Nanobio Technology Enabled Point-of-Care Devices

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Lecture - 17
Strategy for Electrochemical Detection and Tuning of Electrocatalytic Activities (Continued)

Ok students. So, last class I taught you different enhancement method. Now, today again I will teach you the different pretreatment method. Thus, pretreatment means similar kind of we will use different chemical, different electrochemical method and let us enhance the catalytic activity.

This is all similar kind of thing like tuning the electrocatalytic activity and use them for biosensing applications. So, let us continue again like different tuning method. How we can improve and these improved activities also may not stay for longer time. This is the another phenomena I will cover today.

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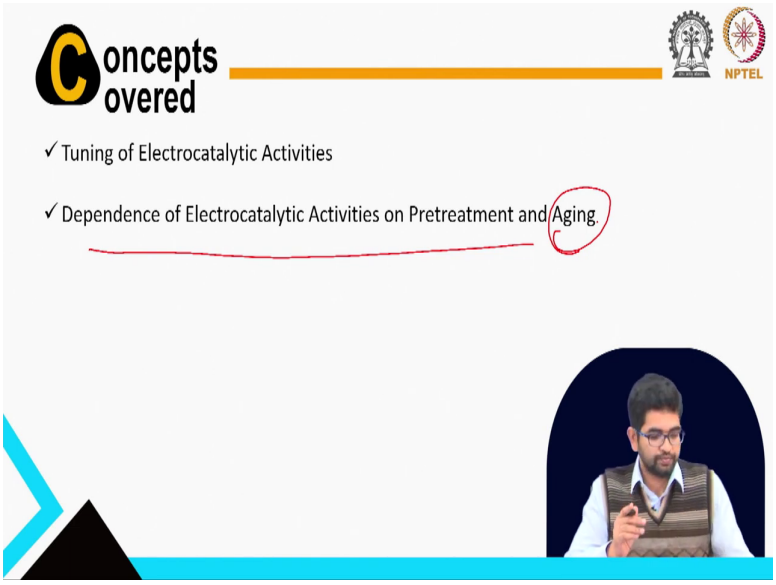

So, what is the main concept for today's lecture? First let us come to the tuning methods that is I taught last time like sodium borohydride on chemical method for tuning. Today, I will teach you some other method and one part that I will add this high activity if you want to store for longer time, they that may not be that may not be possible that can decay, that can change with time.

So, then what is the reason for this changing that also I will let you know. So, this dependence of catalytic activity of the pretreatment also is depend on the aging behavior means with time this highly catalytical active phenomena may be changed right. That phenomena that is why you have to be careful.

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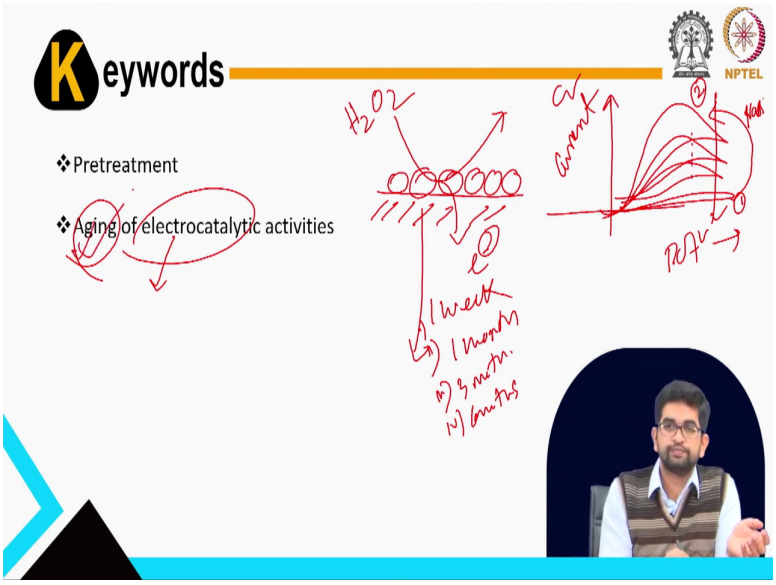

So, you should have this kind of informations. So, this is the main key points of this lectures in the pretreatments and the aging of the electrocatalytic activity. So, what is the aging? Aging means. So, as I told you last class. So, if you have some (Refer Time: 02:14) goal nano material, goal nano particle modified surface and you measure here like hydrogen peroxide oxidations after the enhancement right.

