Carbon Materials and Manufacturing
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Lecture – 54
Transmission Electron Microscopy of Carbon Materials

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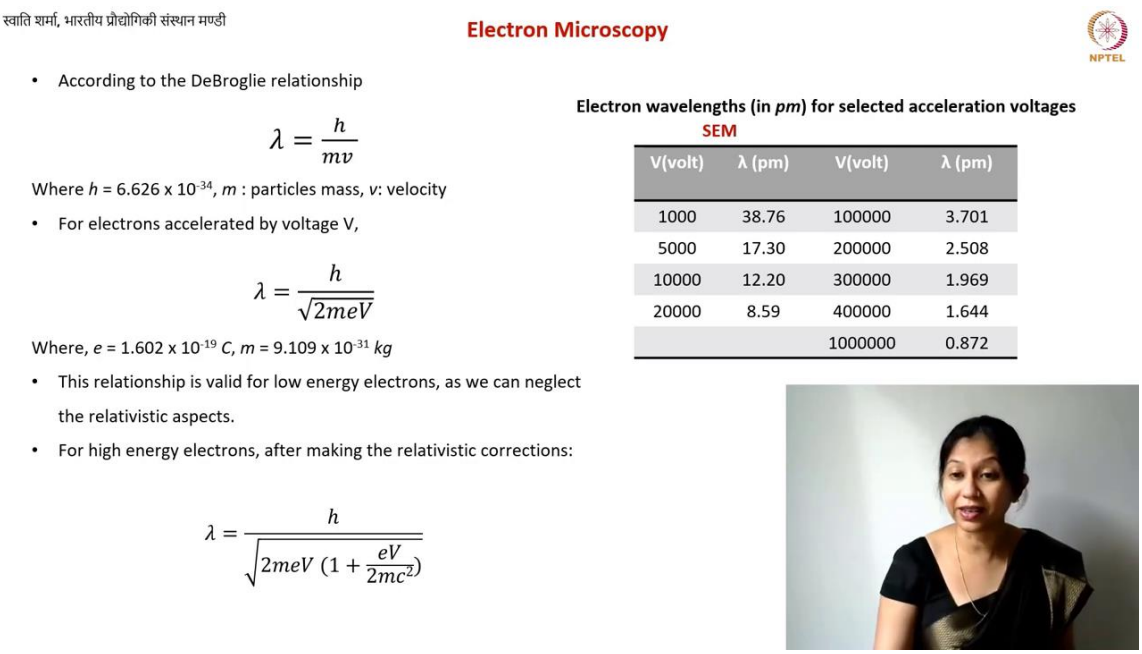

Hello everyone.in this lecture, we are going to discuss another characterization technique for carbon materials electron microscopy. Our focus is going to be on Transmission Electron Microscopy. Because this is the microscopic technique that is used for looking at the microstructure you have. In fact, I have already shown you a couple of transmission electron micrographs or transmission electron microscopy images.

I have shown you before u to help you visualize how your carbon material looks like at a very small scale, at atomic scale. How are the crystals organized? Although it is a very powerful tool, we can visualize, looking at whatever you have made, gives you kind of satisfaction; I wanted to make carbon nanotubes here I have carbon nanotubes.

When you see them that does really help you understand your material, but if the same time there are few small things that we need to take care of because in the transmission

electron microscope you may sometimes also get some wrong impression of the material. So, this is what we are going to discuss.

Similar to the other techniques that we have discussed I am not going to go into the fundamentals of transmission electron microscopy. I will give you references and resources to learn about that, but we will be focusing on how it works for carbon. Especially, these confusions when some planes look like they are on top of each other, but they are actually not. Some planes look like they are intersecting each other, but they are actually not.

So, all of this we are going to discuss one important thing is that and that I will probably again tell you in this lecture is that TEM should not be your only analytical tool. So, whenever you have made carbon material even if you know what material you are making whether it is nanotubes or graphene sheets or a bulk a carbon. In all cases, TEM should be more like a supporting technique and that should not be the only technique. X-ray diffraction often gives you a good average of the crystal structure of the entire material. And in the case of transmission electron microscopy, you are often looking at a very small region. And there the interpretation is not all that straightforward; this is what we are going to discuss.

Before I will not give you too many details but let us at least understand how we can use electrons for imaging something. So, often you would image something using light, or even you can use x rays to get images like in the case of your bones in your body.

So, you can use different electromagnetic rays for imaging purposes but we also use electrons because electrons we do not know whether they are light or particles we do not know.

However, there is one thing that definitely works for electrons is the De Broglie relationship. So, De Broglie this relationship you definitely know

$$\lambda = \frac{h}{mv}$$

Where h is your Planck's constant. And whatever is your particle let us assume that electrons are particles in that case the mass of those particles is your m and then v is the velocity at which they are accelerated. So, this is something very fundamental.

Now, if I take electrons that are accelerated let us say by some voltage v in that case,

$$\lambda = \frac{h}{\sqrt{2meV}}$$

So, that will be because these are accelerated particles. So, this is what your relationship changes to and again here you have to new parameters. So, we know what is the mass of our particles that we are dealing with. So, that is you know the mass of electrons, you know what is the charge on electrons. So, these are the two more things that you need to factor it.

However, what is interesting is this relationship is only valid for electrons that are low energy; low energy means the voltages at which we are accelerating them are not too high and we will see what we call too high, what is not.

So, these are low-energy electrons and for those electrons, this relationship is valid. Why? Because we are sort of ignoring any relativistic factors. So, what happens if we have these very high energy electrons, and we also need to make relativistic considerations? In that case this is the relationship this is what it changes to.

So, now using all of these relationships you can calculate what are the wavelengths of electrons that are accelerated using different voltages and here I have shown one table in which you can see.

So, the left two columns are relatively low-energy electrons which we use for scanning electron microscopy. So, scanning electron microscopy, we are not going to cover in this lecture, but that is something which is mapping your surface. So, that is just taking the image of the structures of your surface but not going through your material. So, transmission as the name itself suggests there is some sort of transmission of these wavelengths through your material.

So, they are transmitting and we are collecting. So, this is your sample, the electron comes from here and then it goes through your sample, comes out with the loss of some energy. So, that is what we know as transmission.

And for transmission electron microscopy the wavelengths that are e in the second column of this table are the ones that are used.

So, now from what do you see here. The wavelengths associated with electrons are in the picometer range. So, they are much shorter than even your X-rays. So, if you remember in the X-ray diffraction lecture, I said that we were talking about the lambda or the wavelength should be pretty much of the same size of the interatomic distances and that is why we use X-rays for diffraction purposes.

