region.

So, what is the XPS that is why if you have to study the photoelectron spectroscopy. X-ray photoelectron spectroscopy it will help you to measure different surface material if it is present and easily you can predict the reason of deactivations hm. And, you can see this 84 and around this region 88 something you can see the gold peak. This region we can see the gold peak, sharp two peak you can see.

So, if your surface cover means if your gold surface is covered by some impurities then definitely your gold peak also can be covered. You can see that also not the advanced not means if it is too many if it is contamination, then it should decrease like this up to here up to here, but not it was not happened. So, it means something else can decrease the activity.

So, I am actually teaching you the sequentially and systematically you should understand how you should characterize the surface if you want to explain a factor for change of electro-catalytic activity.

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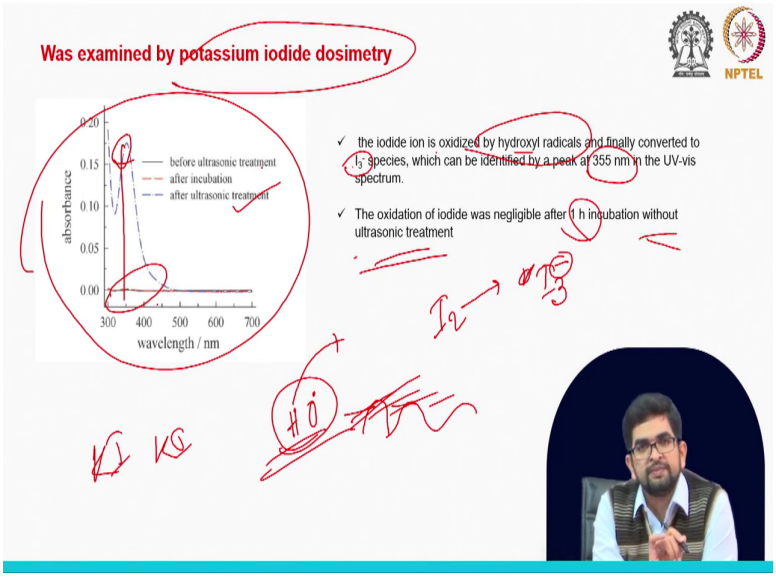

So, in this case also we can imagine that there is no contaminations. Now, let us come the correlation of the Fenton's reagent that I told you know. So, Fenton reagent case you know like OH dot hydroxyl radical actually generating. So, actually it is well known during this sonication, there is a possibility of the hydroxyl radical generations.

But that hydroxyl radical that I taught you that after mechanical polishing that this hill and valley type the surface, it can attack and it will dissolve this surface roughness and you will get the smoother surface you will get the deactivated electrocatalytic activity can be deactivated right. That phenomena we checked it was examined by potassium iodide dosimetry.

What is potassium iodide dosimetry? You can check before and after sonications, before and after sonication you can check if there is a hydroxyl radical is generated or not. See here,

potassium iodide solutions was used hm. So, the during the sonication then the iodide ion that iodide ion can be oxidized during the hydroxyl radical generations. So, iodide it can form I 3 minus and this this can be done this oxidations can happen only because of this generation hydroxyl radical.

So, you can see here this UV visible spectroscopy, this is the UV visible spectroscopy a diagram. You can see the before ultrasonic treatment and after the incubations means we dipped in the potassium iodide solutions for the 1 hour and also we dipped the electrode in potassium iodide solutions up during the ultrasonic treatment. Then we can see this peak, this is this peak we can see only during the ultrasonic treatment, but not just during the simple incubation with the potassium iodide.

So, what is the meaning of this? So, this means oxidation iodide that was negligible means that is almost not done not here during the one incubation with the without ultrasonic treatment. But this peak you can see around 355 nanometre, this is because of conversions of the iodide to I 3 minus and that because of the hydroxyl radical. So, these experiments actually prove that hydroxyl radical is generated during the ultrasonic treatment ok.

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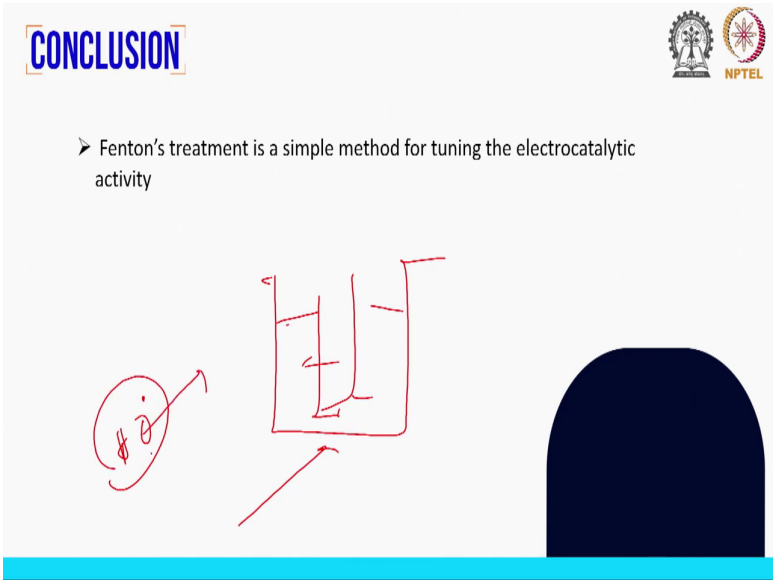

So, we are concluding this that Fenton treatments and ultrasonic treatment there is a correlations, right. So, Fenton treatment this is a very simple treatment, ultrasonic treatment means this is a very simple like you can like just take a water bath and then keep you dip your electrodes and then sonicate it for quite sometime. Then you by this way you can deactivate the surface and what is the reason for this deactivations that we can correlate with the Fenton's reagent.

I mean there is also possibility of the hydroxyl radical generations and that hydroxyl radical can smooth your gold electrode surface and activity can be changed. So, this is the correlations of this two treatment. So, today also I taught you like some another treatment that is the ultrasonic treatment. Again, in the next class I will cover some another tuning method

then I will correlate the all the treatment method and I will explain one by one the reason of the deactivations ok.

Thank you.