So, you got the very high catalytic activity right this type. At the beginning it was this type, this cyclic voltammogram so, in the y axis current x axis potential. Now, if you keep this on for some time like 1 week. Now you have to check this catalytic activity. I mean by measuring just a cyclic voltammogram you can check their catalytic activity. You have to mention the electrocatalytic this is not just a catalytic, electrocatalytic activity.

Then if it is a 1 week you can check you can check after 1 month, then after 3 months, after 6 months then you have to check the this kind of cyclic voltammogram. You may observe this cyclic voltammogram slowly decrease with time. So, you improve first. So, it was very beginning its catalyted with like this.

Then you increase the activity from 1 to 2 up to here this is called the enhancement by sodium borohydride. Now, if we keep for longer time in your laboratory environment in your room temperature then slowly this can be decreased. So, this is called aging ok.

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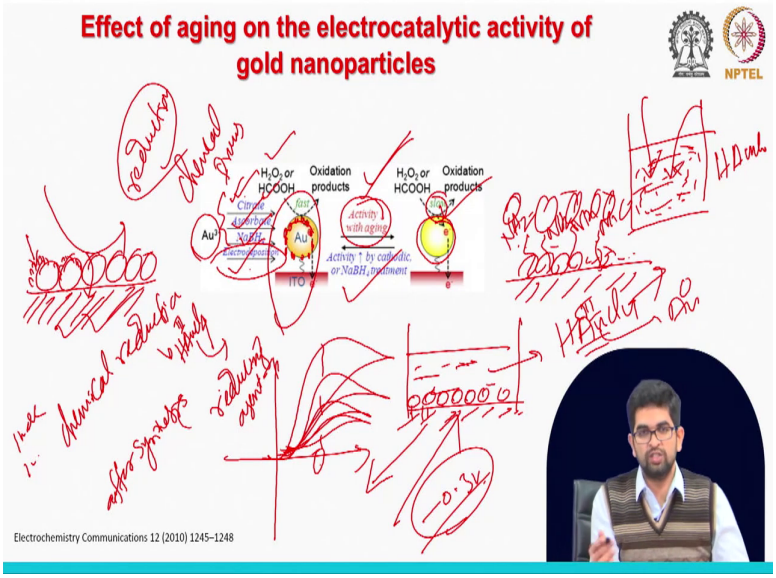

So, let us show you this one schematic for this enhancement and decrease of this electro catalytic activity and what is the reason. See you can see that first time I told that goal you

have a electrode surface that modified with gold. But this gold nano particle can be synthesized in different way right.

At a very I think few class before I already taught you like we can go for the chemical reduction chemical reduction method. So, we can use a gold salt like chloroauric acid HAuC l4 here gold oxidation state is 3 that is why I put the Au 3 here. So, chloroauric acid and we can reduce this one by using chemical.

So, it what kind of chemical some reducing agent? So, see you need some reducing agent. See so, some reducing agent we can use like for example, here I put citric acid sodium citrate ascorbic acid or some ascorbate salt sodium borohydride. So, this all 3 they are the reducing agent this is this all 3 is the chemical process. What chemical process?

Its chemical reduction process and we can deposit we can this chemical process means in a beaker maybe if you use your chloroauric acid HAuC l4and then if you add this reducing agent. So, you get a reddish or pink solutions of the gold nanoparticle. Now, what you have to do on a electrode surface maybe you have the dendrimer or maybe may be you have some other linker maybe mainly if you have the amine modified surface.