What if your wavelength is even smaller? Then you can very clearly see your interatomic distances, you can even potentially see single atom. Although, this is not the case because of the instrumentation parameters; but in principle, you should be able to see single atoms using transmission electron microscopy. And there have been reports where people have observed the hexagonal rings of graphene.

Although, again as I will explain to you, the interpretation can be tricky sometimes also these beams of electrons can damage your sample, after all electrons do have certain mass. So, they might also damage your sample, in that case while imaging your sample you may end up inducing defects and, in that case, you will not be sure, whether the defect was already there in the material or it is because of what you did to the material.

So, all of these things need to be factored in but you see that the wavelengths are in the picometer range; that means the imaging is not really wavelength limited. So, in terms of wavelength we have a lot of flexibility we can go all the way to picometer region.

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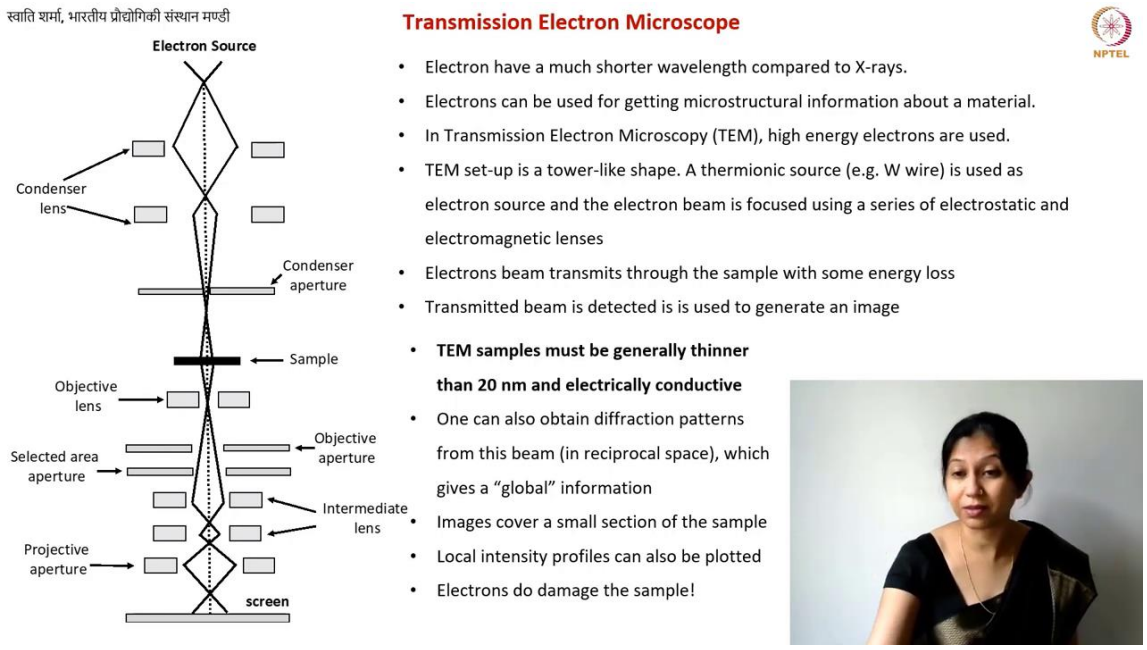

I already said, you have much shorter wavelengths than X-rays. Now, electrons are used for getting micro structural information. Remember that now we are talking about microstructural information, we are not talking about crystal information. Although, microstructural information contain the crystal structure and you remember that you also can now see the defects, the residual stress inside your material.

Now you can actually visualize all of these things but now we are more concerned about the microstructure not the large-scale crystallinity of the material. Although we can deduce it from here as well.

Only the high energy electrons are used in transmission electron microscopy that you already saw in the table before. Now, here I have shown this some schematic, I will again not go into the details of what kind of lenses are used and what is the optics of transmission electron microscopy. But this is some basic schematic of the entire instrumentation and here you can see that this is a very long structure.

So, if you see one transmission electron microscopy in some lab then it looks like a tower. So, it is a tower like structure 6-7 or more feet higher. So, these kinds of towers they contain various lenses and these lenses are not like what you would think of optical lenses and so on. These are electrostatic and electromagnetic lenses. So, these are specialized lenses.

And then you have an electron source, the most important thing for you. So, you will use some thermionic source.in some other lecture I had mentioned thermionic source is when

you heat something and therefore the electrons come out. So, you heat something and you also create a high potential difference then the electrons come out in the source.

So, these thermionic sources, although there are many other more sophisticated sources but you could potentially just use the tungsten wire in both scanning electron microscopy and also transmission electron microscopy. You also have other materials but you have basically one electron source.

Now, you have the beam of electron which is focused through these lenses. Then it falls on your sample and transmits through your sample and at the bottom you have a screen or a detector where you form the image.

So, this is the fundamental principle, basically now, you are using a beam of electron for imaging purposes. However, you should know that not all the electrons will just transmit through your sample and so there may be some backscattering.

And also, definitely some electrons will damage your sample. And definitely, even those which are transmitting through your material will lose some energy. There will be some interaction, some loss of energy when your electrons are going through your material because they are after all interacting with the atoms of your material.

So, there will be some loss of energy. This is the fundamental principle when you prepare the sample. So, now we already come through more of the experimental part and the analysis part.

When you prepare the TEM samples in principle, they should be thinner than 20 nm. If you want that the electrons pass through it and if you want to see the microstructural information. If you have a thicker sample, well nothing bad will happen; the only thing is that you will not be able to see the microstructure. Why? Because if your sample is too thick then the electrons sort of get lost inside your material, they do not come out on the other side and even if they come out there, they have lost a lot of energy.

So, you will lose a lot of information in that sense. You can definitely evaluate if the diameter of your tube let say was 15 nm or if you are using carbon fiber. Well, often I see transmission electron micrographs of carbon fibers that are even 200 nm thick or their diameter is 200 nm.

In that case, well you can measure the diameter of your fibers but that you could even do using scanning electron microscopy 200 nm. In fact, even there are optical microscopes that will give you that information. So, for that purpose in principle, there is no need to use a transmission electron microscopy, especially high resolutions. as the resolution increase, we are basically using higher-energy electrons.

So, that information can also be achieved by other techniques. When you want to essentially get the microstructural information you want to see how your crystal planes are organized in that case the sample should be thinner than 20 nm; and the thinner the better.

