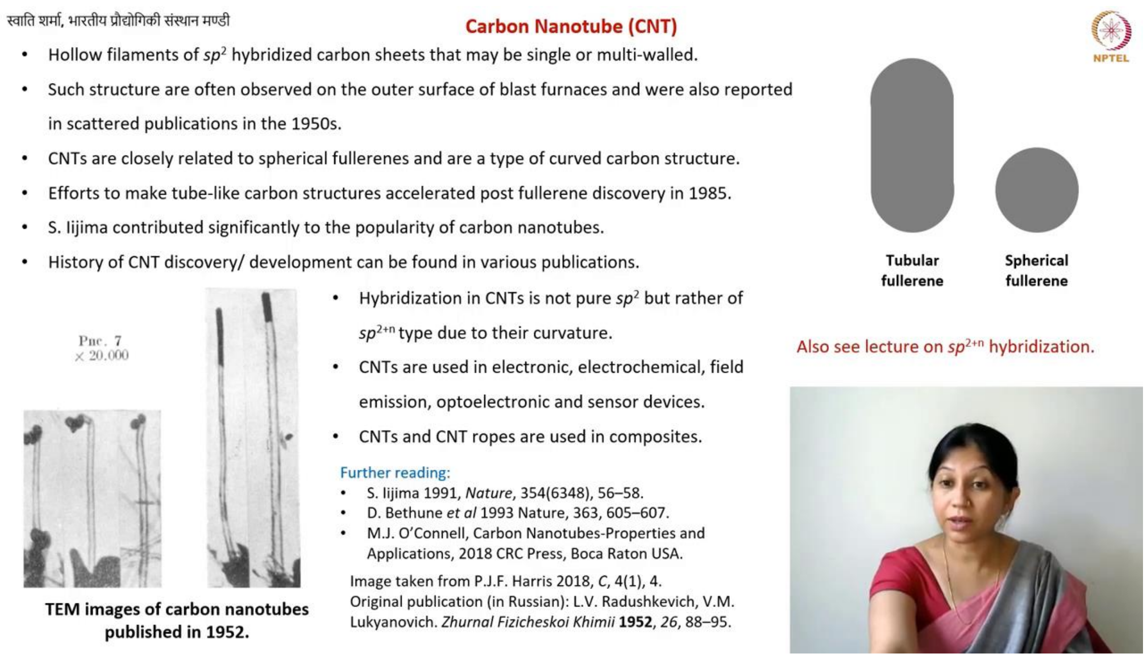
Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 48
Carbon Nanotube: Introduction and Properties

(Refer Slide Time: 00:13)



Hello everyone.in this lecture, let us talk about Carbon Nanotubes. So, carbon nanotubes as the name itself suggest, they are hollow carbon fibers. So, what is a tube? Tube is a hollow fiber. You can also look at it this way that if you take a graphene sheet and you roll it up then what you get is a tube-like structure hollow cylinder basically that is what we are talking about. From the two graphene lectures, now you already know what are (n, m) notations and you also know that when you make tubes then you can have armchair type of tubes, you can also have zigzag type of tubes and you can also then have a mixture of the two, which is known as the chiral carbon nanotubes.

Now, we are still talking about single-walled carbon nanotube. So, whenever whatever we discussed the rolling up the graphene sheet then we are still talking about just one graphene sheet and then we roll it up. So, we get what is known as the single-walled carbon nanotubes.

Now, you can also have multiple walls means multiple concentric cylinders. We are talking about one cylinder, but we can also have multiple cylinders.in that case you can call it multi-walled carbon nanotubes. Again like all other carbon materials, this material also has a history. This material was also reported in the past, there have been publications in the 1950’s and 1960’s where at least hollow filaments were reported.

So, the name carbon nanosheets were probably not used, but hollow filaments were definitely reported. And you see whenever there is vapor of carbon and there is also some metal nearby and there are high temperatures.

I mean, when we say vapors of carbon, typically you are cracking a hydrocarbon or you are performing some very high energy let’s say, let us say manufacturing processes on graphite-like, laser ablation of graphite or any other type of carbon.

So, in that case, you may have these vaporized carbon atoms and they contain very high energy. So, at that time if you also have a metal catalyst present then 99 percent chance, you are going to get some sort of carbon deposits.

Now, if these catalyst particles happen to be particles and they happen to be in the nanoscale.in that case, the deposits on top of them will also be nanoscale. So, you can get these deposits and ultimately a tube can come up.

Basically this these kind of processes were also observed near blast furnaces in the past because in a furnace you typically processing metal and carbon is almost always present because there is some hydrocarbon that is always present. Sometimes, even if you are not intentionally using a hydrocarbon, but you use certain types of oils or you will use some sort of fuel for the furnace. So, some hydrocarbon materials always present.