If you have a amine modified surface and if we draw this gold nanoparticle in this surface then amine and gold they have some interaction and easily gold nanoparticle can be attached on your electrode surface. So, you will get a gold nanoparticle modified electrode surface that you can use for bio sensing applications clear. So, this is the chemical method.

Now, let us come the electrode deposition that also I taught you right let us show you one more time electrode depositions means. So, you have a electrode surface on this bare surface and this bare surface you should have a solution of chloroauric acid HAuC l4. Then you have to apply here a negative potential suppose 0 minus 0.3 volt if you apply then this gold minus 3 2 it will come to Au 0 means gold 0 stage then nano material will be means this is in situ.

Say this is the x situ this is in situ means on inside solution when you apply some potential then this nanomaterial will be deposited. Why what is the here driving force is the negative

potentials this is called electrode depositions method this using. This method you can deposit this nano nanoparticle.

So, here just I give the example of gold you can try some other salt I means metal salt and those metal you will get as the form of nanomaterial or nanoparticle form. Now, we will try the oxidations of the like hydrogen peroxide or formic acid some oxidation will try on this sensor surface.

So, if we see this is very common method you have you can if you have the lab facility you can check also. Just after synthesis citrate ascorbate sodium electrode deposition just after synthesis if you check their electrocatalytic activity you may get very high catalytic activity because you will get this kind of very high signal like hydrogen peroxide formic acid if you measure electrochemical signal you will get very high current and the potential oxidation potential will be very low.

This is I am saying just after synthesis. Now, just after synthesis you modified your electrode on the gold nano particle like this and keep it in the room temperature on the laboratory environment for longer time this is called the aging you may see the activity somehow it will decrease that we observe that we may observe also it depends in which environment you are storing.

So, there may be one problem you may thinks these activity decrease may happen due to the contaminations right in the open air if you keep there is some other carbon contaminant right, they may come on the sensor surface on the. So, there may some there is so many active site of the nanomaterial right this active site of the nanoparticle they can be blocked by carbon material or some other contaminant from the open air.

So, you can try to store that is why this kind of sensor surface inside a solution. If you store it means if it is just a bare gold nanoparticle coated sensor surface or just a gold coated surface. Then just try to keep it inside the solution you can store just store you can store it. Then if you check after a long time their electrocatalytic activity like after 1 week or after a month or after

6 months you may see this decrease of the catalytic activity slower than the open air this is one of the call is the contaminations.

And another reason as I told when you go if you have a like nanomaterial coated electrode surface and you are getting very slow electron transfer rate means your electrocatalytic activity of a sensor surface is very low. Say you want to tune its activity you want to go to the high electrocatalytic activity then you can adjust sodium borohydride. So, then you can get again first catalytic activity.

So, why this happened? Because hydrogen can be adsorbed on this surface also during the sodium borohydride treatment so, in this case also because of surface reconstruction, surface strain you may get higher activity. And when you keep for longer time, but during the aging this surface reconstruction again slowly it may come to the ground stage.

So, there may be some strain on the surface that calls are by reconstruction then again it may come to the slowly ground stage and because of this also electrocatalytic activity will decrease slowly. So, two reason possible one is surface reconstruction and another is the contamination so, how you are storing the electrode that is also very very important. So, if you keep just open air in dirty environment that is not ideal case to keep the high catalytic activity for the electrode surface it can be decreased.

