Carbon Materials and Manufacturing
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Lecture - 44
Graphene: History and Nomenclature

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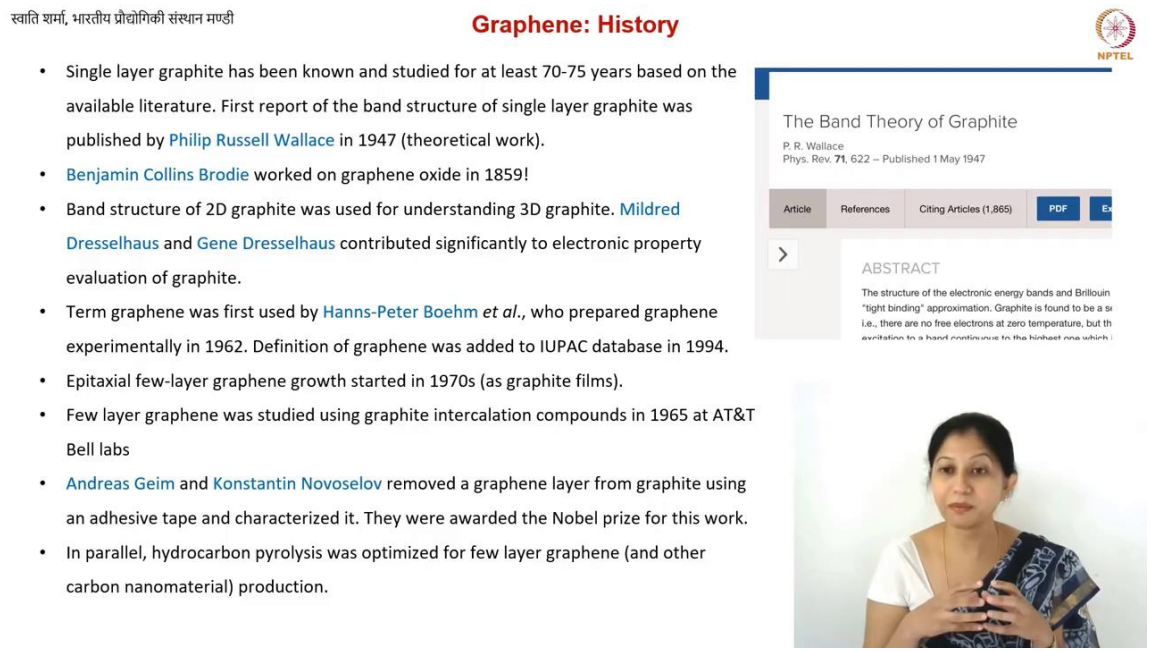

Now, coming to the history of graphene. This is a very important topic for all the carbon scientists. Single layer graphite has been studied for a very long time because first we need to understand a property of single layer, then understand the properties of graphite or then translate those properties to graphite, and the effect of pi electrons. This is also important for a lot of hydrocarbon materials.

The first time it was studied, not necessarily what you call graphene nowadays, but what is known as graphene oxide and reduced graphene oxide. This was studied by Benjamin Brodie in 1859. But the first paper on the electronic properties of single layer graphite was published in 1947.

This still remains a very highly cited paper. And actually, if you are interested, it is a very nice paper about theoretical calculations of the band gap of graphene with very nice explanation. Now, coming to the work of Millie and Gene Dresselhaus, these two

scientists have also contributed significantly to the structure of graphene like sheets and carbon nano tubes.

This is the case with fullerenes, people started studying carbon materials which are not 3D. So, they do have sp^2 or sp^2 like sheets, but they are not 3D structures. One thing that we have now understood is that these materials are also very stable. In the past it was believe that anything that is 2D may not be very stable.

Last 30 years or so, we have been studying non 3D sp^2 carbon materials. And this includes a lot the range of carbon materials like the spherical structures, the tube like structures and also the sheet like structures. And then also single layers and multi layers and bi-layers, and how can you differentiate them using Raman spectroscopy.

So, the characterization of these materials has also been very interesting for scientists. Millie and Gene Dresselhaus have contributed a lot of literature. There are also books review articles and written by them that is also something that I believe everyone should read.

