Nanobio Technology Enabled Point-of-Care Devices

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Lecture - 18
Strategy for Electrochemical Detection and Tuning of Electrocatalytic Activities (Continued)

Dear students so, today I will start again the Tuning of Electrocatalytic Activities of electrodes. So, last few classes I thought that we can tune the electrocatalytic activities with different chemical treatment, electrochemical treatment. Today, again I will continue the similar kind of tuning phenomena, but let us come how we can tune some other treatment method.

And definitely this is a very interesting topic as I told. The, tuning method we can use for high catalytic activity as well as low catalytic activity, right. So, maybe you have to understands why you need and how you can apply those technology for tuning the catalytic activities and what is the reason let us come one by one.

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So, mainly then the basic topic this lectures we cover the tuning the activities and dependence of this activities on pretreatment and aging, as I told last class also this is kind of pretreatment, right. So, when we clean the electrode surface, we are removing the impurities. So, now this few classes I will take basic fundamental things. So, how we can work on basic area on electrode surface area now.

So, I already taught you like development of biosensor now coming back again to the development part then again, we will go to the advance level. So, like we will be going to up and down right let us come again to the surface modifications.

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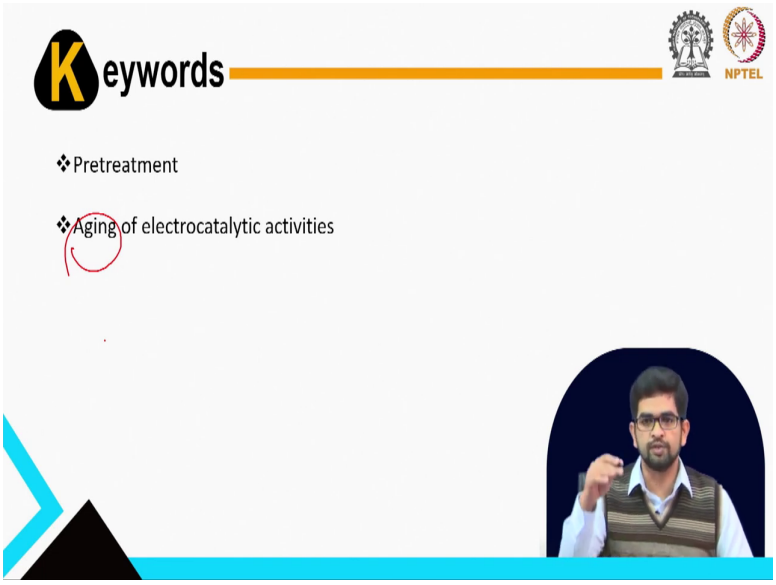

So, main keywords for this that is why pretreatment like as I told this is just enhancement tuning method and tuning means not only the enhancement it also you may need deactivations of the electrode surface activity, right.

And how this after pretreatment as I told the after sodium borohydride treatment you may get the high electrocatalytic activity or after anodic treatment you may get the high electrocatalytic activity. But when you apply the aging effect you know aging means when you store the electrode for longer time in laboratory environment or even in the vacuum conditions or in the solutions medium how it will impact on electrocatalytic activity, right.

This is just very important phenomena for storing where sometime we need know like how long you can store your sensor for checking of the result. So, you should know the story storage conditions and still if you are following all the storage conditions, but you may face

like deactivations of the result. That is why maybe your signals may go down what is the reason that is why you should understand.

