Carbon Materials and Manufacturing
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Lecture - 09
Allotropes of Carbon and Their Classification

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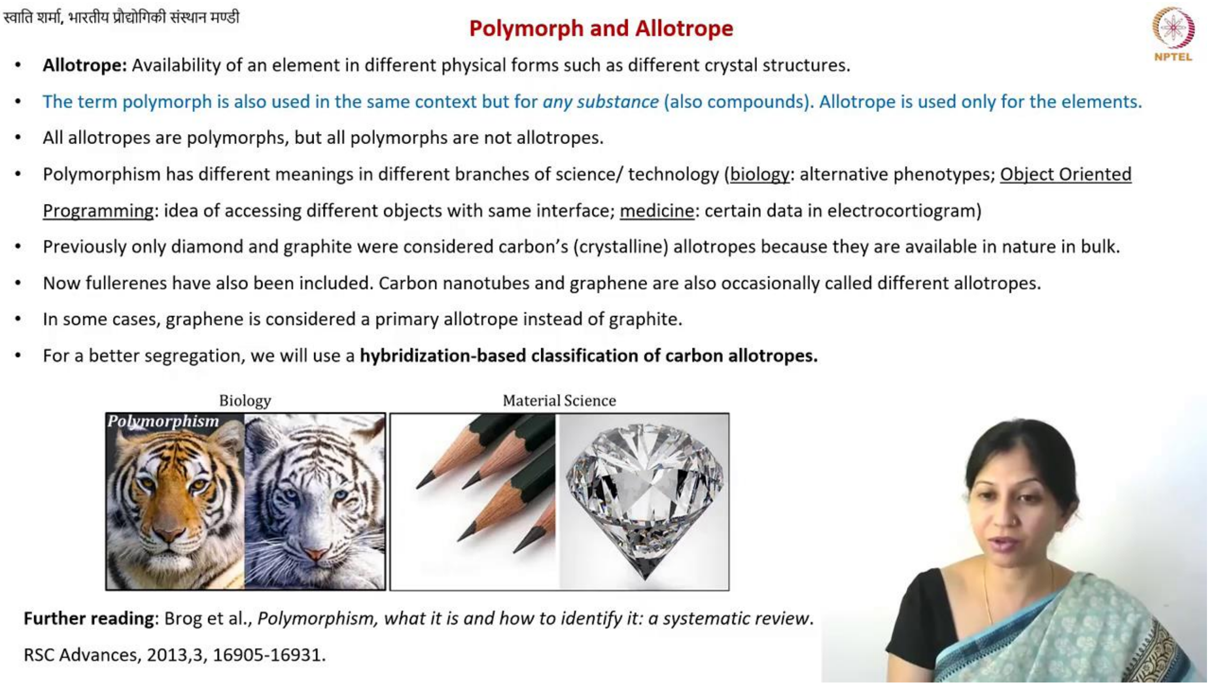

Hello everyone. This is a lecture about carbon allotropes. This is very interesting for us because whatever we have learned till now, all about the hybridization of carbon materials and different crystal structures of carbon materials that are going to be used here.

Now, we are trying to understand the different allotropes of carbon. What is an allotrope? If you remember allotrope basically means if an element is available in different physical forms and these physical forms are because of different crystal structures. However, you know the element, the chemical formula itself are the same, but physically they are different crystal structures. For example, we call diamond and graphite two different allotropes of the same element.

So, there is another word isotope which we learned a couple of classes back. Isotope is when we are talking at an atomic level, in fact at nuclear level then we then these are isotopes. While allotropes are at crystal structure crystal level.

Now, in this context you will also hear another term which is known as polymorph. So, you will also read that graphite and diamond are two polymorphs of carbon. So, what is a polymorph? Polymorph also indicates the same thing that you have different physical or crystalline forms, but the only difference is that polymorph is a more general term. So, you can also use it, for example to indicate some compounds.