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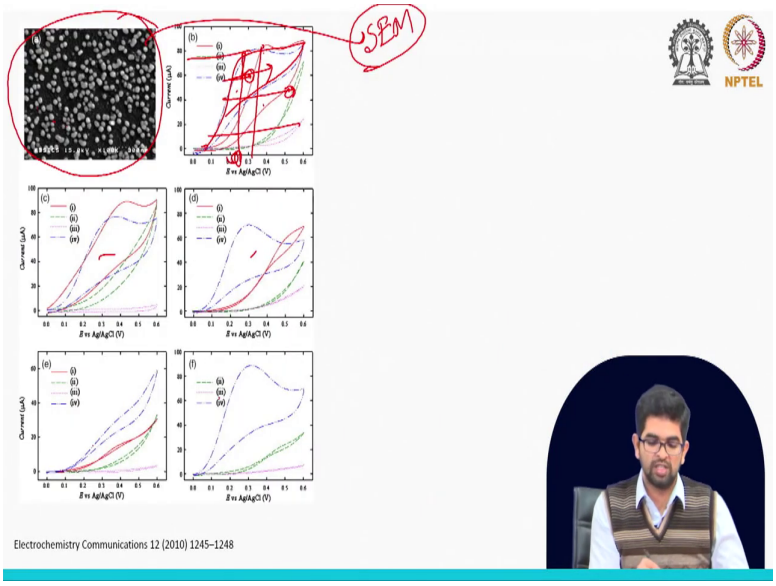

I will show you the example now. See this is the surface just after modifications this is the SEM image Scanning Electrode Microscope that image. See you can see the small small nanoparticle it is size around 10 nanometer the all the gold nanoparticle coated. Now, it can be just after synthesis or just after sodium borohydride treatment, you can see this is the high activity this is the this one you can see the oxidation peak potential also very low current also very high.

Now when you keep for longer time like 1 week, 1 month, 6 months say the activity this peak potential is shifting towards right and current also see in this potential see current decrease this much current and again if you see say here. So, the shifting and current also decrease this shifting current also decrease.

So, it means this is because of aging and it means your catalytic activity decreases. So, there is so many you can see that this kind of diagram this curve. So, this all the things actually tried just after citrate method, ascorbate method, sodium borohydride method and electrode depositions method.

So, here you can see just 1, 2. So, 1, 2, 3, 4. So, these all the methods just we tried just after different different procedures means you can try all the synthesis procedures like chemical procedures, electro deposition procedures, you may see similar behavior, at the beginning you may get high activity then slowly it may decrease.

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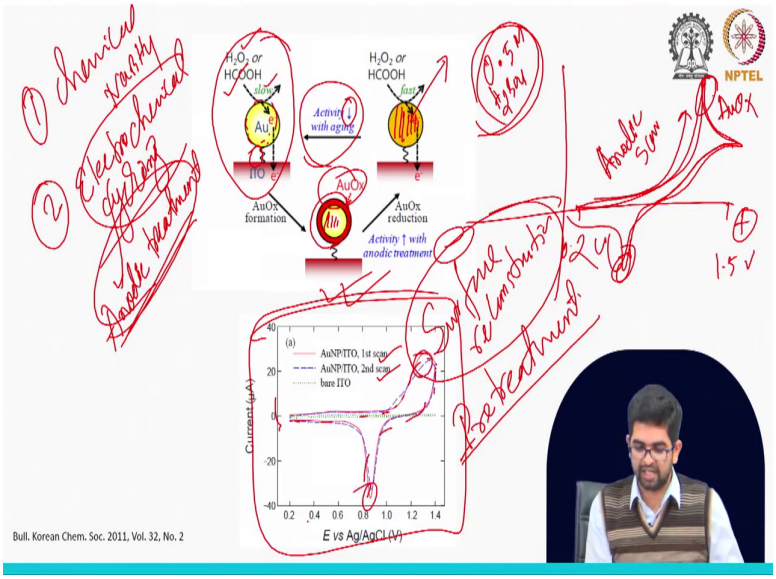

Now, let us come some other factor means if catalytic activity decrease with time, then one method is the chemical method that is sodium borohydride can be used let us use a other procedures also. 2nd method I will teach you now that is electrochemical method what is this

electrochemical. This is electrochemical method or electrochemical cycling; electrochemical cycling you can try this electrochemical cycling that is different kind of electrochemical cycling.