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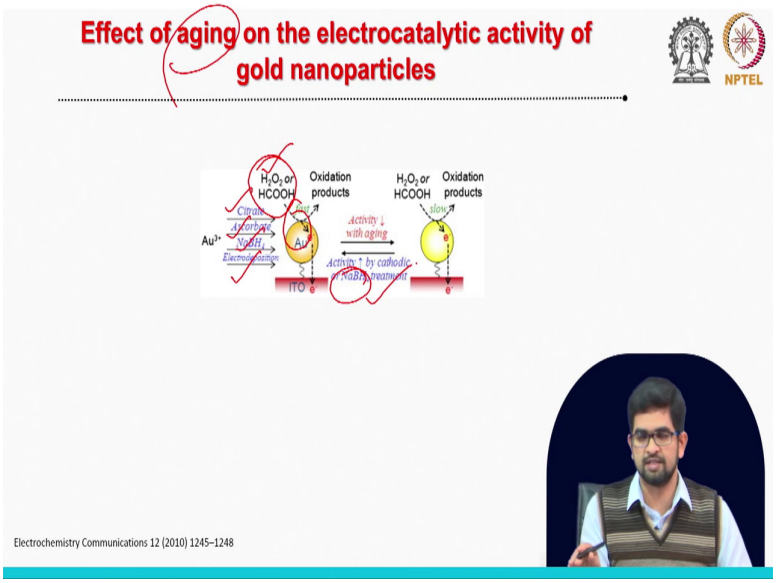

So, one reason that I told you that the aging effect let us come this all the aging factors. Again, like as I told in the last class like citrate, ascorbate, sodium borohydride, electrodepositions all the methods we can use for gold nano particles synthesis.

Now, if we try like forming acid like glucose-oxidation or hydrogen peroxide oxidations you may get the very first electron transfer rate, but when you keep for aging then activations can be decreased. But again, how we can go back again? When you can go very simple treatment like sodium borohydride.

Maybe after a year after storage of the your electrode or you if saw the electro activity is not so good then what you have to do? And you have to go for the sodium borohydride treatment. I am telling not after biosensor formation I am telling this on basic sensor surface.

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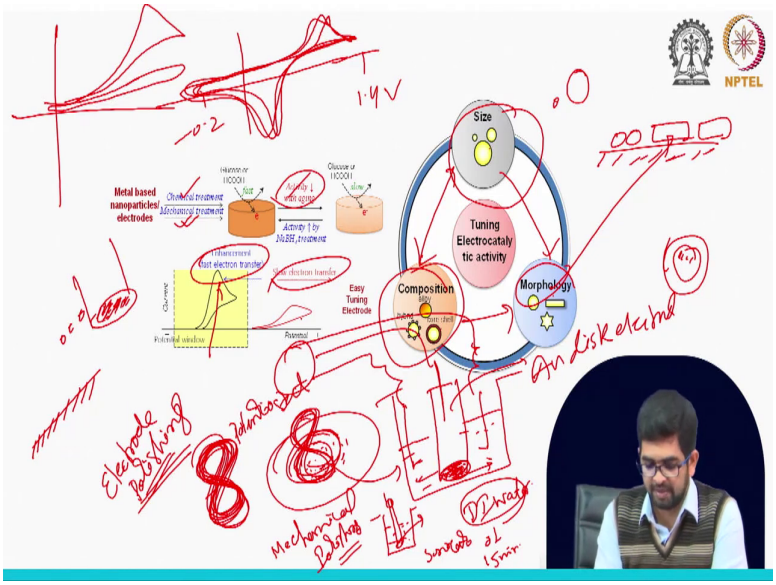

Let us come the tuning. Today I will cover all the tuning method again some new topic of the tuning. Say we can tune the electrocatalytic activity based on different sizes, size of the nano particle also can impact on the electrocatalytic activity. Something, different different size of the nano particle has the different different activity. Also, like sometime like spherical size, sometime rod size, a ribbon size different different size they has the different surface area different activity.

So, based on this we may control the your same compositions were different size your electrode surface activity can be changed because your nano your sensor surface because you

are modifying may be sometimes spherical size or sometime like this like tube size the activity can be changed.

Also like that is called the morphology that the spherical tube at size means like smaller bigger and sometimes we are saying the composition. Compositions mean like you may use some hybrid or maybe core cell or maybe alloy not the pure gold maybe you can iron and gold compositions or maybe some core cell type.