But the term allotrope is specifically used for elements. So, this is the only difference. You can understand that all allotropes can be called polymers but not all polymers can be called allotropes. Now, we are going to use the term allotrope mostly in this particular course. One reason of course is because we are going to always talk about elemental carbon. The other reason is also that the term polymorphism is used very differently in different branches of science. For example, in the case of biology, you indicate different phenotypes as two polymorph. I should show this with a picture, the yellow tiger and the white tiger are considered the genetic polymorphs of each other.

Similarly, in the case of object-oriented programming the idea of accessing different objects but with the same interface is known as polymorphism. In the case of medicine, you have a certain type of data in ECG which is known as the polymorph. In all cases; however, we are somehow trying to indicate that it is the same thing but the physical forms are different. The idea of being the same but difference is somehow indicated by the term polymorph.

But we are going to use the term allotrope in this particular course. If you are more interested in learning about the difference of polymorph in allotrope and how these terms are exchangeable used there is a review article that you can read.

Now, we come to the carbon allotropes. So, I think I told you before that when I was in school which was like 20 years ago, we were taught only diamond and graphite as the 2 allotropes of carbon. But nowadays fullerenes are also taught as the carbon allotropes which is good.

However, we should know that these are only primary allotropes of carbon and then there can be also many elements or materials which are in between and which have this spx hybridization state.

So, carbon materials are actually like a periodic table. You know that these materials should exist but there were so many materials, so many elements in the periodic table which were not discovered at that time when the periodic table was formulated, but people left some blank spaces for them and then later on. Now because we can already guess the properties or the type of those elements then it became easier to guess them or to find them and later on many of those elements were discovered.

So something like that is also true for carbon allotropes or elemental carbon forms. Now we know their different hybridization states and based on that we can have a large number of carbon allotropes.

However we have 3 primary allotropes which are diamond, graphite and fullerenes. You know that fullerene is not just one type of ball, one c60 i.e the buckminsterfullerene, is not the only fullerene. We know that we also can have a range of them we can have different sizes, different curvatures. And at some point the fullerene will not exist anymore, the structure will collapse. You should keep these things in mind also.

Graphite can have slightly graphite related elements or diamond can have diamond-like carbon which we will learn in this course. We learn about not just these different carbon forms but also their technological applications. So, now before we go into that, we need to understand how do we classify the allotropes.

One more interesting question is that should graphene be called an allotrope instead of graphite. are graphite and graphene different anyway? Yes they are different because graphene is the single sheet while graphite contains multiple sheets. Even the more important difference between the two is that the graphene sheets are randomly organized on top of each other while graphite has this ABABA type order in it and that is how you have the crystal structure.

Now we know that, but should we designate graphene and graphite as different carbon allotropes. This is an interesting question in fact, in the literature here and there you will see that there are you know 3 or 2 primary carbon allotropes and people say it is diamond and graphene and fullerene.

So, in my personal opinion it should be graphite and not graphene the reason is the graphite has a certain fixed arrangement of crystal which is not the case with graphene because graphene itself can have a lot of variations because they are randomly oriented sheets. So, they can be oriented in infinite different ways and also the definition of graphene is also not very clear it should ideally be a single sheet without any defects. But in many technological applications you will often not have a single graphene sheet, you will often have multi-layer graphene that will often have a lot of defects. So, this is something that we cannot completely define or at least we cannot reach a consensus that exactly this should be called graphene.

But for graphite, we know what is the crystal arrangement, we also know that how to process graphite, we know what kind of crystal faults it has, for example stacking faults or line defects it can have. So, we know so many things about graphite and also the fact that graphite is naturally available and we can mine it. So, let us call graphite and diamond and fullerenes as three primary allotropes. But of course, these are only primary allotropes that we know and there are many more carbon materials that can exist.

