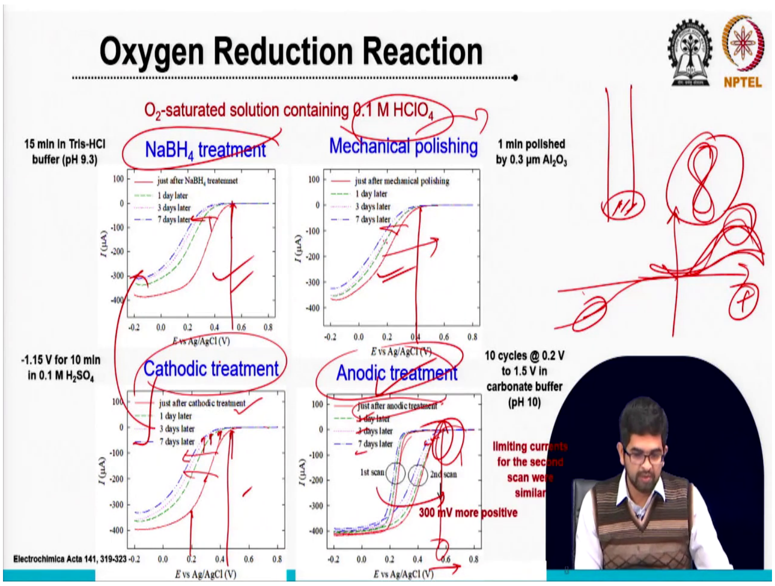
Nanobio Technology Enabled Point-of-Care Devices
Prof. Gorachand Dutta
School of Medical Science and Technology
Indian Institute of Technology, Kharagpur

Lecture - 22
Strategy for Electrochemical Detection and Tuning of Electrocatalytic Activities
(Continued)

Ok students, let us show you again this treatment effect on platinum electrodes that I last class I taught first a gold electrodes. Now, I will show you the pre-treatment effects on platinum, like platinum disk electrode, platinum nanoparticles. So, how this all the pre-treatment effect, or just after synthesis how this aging effect can effect on electro catalytic activity that effect I will continue today.

(Refer Slide Time: 00:54)



So, again, you can see the oxygen reduction reaction that I wanted to show you for the platinum electrode case, right. That you can remember that last class I taught you, like oxygen reduction reactions actually I will select for mainly platinum case because platinum is very much active for oxygen reduction reactions.

And for this reduction space we will choose 0.1 molar perchloric acids because the in this acidic media actually it is showing much better oxygen reduction reaction. I will show you now some effect on this oxygen reduction reactions. Let us see. First, as I told you like you have the platinum disk electrode.

And this disk electrode first we can use for mechanical polishing, cathodic treatment, anodic treatment, and then we will compare with sodium borohydride treatment, ok. So, let us keep first the sodium borohydride treatment.

First, we will I wanted to show you if we compare like other treatment like mechanical polishing; like we have to polish the electrode on a pad and just make the aid, and then clean it, and just check the oxygen reduction reactions. You can see this one just after the mechanical polishing. Then, we stored this one for 1 day, 3 day 7 day or even the 1 month we can store it. Then, you can check the oxygen reduction effect on the platinum electrode.

You can see the cathodic treatment here. Cathodic means we will apply some negative potential or more negative scan; that means, maybe you can take in the sulfuric acid medium or maybe you can take the perchloric acid even. Then, you can scan your platinum electrode in the negative window, for the 10 or 20 times you can scan. And that treatment can also activate your platinum electrode.

You can see just after the treatment, again you can see the high activity. So, why I am saying this one high activity? You can see that it started the oxygen reduction, see in this potentials. And almost the highest reduction speak we are getting here. And see, but when we kept this electrode for longer time in laboratory environment; see the oxygen reduction start again towards the left.

It means it is deactivated again after maybe 3 days, after 7 days, you can see it started actually from the left side. It means it is deactivated, an anodic treatment. Anodic treatment is again, this is in if it is the window of your potential scan. So, this is the positive side, this is the negative side. So, you have to go for some anodic treatment means this positive side you have to scan, for again 10 to 15; 10, 15 or 20 times you can scan. And then, you can check immediately, after the treatment you can check oxygen reduction.