So, inside you have like a like silver and outside you may have the gold this is called the core cell type. This core cell type also nanomaterial has the different activity that also you can tune, ok. So, this all the things you should know like how you can tune. So, that is why I am saying the tuning the catalytic activity they are very much related size, morphology and composition.

Now, let us come a very basic concept that I am going to tell you like chemical treatment I already taught you like sodium borohydride treatment one. So, if you have metal based nanoparticles not only the nanoparticles today I will show you if you have the electrode itself. So, you can go for the treatment. Sometimes the mechanical treatment. What is the mechanical treatment? Like electrode polishing, electrode polishing.

So, from the name of the policy you understand, right. So, you may have a pad and it will contain some alumina salari alumina. So, those alumina you can use for polishing your kind of disk electrode. This one thing you should remember which electrode you should go for the polishing. So, if you have the pure gold electrode kind of the disk electrode you know the gold disk electrode available this is the pure gold that you can go for the polishing.

You can polish here generally we are polishing something like this we are making 8 and we can polish ok, like this way maybe we can polish for 1 minute you can do the alumina powder here alumina different sizes alumina powder available you can put the alumina powder. And then the disk electrode this is the disk electrode something like this you can put here and then you can polish it on the on here on this pad.

Then after polishing you have to wash it with the DI water and then in a small beaker take few DI ml DI water and keep your disk electrode and sonicate you have to sonicate it sonicate it for like may be 15 minute. So, if you have any other alumina powder here if you attach, they will be removed from the surface, ok.

And also after the mechanic this is called the mechanical polishing electrode polishing this is called mechanical. So, this is mechanical treatment or mechanical polishing, ok. This polishing will definitely will help to remove all the contaminant you have on the electrode surface because it is the mechanical.

So, you may think like after the polishing after the D DI water washing and then sonication for 15 minute if some steel some alumina powder there, then you can go for the another treatment after the polishings this one maybe you can take a electrochemical cell. Fill it with means after the polishing and you your disk this is the gold disk electrode right, Au disk electrode, ok.

This is gold disk electrode then put here reference electrode and put here counter electrode then add this all the three electrodes with the potentiostat, potentiostat and then you can go for the potential cycling which potentio cycle you may use like a minus 0.2 to 1 point may be 4 volt.

So, this potentio cycle it is the gold disk electrode if you go for the potentio cycle for 20 times something like this you may see this kind of cycling voltammogram or oxidations of gold, the reductions of gold oxidations of gold, reductions of gold something like this.

So, like this way you can you can after the mechanical you can go for electrochemical polishing again. So, almost your surface will be clean and this surface will be highly activated then your before the your electrode that you received from any company or from any other source your vendor.

So, you should go always this kind of mechanical polishing treatment so that you can remove all the contaminant. So, this is also kind of tuning of electrocatalytic activity. So, if you polish it then you may get. So, if you check like before polishings if you check the like forming acid oxidations before polishing you may get something like this cyclic voltammogram for forming acid oxidation after polishings you may get something like this.

So, why improve? Because it will it removed all the contaminant also at the same time it enhance the catalytic activity. So, this is another treatment that you should keep in mind may be after polishings you may need may be suppose you clean today and you want to store you have to store it because may today you cannot fabricate your sensor surface gold surface within today may be you are not able to fabricate your biosensor on that surface.

So, which conditions you will store this electrode. So, that I am going to tell you now. But if you store it for a quite longer time. So, you should check the activity basic surface activity then you have to check why? Because there may be aging effect. So, aging effect also can call the decrease of the electrocatalytic activity. So, it can call the reproducibility problem that is why clear.

So, what you will do then? You have to store it fast in the proper conditions which conditions may be you should avoid the contaminant or even you may store this one vacuum or in the solution conditions may be in the DI water or may be at very pure water you have to use and store the this kind of disk electrode and this surface can be dipped and you can store for the longer time.