Now, we are going to use a hybridization-based approach for classifying the carbon allotropes. In fact, one of the biggest difficulties in teaching carbon is that there are so many carbon materials and if we directly start with the material, the properties and the manufacturability itself then we often cannot study other carbon allotropes in the same context. Then we end up studying only one carbon material and we cannot study or we cannot relate different carbon allotropes with each other.

So, we are going to do this hybridization-based classification after that we will go into individual carbon materials. So, in the next 2-3 slides, you are going to hear some names of carbon materials that you might not have heard before. Some of these are in fact very fancy names and this is a good question whether or not we should call them allotropes. But if you understand how they are hybridized and at a crystal level how do they look like then it does not matter whether you call them an allotrope or not.

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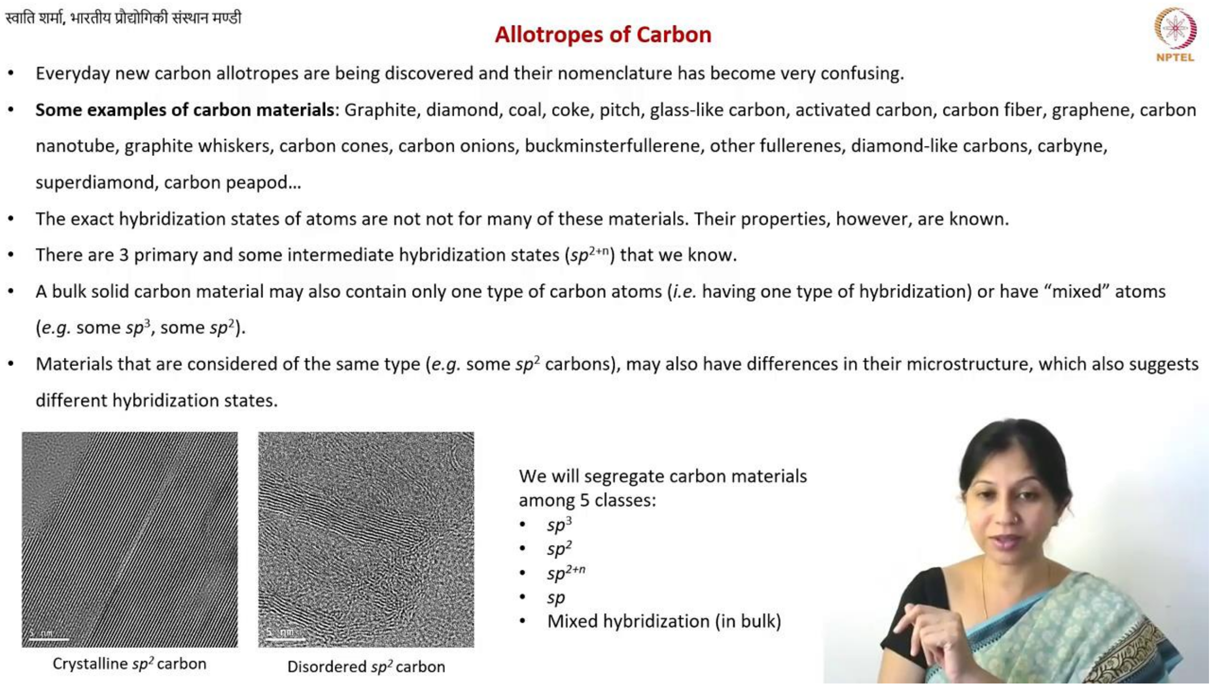

I mentioned before every day scientists are coming up with new different types of carbons. By the way here and there I will use carbons which you will not use probably for any other element like you will not say coppers or irons at least I have not heard that. But carbons is like a plural of carbon because you see there are so many carbon materials available in nature. Then you do not always have to say carbon materials, you just say carbons.

So many carbons are being discovered every day. We do not even know when we are discovering them if they were already existing in another form or a slightly different form. But we are definitely developing techniques of making them artificially and making these different types of carbons. And that is why you can say that every day a new name is being added to the list of carbon allotropes, but we know there are 3 primary ones.