So, if you have a sample that is 5 nm thick that will give you more information because you will have only a few planes of your sample within the focal length.

So, this is something we are going to also discuss. The point is that you need to spend some time preparing your TEM sample. And that is why it becomes a little bit tricky when you are using let say bulk carbon materials. If I want to take the transmission electron micrograph of glass-like carbon material and I purchase a glass-like carbon in bulk. In that case, I need to make either powder or a slice which is thinner than 20 nm which you cannot use just some kind of milling or ball milling or something like that to make the kind of sample because 20 nm believe me it is very small.

So, you will have to prepare a slice using what is known as focused ion beam milling, we will not again go into details. But as the name itself suggests there is an ion beam, which can be used. An ion beam is a high-energy beam that can be used for slicing your sample. And that also needs to be done under inside a microscope, because you should be able to see what you are doing there.

Often the scanning electron microscopes are also equipped with this ion beam setup or you can buy a separate focused ion beam setup. There you can actually slice your sample and then get this very thin ultrathin sample. you also know that you might be inducing some stresses in your sample or if you are using any technique for making powders, in that case also you need to make really thin powder. So, the sample preparation is not all that easy.

Now, can you get only images from transmission electron microscopy? No, there are many things that we can do with this machine. But the most common application of transmission electron microscopy is imaging because as I said it helps you visualize your material, that is very good.

But you can also get electron diffraction patterns. You already now know about X-ray diffraction patterns, the only thing we are doing here changing the wavelength, but we can also get the diffraction patterns. The diffraction patterns are often in the reciprocal space. So, that is why you can get more global information because then you are getting the reciprocal. So, it is like for the entire sample, you can get the information that is sort of localized. While imaging will give you more local information; the diffraction patterns can give you relatively global information. It does not help us very much with non-graphitizing carbons. So, again we are going to discuss that.

Non-graphitizing is turbo strategically arranged. In that case, there is the 3D crystal structure is missing, so we have a crystal in 2D. And whenever there is 3D arrangement missing it becomes very difficult, even with extra D is difficult. But potentially you can get electron diffraction patterns as well using your transmission electrons microscope.

This, I already told that you images covered a very small space; typically what you are looking at is this information within 50 nm of your sample. So, remember that if your sample is not uniform sometimes, this has happened to me that I thought I found something really amazing in one corner of my material but that was really just one corner and not the rest of the sample and it could even have been some impurity. Let us say if you have some non-carbon atoms in your material. So, they may change the shape of how your six-member rings are organized.

So, because of defects, you can have different strains in the sample. So, because of that if you are sampling only one part of your material then you may end up getting misleading information. So, you need to often perform the microscopy at different samples. You need to do the sampling at different positions on your sample on your specimen.

One more thing is that you can plot the local intensity profile. So, I am mentioning this because this is also very commonly seen in a lot of publications. You will see this intensity profile, I will show it in the next slide.

So, intensity profiles are still something done by the software. You can just take a TEM image and you can do this processing by yourself using practically any image processing software.

You taking the profile if you have a dark line and then bright and then dark and so on. So, what you want to see is the spacing between them. So, you will just take the peaks or the profiles as the intensity increases and decreases and that helps you understand the D spacing. D spacing is very important to us and that is why often you will see intensity profiles in many publications related to carbon materials.

Electrons do damage the sample and this is something especially when your samples are sensitive and carbon materials are sensitive. So, they are definitely sensitive especially if you are working with these few-layer graphene structures. These materials are sensitive to electron beams and you need to be careful. Also, if you are working with carbons that are prepared at lower temperatures which may potentially contain some impurities and may not be perfectly electrically conductive.

You know that electrical conductivity increases as we increase the heat treatment temperature. So, if you prepare something at let us say 800°C, you may not even call it carbon that is a different thing but let us say if it is a pyrolyzed polymer. So, in that case, these materials may not be electrically conductive and one condition for a TEM analysis is that you need to have an electrically conductive sample.

So, electrons need to go through it. You can imagine that you need to have something that is conductive that allows the transport of electrons. And materials that are not electrically conductive often are sputtered or coated with a conductive material. You can use any metal to coat like gold. That you will also do for scanning electron microscopy because electron microscopy requires the samples to be conductive.

But you should understand that if you are working with for example, single or few-layer graphene sheets, in that case, you may end up losing some information because of this sputtering. But graphene happens to be anyway electrically conductive. So, it is not a problem, but I am talking about the defect containing or impurity containing structures graphene-like sheets because these kinds will also exist in the material that is at 800 °C, but they are definitely not pure carbon. So, you need to be careful, your samples are

sensitive to electron beams and the electron beam can potentially cause damage if not the entire sample surface of the sample, but it is pretty thin already.

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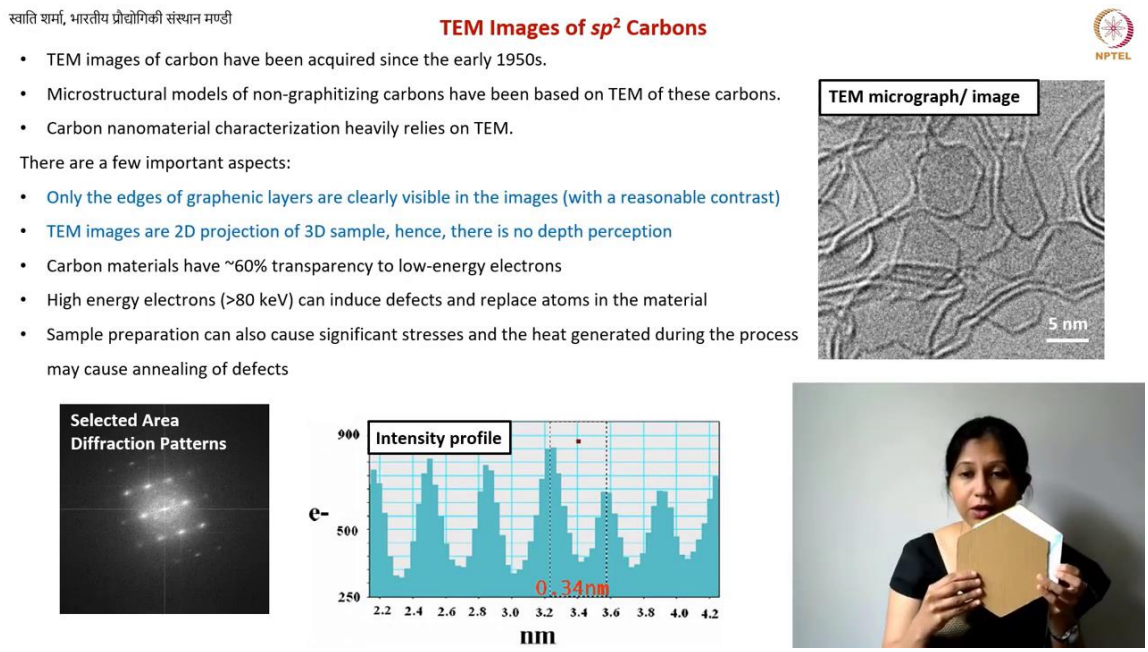

Transmission electron microscopy has been used to image carbons for a very long time since the 1950s. In fact, when we were learning about carbon nanotubes, I showed you an image of these hollow carbon filaments or carbon tubes that were observed in 1952 and those were TEM images.