But still, you may face the some amount of deactivations if you store for quite longer time. So, that is called the aging effect, ok. So, that you have to check. So, enhancement or faster electron transfer whatever you are facing that is just after the pre-treatment or after the mechanical polishings and this electron transfer can be slowed down ok, that you should remember.

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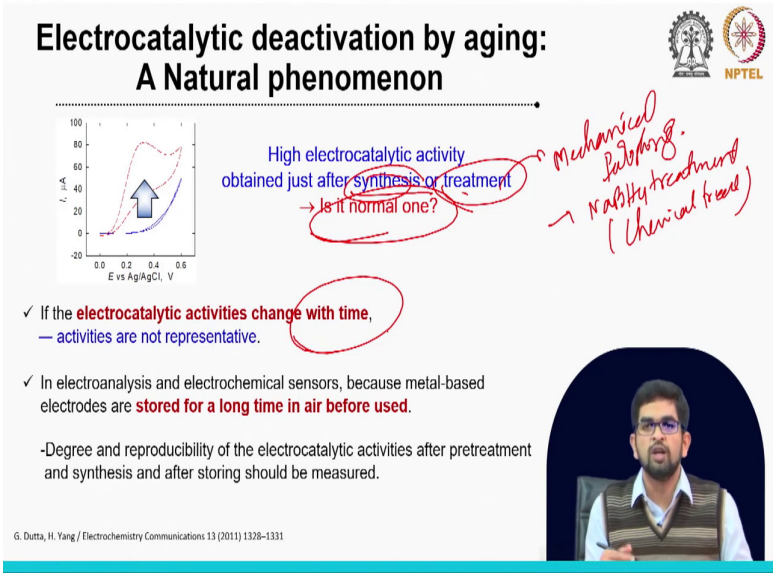

So, electrocatalytic deactivations by aging this is a natural phenomena. So, high electrocatalytic activity that is you are getting or you are obtaining just after the synthesis. So, why I am saying the synthesis because you know last time I taught you like if you go for the nanomaterial synthesis just recited or maybe ascorbate method or by any kind of reductions method from the gold salt.

Then you are getting gold nanomaterial. But after storage for some long time, you are getting the lower activity. So, that is why just after the synthesis or after treatment. Treatment means it can be the mechanical polishing mechanical polishing or it can be sodium borohydride treatment. Sodium borohydride It is called chemical treatment right, chemical treatment.

So, is this normal one? This is the questions after this treatment after the synthesis if we get the deactivations what is the factor? So, if the electrocatalytic activity change with time. So, you have to take care of this. So, you have to properly investigate this phenomena.

So, activate is the way you are measuring if they are not reproducible every day with time to time then there is some definitely some cause. So, we cannot store for the longer time. So, what is the meaning of the degree of reproducibility of the electrocatalytic activities after the pre-treatment and synthesis if we store for the longer time?

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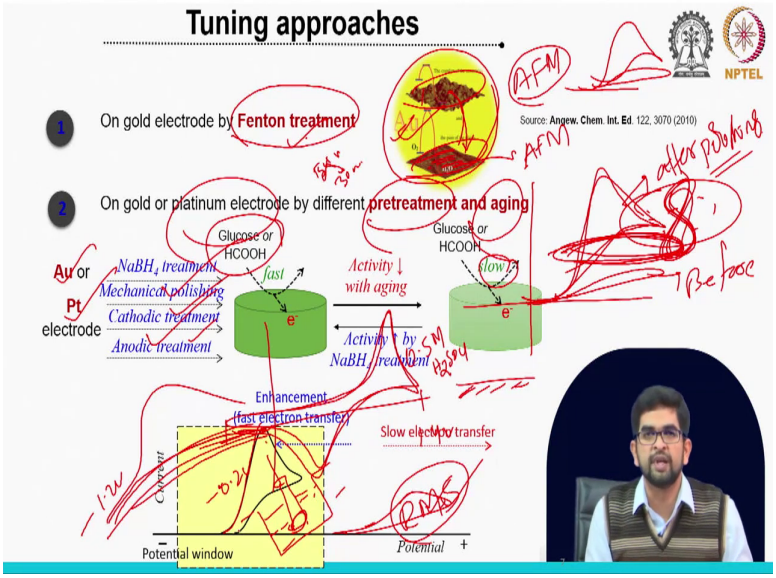