The term graphene, as I also mentioned that it was suggested or officially recommended by IUPAC in 1994. However, this term was also used before by Hanns-Peter Boehm and his team.it was used actually as early as 1962. It did become popular only in the late 20th century or early 21st century.

There are also some other studies. So, these are rather scattered studies, but you can find papers from 1960s and 70s which talk about few layer graphene. They also talk also about different you know fabrication methods. For example, epitaxial growth we will also talk about that. So, there are also papers from the 60s and 70s that you can find.

In 2010, the Nobel Prize was given to Andreas Geim and no Novoselov, this was given for the for discovering a new method of graphene preparation. And this new method is basically removing one layer of graphene using a scotch tape from highly oriented pyrolytic graphite. For developing this method, they were given the Nobel Prize.

So, all of these things were going on in parallel. Also, we have been developing the industrial methods of graphene production whether it is for the purpose of making

graphite or it is for the purpose of getting graphene itself. The point is that CVD methods and pyrolysis methods have been being discovered or being optimized in parallel.

So, this has also been going on for let us say 100 years. And now we have reasonably good methods to produce whether pyrolytic graphite at industrial scale. Then you can also optimize these methods to now get single and bi-layer structures because now that is more important to us. So, this is the history of graphene is very important for you to know.

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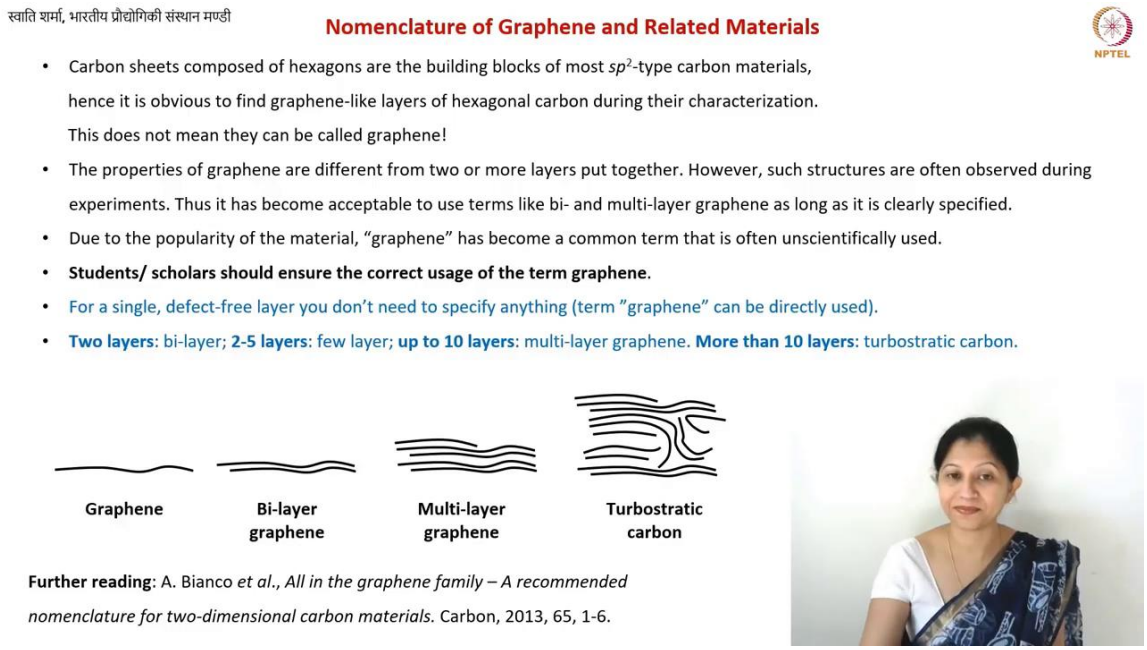

Since we are on the topic, I thought I could also introduce a few concepts of the nomenclature of graphene and related materials. And we do know that nomenclature is important. So do not say what is there in the name, I mean we all write our names on our publications. So, names are important right.

