Carbon Materials and Manufacturing
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Lecture – 18
Highly Oriented Pyrolytic Graphite

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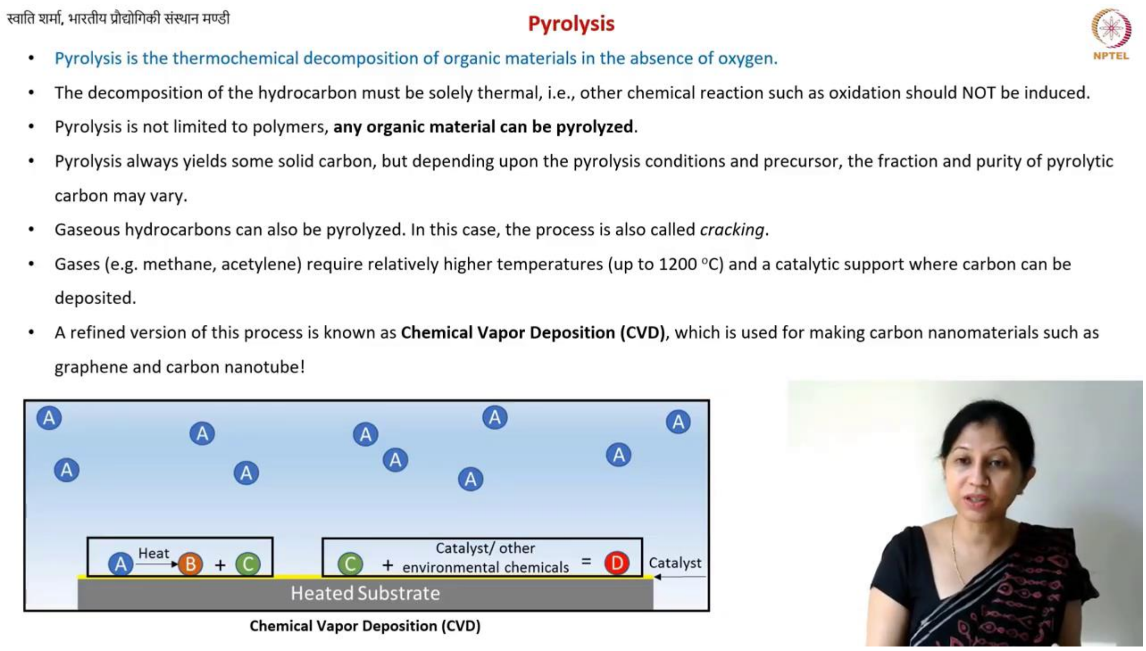

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Pyrolysis

- Pyrolysis is the thermochemical decomposition of organic materials in the absence of oxygen.
- The decomposition of the hydrocarbon must be solely thermal, i.e., other chemical reaction such as oxidation should NOT be induced.
- Pyrolysis is not limited to polymers, **any organic material can be pyrolyzed**.
- Pyrolysis always yields some solid carbon, but depending upon the pyrolysis conditions and precursor, the fraction and purity of pyrolytic carbon may vary.
- Gaseous hydrocarbons can also be pyrolyzed. In this case, the process is also called *cracking*.
- Gases (e.g. methane, acetylene) require relatively higher temperatures (up to 1200 °C) and a catalytic support where carbon can be deposited.
- A refined version of this process is known as **Chemical Vapor Deposition (CVD)**, which is used for making carbon nanomaterials such as graphene and carbon nanotube!

Chemical Vapor Deposition (CVD)

In the previous lecture, we talked a little bit about pyrolysis. You learnt that when you heat a polymer and then it gets thermochemically decomposed, that is something which is known as pyrolysis. And after that what we get? We get carbon, we also get some gaseous materials and some smaller hydrocarbons and at the end you get carbon. We learnt this technique in the context of graphite preparation. We just learnt that there is polyvinyl chloride and certain graphitizing polymers when they are pyrolyzed, they give you graphite.

Now, I am going to tell you more about this method, which will take us to the graphite preparation method. What is pyrolysis? You learnt it only in the context of solid polymers but can we also apply it to other organic materials? We are going into more details of this process first.

You learnt that, if you keep something in the furnace and you have no oxygen and then these molecules break and then leave, that is what you know as pyrolysis. But how do you formally define it? So, that was the process that you do inside a furnace, you call pyrolysis. But chemically what is the definition of pyrolysis? You can derive it yourself that pyrolysis is basically the part where the thermochemical decomposition of your polymer taking place.