And then you can find these kinds of deposits where you have carbon nanotube, carbon fibers, filaments that are hollow or not hollow. All of these kinds of structures can be observed and they have also been analyzed and reported in the past.

Let us get started with this.as I already mentioned all of this to you. This is one picture that I have for you from 1952. So, this is any transmission electron micrograph of hollow carbon filaments which was published in a Russian journal. So, here I have mentioned also. Recently it was published in a review article. So, I have mentioned both the review article and the original publication. The point is that these reports were already there in the 1950s and what is also interesting is that transmission electron microscopy also existed.

Actually, this electron microscopy has also its own history, already started in the 1930s and it was in a reasonably advanced form in the 1940s and 1950s.let us talk about carbon nanotubes. One interesting thing about it is that although for understanding the crystal structure, we often say that these are rolled-up graphene sheets because that makes it easy for us to understand especially in the terms of (n, m) notations and so on.

But chemically these tubes are more closely related to fullerene-like structures. Why? Because these are curved structures. We have curved carbon structures, this is one schematic of some spherical carbon structure, let us say Buckminsterfullerenes.

Now, you see this is your tube which is capped at one end. So, I am talking about capped tubes. Most of the tubes are actually capped at one or both ends, but you can also have open cylinder-like tubes. But when you have the cap, now you see this curvature in the bottom, the same thing that you see in the fullerene. What does this mean? This means that you have to have some non six-member rings, only then you will get this kind of curvature.

This is actually a type of curved carbon and in fact, that is the reason you will even find these statements that the carbon nanotubes are fullerenes. So, do not get confused. This is how we learned in this course that carbon nanotubes are a part of the fullerene family because of the fact that their hybridization state is not necessarily sp^2 type but of sp^{2+n} type.

That is why this lecture where we talked about sp^{2+n} type materials; you should also definitely go over it one more time. For you to understand that, if in order to have this kind of curvature, you should have some kind of sp^2. If you have completely sp^2 type hybridization then you are going to have completely flat structures. Here, it is also important and definitely in the case of capped carbon nanotubes we have some non six-membered rings.

But what about the hollow tubes which are open on both ends, just roll the graphene sheet. In that case, well there is a certain curvature because we are talking about the cylinder here. So, again in this direction there is definitely some curvature.

We still do not have a pure sp^2 type hybridization, we have still sp^{2+n}. However, in that case, the value of n can be much smaller. Compared to a completely closed structure, you are going to have the value of n much smaller, but you will not have a perfect sp^2 hybridization in the case of carbon nanotubes.

What else? The point is that I told you that carbon nanotubes and similar structures were observed on glass furnaces, but still dedicated efforts to understand carbon nanotubes and their utilization in the technological application that only started after 1985 because in 1985 fullerenes were discovered. So, Buckminsterfullerenes and that discovery really helped the entire carbon community.

Because it told us that curved structures can also be highly stable. So, when we saw fullerenes then people went back to carbon nanotubes like we also have seen a tube-like structure. And also by that time transmission electron microscopy had become a very common technique, although it did exist in the past also. But in the past only very few universities had TEMs, but then by 1980s and, it became more and more common technique.

Nowadays, pretty much many universities have TEM setups. So, after 1985, many people started working on carbon nanotubes. And especially one particular paper that is worth mentioning is the paper by Iijima. This paper was published in 1991.this paper actually helped a lot in making carbon nanotubes more popular. There are many other publications as well as I mentioned that, I will not go more into the details of the history of carbon nanotubes in this lecture.

But similar to graphene you can definitely find it. If you are interested then there are many resources that talk about the history of carbon nanotubes. The applications of carbon nanotubes, again I will not go into the details because there are so many applications of this material.

What you need to understand is we already know that the electronic properties of this material are interesting; something that can be conducting and semiconducting and if you join one conductor and one semiconductor then you can get these single element conductor semiconductor junctions.

There are so many things that you can do with it. There are a lot of electronic applications especially field-effect transistors, there carbon nanotubes are used a lot. There are various other different types of sensors that can be made using carbon nanotubes.

There are electrochemical applications; carbon nanotube can be used as single tubes as well as the bundles of tubes or the forests of tubes; when a lot of tubes grow together parallel to each other, then you get what you call a forest of carbon nanotubes.

So, vertically aligned carbon nanotubes, you can also get not aligned carbon nanotubes that will depend on your CVD parameters. So, we are going to talk about CVD after a couple of slides. The idea is that you can use carbon nanotubes for a lot of applications. What is also interesting is the mechanical strength of carbon nanotubes.it has been predicted that it is thousands of GPa, this has not been experimentally validated but there are scattered studies.