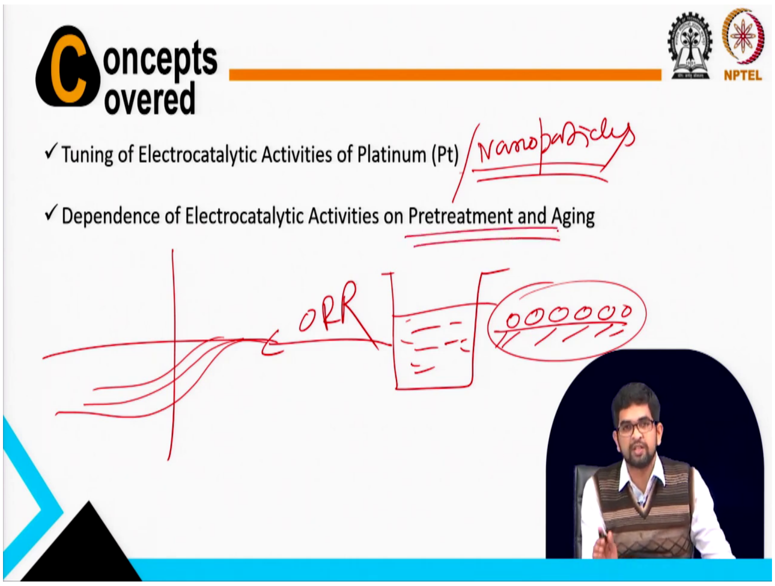
You can see just after anodic treatment, at the first chance its showing something like this. Why? Maybe this is because of maybe somewhat effect on the because of the oxidations. But just after one scan if you go to the second scan actually you can see the peak like this. So, it is just the behavior on the platinum surface just after the anodic treatment.

But still if you see like 1 day 3 day 7 day there is very small change, very small change still you can observe. That also I will again I will show you the surface phenomena. But just the result is this that it means show you some deactivations. Now, let us compare with the sodium borohydride treatment, because this is the very simplest treatment for the platinum case, the oxygen reduction again is started in all cases you can see the oxygen reduction is started around here.

So, it means they are actually very much, but in the anodic case its little bit positive side its reduction start. So, then which one showing the best oxygen reduction reaction, in this case, because it is started the reductions little bit right side, right. If reduction started right side means it is much better active compared to other 3.

But this 3 is almost you can say similar, but their deactivation is something different ok, say for the sodium borohydride case, and mechanical polishing case, and cathodic case. But cathodic and sodium borohydride treatment in this case is almost a similar. But anyway, we can observe the activations, but they are not stable. This is the conclusion.

(Refer Slide Time: 05:43)

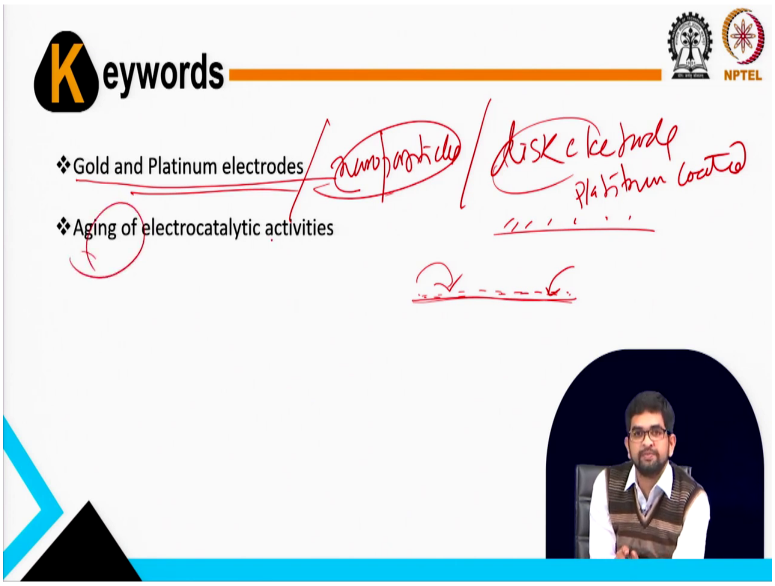


Now, let us see the factors that I am going to cover in here again. So, mainly the platinum electrodes, not only this, here also I will cover some nanoparticles now. So, why I am going to cover today again the lecture in the nanoparticles?

Because as I mentioned like just after the synthesis, if you coat this all the nanomaterials on the electrode surface may be immediately if you check the oxygen reductions, ok; if you check immediately oxygen reductions, just after nanoparticle synthesis, you may see the reductions like this.

But now these electrodes you just store it then you may see the reduction again shifted. It is I am saying this is just the hypothesis now I will show you some result and then I will explain you for the nanoparticle case also. And then, this activities why is different on the aging that side that also now I am going to explain for the nanoparticle case also, ok. So, just try to remember, these activities actually not stable that is why I am saying.