So, TEM itself has a long history. The first electrons were used for imaging purposes as far back as 1930. So, in 1931 we had the first TEM set up.

But of course, then there were various modifications and now it has become a more common technique. The point is that if we relate the history of carbon materials development and the history of transmission electron microscopy; these are connected because we have always been using TEM to visualize the carbon materials. So, as far back as in 1950s, we used it.

One very interesting development in the entire carbon community was the fact that, we understood what non-graphitizing carbon right. And a lot of carbons are non-graphitizing we know that now. The discovery of non-graphitizing carbons or how we understood the

microstructures or when there were microstructural models proposed, many of them were very strongly related to TEM imaging.

So, not the first one, not the one that Rosalind Franklin described that was based on a completely based on X-ray diffraction and of course, some properties of the material that you need to correlate. But the other models the Jenkins carbon model and then the model provided by P. J. F. Harris and also the recent study then I have done and I have shown you also the in-situ electron microscopy which gives us some more information.

And recently you will find many other publications. Nowadays we understand the microstructure of non-graphitizing carbons reasonably well. So, yeah all of these studies have been very much dependent and very much related to transmission electron microscopy. So, this is a very important imaging technique for us. I told you never seen a carbon nanotube.

You only believe in what you see inside the TEM not just carbon nanotubes but there are also carbon nanoparticles and various carbon nanomaterials. And in fact, some fancy carbon materials fullerenes we know and using chemical synthesis we also know how they are agglomerate then they form FCC crystal and so on.

We know what is the structure of fullerenes, because of the other characterization and other information that we have about the material. However, in order to visualize them, this is a very interesting tool. When I see fancy carbon materials you have carbon nanotubes and you have fullerenes filled inside them. These kind structures, the TEM provides. It is a very good tool to see these structures and then understand and correlate the rest of the data.

So, carbon nanomaterials heavily rely on transmission electron microscopy but then now till now, I have only been telling you all nice things. It is nice, everything is nice about TEM, we will talk about that it is a very important tool. But there are also certain things that we need to take care of. So, when we are interpreting the images especially at that time, a lot of things become important, that is what we will now discuss.

These are two aspects I have highlighted. So, two things when you see any carbon material let us say I have this. If I see this what is going to be visible? Only the edges,

you will not see this central part because our carbon materials seem to have reasonably high transparency to electrons; at least the lower energy electrons.

So, it is only the edges that are visible that is number one. Number two — this is not just valid for carbon, but for everything. Those transmission electron microscopy images are basically 2D projections of a 3D material because your entire sample which is your 20 nm or thinner sample that is in the focal length. So, what will happen when there are two objects for which you cannot get depth perception.

If I have this one sheet and this is my other sheet. So, they are like this. They are far apart from each other and if I rotate them, then they are like this I hope this is clear.

However, what you see is just the edges and it looks like they are both in the same plane. So, you cannot differentiate if they are like this or they are like this basically because you are only seeing the front view and in the front view, you always see the edges and you cannot get any depth perception.

So, this is something very important. These two things if you understand then you should be able to analyze your imaging at least. So, the problems during imaging are different, but once you get the image interpretation, at the time of interpretation you need to understand these two things completely.

As I said that we do have carbon materials that are also transparent to X-rays and to various other wavelengths, but also for electron wavelengths they do have reasonably high transparency especially for low energy electrons. But we need to use low-energy electrons because high-energy electrons damage your sample.

So, most of the TEM equipment that is available often operated 300 keV, but they can go down to 100keV, but it is really difficult. In fact, a lot of instruments do not allow you to go below 100keV.

That means, what is the optimum voltage is below 80 keV. So, if you want to image carbon samples in principle you should image them only below 80. Because 80 is the energy required; not exactly 80, but slightly above 80 is the energy that is required to remove one carbon atom from your six-member rings which basically means that above

80 keV you can potentially induce defects while imaging. So, this is another aspect that we need to be careful about.

Sample preparation, already I told you that this can already create defects. So, you are often using either this focused ion beam milling or some sort of technique for making powders. But in that case, you are using definitely using very high energy to make these slices or to make the powders and there you may also have higher temperatures occasionally depending upon how you are making your sample.

But if you have a high temperature, our materials are temperature sensitive you know that I mean; all we are trying to study about carbon especially pyrolytic carbon; all we are trying to understand about these materials and you know what is the influence of temperature on the microstructure. And if you induce high temperature during your sample preparation in addition to the mechanical stresses. So, in that case, you may end up changing the microstructure of your material.

However often it is not so significant that it will completely change and as I said you are doing the imaging at different locations then you will get certain idea of the material anyway. So, all you need to know is that do not do very extensive sample preparation, do not use technique that would also depend on what kind of carbon material we are using.

So, just be sure that you do not damage your sample, and if you do then still try to do the sampling at different locations just to make sure that your data is correct.

So, now I will show you how does the transmission electron micrograph look like. Micrographs are the term that we use often you can also just call it a TEM image. This is one example of one carbon material. How does diffraction patterns look like? This is how it looks like. We call it a selected area because it is often done in a very small region of the sample altogether.

Selected area diffraction patterning: we select an area in the image and this will be important for many materials, part of it is crystalline and some part is not crystalline. So, these are the diffraction patterns this is how they look like.

Now, what often people do what is known as indexing of diffraction patterns, indexing basically means you will take two planes. So, you what you see here these are lines, they

are planes right. So, you have one plane like this and another plane. Let us say like this and you will measure the lengths of these distances. So, between two spots.

