Carbon Materials and Manufacturing
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Lecture - 49
Vapor Phase Growth of Carbon Nanotube

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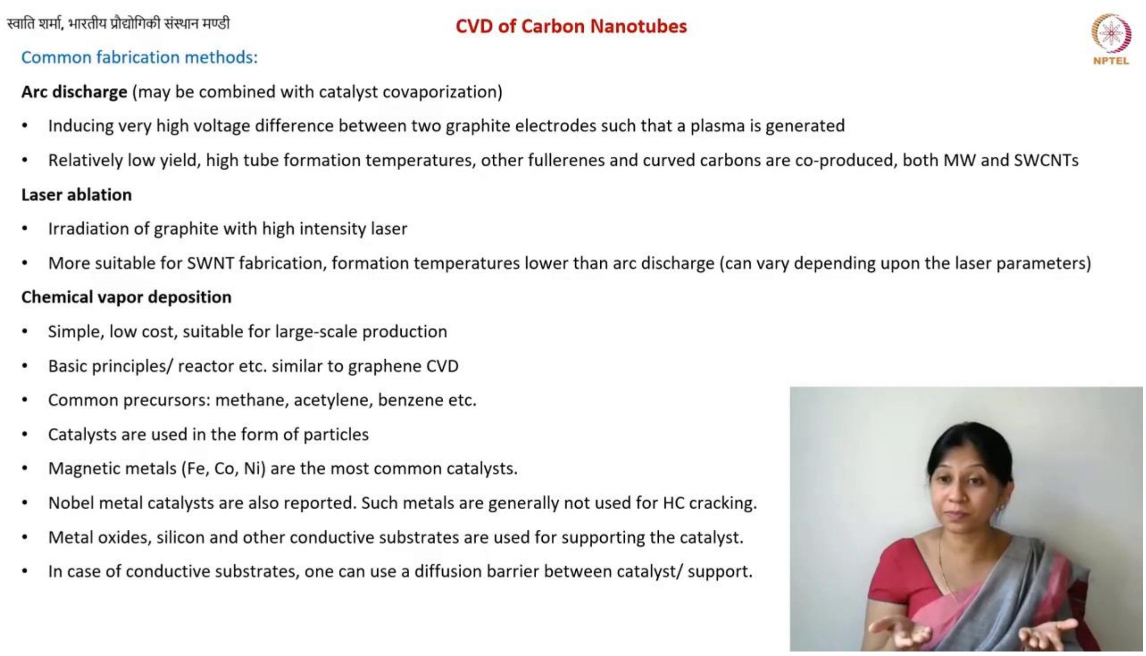

Hi. Now, let us talk about the fabrication processes for carbon nanotubes. You can again call them synthesis or fabrication or manufacturing as you like. The idea is that for making carbon materials especially nanoscale carbon materials, if you want to do that at a larger scale, the most cost-effective technique is chemical vapor deposition.

This is the same thing when you are working with graphene or other various carbon materials, maybe we learn also about diamond-like carbon. CVD will yield a lot of carbon material on the entire surface, but at the same time the quality may not be that great, but the extent of production of the quantity can definitely be scaled up. So, CVD is still the most common technique for making carbon nanotubes.

What else can we do? You remember that how do we get fullerenes and where do we get fullerenes, the completely closed ones that I am talking about. You remember, we get them out in the outer space, we get them when some meteorites hit the earth, then we get some fullerenes. We can also get carbon nanotubes in such cases because carbon nanotubes are also formed during such high-energy events.

For any carbon sheet to take a curved structure or curved geometry, high energy and impact always help. Similarly, we also can try out some processes where we have artificially induced impact or artificially induced high energy process; plasma comes to your mind, lasers come to your mind right whenever we talk about these high energy process.

Yes, we can also perform these things and obtain some carbon nanotubes, but CVD still remains the most important chemical process for the manufacture of carbon nanotubes. Also when you purchase carbon nanotubes and if somebody has produced them in some industrial-scale process then most likely those are CVD-grown carbon nanotubes.