(Refer Slide Time: 06:55)

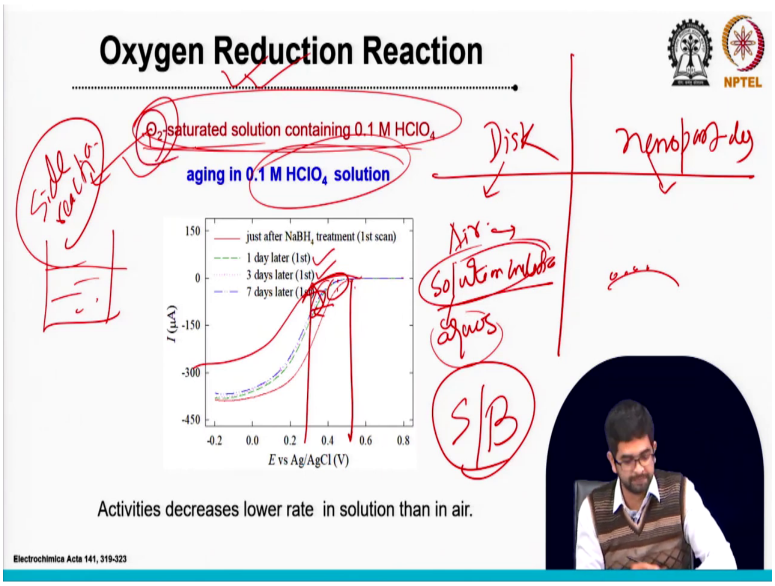


So, for the main today's talk you are let us go to the platinum all the electrodes this is nanoparticles, disk, ok disk electrodes also may be platinum coated electrode, platinum coated. So, why I choose different different substrate? Because when we will develop some lab on a chip right, we will not use always the 100 percent pure platinum.

There maybe we may use some glass surface, on that surface we will use some some supporting material, on that surface then we will use some gold or platinum. Let us see their behavior may be underneath that we are using some other material, they may also effect on the aging factor they may also can hamper their electro catalytic activity.

That is why we change like from nano material to disk to platinum coated, then we can see the actual phenomena and then we can apply this one on a lab on a chip design. So, that is why. When you will go for the cures for this all the lectures, let us cover now like this way, like platinum nanoparticle, platinum disk, platinum coated electrode and their aging factor.

(Refer Slide Time: 08:20)



Now, let us come back the oxygen reduction reaction for now disk and nanoparticles. See, as I told you like although you are checking like disk and nanoparticle, let us compare in the different environment. You can store this disk and nanoparticle you can compare one in the air conditions and another in the solution conditions.

Mean, solution condition means that I can say in the aqueous conditions. Why? You can dip the electrodes or coated electrodes inside a maybe aqueous solutions or inside a buffer solutions you can store it. Why I am saying? Because platinum is highly active towards oxygen reduction reactions.

But if you keep it the longer time in the laboratory environment, if somehow the platinum active side is blocked very little contaminant, immediately, you may see this deactivations. But if you store it in the solution stage, in the aqueous stage, these contaminations may come very slowly or almost no, then you can easily can decide this deactivation is because of the contaminations or not.

And as I told you we choose the oxygen reduction reactions, because it is very very rapid for the platinum case, and if there is any single and small change of the contamination small deactivation you can easily see this change see. Means just after see the sodium borohydride treatment you can see it started here. But because of little maybe contaminations or maybe surface reconstruction you can see it started from here, little you can see this deactivation.

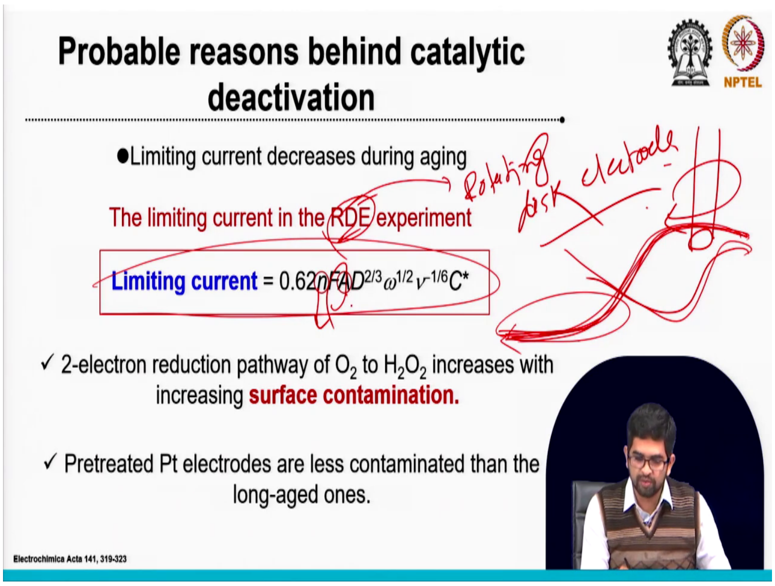
But when this things means this activations we check in a solution stage, you can see this deactivation rate even after the 1 week is so slow almost nothing, but if you go back like last class I taught you this deactivation up to this much, it was started around here this reduction in the ER case.