But what happens when it comes to carbon materials? It is not just graphene, even in the past graphite has been used in incorrect fashion. So, for somebody who is working in the field of carbon, the confusion of nomenclatures is kind of unsurprising. But, let us talk about graphene, so you know that a lot of bulk carbon materials especially graphite-like materials, highly oriented pyrolytic graphite or just pyrolytic graphite. These materials will very well contain graphene like sheets.

So, sheets of hexagonal structures sp^2 carbon, in some cases you will have defects or point defects. If you are taking a transmission electron microscope image, then you take the image of a very small and well-defined area in that case, there is a high probability that you will find some graphene-like sheets or sheets of perfect hexagon. But, that does not mean that this entire material should be called graphene even whether or not these sheets are bonded. So, if they have 3D structure or not or in the case of non-graphitizing carbons, you may have correct carbon structures, but you will also have some short-range order, so there you can also find some flat sheets.

So, in all of these cases, it is not necessary that these sheets are bonded with one another or not. The point is that when you see a graphene-like sheet in a bulk carbon material, then you do not call that bulk carbon material graphene. The term graphene should only be used for single and defect-free layers. We will come to that,.

So, you should also understand again why the nomenclature is important because when we are talking about the single layer, then we are talking about one very specific set of properties that is not valid for multi-layer or even bi-layer graphene. The effect of the pi band is completely different when we talk about single layer defect-free graphene, or when you have two layers; you do lose that effect.

So, this confusion is not right. If you tell somebody these are the properties of graphene then you should only be talking about single layers because those properties are not valid for large-scale materials. Now, as I mentioned that because graphene has become a very popular material that is the reason that is attributed to this confusion of nomenclature.

Anyway, if you are a research scholar or even for all the students I would say that you should use the term graphene in a very way. You should judge it for yourself what is correct, and you should definitely follow the recommendations. There have been several articles. I am going to provide you with the reference to some of these articles, and you can actually find out. Also you of course, always have the IUPAC gold book for your reference.

So, whenever there is confusion, please look up what is the correct terminology and only then use the terminology. Even if some very popular or highly cited publications have used the wrong terminology and you think that this is not correct then it is your responsibility to find out what is correct.

So, this article is the one that I was talking about it was published in the journal Carbon, there you can find out a lot of guidelines. So, I have not repeated all of them just because there is no point. You can find out these details in the article in fact, it is very detailed not just for graphene, but all the bulk carbon materials also which contain graphene. There are certain recommendations that you might want to follow.

So, however, I have provided a summary here. Again I mentioned that the term graphene without another word attached to it, just the word graphene and not graphene layer. Graphene should only be used for single-layer defect free hexagonal structures sp2 hybridized.

But if you see these sheets as I said in parolytic graphites or any other carbon materials, in that case you can say graphene layer. So, the term graphene alone should be used only when you are talking about single layers, there is nothing around it. So, these are single layers.

But if these kinds of layers are found inside a bulk carbon material, then you can say that graphene layer or graphene-like structures. I personally prefer to use the term graphene-like structures especially when I am talking about non-graphitizing carbons because I do not know exactly what the extent of defects is.

Maybe in the transmission electron microscope, I can see a certain type of defect or I can even see a defect-free layer. But it is quite possible that in the same material at another point or another location you will have defect-containing layers or you may even have voids, you may have a very strong curvature and so on. So, in that case I personally prefer to use the term graphene-like sheets or graphene-like layers.

But if you can find a good graphene layer inside a carbon material, you can use the term graphene layer. So, remember graphene and graphene layer are used differently. This publication will probably also explain this in more details. Now, I said that we use the terms like bi-layer, multi-layer, few layers layer, so how many layers are acceptable? In the case of two layers, sometimes also three, but typically two layers is bi-layer as the name suggests.

Few layer graphene is the term that is used for 2 to 5 layers. So, if this is 2 or 3 layer, even up to 3, people end up calling it bi-layer graphene. But then between 2 to 5, up to 5

you can call it few layers. But if you have more than 5 but still less than 10 layers, you would call it multi-layer graphene. If you have more than 10 layers of graphene, then the material should not be called graphene.

It should be called a turbostratic carbon material. Turbostratic again because of the turbostratic arrangement of the sheets. But if you have more than 10 layers, then you are not talking about this 2D material, then you are actually talking about the 3D material even if it is in the powder form.