So, one very important method is the anodic treatment I will come this treatment you may tell this is the a kind of pre-treatment that is where we do not need any kind of reducing agent, but this is just a potential cycling method we will try and it can improve the activity. Let us show you. So, suppose you have a this kind of electrode surface ok.

So, your electrode surface is coated with gold nanoparticle and so, what electrode surface we are using here indium tin oxide coated electrode surface. So, this is a linker and we tried the gold nanoparticle and you can see that gold nanoparticle can oxidize hydrogen peroxide formic acid, but at the beginning we are getting slow. Now when we try the anodic treatment what is this anodic treatment? Anodic treatment means plus minus.

So, suppose you have to use a 0.5 molar sulfuric acid solution means anode even oxidations means on your gold nanoparticle coated surface you can try a higher potential window this cycling you can try. Suppose you can try like 0.22 around 1.5 volt this volt to this volt.

Then if you cycle in the 0.5 molar sulfuric acid medium you may get something like this something like this means your gold can be oxidized at the higher potential your gold surface your potential cycling in a sulphuric acid medium then it will form gold oxide then gold oxide again reduce. Then this can you can go like 20 times, 50 times you can try.

So, first during the anodic scan you know right when we go from left to right this is called anodic scan right anodic scan. So, this is called that is why anodic treatment. So, in the higher potential we are scanning and gold oxide AuOx we are forming. So, if that is why you see in this schematic.

So, here a gold nano particle one gold oxide layer will form during this treatment. And when your this gold oxide when you reduce then these gold oxide again this gold oxide reduce back

here. And during this potential cycling your this gold surface will show high catalytic activity this is again because of kind of surface reconstruction.

Because this potential cycling potential cycling potential scan again the surface energy can change this is the assumption just surface reconstructions, but you may see the gold oxide oxidation reductions also on the surface. This may further improve your gold coated surface electro catalytic activity you can improve.

So, this is called anodic treatment or electrochemical cycling this is another pretreatment. Now these highly catalytically active sensor surface, now let us store again in the room temperature for some time for long time there is a possibility of decrease of the electro-catalytic activity again.

Let us show you something. So, here is the a data. So, you can see when gold nanoparticle at the very beginning. So, you may get very low catalytic activity and then you can go for the first scan, second scan say first year gold oxide forming and then gold is actually reducing it is actual data.

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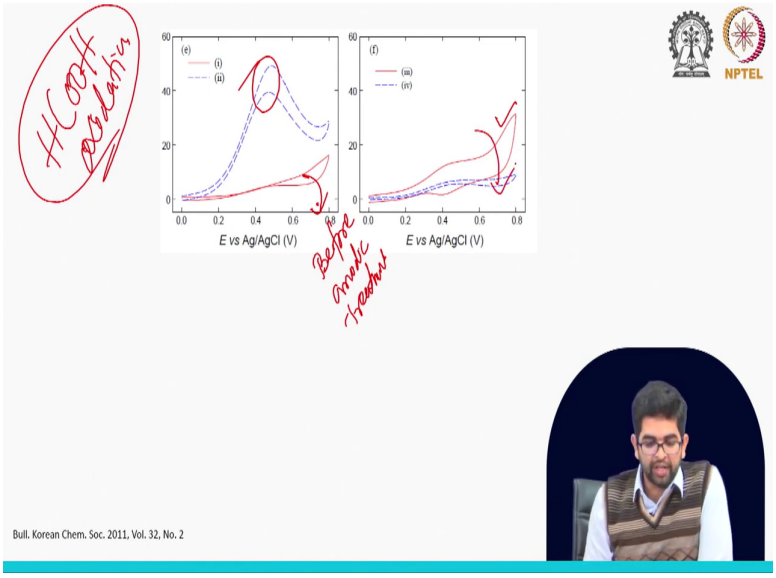

Now see here the formic acid oxidation. So, formic acid oxidation we tried when before anodic treatment and after the anodic treatment you can see this one is the before anodic treatment. See formic acid oxidation is very low, but if you go for the anodic treatment you can get the highly catalytic activity. Now, if you keep it for the longer time like one week or more than 1 week, 1 month, 6 month you can see the activity actually decreasing ok.