So, you will measure distance between two spots like this and then also two spots like this whatever it is, not necessarily perpendicular angle. But these are the two planes, you will measure the lengths and then you will find the ratio of these of the lengths.

And accordingly, for all types of structures FCC, BCC or different crystal structures there exist some rules of thumb that if this is the ratio of the two then it could be potentially an FCC.

It is not that simple. But the point is that you can obtain this information just by looking at the diffraction pattern, you can potentially see that. Then you can say this is FCC, this is BCC; that much information you can generally get, but that is very difficult in the case of carbon, especially non-graphitizing carbons. It is very difficult to get this kind of information and diffraction patterns can often be misleading.

So, if you even try to analyze this particular index or this particular diffraction patterns; it is very difficult to get any information because when you have pure graphite you do not have hexagonal closed packing; you have a hexagonal structure, but not close packing. And all of these rules allow you to find the potential crystal structure; they are for well-defined crystal structures; they are for HCP. In this particular case and our material is not HCP.

So do not get too confused by the diffraction patterns that is what I am trying to say. Intensity profiles, they look like this some green-blue color. It can be any other color because as I said that this is something that you externally plot. But what you doing here is you take any region, if you see stay stacks of a few sheets.

So, if you were looking at the cross-section, here we have these two sheets. In that case, if you plot, if you draw a line here and you plot the intensity profiles. So, in that case, you will know where do you have your darker regions and where do you have your lighter regions or brighter regions, and then you can basically just find out using post-processing what is the separation.

here in this case, you see 0.34 nm, does that remind you of something? what is the layer separation or what is the D spacing for graphite perfect graphite? 3.335 Å. So, this is for perfect graphite.

But if you have something between 0.335 in terms of nanometer; 0.335 and 0.344 in that case we call the turbostratic more than 0.344 also can be considered some curved carbon structure. If the spacing is too much like 0.4 or something like that, in that case, you will say that it should be considered a completely disordered carbon.

You might actually be looking at the top view and not the stacks. So, you might actually be looking at something like this. So, this white line and then this brown one rather than this then you probably looking at this. So, this is what we will come to.

So, these are the type of images that you get. There are many more, by the way transmission electron microscopy can be used for various purposes and various types of imaging. But these are the types of images or patterns that we use generally for understanding carbon materials.

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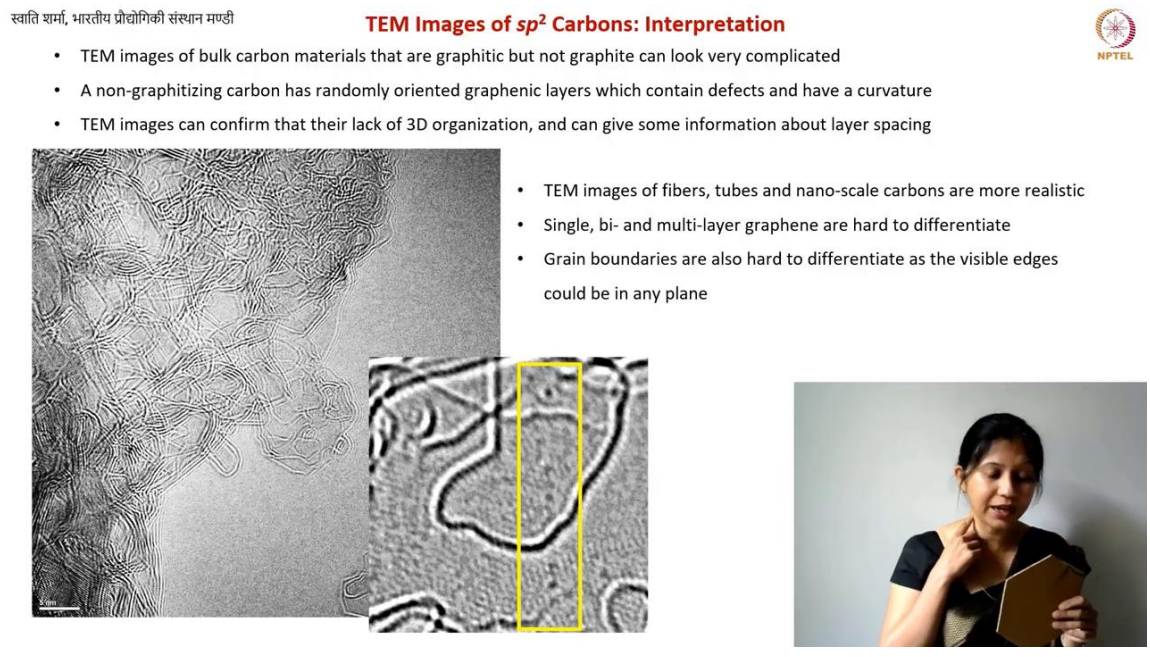

TEM patterns of non-graphitizing carbons or whatever written here is graphitic. But non-graphitizing, these kinds of carbons are most extensively studied because these are important to us for a lot of manufacturing purposes. Now, for a lot of device application

purposes. So, other than carbon nanomaterials what you study the most is these non-graphitizing carbons.

If you graphite crystal is perfect then you already know it from XRD and then you probably do not need to go into very sophisticated techniques that you can learn it for understanding the technique itself, but as such for characterization XRD good enough for perfect graphite and also Raman's spectroscopy will give you one good sharp peak.

So, what is difficult to understand? What we are trying to learn is this graphitic but not yet graphite type carbons. They can also be graphitizing carbons, by the way not necessarily non-graphitizing. They can also be graphitizing, but the point is that they are not yet graphite. So, these kinds of patterns can look very complex because we have multiple planes in these materials.

And some of them are often turbostratic. In that case, it is very difficult to find the alignment of these planes and you are never going to get these perfect crystal planes in 3D. So, these are the interesting materials and here I have shown you one image.

This is an image of a glass-like carbon or at least the material that was prepared using a phenol formaldehyde resin at around 1200 °C. But the film itself was extremely thin. When we were taking this particular image, we did was something known as in-situ TEM. In-situ TEM means you heat your structure inside the TEM itself; using a Joule heated substrate. You can purchase different types of substrates for transmission electron microscopy; typically what you use is known as TEM grid.

Grid as the names suggests it has like these kinds of structures, it looks like a net pretty much, but it is made of metal. And it is circular and it is about a few couples of millimeters in terms of size. So, you will use this kind of grid, and then you will place your sample on top of it and then perform the imaging. When you are performing the slicing using FIB then you may already place your sample on top of the grid inside the FIB system.