So, let see this all the tuning activities and their aging effect. Today I will teach you one more factor the of the tuning that is Fenton treatment. This is again some tuning and we will check their storage effect for this catalytic activity.

As I told like just after mechanical polishing, right. So, if you have the pad alumina so, if you polishing like 8 then you can see the catalytic activity as I told if you check like hydrogen peroxide oxidations or glucose oxidations as I told you get the very high activity right, like this. But before the polishings you may get like this activity this is before polishing this is after polishing after polishing.

Now, you have to consider to development some biosensor you do not need that much activity means even your basic surface so, that you may get very high background current, right. With just after polishing or just after sodium borohydride treatment if you get very high activity it may cause high background current.

So, let us tune the activities such a way so, that you want to get a moderate activity means in between. For that you may go a treatment that is called Fenton treatment. So, you understand the story, right. So, sometime you may need very high activity, sometime you may need moderate activity, why? To avoid the side reactions or background current you may need to decrease you do not need very high background current. So, you may need the moderate activity.

So, you need to tune the activity that is why you can use Fenton treatment. What is this Fenton? Fenton that is this is a chemical treatment chemical compositions that I am going to tell you the mixture. So, first let tell you that if you see this image see this kind of you can see valley and hill and valley type of the structure this is the AFM structures of the gold surface just after the polishing.

Now, this surface it is not the comforts I mean it not it filled some strain I told you know in the last class or because of the structure reconstructions the surface activity will be very high. Now, you want to make this surface may be some smoother. So, this kind of Fenton treatment this is a just chemical, but this chemical composite let you know it can smooth the surfacing it was hill and valley type and you are getting very high activity.

Now, if you go for the Fenton treatment your surface also becomes smooth, this is again you have to take the AFM image atomic force microscopy image. You can see the surface smoothness this is called RMS like root mean square value if you can determine from the AFM I am going to show you more surface images next line, this RMS value we are going to detect.

If you detect here the RMS value is very high and here you will see the very low almost becomes smooth and you will get the lower activity. Depend on degree of this treatment like how long you may be 15 minute treatment or may be 30 minute treatment, depend on this treatment time you can change the surface roughness this RMS value root mean square value surface, roughness you can change and you may get different different activity, clear. And like this way you can tune the activity.

So, this is this kind of phenomena can be tried with others materials also. So, you have the huge scope of the research itself not only the gold you can try with some platinum electrode also why is only gold. So, I just kept it here gold you can try with the other also platinum electrodes or some other electrode also. So, this is also kind of pre treatment we can try not only Fenton like other pre treatment you can try and you can check their aging effect.

Now, I am going to show you all the respective data. So, we can choose gold, platinum just for example, and we can go for the sodium borohydride treatment, mechanical polishings you can go for the cathodic treatment. So, another treatment just I am going to introduce you. What is cathodic treatment? This is the negative potential you can apply on your electrode surface. I told you this is the anodic treatment, anodic treatment just you can take a 0.5 molar sulfuric acid.

And then you can scan the gold surface I told you can get like this like oxidations of gold reductions of gold like this right, 0.5 molar sulfuric acid like in minus 0.2 volt to suppose 1.4 volt then you are scanning for few times this is the anodic treatment. Because anode you are mainly the positive side you are.