And sometimes the nomenclature becomes confusing because you have even graphene and graphite. I would say the nomenclature is a little bit confusing here, but the point is that new types of carbon materials with different properties and probably also different hybridization states are being discovered every other day.

So, here are some examples and I would like you to do some more internet search and try to find out what are the new carbon materials or different carbon materials. You will see a lot of names, some of them would be even very fancy like when you say this is carbon onions. Then you will see or you will think or you can imagine about carbon onion that it should have some sort of layered structures. This is true and that is because of its similarities to the physical structure of onions as it was given the name carbon onions.

Now, if I ask you what do you think is the hybridization state in the case of an onion that is a difficult question because also then you need to know the exact curvature of the onion and not all onions have the same curvature. But because of the similarities with certain things, whatever is the best way to describe the materials, that is how the names are given and every day you will then see many different names coming up. Many elements are similar to graphene, many of them are made by folded graphene or curved graphene and so on. You can read about it.

What is not known is the exact hybridization states. The properties are known if you can physically make something then you can measure the properties this is always the case. Then you can also back-calculate the hybridization to some extent. So, you know 3 primary hybridization states and 3 primary allotropes.

Now, if I give you a bulk solid carbon, you can understand then I am not talking at nanoscale, I am not talking at micro-scale either, I am not talking about the individual crystal units or individual molecules, I am talking about a powder or a bulk solid or a piece of carbon. In that case if you are given a piece of diamond then if all the atoms are sp3 hybridized or most likely most of the atoms. If I give you a piece of pure graphite, in that case most of the atoms are sp^2 hybridized.

But there are many other carbon materials that will have all types of atoms in them. Even if you take coal as an example if I let us say remove the impurities from coal if I just take elemental carbon which is a kind of disordered structure. Now, when you say disordered structures you will have some crystalline parts and you have some non-crystalline parts. In the crystalline parts you will then have sp^2 hybridization but in the non-crystalline parts you might even find traces of sp^3 carbon, you might find traces of sp^2 carbon and you might find sp^{2+n} for sure especially if you have some curved structures which is the case with the disordered carbons. So you will have these materials, if you talk about them in bulk then you can call them mixed carbon allotrope. So, I have used here this terminology because I thought about this is the best way of describing such carbon materials.

So, I think we can just call them mixed carbon because we do not know what exactly is the hybridization state for each individual carbon in this bulk carbon form. And it is also very difficult because even each sample might significantly differ from the other.

So in this course, we are going to call them mixed carbon allotropes. For example, so here are 2 pictures where you would see the scale bars 5 nanometres. These are transmission electron microscope images. What can you see? You can see the microstructure of carbon in these images, Now you see both of these images indicate somehow an sp^2 type carbon. Whenever you see these lines, these are basically crystal planes. And these are sp^2 type planes, you cannot say just by looking at the image, you have to do some other calculations. You have to see what is the distance between these 2 planes. You know if it is graphite then the layer separation will be different compared to when it is not graphite, but slightly it is graphitic carbon.

So, you see these both are images of sp^2 type carbon, but one of them is crystalline and the other one is disordered. But even in the disordered image, you can see some of these lines. So these regions of that material are graphitized or are graphite-like. You will say in the first image you can say that most of the carbon atoms are sp^2 hybridized. So, we just call it sp^2 type carbon.

The second image, we will say is a mixed carbon atom form because it has sp^2 but it also seems to have other types of hybridization states that we do not know. We just call them amorphous when we do not know of them. So these are amorphous regions and crystalline regions that is how we call it, but within the amorphous region we do not know each individual atom what is happening to it. So, in the second image these types of allotropes we will call them mixed carbon allotropes.

Now we are going to have these 5 different sorts of columns y for the classification of carbon allotropes based on sp^3, sp^2, sp, sp^{2+n} because that is the known thing to some extent and then whatever is leftover we call it mixed carbon allotropes.