So, this is how you analyze them but you can also perform the heat treatment inside the transmission electron microscope, given your sample is extremely thin. So, when I said you should in principle go below 20 nm, why? Because you are going to carbonize a

polymer. Then you will also have some by-products, there are some tarry materials and you do not want to contaminate these very expensive machines.

You want to make sure that the quantity of the material is as small as possible anyway. So, this is the image of some non-graphitizing carbon. What do you see here? This is a crazy image. What can you say? Maybe all you can tell from this image is that this material is definitely not graphite and definitely there is no 3D organization in the material, that is all you can say right.

You can really not tell anything about the material itself about how the crystallites are organized and so on. We can say that crystallites are randomly organized, that much also you can say, but how exactly are they organized? What is the crystallite size? What is the type of organization? Whether you have all the planes these two planes?

If we talk about whether all of them are of the same size or different sizes, whether they have the curvature or whether they are flat; none of the information is available from this kind of TEM micrograph.

So, this is for the bulk carbon materials, what about carbon fiber tubes? There you can get relatively more realistic information if your fibers or tubes are thinner than 20 nm. If they are larger than 20 nm as I said that you can measure the diameter, but there is little information you can get about them. But sample that is thinner than 20 nm and they are individual tubes or let us say fullerenes and so on. Then you can get more realistic information so to say. Similarly, what about single, bi and multilayer graphene; you can see them, yes. But it is hard to say that this is single layer graphene, you should not do that unless you are really 100 percent sure and you also have some other data to show that.

For example, Raman spectroscopy can be used for differentiating between single and bilayers. So, if you have any minor disorder or the turbostratic arrangement within your sheets you should definitely make sure that you have some other characterization technique that gives you more information about this kind of arrangement.

Because in the TEM images, it is hard. You are looking at this, it is hard to say what it is. If these two are your graphene sheets (refer to the video at 39:15). Let us see you have

bilayer graphene, but it looks like this then you might end up thinking that this is a single layer, but it is not the case.

You also need to understand grain boundaries because we are trying to understand mechanical properties of the materials, of the crystal. So, grain boundary analysis is also one of the important applications which is often used for various metals. TEM is a very good tool for understanding grain boundaries, but again in the case of carbon try not to do it because you do not know where your planes are; one is here and the other one is here.

So, if you see some boundary, you do not really know if this is really a grain boundary or these are just two different planes at two different locations. So, again this is where you need to be careful. So, here I have shown this example of a grain boundary if you see with this box I have shown.

Do you see in the box there is some sort of this broken line? And this broken line can be thought of as a grain boundary. Because these kinds of grain boundaries have been observed in graphene-like structures, but at the same time we can never be sure if this broken line exists in just one plane or there is some other graphene plane that is far from your original plane.

But at the same time, it has some defective edges. So, this is also common in the case of graphene and graphene-like structures to find edges that have a lot of these unpaired bonds which basically means that you may have the defective edge which may be far from plane. So, just be careful with these things.

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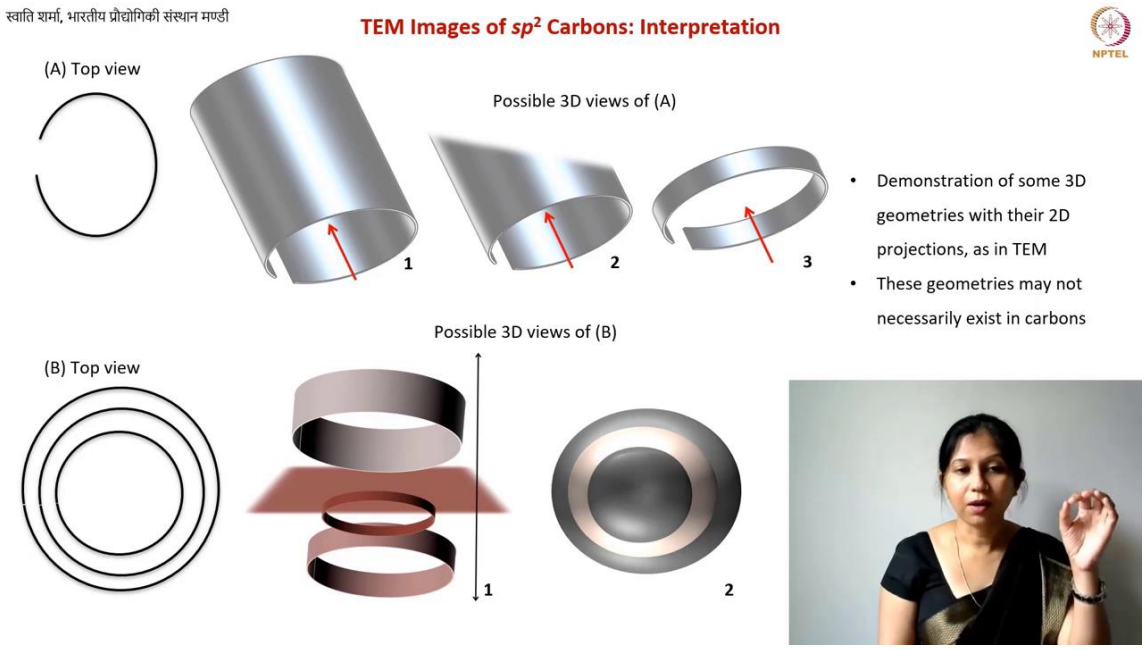

Now coming to some more structures that you can potentially see in your carbon materials but not necessarily. So, I am just taking some very simple geometrics to explain whatever I had just said. You see some circular ring line structure in your carbon. you can go back and again see that the TEM image that I have shown. You see a circle or not a complete circle this screen-like structure whatever it is.

What are the possible 3D arrangements that you can think of? What is the 3D shape that you can think of?. If I see a ring, I can think of it as a particle. I can also think that maybe it is a tube because I am seeing only the 2D structure right. So, maybe it is a tube, that is possible but it could also potentially just some randomly organized sheet. So, it can be something like this which is not completely closed right and this is not really a tube this is just some graphene plate that is just folded which has a curve.

We can have various possible 3D shapes to will give you this 2D projection. So, the first one is more like a tube again because I did not draw a complete tube, but it is this basically. So, this is your first one. The second one as I said that could be some randomly folded graphene sheet. And the third one can also be more like this annular structure, more like very thin ribbon-like structure.

Why am I describing this ribbon-like structure? Because this has caused confusion, if you remember some of the microstructural models of non-graphitizing carbons especially glassy carbon. They suggest that you have really ribbon-like geometries, long

ribbon-like geometries but in principle if you think about the fabrication techniques if you think about the energy of the overall structure.