So, definitely, platinum can show faster deactivations for the oxygen reduction reaction case if you store for the longer time in the ER. This is a good informations because as you know another factor the oxygen also thus side reactions always in the biosensor, right. That is why.

Why I am teaching all this topic? You have to understand all the side factor on your electrode surface what is going on. That is why this is a few classes I am teaching this all the basic stuff. If you can understands like the electrode to electrode change, see as I told you the platinum electrode is highly active for oxygen reduction, right. So, that is why you have to keep in mind if you wanted to use the platinum.

So, you have to think about the oxygen reductions, otherwise you may get the higher background current. You can remember the signal to background ratio is very very important for your ultra-sensory biosensor. But if you want to use the platinum electrode then you have to very much cautious about the oxygen reduction reactions.

(Refer Slide Time: 11:55)



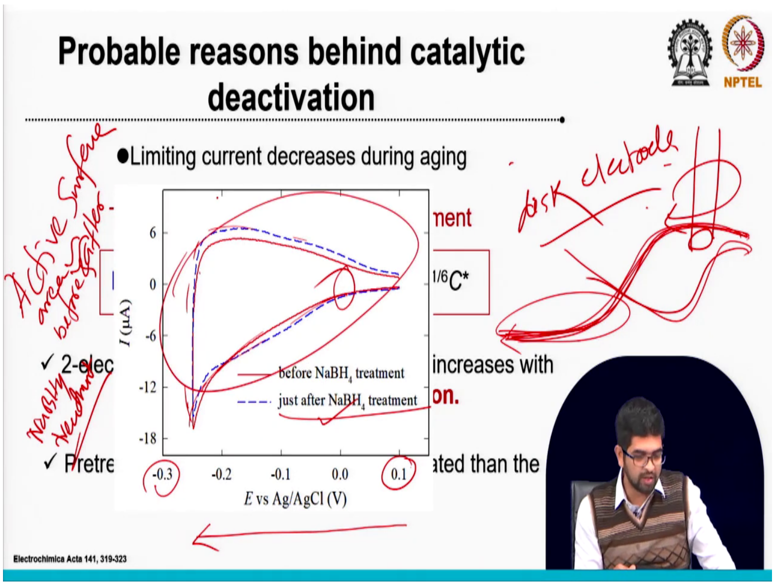
So, let us tell you the probable reason again for the platinum case actually, this all the studied have done in the rotating disk electrode why we use the RDE means rotating disk electrode, rotating disk electrode. So, why is the rotating disk electrode; then, means generally what happened in a rotating disk electrode in this mechanism your disk electrode will rotate in the different rpm means rotation per minute. So, it will rotate. And we will get the this current.

Generally, what happened? If you can remember the reductions current generally showing like this. But when you measure the in the rotation conditions, you will get almost the a the linear in the case of the reduction, this linear current. So, this is because a diffusions this will be a very much constant and you will get this phenomena only for the rotating disk electrode case, not for the simple case. In the simple case, you may get like this reduction.

So, that actually we wanted to see the very sensitive change, that is why we use the rotating disk electrode. And the rotating disk electrode case this is a just limiting current factor I think, and this is just the equations why I use. That is why we wanted to show you that this oxygen reduction reaction that is happened on the platinum electrode and what the change happened on the active surface area.

So, these equations actually will show you the actually if there is active surface area is changing or not during the storage conditions in the laboratory environment. See so, this number of the electrodes this A factors, this is the area factors, this all we can see from this equations and from the experimental study you can compare the data.