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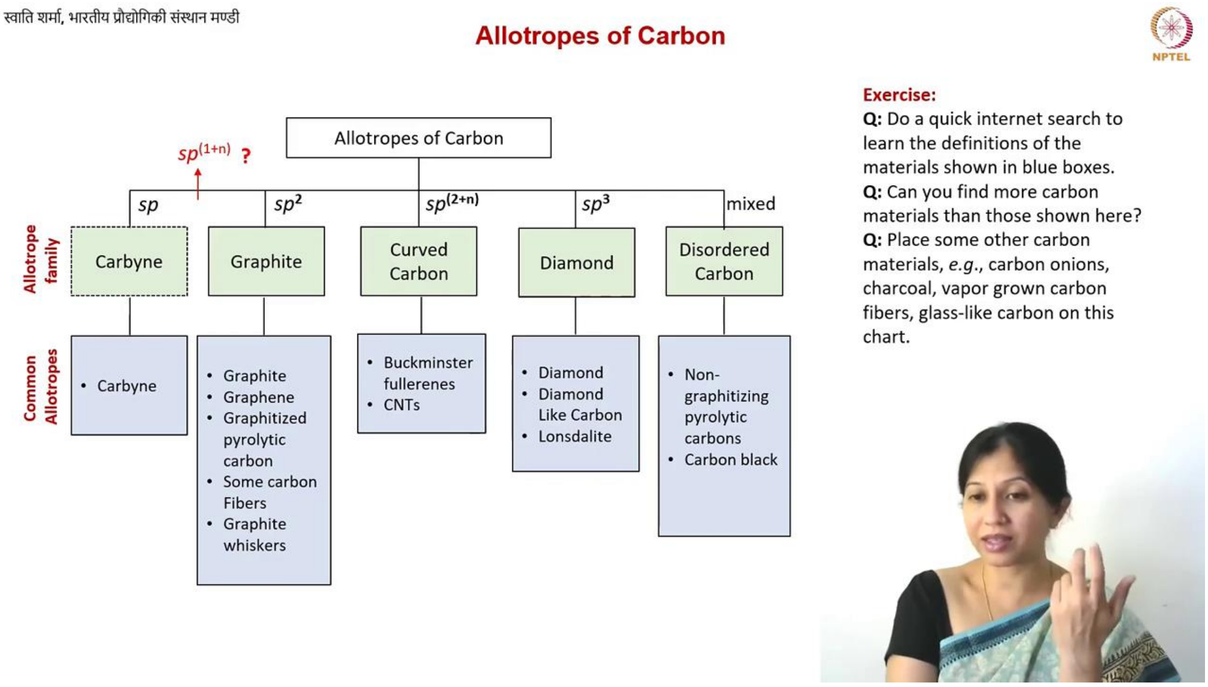

As I mentioned we have these 5 columns that I have prepared. And in this column, I am going to first write the family of allotrope. So, again this entire thing is a new nomenclature. I am not calling them diamond or graphite. But I am indicating that there is a graphite family and there is a diamond family and there is a fullerene family. So, we call them allotrope families where the primary allotrope of course is also the part of that family, they are the main member of that family.

Carbyne I have written it in this dashed box because this is still something that is being discovered right now. So, this is carbyne family. In sp^{2+n}, I did not write fullerene. I rather wrote curved carbons as I mentioned before because in order to avoid confusion that you will always think of fullerenes as ball-like structures. But curved carbons can be other curved structures as well, for example carbon nanotubes. Now, at the end we have the mixed carbon allotrope. In most cases mixed carbon allotropes are disordered carbons. So, that is the primary member of that family. These are the main members.

What about the further other members of that family? In the case of carbyne we do not quite know, so carbyne is the only kind of the known member of that family. However in the case of graphite, you have graphite as the main member of the family, but then we also have graphene which is the structural unit of graphite, but the only thing is that it is not as organized as graphite when it comes to bulk form. Now, you also have some other names here.