These will be very high energy structures and there is a very low probability of finding these ribbons in any carbon material, but the point is that you could potentially misinterpret the TEM image to think that this is ribbon-like structure; there may also be some ribbon-like structures. So, the point is that from TEM image, do not just use this technique for developing a microstructure model.

But of course, if you know other things about the material like you already know how the Xray diffraction pattern already and other information like chemical information, also surface property information, porosity information whatever you have some other information like density; density becomes important in the case of non-graphitizing carbons because you may have closed porosity. So, all of this information you can integrate then with your TEM info.

What else? Some couple of these little structures, I have made just for your understanding? What you think of these? These can be three concentrated tubes, why not multiwalled carbon nanotubes? And I am seeing just this view and very well it can be multiwall carbon nanotubes, but it can also have some very funny structures.

So, I have shown this, let us say you have these ring-like structures then there is one over here and the other one is over here and then there is a smaller one over here.

And then there is also a complete plane in between which you do not see because you are only seeing the top view and the edges are not present within the structure. If you look from the top, will also give you these kinds of three rings. this will be the projection or similarly if you have three concentric particles. So, you have these carbon particles or carbon onion-like structures even they will look like this.

So, basically these are one sphere and then one on top and the other on top of another. So, these are basically particles, multilayer all of these are possible. So, the point is that the projection itself may not be sufficient, you should know other things about the material, some more example.

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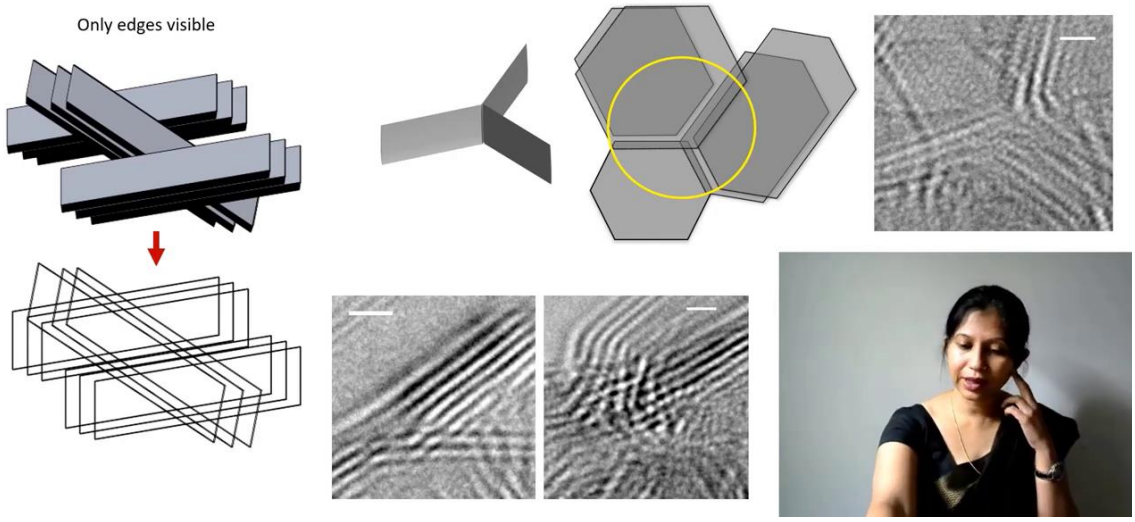
TEM Images of sp^2 Carbons: Interpretation



Here is another example. This is of this kind of structure you will often see. If I have these two things, here these two planes. So, let say this is how they stacked and what you see is just these lines and you often will have these lines and then also some intersecting planes and so on.

This kind of structure you will often find. If I just remove the solid part from this image and I just take this wire frame image of the exact same structure then this is how it looks like. Now you see it looks already so complicated. these are actually real images from glass like carbon. You often feel that your two planes are intersecting while they are not. They are actually far from each other.

But they look like they are intersecting. So, these intersecting planes, this is also something you need to be very careful because here the other thing is important that what you see is just the edges and not the entire solid material. What else? This image I will show. This image, I show this multiple times. What I thought when I first saw this image it looks like this it could potentially look like this.

You have these kinds of these triangular junctions are present in sp^2 type carbons. They have 120° and they are present. And if you read some of very old books and so on. There has been a reasonable description of these kinds of structures as well. So, these kinds of structures when I saw it, I was like really happy that I saw this triangular junction, but

while it can be this kind of junction, it can also be just the top view of these varies hexagon.

If you see the circle, if I am looking at that region; what I also see these can just be hexagons which are on top of each other one. So, basically there will be some triangular junction they will make. So, the point is that these maybe these triangular junctions may have a depth or not because we cannot say that from the projection. So, what do you do in that case?

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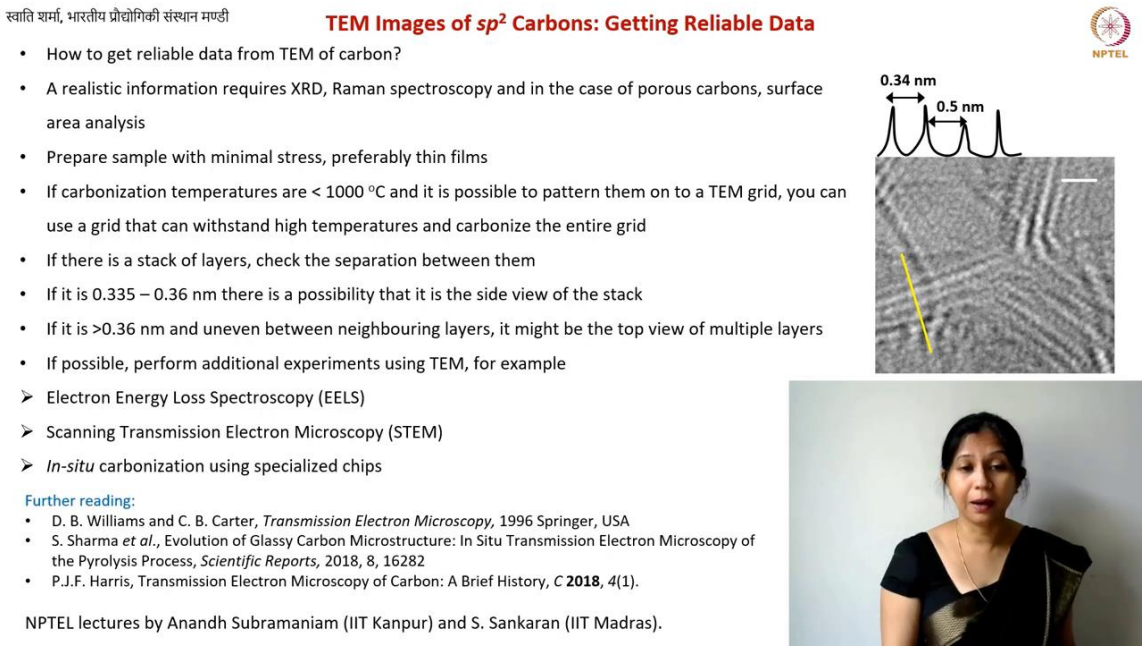