However, the common fabrication methods anyway are CVD. But, what else? Arc discharge: what is arc discharge? Basically, you induce a very high voltage difference between two graphite electrodes. So, arc discharge between graphite electrodes.

The one interesting thing is that graphite of course is very much electrically conductive. So, it is already used for making electrodes. You can take two electrodes and keep them very close to each other, like maybe 1 millimeter apart. And then connect them to external circuitry, and then have very high voltages.

What is going to happen in such cases? These kinds of processes are used for making plasma. So, if you also have some gas, for example, argon-filled inside that chamber where you had your two graphite electrodes very close to each other, and now you created a very high voltage difference.

What will happen is that? You will have some plasma created and that plasma will also contain some vapor phase carbon. And that vapor phase carbon then contains carbon nanotubes. It may also contain fullerenes by the way. So, these are very high-energy processes that can yield curved carbon structures. So, this is also one method of producing carbon nanotubes.

Of course, you can also then optimize it such that you can get more carbon nanotubes and fewer fullerenes and Buckminsterfullerenes. You can then perform a little bit of process optimization. So, typically you will have some inert gas-filled inside, and then you create a plasma that contains carbon vapors, there you will find your carbon nanotubes. This is your method number 1.

What happens in this method? You can imagine that you will have one problem is that you will not get just carbon nanotubes, you will also get other types of carbon structures. So, that already means that your yield is a bit low. The isolation of carbon nanotubes from this mixture may also be difficult.

Although if the rest of the fullerene-like structures or curved carbon structures are not metallic which often happens in the case of Buckminsterfullerenes, they are not metallic, they are semiconducting. So, in that case, it becomes easier to separate out the carbon nanotubes, but anyway you have to perform an additional step for the separation or isolation of carbon nanotubes. So, that is one disadvantage.

But you can get both multi-walled and single-walled types of carbon nanotubes. And definitely, you do have certain optimization flexibility. One good thing about this process is that the temperature at which these tubes are formed is extremely high. So, they can be as high as the 3600 up to, even 4000 Kelvin that has been reported.

You do not want to go into the sublimation zone still, you have really high temperatures and that is why the purity of these kinds of tubes is pretty high. Also at these formation temperatures, there is also a very low probability that your tube will contain defects. So, these are also some advantages of our discharge method. Of course, this is a relatively expensive method with a comparatively much more much less yield.

The second one is laser ablation, again laser ablation of graphite.as the name itself suggests that you irradiate. So, you have laser pulses. You hit your graphite again and again with your laser pulses and during this high energy operation, then you will have again different types of curved carbons produce, carbon vapors produced basically in which you can find all kinds of interesting carbons. It is not just carbon nanotubes and fullerenes. You can also find other carbon stuff, you can find carbynes, you can find C_2 C_8. So, many structures that are believed to exist and they have not been experimentally validated. Some of them have already been validated in carbon vapor.

So, carbon vapors are very interesting mixtures of carbon species and they are studied for understanding different carbon allotropes, understanding the hybridization and understanding the carbon itself. So, you do irradiation of graphite with high-energy lasers, high-intensity lasers. This kind of process interestingly yields more single-walled carbon tube rather than multi-walled.

It's not that you have no multi-walled carbon nanotubes at all, but you have a much larger region where you have a single-walled. If you see the distribution of the diameters or the type, then you will find more single-walled carbon energy using this process. And here also the temperatures are relatively high, but lower than that of the arc discharge methods.

And also depending upon the laser, depending upon the parameters, you can also tune the fabrication temperature. So, this is another method. And then we come to CVD. So, CVD we are going to discuss probably in a little more detail, so you already understand the fundamentals of CVD. It is very similar to what we learned in the case of graphene and also the fundamentals of CVD reactors.

And so I would again suggest that you go through that lecture of the hot wall reactor, the cold wall reactor. The fundamental things that remain the same, and even the pyrolysis process remains the same. So, you have a hydrocarbon, again you can have methane or acetylene, you can have aliphatic linear hydrocarbons or you can also have aromatic hydrocarbons such as benzene and even some larger molecules.