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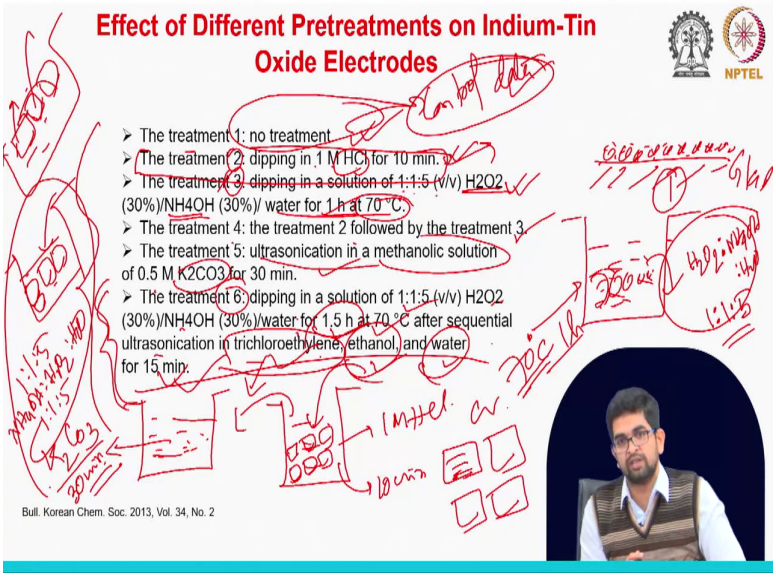

So, this phenomena you observe. Now let us show you some other pretreatment method so, that we can improve the catalytic activity. So, this is this kind this all the pretreatment method sometime you may see maybe after some class I will show you some scanning image or some AFM Atomic Force Microgram image means you can see the actual sensing surface if there is some contamination is after this pretreatment is actual contamination is removing or not.

If surface roughness changing or not this all the characteristics also I will show you next class. So, today again I will going to show you some other treatment let us cover all the treatment name then how we are improving then I will come step by step. Let us will focus the surface images a kind of change you can see after the treatment.

So, there is some possibility. So, one big possibility after the treatment or pretreatment or after this anodic scan anodic treatment the why we are getting improve activity there may be a

contamination removal another thing that was a surface reconstruction, but that is just the assumption.

But surface if it has the contaminations and after the treatment if you can remove and if you get the higher activity that image if we analyze the surface by AFM or SEM as then definitely you can see by a AFM you can see the roughness change, but SEM also we can see the clear image of the surface that if there is a contamination present or not that I will show you next class.

So, today let us cover some other treatment this is treatment and I will show you some actual data and I will compare all the treatment let us compare. Today I am going to show you here you can see like total six pretreatment of ITO electrode ITO means you have a glass ITO means glass surface with indium tin oxide coated nano particles right.

As I told you when you receive this kind of electrode from any company and any industry, they have lots of contaminations and they cover the active site of the sensor surface. So, we have to remove them. So, how we can remove? So, we tried different different process 1, 2, 3, 4, 5, 6 different different process I will show you. So, definitely you should have a control experiment that is called no treatment.

So, one electrode will check just after when you get the electrode from company from any industry or from any vendors in the source. Let us check the cyclic voltammogram by using a forming acid oxidation any hydrogen peroxide oxidation glucose oxidation and let us get the cyclic voltammetry that will be your control experiment control data and then compare with other treatment.

So, we compare here one method is the one molar hydrochloric acid. So, you can take in a beaker, 1 molar hydrochloric acid then you can dip to your small small ITO chips you can dip for 10 minute then throw the all the HCL and then wash it with the di water, deionized water; very clean water then clean the ITO surface all the indium tin oxide coated glass surface you

can clean then measure again cyclic voltammogram. Then you can see the change and then compare with the control data.