(Refer Slide Time: 13:50)



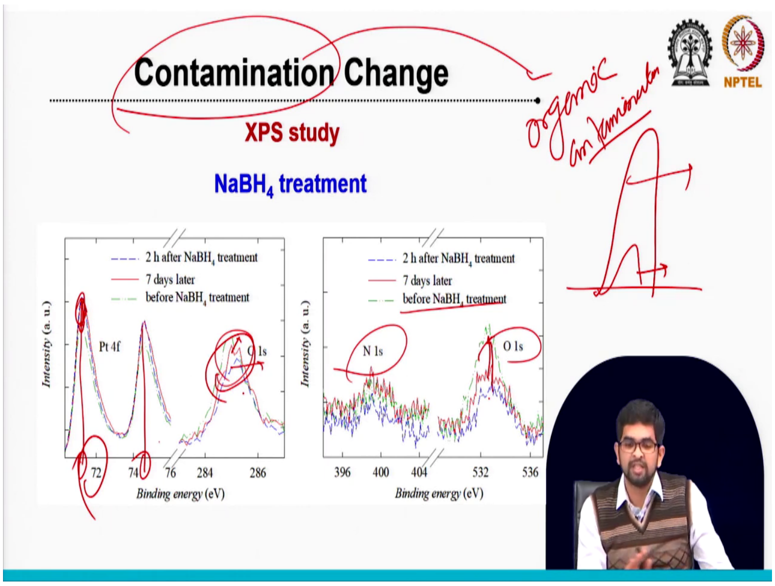
So, here I wanted to show you, you can see let us remove this, you can see the reduction zone. See, this is the reduction, 0 point actually we start the 0.1 to 0.3 in this region which scan, so from positive to negative. You can see the red one that just before the sodium borohydride treatment and this region.

So, you can calculate the area in this region, and then just after the sodium borohydride treatment in this area. So, this if you calculate this reductions area, then we can measure that active surface area on the electrode is blocked or not. So, from these equations, we can measure actually the active surface area of your catalyst or of your transducer surface. So, as you see from this curve that before treatment and after treatment, this see this surface almost similar you can say, not that much change.

Then, what is the conclusion from here? That your active surface area is not change, active surface area almost similar we can say almost similar, before and after sodium borohydride treatment, right. Then, why you are getting deactivations after the sodium borohydride treatment?

That also we may have to think using our hypothesis that is the surface reconstruction. That is why the surface reconstruction this phenomena came for this aging effect. Although we may think the contaminations won the effect, and another thing, why we are we are making this hypothesis surface reconstructions; because there is not that much change of the surface area.

(Refer Slide Time: 15:57)



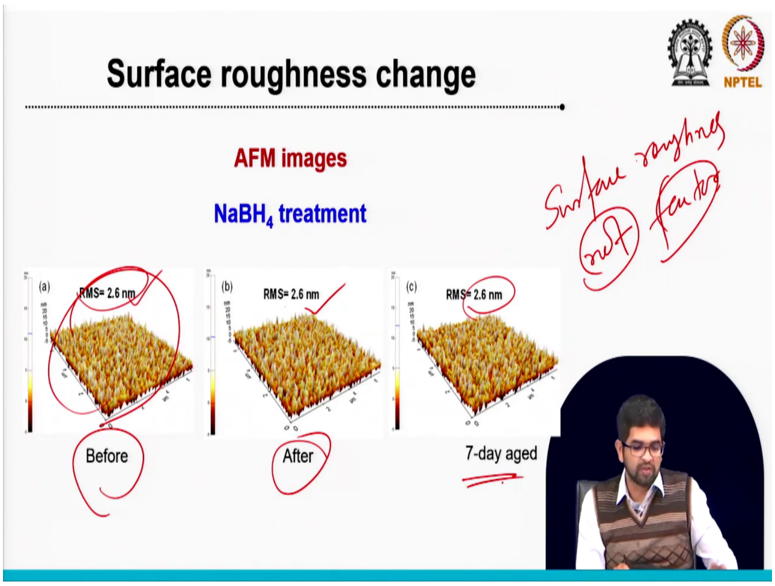
I will show you the XPS now. So, when to check the contamination, XPS can effect if there is a mainly we may think any organic contaminations, right. See platinum region, so last class I showed you the gold region, now I am showing you the platinum region; 72, in this region here and here also another.

In the here you can see the platinum 2 peak, that is before and after. But here you can see the platinum peak is little bit still change. From the electrochemical data also, there is very small change, and from the XPS data is very small change still there after the aging. Carbon, we can see this is the almost similar, all small change. You can see the after 7 days, it is little bit. Then after treatment you can see this one.

If you see the nitrogen peak, oxygen peak, oxygen peak you can see little bit increase. Just after the before sodium borohydride treatment, then after the sodium borohydride treatment, and then after 7 days, you can see little bit increase.