But if you apply negative potential some maybe you can you can apply you can check a gold electrode, gold disk electrode just then you can go for the cathodic treatment just inside the sulfuric acid. Medium you can go for the like negative side or maybe you can apply some negative potential, some negative potential or you can go like negative scanning minus 0.2 to suppose here you can apply like minus around 1.2 volt.

So, you can get like here reductions then something like this. So, this negative side treatment that is called the cathodic treatment also can help the kind of reconstructions of the your electrode surface. And you may get the higher activity before and after you if you check. So, this is also new treatment that I am introducing, now an anodic treatment just I told you.

And if I have to measure like glucose or forming acid we will get the faster electron transfer rate. Now check the activity with the aging then you will get the slower and that can be activated again by sodium borohydride treatment, right. So, this is the tuning effect. So, now let us come back with one by one treatment and how your surface can be affected with different treatment.

So, systematically one by one treatment I will come. So, like this like you are getting the higher activity and electron become the slower then you will get the lower activity. This is just a schematic and you can get the enhanced transfer rate when you apply against sodium borohydride.

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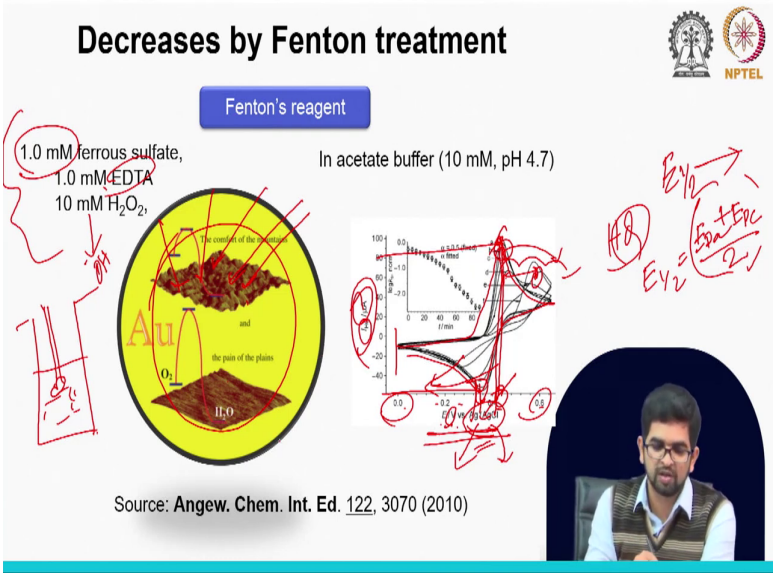

Let us comes a Fenton treatment now. See Fenton treatment it is just a chemical mixture. It is 1.1 molar 1.0 millimolar EDTA and 10 mill molar hydrogen peroxide mixture with 1 millimolar ferrous sulphate. In this chemical mixture is called the Fenton's reagent. This Fenton's reagent if you dip your electrode inside this reagent just make a beaker small beaker make this Fenton mixture and dip your gold electrode and check with different time interval.

You can see this phenomena at the beginning just after may polishing or just before Fenton treatment you may get you may see the AFM structure is very high and you will get the high activity and slowly it will decrease. So, the surface become slowly plain. So, something as a striking on your surface right, what is that? That is something radical actually it is generating this is the hydroxyl radical OH dot. This hydroxyl radical is generated from Fenton's reagent.

This radical actually hit here and the surface become smoother and you can see the cyclic voltammogram. I told you last class also if you check cyclic voltammogram this is just kind of hydroquinone cyclic voltammogram. So, we measure 0 to 0.6 is the hydroquinone see just before the Fenton treatment see. So, we are getting something like very high catalytic activity right, because there are oxidations peak and reductions peak they are very close right, they are very close and high current you are getting I told you know.