But the idea is that if you think about it when we were talking about carbon fiber. Because its fiber-like structure so, let us compare it with carbon fibers. Carbon fibers, why do they have cracks? And why do you have weak links and weak points? Because these are the points where you have voids or because you were deriving the carbon fibers from polymers by heat treatment of polymers. There is a higher probability of containing defects.

So, defects and voids are your weak links and those defects can come all the way from the polymer in the beginning itself if you had some lump of polymer or something like that. So, that is the reason, that is where your fibers can break. But that is not the case with carbon nanotubes because in most cases carbon nanotubes are prepared by bottom-up processes; this is an atom by atom deposition or if not atom by atom, at least it is smaller units coming together.

So, it is a bottom-up process, and in the case of bottom-up processes the defects are much less. And especially, when you have extremely thin walls whether it is single or multi-walled carbon nanotubes. You have very thin walls of these tubes, there it is not even possible for very large defects to exist. Even in the case of carbon fibers when as we keep reducing the diameter of the fiber at some point, the defects cannot be there anymore because that becomes a very high energy structure then.

So, that is why it has been predicted that carbon nanotubes have thousands of GPa that is the Youngs modulus. But some of it has been experimentally validated some not because you can imagine that you have these extremely thin structure single-walled carbon nanotubes that can be 1.72 nm in diameter. The aspect ratios are typically high for carbon nanotubes.

Even there have been reports of several centimeters long carbon nanotubes, but the point is that it is also a very sensitive thing. If you have single-walled nanotubes, if you have multiple-walled nano, already the properties differ a lot, also the electrical properties differ a lot.

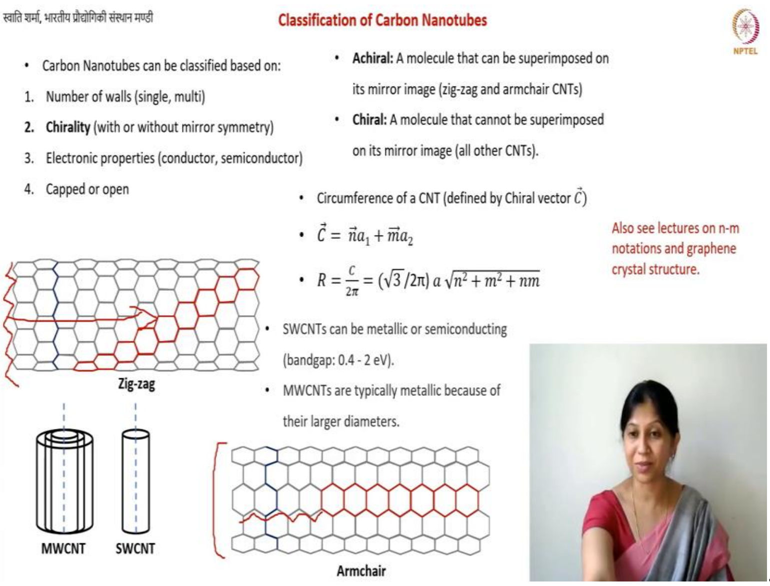
If you learn that when you have zigzag type carbon nanotube, in that case, when the phase of your tube is zigzag type the path that electron needs to take that is perpendicular to it; the paths during the electrical conductivity. So, for the zigzag type carbon nanotubes, you actually have armchair type of paths for the electron and for the armchair type of carbon nanotube you actually have a zigzag path where electron can easily travel. These type of carbon nanotubes are then pretty much always metallic and the zigzag type, however, can be metallic as well as semiconductor.

So, when I say zigzag type, the path of the electron is armchair type. And the chiral nanotubes can also be both semiconductor metallic.in most cases they are metallic because once the diameter of the tube increases. In that case, they are more towards being metallic rather than having a bandgap. So, all of these things we will discuss briefly, because of the mechanical strength of the carbon nanotubes whether it is validated experimentally or not, but the point is that carbon nanotubes are already extensively used in composite materials. So, you can add tubes directly like what we did with the short fibers or you can also make ropes of carbon nanotubes. Now you have strands.

And with the strands you can either break the strands and then make these nice preforms or you can directly add these strands inside your polymer matrix. So, you can also make carbon-based composites. Carbon nanotube reinforced plastics that is also a new and advanced area of research.

Here are some more publications. So, the one that I mentioned the Iijima's publication and also at the same time Bethune et al also published his paper in Nature. So, these two papers actually are very commonly cited when it comes to carbon nanotube.