It means there is some carbon oxygen material may be there, but it is not huge change. If it is there too much contaminations may be your peak, and this is just I mean for the carbon case, carbon contaminations case this is just after the treatment. And if it is then you can see may be the huge change of the carbon peak. But that is it is not like this. So, we can say, it is not that much level.

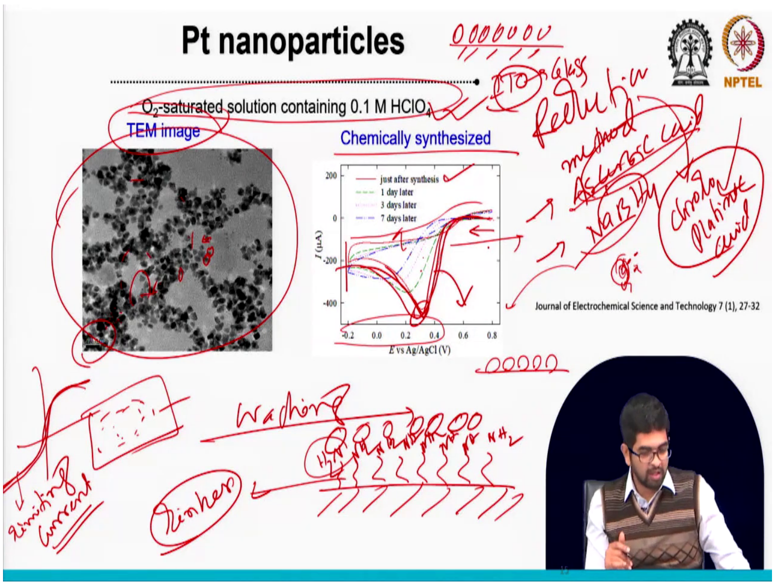
(Refer Slide Time: 17:24)



Now, let us see the surface roughness change. Maybe after the storage for the long time around 1 week or maybe 1 month, we may see some change on the surface roughness. You can see the RMS value again, this is the before treatment of this gold electrode surface then after treatment, so 2.6 nanometre, 2.6 nanometre, again the after 7 days almost 2.6 nanometre in the same surface.

So, it means you can from here you can conclude that surface roughness is not effected, right. It is not it is not a factor for this electro catalytic activity change so, that we can conclude from the AFM analysis.

(Refer Slide Time: 18:29)



Now, let us see for the disk electrode for the coated electrode case it is almost clear that they will deactivate and they will show you some contaminations issue. But let us see for the nanoparticle case, what will is there anything different for the nanoparticle case or it is also similar, right.

So, from after this nanoparticle study, now we can say that this aging effect is really is important for all the cases or not. But still, we may need to investigate for some other material or other nanoparticle, but from here we can conclude on fundamental things that we should not store your nanomaterial or your disk electrode even or maybe you can say in general your transducer surface for longer time.

But if you want to store which condition you have to store and how you are modifying the surface that actually directly depend on your electrocatalytic activity is changed during the time. Let us come to the nanoparticle. So, here also again we checked oxygen reduction reaction, in the acidic medium.

So, here this is a transmission electron microscope image or you can say the TEM, here we synthesized the platinum nanoparticle after some chemical. Like you can say the reductions method, reduction method as you I think I remember reduction method like ascorbic acid.

So, you can use ascorbic acid or you can try some other reducing, other reducing agent like sodium borohydride also you can try. Then, you may get some platinum nanoparticle. And from which salt you may get platinum nanoparticle? Here we are in a chloroplatinic acid, chloro chloroplatinic acid.

So, if you use this salt, and then use this like ascorbic acid sodium borohydride, then you may get something like this platinum nanoparticle. You can see they are very very small size. So, in the scale world is 10 nanometre. So, it means this size is really small, right. It is like a almost 1 nanometre, something like this, very small size nanoparticle you may get from chloroplatinic acid and after the reduction.

And one thing I just tell you again when you use this kind of reductions method for synthesis of platinum nanoparticle or any nanoparticle, you have to use some stabilizer. Otherwise, you may get some different result or maybe deactivation may happen, then you can claim that it is because of maybe agglomerations.

What is that? If you not use here in stabilizer, generally we are using some sodium citrate as a stabilizer. What is the role of the sodium citrate? During the synthesis, when you add some ascorbic acid or sodium borohydride in the chloroplatinic acid, you can add sodium citrate.