If I explain all of them in this lecture it is going to be a very long lecture. So the idea is that by the end of this course you will know about all of these different carbon materials. For now, out of interest you can just do a quick internet search and see what do these forms of carbon mean? So, pyrolytic carbon, carbon fibres but not all carbon fibres are graphitic. So, some of them are also disordered that is why I said some carbon fibres. There is something called graphite whiskers and there are many other elemental forms that can be put in the graphite family. So, you can learn about it on your own.

In the case of curved carbon of course the primary member is the buckminsterfullerene. As I said carbon nanotubes are more closer to graphite than to fullerenes, but since they are curved I have written it here. This explains that they do not have pure sp2 hybridization. There is some slight curve due to the curvature. They have slightly different hybridization states.

Now you know what is diamond-like carbon? It is a carbon that is like a diamond but still not diamond. So, this is also what we are going to learn in this course. There is also something called lonsdalite which is a form of diamond that is something between diamond and graphite, but closer to diamond. We are going to learn about all of these things later.

There is no primary member in the case of disordered carbon, but there are something called non-graphitizing carbons and we will learn about that. Non-graphitizing carbon is very important for us because when you make micro or nanodevices then you are pretty much always using the non-graphitizing carbon. Also for battery applications for supercapacitor manufacturing and so on it is mainly the non-graphitizing carbons that are used. So, this is also something that we are going to learn. In fact, you will often hear commercially that this is these are graphite batteries graphite. It is not really graphite, it is close to graphite. But it is this non-graphitizing carbon that may have parts of its structure as I showed in the previous TM image, parts of it are graphitized. They have this graphite-like crystal arrangement, but they are actually disordered carbons. So, all of these things we are going to learn. But the idea I hope you understand is that we have a certain allotrope family and we have different members and I think if we have these 5 different families then we should be able to put everything in here.

Even if you come up with a new carbon material then you should be able to place it on this chart so to say. As I mentioned before this is like a periodic table the elements of the forms that I have mentioned. They are the known forms and there may be many other known forms that I have missed out. But we can also always find more forms of elemental carbon and then we can put it on this chart and then maybe in another 30-50 years we will have a much longer list.

This is another interesting thing is that we know that there is sp^{2+n}. So, there is something between sp^2 and sp^3 that we know. But we do not know if there is something between sp^1 and sp^2. In my personal opinion that should also exist when we have something between sp^2 and sp^3. But the point is that right now we do not even know about sp^1 or carbyne type of carbon structures properly. So, first that needs to be discovered and then we will probably go into what is between sp^1 and sp^2. And in fact, there can also be something between sp^1 and sp^3 which is also an interesting thing. All of these materials are yet to be discovered. So, this is our sort of very basic periodic table of carbon.

Now, I would like you to do a few things on your own. First of all, do a quick internet search and try to find for yourself about these materials that I had written. Then you can try to find more materials than what we have on this chart because definitely there are more materials. And now you take some of these materials, for example I said carbon onions in the previous slide, but I don't think I have shown carbon onions here. So try to figure out what carbon onions are? What could potentially be their hybridization state? Are they of mixed hybridization state or are they primarily curved carbon type of carbon? If they have a lot of graphite-like structures then will you put them in the graphite family or will you put them put these materials in the curved carbon family? If you think that they have mixed hybridization or we don't know anything about their hybridization then maybe we could also put them in the mixed the disordered carbon family. Maybe it will be a good exercise if you do it by yourself.