For example, alcohols or even from any natural source, any organic material which is in the gas phase can in principle be used as the source of hydrocarbon. So, some these things remain pretty much the same. The major difference is that now your catalysts are in the form of particles rather than films.

If you give a very small surface for your carbon to deposit, then it will deposit on top of each other. Rather than having one single film, even in the case of graphene it is very hard to get one single film right. You get one film; on top of that, you get another film, and then another film and then another film. So, it is difficult to stop the process at one single film.

This means that the second layer of carbon also serves as a catalyst for the third layer, and the third layer serves as a catalyst for the fourth layer. So, carbon can deposit on top of carbon. In fact, in the case of pyrolytic graphite production, we are using graphite itself as substrates.

The point is that, if you have a catalyst particle then you have one layer of carbon deposited on it. Then there will be another second layer deposited on top of that and the third layer, and the fourth layer, and the fifth layer. And then you can get a tube-like structure that is what we call carbon nanotubes.

So, how we are controlling the diameter for our nanotubes here? By controlling the diameters of our catalyst nanoparticles. Nanotechnology has really helped us, and that is why also carbon nanotube production has become relatively much easier in the past.

Anyway how do you prepare catalysts? Do you always have to have particles? Sometimes you can also have particles but not just made of one metal, but made of alloys and that is how you can play with the geometry of your carbon nanotube basically by modifying your catalyst. Most of the other things are very similar to what you will have in the case of graphene.

So, yeah this is what I have mentioned here, and the common precursors again as I said you can have any hydrocarbon again. And catalysts are used in the form of particles. Now, what is very interesting is the most common catalysts that are used or that have been reported for carbon nanotube growth are the transition metal catalysts, but these are magnetic types of metals, so iron, nickel and cobalt.

These three metals provide the best kind of carbon nanotubes or at least that is how it has been reported. Again, nickel we also use for graphene synthesis, but then we also use copper. We typically do not use iron very much in the case of graphene, although all of these metals have been reported. But the commonly used catalyst in the case of carbon nanotubes is these magnetic metals iron, nickel and cobalt.

Maybe you can think about it, why would you use magnetic metals or does it make any difference? although there have been also noble metals and other metals that have been tried out; even gold as a catalyst for making carbon nanotubes. Now, noble metals are generally not very good catalysts especially when it comes to carbon production.

If you want to make bulk carbon, you will most likely not use a noble metal. But they are fine when it comes to carbon nanotube production, then those catalysts even which cannot be used for other bulk carbon production or carbon film production, even they are actually reasonably good for carbon nanotube production, which still tells us that there is something very interesting going on when it comes to the mechanism of carbon for of tube formation.

It is not just the same mechanism as in the case of graphene. He mechanism by the way I will discuss it a little bit on the next slide but let me tell you that this is still being investigated. So, the research is going on in this field.it is not completely understood yet, but we do know a lot of experimental results.

And we know that if you perform the process in this way, this is what you get. Every time, we can come up with a different mechanism of our own, but then after some time, there is another study that proves the previous mechanism wrong. So, this is something that is still an ongoing field of research.

Yeah, one important thing is also in the case of carbon nanotubes which is not really a concern for us in the case of graphene manufacturing, is that the catalysts need to be supported here? So, you can also have floating catalyst, that is a different thing all together, then you have a hot wall type of CVD reactor. But if you have the seeded catalyst, then the catalyst is seeded on metal oxide substrates or alumina substrates.

Also, you can have them on silicon substrates and people are using conductive substrates especially when it comes to electronic devices. Sometimes you can already pattern your electrodes, your contact paths, and then on top of them, you grow your carbon nanotube so that then later on you do not have to worry about forming the contacts.

Often it happens that you have different types of substrates and the interaction of the substrate with your nanotubes. So, the interaction of your substrate with the catalyst particles also plays an important role in the growth of your carbon nanotubes.

Again, the different supports behave differently. But in the case of conductive substrates, often you will also have a diffusion barrier just because you do not want the dissolved carbon species to diffuse through your substrate or the support that is there for the substrate.