So, in that case, you should just call it turbostratic carbon irrespective of the defects. its interesting that defect containing graphene has become a very common term. So, graphene is a single layer defect-free. In one of the lectures, I will be talking about what are the commonly found defects in these graphene sheets and some of them have also been well characterized and defined.

Sometimes these defects induce very special properties to your graphene sheets. So, in that case, if you have well-controlled defects or if you have intentionally created or induced these defects, in that case, it is alright to call it defect containing graphene. But if unintentionally you just got a lot of defects and you did not want them, in that case that material might not be graphene at all.

And again, when you say defect containing graphene and if it is a single layer you still call it defect containing graphene, or you say defect containing graphene layers in a bulk carbon material.

here I have also shown it with some pictures. So, the first picture here you see, this is what you will call graphene. You will see that it is not a perfectly flat sheet, and there is some waviness. There is some natural waviness when it comes to graphene structures because the bonds are always vibrating.

So, you do get some waviness that is not necessarily because of defects. However, when you have so many defects, means non-six membered rings and when you have these non-six membered rings then you have a stronger curvature. This kind of waviness can also be thermally annealed out.

This is Bi-layer graphene, two layers. Multi-layer graphene is an acceptable image of multi-layer graphene. So, you see that these are layered structures and they can be converted into graphite if we anneal them. But, in any case, if you want to use them also directly, then up to 10 layers can be called multi-layer graphene structures.

However, if you see something like this, where you do see these multi-layer graphene-like structures, but you also have some curved carbons or if you look at other locations in the same material you may find something else, in that case, you call it turbostratic carbon.

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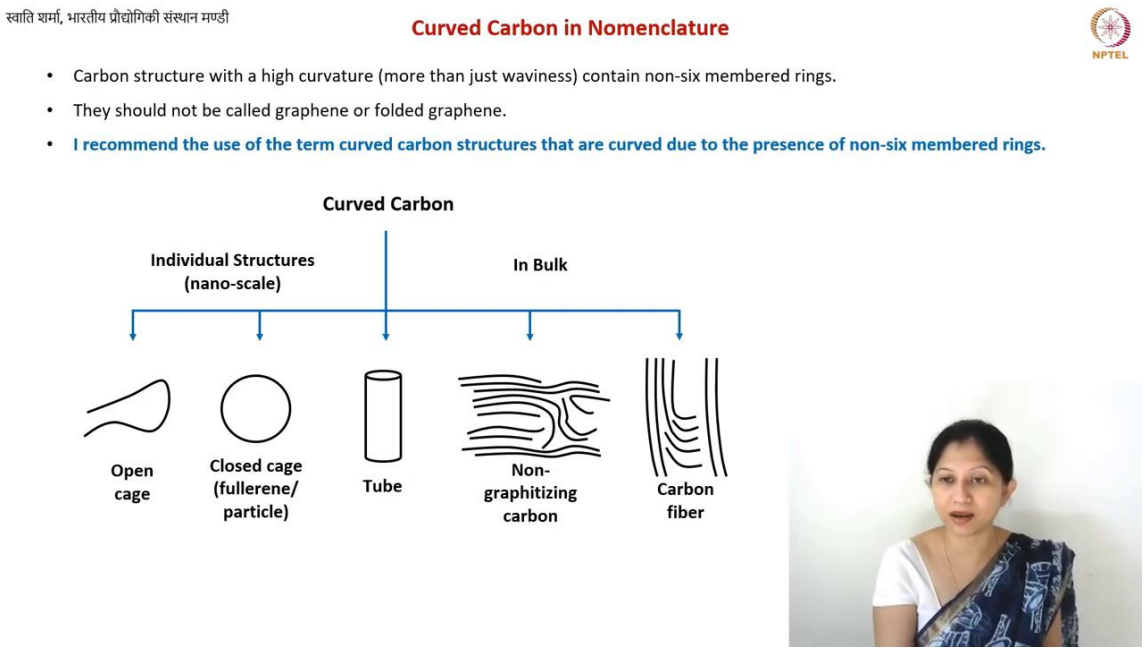

On this slide, I have mentioned the curved carbon terminology. So, this is something that I have proposed and that is why I do not impose it on anyone. You may or may not use it, and I am explaining it here because I have used it in this course.