So, what we can do? On this slide, now I am telling you how to get reliable data from TEM or how to do a reliable interpretation. This is a very expensive equipment and it is not like you can never get any reliable data from this terribly expensive equipment.

But there is just a few things, few tricks that you need to make sure that you are factoring in everything. So, first of all, this is again important that you need to have other information about the material.

For example, if you want to see some closed structures, you see these particle like structures that I showed you before in non-graphitizing carbons. Now we know that these completely spherical fullerene like structures exist. We also know that if not completely spherical, highly curved structures definitely exist.

This we already know. also this information can be deduced also from the density of the material because for example, these non-graphitizing carbons they are very low density materials. So, in principle they should have some porosity, but at the same time they are impermeable to gases and liquids which means you have pores, but closed pores and closed pores also are not really visible.

You can also not a evaluate closed pores other porosity measurement techniques. It is very difficult to understand them. TEM in that case has been really helpful, that is how we understood that this was a question for a very long time that we have some sort of pores, but they are closed because the material is impermeable.

All of this information is definitely, we can get from TEM imaging, but it needs to be correlated with the other information that we have about the material. So, what you can do. Here I am telling you the techniques that will help you get reliable data. Make sure that you minimize these stresses when you are preparing the sample, sometimes it may be inevitable, but sometimes you can avoid it.one thing that I have used this trick that the some TEM grids that are made of molybdenum. they can withstand relatively high temperatures. So, you can pattern if especially when you are working with carbon nanofiber. So, electrospun carbon nano fiber or even when you are using any other polymer you can make thin film. What I am saying here is valid for polymer carbonization not for hydrocarbon pyrolysis or other methods.

But for the paralysis process if you could already prepare your sample on top of the TEM grid and then then heat treat the entire grid; that of course will depend on the heat treatment temperature that you want to use but if it is let us say 900-1000°C, molybdenum grid will work.

You can place the sample already on your grid then carbonize your sample which will then minimize these stresses in sample preparation. So, this is something you can do also, by the way if you have hydrocarbon pyrolysis. So, if you are making graphene if it is possible; graphene is often made on copper grids, on copper catalyst.

So, if you can take a copper grid and a try to already grow your graphite sheets on top of it then you can analyze it and that that also helps you in sample preparation. I do not know maybe you can use some of these things.

This stack of layers is the most important and interesting thing. Because you know that all the planes they are crazy, they look like intersections of several planes but this is something that you need to be careful. Now what happens if you see two planes.

So, I do not know the cross section is visible but these are two sheets right. So, if you see something like this and you have confused if you see the side view of these this stack or the top view.

Let me make it white (refer to video at 51:50). So, if you are confused what you see is this view from here or this view; in that case one potential thing that you can do and this is often done is this intensity profile. as I said, you draw line here and you take this kind of some intensity profile that you get.

Now, you measure the separation. If the separation is between 0.335 and 0.36 I have written 0.36 and not 0.344 because up to 0.3 this I have written. Specifically, because there is definitely manual error when you are measuring the separation because this as I said that this is done by software image processing software and also often you will manually place your cursor when you want to measure the separation between the two intensity two in peaks.

So, in that case there is some manual error, but this gives you some information up to 0.36; you know this might be the side view. However, if this is a much larger let us say you have something like a 0.5 nm between the two layers then in that case this is higher probability that you are looking at this. Because you see this separation is not necessarily 0.335 or anywhere close to it.

So, this is one thing that you can do if you are a little bit confused. What you can also often see in these kind of stack is that are you getting repeatable sort of information.

So, if your the intensity profile between two layers is 0.34, but the second one is 0.5 the third one is 0.4 again something like that; if you have lot of variations between the neighboring intensities, in that case again this may not be a stack. So, if you however are getting 0.33, 0.34, 0.35, 0.33; this kind of the profile, in that case most likely you are looking at side view. What else? Yeah, in the TEM machine itself is possible use other techniques.

For example, there is something known as a electron energy loss spectroscopy EELS and as the name suggest it is a spectroscopy. What is spectroscopy? When we somehow measure the loss of energy or gain of energy in the spectroscopy techniques that is what you are doing. So, energy loss as the name indicates that electron goes through the material and loses some energy and that is what we measure — the loss of energy. This you can do this will give you some more information.

There is also something known as STEM which gives you some idea about the depth of the structure. So, if your equipment is with these kinds of things then you can definitely do that; not necessarily all the TEM setups are equipped with these additional things. Because already these machines are very expensive and also the maintenance of the machine is also very expensive. It also requires the continuous high vacuum.

So, it is not something that you should definitely respect it is a very expensive machine, but in the same time you may not always expect that you will have all the features in your TEM and also the these features are changing every day. So, if somebody purchases the TEM microscope 5 years ago that might already not have some of the recent feature and so on.

So, this is also a constantly changing field and you cannot just buy a TEM every other year for sure. The third one that I have written is this in situ carbonization. So, I will also provide citation of my own paper where I have performed this. So, maybe you will get some idea from that paper. I have also taken some of these images. So, this is also for the citation, the acknowledgement.

If possible then ensure make sure that you do not contaminate the TEM setup, but you can perform in-situ experiments as well. Further reading: the some NPTEL lectures by Anandh and Anandh Subramaniam and Mr. Sankaran from IIT Madras. So, there are definitely other lectures as well on microscopy. So, from there you can learn the fundamentals of TEM which I have not described here.

This book however, by Williams and Carter is one of the standard books for understanding TEM. And so, the second one is my paper from where I have taken some for some of the pictures. Third one is a review article written by P J F Harris, which gives you a very interesting history of how TEM and carbon materials have been

connected and what were some of the first carbon materials that were analyzed using transmission electron microscopy.