And that is why you want to keep it limited to the catalyst itself and you do not want your carbon species to go into the support and that is why you might create a diffusion barrier. So, this is also an important parameter.

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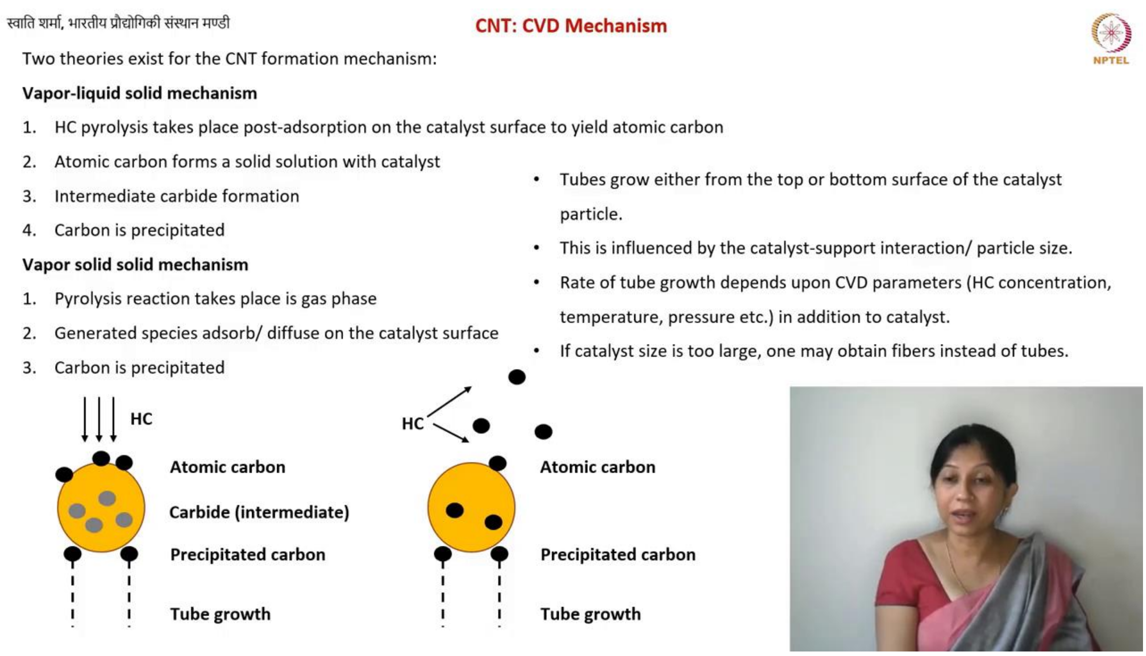

Let us talk about the mechanism of carbon nanotube growth during the CVD process. So, interestingly different mechanisms have been proposed. You can try to relate it with the graphene CVD, try to relate it to the idea of hydrocarbon pyrolysis, and then the dissolution of some carbon species on top of your catalyst material. And then the desorption of certain byproducts as well as the deposition of carbon. This is a fundamental idea also in the case of carbon nanotubes.

Also, when you have vapor grown carbon fibers, this is the very idea, you are just changing the type of your catalyst and shape of your catalyst. Of course, there are minor changes in the process, but to be honest there have been a lot of variations in the process, and even though you can vary the process a lot. You can still get carbon nanotubes as long as the catalyst is right.

So, now think about the mechanism of carbon nanotube growth; as such there are various theories, but there are two main theories that we are going to discuss here. The first one is known as the vapor-liquid solid mechanism. There are various steps in this particular mechanism that have been proposed.

So, you remember that we always had this dilemma in all our carbon whenever we were talking about hydrocarbon pyrolysis, whether the pyrolysis reaction is taking place in the gas phase or it is taking place on the substrate. And what did we do before? What we can in principle do is you take the hydrocarbon itself, whatever is your hydrocarbon whether it is methane or acetylene or any other bigger aromatic hydrocarbon, what you can do is you can just pyrolyze the hydrocarbon itself.