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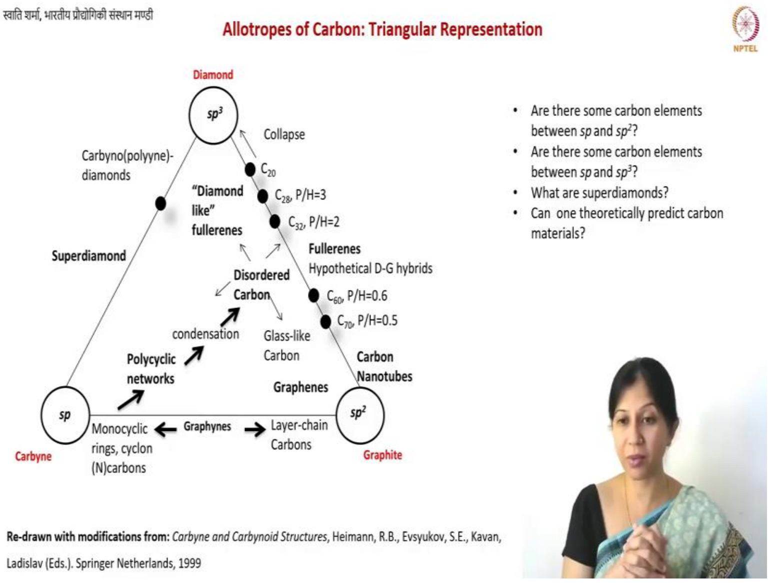

So, in the context of this hybridization-based classification of carbon allotropes we also have another diagram, which is a triangular diagram. What I showed in the previous slide is something I prepared in these different columns. There are 5 different types of allotropes which makes it easier because you have 5 primary families and then other materials you can fill in.

But there can also be more complex representations. Like I have this particular representation, was already suggested by someone. I have also given this reference. In the preface of this book, this kind of diagram was suggested which gives rise to some interesting questions.

First of all, do we have anything between sp and sp^3? So, I also said before, that we do not know right now know if there is anything between sp and sp^2 also. We only know these sp^{2+n} or fullerene structures. They are between sp^2 and sp^3. And if there is something that exists between 2 and 3 there should also be between you know 1 and 2, some something should be there. But, should we also have something between 1 and 3? That is also a good question.

So, we do know some. Here and there you will read about some super diamonds or graphynes and I am sorry, but these names are just confusing people a little bit more. I am not saying that it's wrong that we find these elements and it's very nice and it's very interesting. If we have very you know completely new properties or if we can even synthesize these kinds of allotropic forms of carbon. It is very good and wonderful but sometimes the names become confusing.

Because, now if somebody starts doing his or her research on graphynes. Now it is very important that that person first understands graphite and then graphene and then the allotropic forms of carbon and then the classification of carbon allotropes then only after when you know this picture is clear in your mind then you think of whatever is the new thing.

You can give it any name, but what is more important that fundamentally in terms of hybridization you understand it. But, this anyway is a good classification because here we see that there is a possibility of finding something between sp and sp^3 or sp and sp^2. And we do not know them yet and these are found in recent. Maybe one of you in the future will find one such new allotropic of carbon.

So, these are some interesting questions that arise. We also do not know much about these super diamonds. I also do not know some of the names that are written here because as I said that these terminologies are a little bit confusing and I may not know these materials by their names. I do probably understand how they look like and what should be their property. But I may not really know the names because the names are being coined every other day. You guys do not get confused about it. The point is that it will be nice if you can try to Google or try to do some little internet search about these names and then figure it out for yourself what is what.

Now, the most important question here is that whether can we actually have this kind of chart where we can have a periodic table-like thing, where we can discover further forms of carbon and we can fill in the gap? So can we do that? Can we actually make them? Can we synthesize these kinds of carbon materials? That is question number 1.

Question 2 is that if we cannot synthesize them can we at least theoretically predict them? I personally think yes if we understand the hybridization then you know you can definitely predict new carbon materials.

And then at some point, they may or may not exist because it is quite possible that theoretically they are possible but in reality, their energy of formation is too high or they are very unstable. But at the same time theoretically, it should be possible to predict.

So, these are the questions that you can also think of. The very idea in this lecture was to tell you the best way to classify carbon allotropes and to clean up the mess a little bit when it comes to carbon materials. The best option is to classify them based on their hybridization states.