So, if their oxidation reductions peak are very close it means E half value that is very E half value very low and you are getting high oxidations current reductions current. It means your surface is highly electro-catalytically active. Now, if this peak shifted oxidations peak, if shifted towards right and reductions peak, if shifted towards left and current also decreased right, it means your electrocatalytic activity also slowly decreasing. See, we increase the dipping time inside the Fenton's reagent and then we measure this hydroquinone oxidations and reduction.

Then we see then see the peak current also decreasing and peaks potential also shifting right, slowly it is shifted. And after a quite longer time you see is almost shifted towards right and reductions peak also shifted towards left. So, E half value slowly increasing E half value E half value means you can remember like peak potential of the EPA means anodic peak potential plus APC cathodic peak potential divided by 2 right, this is the E half value.

So, this E half value will increase. And every time when I am showing you some cyclic voltammogram you see in the x axis we are showing the E versus V, E by V versus Ag Ag cell. What is the meaning of this? So, we are using which reference electrode that is the meaning of this.

So, we are using here silver chloride reference electrode. Because these peak positions is highly depend on your reference electrode if you use a hydrogen reference electrode, calomel reference electrode then these peak position will be changed.

That is why which reference electrode you are using that you have to always mentions this is not like very standard oxidation peak potential which depend on your reference electrode. That is why always you have to mention when you represent a cyclic voltammogram always you have to mention which reference electrode you are using.

So, here I am using silver chloride reference electrode. And by V means here we are representing this is the as a voltage and in the y axis this is the current of hydroquinone in micro amps in it, ok. This is clear? The cyclic voltammogram for Fenton's reagent, ok.

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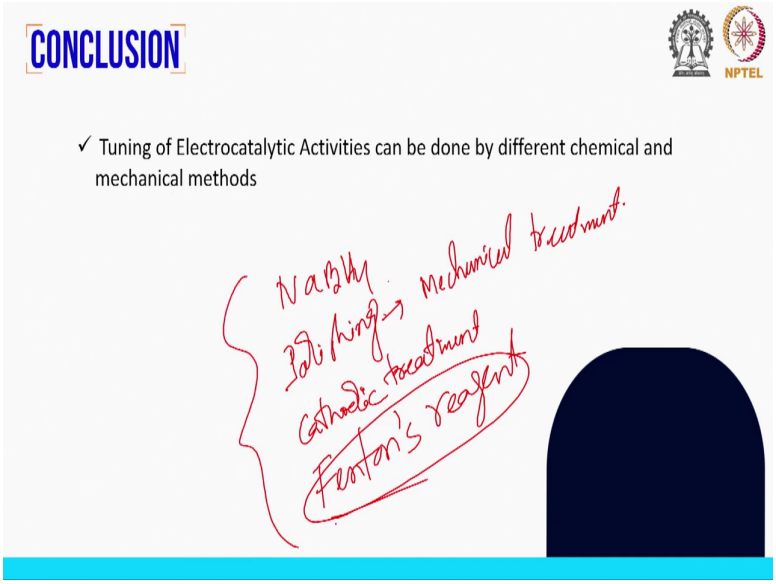

Now, I will come back again in the next class with some another treatment. Fenton treatment also again I will cover like what is the reason of these, why the surface changing of the roughness that I already just mentioned the hydroxyl radical. Now, I will come with proper

reason, with proper informations, proper surface images and we will show you more tuning method its very interesting right, many treatment methods you are learning here.

So, first you learn sodium borohydride treatment that is chemical treatment right, today I show told you the polishing that is the mechanical polishing mechanical this is a mechanical treatment right, mechanical polishing and also you learn cathodic treatment right, today. Cathodic treatment means you are applying some negative potential or negative area you are scanning your electrode and also you can improve the electrocatalytic activity. And another treatment Fenton Fenton's reagent and its effect.

So, this one I will continue again in the next class. So, tuning of the electrocatalytic activities that can be done very easily, right. And this of all the things can be explainable and this we can explain easily. So, let us come in the next class.

Thank you all thank you very much for this class.