Third method is the dipping is 1 is to 1 is to 5 hydrogen peroxide, ammonium hydroxide and water mixture and we can heat this solution for 70 degree Celsius this cleaning method I already taught you at the very first class. So, if you clean this surface by using this chemical this is very very I mean you can say very important treatment method they can remove many contaminations like organic contaminations.

So, like you can take a beaker and you have to take hydrogen peroxide, ammonium hydroxide and water mixture. So, this mixture 1 is to 1 is to 5 ratio and then heat this solution at the 70 degree Celsius for 1 hour with your ITO chips you can put all the ITO electrodes here and heat it.

Now, after that bring the room temperature, clean it and after the cleaning let us check again cyclic voltammogram of formic acid or hydrogen peroxide. Then compare with your control data ok. So, this is another method. Fourth treatment, treatment you can try this hydrochloric acid treatment and after that you can try this treatment.

So, after hydrochloric acid treatment maybe we may we may think that this is may not a good enough forming all the contamination then 1 plus means 2 and 3 both you can try then let us try to see if both they can make further improvement of the electrocatalytic activity or not. So, treatment 2 followed by the treatment 3.

Now, we can show another treatment that is again there are some chemical treatment we can take your ITO chips in a ultrasonic bath in a methanolic solution that content potassium carbonate. So, in a beaker also you can take in a methanolic solution that content K 2 CO 3 and you can bath sonicate this one for 30 minute then clean this one then again check the cyclic voltammogram of formic acid or glucose or hydrogen peroxide, whatever you choose the substrate.

This is another then another treatment you can dip this one is to 1 is to 1 is to 5 and this method you can try and water and you can increase the time at the 70 degree means last time we try for 1 hour you can increase 1.5 hour after sequence were ultrasonications of the trichloroethane ethanol water means that is that also another cleaning means what you can do your all the ITO chips.

First you can clean this one with some acetone or means trichloroethylene means (Refer Time: 26:15) they are very much non-polar solvent that also I taught you at the beginning that you can try first means in a beaker you can take all the ITO chips put it acetone or trichloroethylene sonicate it for 15 minute wash it then take again ethanol sonicate it for 15 minute wash it again and take the again water sonicate it 50 minutes wash it then I mean this is the many steps washing and cleaning.

Then after that all the chips after this cleaning you can take 1 is to 1 is to 5 ammonium hydroxide, hydrogen peroxide and water mixture 1 is to 1 is to 5 ratio and then you can heat this solution for 1.5 hour at 70 degree Celsius means we tried very strong cleaning now.

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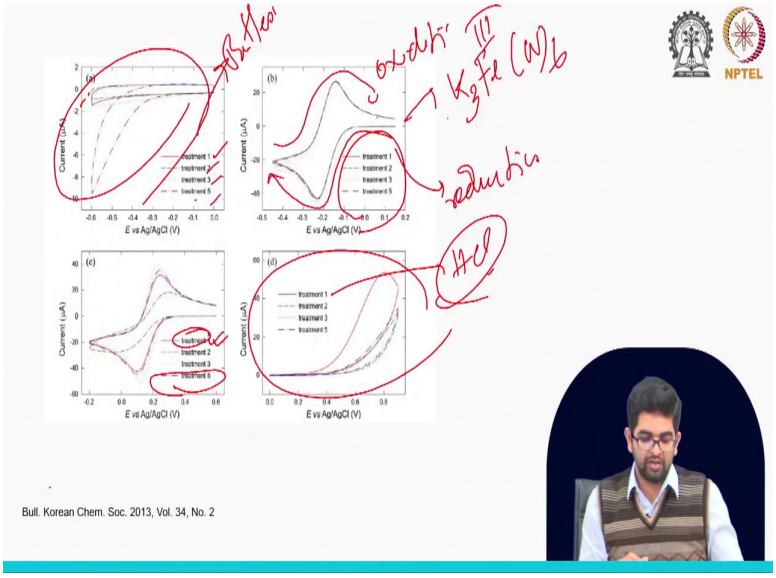

And we can compare through its all the data and we can see that further where we can we may get the further improvement. So, treatment 1, 2, 3, 4, 5 so, we just compare all the things. So, we saw that that last treatment actually it is showing you can see here actually we checked this is just a buffer solutions.