At the same time when the nanoparticle will form and before the aggregation each other, this sodium citrate can help not to aggregate to each other. So, this is that is why we are saying sodium citrate is a stabilizer, they can stabilize, you can see this nanoparticle is not that much aggregate.

But still, you can see maybe one each other, this is because maybe if you use when you take the TEM image do not use very high concentrations. You have to use very low concentration; otherwise maybe one nanoparticle can overlap the another. That is why you can see you can see dark color.

This is because one each other they actually overlap. That is why you see this dark color. Otherwise, this nanoparticle almost see they are almost separated because they are on they are very good they stable nanoparticles. Why? Because during the synthesis, we are using stabilizer like sodium citrate.

So, after the synthesis let us drop this nanoparticle on a electrode surface. So, for example, here you can use indium tin oxide ITO coated glass surface, On that ITO coated glass surface you can just drop cast here platinum nanoparticle here, and then you can dry it, but there is a there is the on disadvantage, just drop casting and clean a washing the surface, where they can be detached from the surface.

And you may think this deactivation maybe because of the detachment of the nanoparticle from the surface, right is possible because platinum nanoparticle only give you the active surface area. If they detach, the definitely number of nano nanoparticle decreasing, active surfaces also you can decrease.

So, you have to very much cautious, you have to think about the number of the particles should be the same, so that only you can compare. So, nanoparticle it is not like the disk electrode not like the platinum pure electrode. So, in this case you have to think about that nanoparticle should not be detached from the surface, then only you can compare.

So, one thing that is why you can think like your ITO Indium Tin Oxide coated that glass surface you have, just after cleaning you can use some amine modification, amine modification N H 2. How you can do the amine modification? So, that I already taught you in the very first class, you can see that we can modify some amine molecules, then and the also you can use some dendrimer. They also have some amine dendrimer or some amine related thing, you can try.

Now, these amine and nanoparticle this gold or platinum they have some interactions. So, they will be very easily, they will be attached on the surface and they will not easily detach when you will wash because you need some washing [FL]. So, when you are washing the surface just after synthesis they will not easily detach. That is why it is recommended when you drop some nanoparticle let us use some linker, this kind of linker you can use. They will help bind the nanoparticle on the surface.

Now, let us check just after synthesis you see when you check the oxygen reduction. Here we are not using the rotating disk electrode because your chip that is ITO chip that is coated the platinum nanoparticle, if it is very difficult to rotate them. That is why last time we saw the oxygen reduction reaction something like this. This is a this is kind of limiting current, is kind of limiting current.

But here we are getting like simple reductions like the cyclic voltammetry as I taught you know last class, like we will get like here also we check the cyclic voltammetry only because you started from right side and then which scan to towards the left. So, I stopped here. Then again oxidation, but here we are not getting any peak oxidations peak because we just tried the oxygen reduction peak. There is no other substrate, so that they can show the oxidations peak. You are slowly you are understanding right.

So, sometime that is why we are measuring only this scan, reduction scan. No need to measure the oxidation scan because your oxidations peak or not peak no peak here. Your oxidation scan is not that much informative. It is not giving any kind of information. So, you can eliminate the oxidation. That is why scan, just reduction scan you can make.

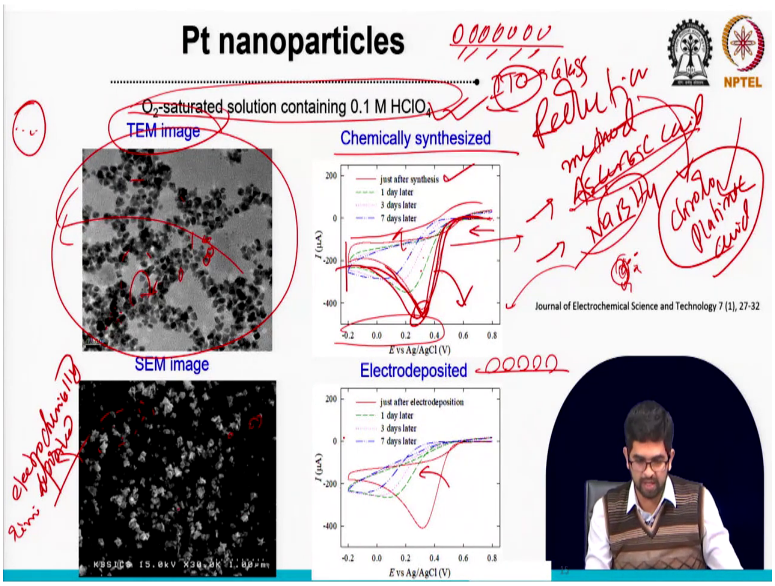
This is called the, I mean as you are taking here reductions and then oxidations that is why it is cyclic voltammetry. But when you are taking only reduction, this is just a one scan, this is called linear sweep voltammetry. That is cyclic; this is a linear sweep, only one sweep.