You just have a heated chamber and it needs to go above the temperature where the enthalpy of formation becomes positive for that particular hydrocarbon. And then at that temperature, you can then flow your gas or hydrocarbon through it, and then basically just observe the byproducts of the pyrolysis of the hydrocarbon itself. We also discussed this during the graphene CVD.

So, when you get the byproducts of the hydrocarbon pyrolysis, then you can kind of guess what is happening. But there is one difference here compared to graphene, because in the case of graphene even if you had a larger aromatic structure, for example, naphthalene. So, you have two rings there, two aromatic ring-like structures.

And if you have this naphthalene, and also the naphthalene was absorbed on the surface of your catalyst film – in that case copper film – in that case, it is possible for the naphthalene to later on convert into carbon because this is a film. But when we think about carbon nanotubes, then because the catalysts are so small, there is lower probability that they can accommodate a lot of larger species on top of them.

Then we believe that if these are atomic carbon species in this particular case, but we just believe that we do not know that because again the results of the hydrocarbon pyrolysis indicate that there are larger aromatic structures that might exist at higher temperatures. So, whether it is these species, the cyclic structures that are depositing on top of your catalytic catalyst surface, or it is the atomic carbon; that is the interesting question based on that, these mechanisms have been proposed.

In the first one, this is what is proposed that you have this hydrocarbon pyrolysis taking place not in the gas phase, but on top of the catalyst surface. So, you basically have the reaction taking place post adsorption. So, that is when the pyrolysis takes place. And that happens on the surface of the catalyst itself. And then after decomposition, you have the atomic carbon species.

And there is one more interesting thing that you have carbide formation. So, we know that in the context of catalytic graphitization, we know that whenever we have transition metals, there is a high probability that some carbide will be formed, and then you can have carbon precipitating out of the carbide. So, this is a very well-known theory. In fact, even catalytic graphitization is industrially used for a lot of purposes.

So, this theory is also then sort of applied to understanding the mechanism of carbon nanotube formation. This is what is believed that you have carbide formation, but where does the carbide form? Inside the catalyst because you have a solid solution that we have discussed in detail during the solubility of carbon in various metals in the graphene CVD lecture and in the lecture before, not right before that but at some point when I was talking about the pyrolysis of methane.

So, carbon solubility becomes very important. In different metals, you have different solubility and you have different solubility curve curves, and accordingly, you collect your carbon at different temperatures. The idea is that the carbon atoms go inside your catalyst and then there is a carbide formation, and then from that carbon precipitates out.

Let me also show it with the help of a diagram. This is your hydrocarbon gas. This is your catalyst particle. Then the kind of deposits on top of the surface of your catalyst, and that is where you have the pyrolysis taking place. And now you have atomic carbon species.

These carbon species then go inside your catalyst particle. And now you have a metal carbide there. It seems this is a metastable state. So, this is an intermediate state. It is not your final product. Now, your carbide precipitates carbon out.

And often that is why it is believed that from the other end the carbon is precipitated out.by the way the catalyst particles are not necessarily spherical, depending upon the crystal structure, they can have various shapes. Anyway, the idea is that the carbon is precipitated out. And once you have the carbon precipitating out, then this is a deposition of one layer on top of another and you then ultimately have your tube growing out of it.

So, this is mechanism number 1. And the number 2 mechanism is known as the vapor solid mechanism although even in the first one there was no really there is no liquid phase as such, but it is believed that when there is solid solution being formed. Because it is a solution being formed, then it may have a liquid-like intermediate state.

Now, in the second one — in the vapor solid mechanism, what is believed is that the pyrolysis is taking place in the gas phase. Now, whatever species are generated, and again it is believed that in the case of carbon nanotubes, they are rather atomic species or at least very small ones. They get absorbed, and then they diffuse through your catalyst substrate.

This sounds very similar to what we learned also in the case of graphene especially with the nickel catalyst. And then ultimately carbon is precipitated out. So, in the second mechanism, we believe that carbide formation does not take place. Here again with the help of a diagram, this is your catalyst particle, but here the hydrocarbon is dissociating already in the gas phase and converting it to atomic carbon.