So, just the buffer and here we use potassium we tried the reduction then oxidation. So, this is K 3 Fe Cn whole 6 this is iron third stage right. So, here we first tried reduction right this is the reduction then oxidation see in the case of potassium ferricyanide in this case we tried all the treatment, but we did not see much observable change.

But means why in this case? Because your all the electrodes may be not that much contaminant, but some electrodes case if it is contaminant then electrode means if it is very much contaminant then treatment 1 may not be effective, but you can see the treatment 5 is

very very effective means I can say from here treatment 5 is very much effective to remove all the contaminant you can try others, but treatment 5 is the very much effective for here and you can see here also some data.

So, we observed treatment 1, 2, 3, 4, 5 and here also we can see the observable change or some cases HCl actually show the very high cleaning, but one thing just you have to remember that some cases you may get that HCl can remove the maximum contaminant, but some cases may not.

But in the last method that 1 is to 1 is to 5 mixture the hydrogen peroxide, ammonia hydroxide and water just after sequential ultrasonication of trichloroethylene ethanol and water mixture for 15 minutes, sonication and then dipping inside this is a very good cleaning method and they can remove maximum organic contaminant and you may get very high catalytic activity after the removal of this contaminant.

And if you store again for the room temperature for some time this activity also can be decayed can decrease then activity can be changed. So, this can be happened because of again contaminations because some of the air again some contaminant may come and they can cover the active surface ok. So, these things you can we should remember during the biosensor formations.

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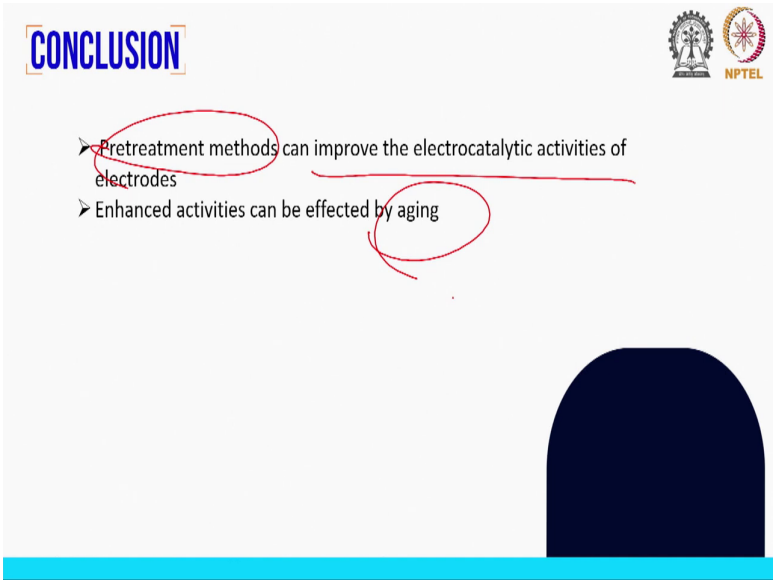

So, what is the conclusions of the today's talk? So, we can use different pretreatment method to improve the electro-catalytic activities and this kind of improved activities may not stable for a longer time if we store for the longer time in the room temperature this activity can be decay, this is effect is called the aging of the electro-catalytic activities and this is because of another reason also surface reconstruction or maybe the contaminations this is the factor.

So, thanks that is all for today. So, next class again I will teach you some other methods of enhancement and use for the Biosensor Application. That is all.

Thank you.