(Refer Slide Time: 14:46)



Now, let us talk more about the properties, and then we will talk about the manufacturing. So about the properties of carbon nanotubes. I already mentioned that you have single-walled carbon nanotubes, you have multi-walled carbon nanotubes.

Now, the electronic properties can also be used for classifying your carbon nanotubes. So, couple of different types of classifications that I have mentioned here.one is based on the number of walls. So, here probably with this picture, it will become more clear that you have a single cylinder or you have concentric multiple cylinders.

Yes, one important thing is that these multiple cylinders if you see it as a cross-section, then they are not AB AB A type arranged. They are turbo statically arranged. So, there is no 3D crystal geometry also because it is a curved carbon structure.

So, it is difficult for such structures to have a 3D arrangement anyway. So, this is one type of classification. The 2nd one is based on chirality. We already talked about chiral and achiral type carbon nanotubes. There are two achiral types of carbon nanotubes zigzag and armchair. And the chiral ones are everything that is not zigzag or armchair or whenever it is a mixture of the two. Then, you can imagine there is a higher probability of finding chiral nanotubes.

And also zigzag and armchair geometries only exist when you have single-walled carbon nanotubes and not in the case of multi-walled. Often in most cases what you have is a chiral structure. Now, by the way, what is a chiral structure? What is achiral structure?

Achiral structure is something that can be super superimposed on its mirror image and on the other hand, chiral cannot be superimposed on its mirror image. So, this is the definition. So, basically sometimes people also explain it with handedness or not. But in terms of chemistry, this is the definition.

So, if you have the mirror image. So, you can imagine that for the zigzag type of carbon nanotubes you can superimpose it on its mirror image and that is why that is known as achiral and the others when it is a mixture then it is difficult, so the left will look right in the mirror and you cannot superimpose it.

So, again I have drawn these two images here and I was also mentioning before is that, if you have a zigzag type of geometry here. So, this is your zigzag type of carbon nanotube, but if an electron has to flow through this, then there is no zigzag path, if the electron moves in this direction.

So, in that case, you can see that the electron path is not zigzag. On the other hand, here you see the phase of your carbon nanotube is this armchair symmetry, but here you can find the zigzag path for the electron to travel during electrical conductivity.

Please also look at the lecture on graphene and also the crystal structure where we also talked about the (n, m) notations and so on. What else? This was the classification based on the structured crystal structure as well as the number of walls. What else?

We can also classify carbon nanotubes based on their properties. So, I already mentioned that you have either semiconductor-type carbon nanotubes or you have metallic type. This is already a very easy way for us to classify. However, what is also interesting is the reasons for carbon nanotubes to be semiconductors. We know a little bit about the path of the electron. We know a little bit about the zigzag and armchair type symmetries and where it is easier for the electron to travel.

However, one thing is that as the carbon nanotubes become larger in terms of diameter, as their diameter grows even if they are single-walled, although single-walled carbon nanotubes typically do not have much larger diameters because then their formation becomes difficult, their enthalpy of formation goes very high. But still whenever you have larger diameter carbon nanotubes, they tend to be conducting rather than semiconducting.

I will mention the band gap somewhere. The point is that the conductor nanotubes have 0 band gap and there is a higher probability for you to find them. And that is why this is also one way of classification of course, capped and open is also another way of classification. Now, you learned in the (n, m) notations lecture, how to calculate the chiral vector for a carbon nanotube.

(n, m) notations; again n is the number of times that you travel along the lattice vector a_1 and the other lattice vector whatever you can call it a_2. The other lattice vector whatever distance you travel along that that is your m. So, I am saying a_1 and a_2 are exchangeable that is why n and m do not have to be associated because you can take your vectors in any direction.it is a 6 fold symmetry in your graphene sheet.

See this is how you represent your chiral or circumferential vector

$$\vec{C} = \vec{n}a_1 + \vec{m}a_2$$

So, the second important relationship for you is how do you calculate radius of a carbon nanotube?

$$R = \frac{\vec{C}}{2\pi} = (\sqrt{3}/2\pi)a\sqrt{n^2 + m^2 + nm}$$

there is this particular formula that relates it to the n and m coordinates. Here I was mentioning that I will say I will tell you what is the band gap. It is 0.4 to 2 eV. There have been different types of carbon nanotubes, different lengths also can affect the band gap and different diameters of course, influence the band gap.

So, in different publications between 0.4 to 2 eV of band gap has been reported for carbon nanotubes. So, as I mentioned before these multi-walled carbon nanotubes because of their larger diameters they tend to be often metallic rather than semiconducting. Now in the next couple of lectures, we are going to talk about the Fabrication Techniques for Carbon Nanotubes.