This atomic carbon then deposits on top of your surface, and then it precipitates out. Also in this particular case, carbon does dissolve. There is some sort of solubility that we need to still understand, but the carbide formation is not taking place. So, this is the second proposed mechanism and of course, the tube growth mechanism remains the same.

Whether the tubes grow on top of the catalyst or below the catalyst that is also an interesting thing. And in fact, I have not shown an image; there is a very popular image where you can see that there is a catalyst particle and the tube is growing on top of it. And in the second strategy, there is a catalyst particle, and the tube is growing below it, and as the tube grows the catalyst particle goes up.

So, these two mechanisms, I think this is known as tip growth and base growth. So, this is also very common. This is another way of describing the mechanism of carbon nanotube formation. There are two things here the physical mechanism of formation and chemical mechanism of formation. So, the chemical mechanism is what we discussed here whether or not we have carbide formation we still do not know.

So, these are the two proposed method of the mechanisms. Whether the pyrolysis takes in the gas phase or on the surface or both, there is no very clear understanding. It is also quite possible that depending upon the reaction parameters or the pyrolysis parameters for that particular setup, under certain conditions it is quite possible that the gas phase reaction takes place or the solid phase.

This will also depend strongly depend on the temperature that you have inside your CVD reactor. So, based on all of these things, then this is what is happening at a chemical level. But at a physical level what is happening is whether or not your catalyst is on top or bottom. And what would influence that? Number 1 — the weight of your catalyst particle, if you have a very large although very large particles, you will not have in the case of carbon nanotubes, but still within the range of the particles.

Whether you are on the lower side or on the higher side? There is something that strongly influences this process is the fact that do you have very good adhesion of your catalyst with your substrate, we also have this alumina substrate or some other substrate.

So, in that case, the adhesion will also play an important role. Basically, during the deposition of carbon, when the tube was growing, did you have enough lift force to lift your lift your particle up or not? Either way the carbon does get deposited and the carbon tube does grow, which also definitely confirms that the carbon particles do go inside your catalyst.

And that is why they can come out of any surface of the catalyst, whatever is more convenient at that given point. So, that is something which we understand about carbon nanotube growth. Now, what is also one more thing is the rate of growth. So, that will depend of course, similar to graphene and other materials.

For that matter all CVD processes have various parameters that need to be optimized. Number 1 is the temperature – between 600 and 1200 °C. A lot of temperatures have been tried out for different types of precursors. Different pressures again; lower pressures or higher pressure. High pressure is not higher than atmospheric pressure, but what is the pressure that you would like to use, that is also important.

You also have some other parameters such as the concentration of your feed gas and the residence time of your feed gas typically is between 15 to 60 minutes, all of this has been reported. Based on all of these parameters, then you can optimize the growth of your carbon nanotubes and the rate of the growth of the carbon nanotubes. Also the carrier gas can become important.

And so all of these factors similar to any other CVD reaction, you can perform the optimization. another closely related material is vapor grown carbon fiber. We can have fibers also through CVD process.

So, if you keep on increasing the size of your catalyst, then at some point, it is more energetically favorable for the fibers to form because you can have single-walled or multi-walled carbon nanotubes. But if there are way too many walls, then there is also an interaction between the walls between these sheets.

Because after all they are carbon sheets and they definitely influence each other when it comes to the formation. Then of the overall geometry that is more favorable then it becomes more like a fiber. So, a solid fiber rather than a hollow fiber or a tube-like structure. So, at some point, you start getting carbon fibers.

Now, there are also some other optimization processes that you can learn on your own. For example, you can create a magnetic field because you see that the catalyst particles that we are using are typically these magnetic-type metals; most of them have ferromagnetism.

So, nickel, cobalt, and iron. So, you can even use magnetic field to align your carbon nanotubes. You can also use certain other parameters in order to improve the quality of your carbon nanotubes. Of course, you can keep on reducing the size of the catalyst which definitely will help you in reducing the diameters of your tubes.