So, here also as usual like chemically synthesized case, just after synthesis you can see there will be good reductions of the oxygen. And then, after 1 day, then after 3 day and 7 day there is some change, again you can see in the case of nanomaterial. It means your nanomaterial coated surface, but here actually also we kept in the year.

So, if you keep this surface in the year, this surface also not that much stable. So, if you that is why if you modify some sensor surface, you have to think about, if you like if your surface is very much highly dependent on the oxygen reduction reaction, then you have to be careful.

That is why you do not you should not try with your platinum electrodes in this negative region. So, it is recommended let us go to the right side so, that you may not see the oxygen effect. That is why I am just teaching this all the phenomena.

(Refer Slide Time: 28:03)



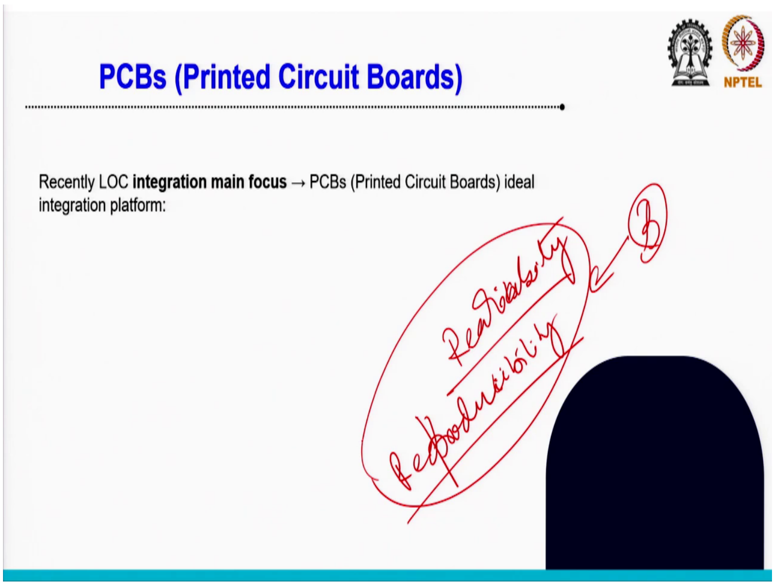
So, here again in this is the SEM image. I am just showing you in this case. This is the another image. Why I am showing this one is same image? Because in this case we deposited the platinum nanoparticle on the electrode and ITO surface electrochemical. I mean it is the electrochemically deposited one, electrochemically deposited, ok. And this one chemically synthesized.

So, electrodeposited one case means as it is already on the surface. So, we cannot take the TEM image; let us take the SEM image because it is a solid surface you can take. And in this case, we are taking just it is the solution, we are dropping on a TEM grid and they are waiting TEM image.

But in this case, SEM case, you may have a big surface, a 1 micrometre by 1 micrometre in this region you can take, the image. And in this case, we can see the still here the platinum nanoparticle size something different for the electro depositions case. They are, as I told you know last time, we can tune the activity by based on the size, based on the shape, based on their morphology, like alloy type, or core cell type, but is this kind of nanomaterial still showing the aging effect or not.

That is why we check the electrochemically deposited one also. And here also we can see that this one also again is deactivated after some longer time. So, that is why it is not recommended ah this kind of electrode surface to keep for the longer time in the room temperature, ok.

(Refer Slide Time: 29:51)



Now, that is all for the platinum case. Now, I will come back again the other electrodes, like printed circuit boards and use them for the again modifications for biosensor development. And let us see is this kind of side effect really effecting on their background current or not.

Mainly, why I am teaching this one, this all the deactivation treatment? This, the factor is a reliability. Reliability means your reproducibility, reproducibility. Means if you want to commercialize your sensor surface, so if you develop today is tomorrow you will get the similar result or not. So, if not, it is not reproducible, it is not reliable; nobody will accept this development. You cannot commercialize. That is why I taught you all the phenomena, ok.

That is all for today's class for factor effect on the pre-treatment or some other case for gold platinum, disk and nanoparticle. Next class onward, then again, I will come to development of the sensor surface based on this factor show that we can avoid and we can develop some very good reliable and reproducible sensor. I think you understands the factors that effecting on the reproducibility. That is all for today.

Thank you.