I personally find it convenient to sort of group all the curved carbons together and that is because these curved carbons do not have perfect sp^2 hybridization they may have sp^{2+n} hybridization, so in order to explain all these materials which have sp^{2+n} hybridization the term curved carbons can be used.

So, this is again this is my rather personal recommendation. So, it is up to you if you would like to follow. If you are doing this course in that case this is important in the

exams and I might use the term curved carbon. The point is that you can find these kinds of curved carbon structures. Sometimes you do not have much curvature, sometimes you have a lot of curvature, sometimes you have completely spherical structures.

But this is beyond the waviness of graphene. So, remember that the term curved carbon should only be used when you have non-six membered rings in your structure and that is why you are getting the curvature. So, we are not talking about the waviness. You will find these kinds of carbon structures in nano scale materials and also in the bulk carbon material.

Here are some examples. So, the first one; the open cage structure that I have written or even the closed cage structure that I have written. These kinds of structures are also found in non-graphitizing carbons, but they can also be found individually when you are preparing graphene using chemical vapour deposition. You may end up finding these open cage kinds of structures, not fullerenes but open cage.

So, whenever you have a lot of defects in your graphene or find defects in your graphene-like sheets, in that case they tend to fold. And then when they have a very strong curvature, then you should not call them graphene even if they are single layers because they do have a lot of non-six membered rings in them.

So, these are then called curved carbon structures. Fullerenes, of course, are curved that we know. Tube like structures also have a certain curvature. So, those can also be then included in this category and in the case of non-graphitizing carbon as I mentioned already and electrospun carbon fibers you often see these curved carbon sheets. So, all of these materials then can be called curved carbon structures.

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Further Reading: History and Development of Graphene

- P.R. Wallace The Band Theory of Graphite. *Phys. Rev.* 1947, 71, 622.
- N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, and D. MacNair. Superconductivity in Graphitic Compounds. *Phys. Rev. Lett*. 1965, 14, 225.
- V. K. Challa, A. Pattammattel. Discovery of graphene and beyond. In *Introduction to Graphene Chemical and Biochemical Applications* 2017, Elsevier Inc.
- M. S. Dresselhaus, G. F. Dresselhaus, M. S. Hofmann. Raman spectroscopy as a probe of graphene and carbon nanotubes. 2008 *Phil. Trans. R. Soc. A. 366, 231–236.*
- H. P. Boehm, R. Setton and E. Stumpp. Nomenclature and terminology of graphite intercalation compounds. *Pure and Appl. Chem.* 1994, 66(9), 1893-1901. (IUPAC Recommendations 1994)

NOMENCLATURE AND TERMINOLOGY OF GRAPHITE INTERCALATION COMPOUNDS

(IUPAC Recommendations 1994)

Prepared for publication by

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Further learning (electronic properties and physics of graphene):
NPTEL lectures on relativistic quantum mechanics by Apoorva Patel, IISc, Bangalore.
NPTEL lectures on electronic theory of solids by Arghya Taraphder, IIT Kharagpur.

So, on this last slide, I will briefly tell you what are the reading materials.so all these publications that I talked about in the case of history of graphene, some of these papers are mentioned here. And these are review articles then in these review articles you can find the citations and read further.

And then it is very important I would like you to judge it for yourself whether you should call graphene a new material, whether you should say that it was discovered in 2010 or 2005 because the discovery is a big word. So, you should judge it for yourself what is the history of graphene. My job here is to provide you with all the relevant literature.

Now, if you are more interested in the electronic band gap and in the calculation of Hamiltonian as I had mentioned in before, if you are interested in physics of graphene, then there are already some lectures that are available on NPTEL. So, I do not want to repeat these properties.

But here a couple of lectures that are mentioned. Also, you will find small topics or lectures here and there on graphene materials or on crystal structure of graphene especially. You will find in the basic material science courses, material science engineering courses which I had mentioned also in my previous classes.