Now, it is not really the process which you perform in the furnace, you should not call that pyrolysis. It is the chemical process that is called pyrolysis. But it is like any other process. For example, freezing is actually happening at the molecular level. But when you freeze something inside a refrigerator, you also call it freezing.

It is like this is the process that you are performing; but at a chemical level, the definition of pyrolysis is the thermochemical decomposition of any organic material. And that must happen in the absence of oxygen. Why is it so important that we do not have oxygen to prevent burning? By definition, this thermochemical decomposition must be solely thermal. What does that mean?

That means that there should not be any other reaction, such as oxidation. So, you are losing non-carbon atoms, but you must be losing them because of only heat treatment and nothing else. So, it should be purely a thermal process and that is why we make sure that there is no oxygen, except for whatever the polymer itself contains.

I have not written polymer; I have written any organic material and that is something very important to us. We use it for polymers, but this is not really limited to polymers, any organic material like it can also be gaseous. Methane is also organic material.

In fact, pyrolysis was initially done more for the gaseous hydrocarbons rather than for the polymers. So, the point is that any organic material, because it is carbon-based material will always yield some carbon after thermochemical decomposition or after pyrolysis. It does not matter whether it is solid hydrocarbons or liquid hydrocarbons. For example, pitch is your liquid hydrocarbon and any gaseous hydrocarbon; for example, methane, acetylene you can think of many gases. All of them whenever they are decomposed will always yield some fraction of carbon. The fraction may differ, but you will always get a certain amount of carbon.

Now, by tuning the pyrolysis conditions that we also learnt in the previous lecture for example, the rate of heating or changing the catalyst or changing the chemical properties of your precursor, now you can get a different fraction of pyrolytic carbon.

What is pyrolytic carbon? Pyrolytic carbon is prepared after any organic material is thermochemically decomposed. Now we are going to talk a little more about this pyrolysis of gaseous hydrocarbons. How do you heat gas?

Well, it is not that difficult. If you have a chamber and the chamber itself is heated, let us say about 1200 °C, then the gas will heat up. But it is not as easy in the case of gases, because also even if they heat up then what happens? Where does the carbon go? You need to make sure that you are somehow able to collect that carbon.

What we can indeed do is, rather than heating the entire chamber, we can have a substrate. What is a substrate? Any sort of solid surface where you can deposit something or pattern something that is known as substrate, for a lot of fabrication purposes, you use silicon wafers as substrates, or you can use also quartz substrates or metal substrates. So, anything, where you can collect something, is known as the substrate.

So, what we can do now? In a chamber, we flow one hydrocarbon, typically with a carrier gas because you want to also control the concentration of this hydrocarbon. So, you will have a carrier gas and the carrier gas should not be participating in the reaction, so that will be an inert gas.

Also if you want the carrier gas to somehow induce catalytic activities then you can choose a different carrier gas, but typically you will have one hydrocarbon that flows inside your furnace. Now, if you have a heated substrate that also serves as a catalytic surface then your hydrocarbon will only crack on top of or around that surface and not in the entire chamber.

If you crack the hydrocarbon in the entire tube of your furnace, then the hydrocarbon will also deposit on the entire tube of your furnace. You do not want that. You do not want to make your entire furnace full of carbon every time.

You will collect this carbon which comes from the hydrocarbons, that you will collect on catalytic support or catalytic surface which is heated.

Now, this process has been used for a very long time and not just for carbon, it has also been used for silicon, some other elements, in fact, compounds can be deposited by this method. A refined version of this process when it is used for not just carbon, but for anything is known as chemical vapor deposition.

You will hear this term a lot. Whenever you do any fabrication especially any microfabrication, you will hear the term chemical vapor deposition a lot. That basically as the name itself suggests, there is a chemical vapor and then there is something that is being deposited from it.

So, this I have drawn here, this is the schematic. What do you see here? There is a heated substrate and on top of that you see this thin yellow line, that is your catalyst and this is heated in most cases. Now, let us say you have a gas A inside your chamber. Now, because of the heat, purely because of pyrolysis that gas cracks into B plus C. Now, if you want C itself to be your final material, then you are good to go already.

Now, if you want something else, you can modify your catalytic support or you can also add some other support gases or carrier gases then you can actually get another chemical reaction, where this catalyst or some something else from the environment reacts with your material C and gives you some material D.

This is a very general form, as I said that this can also be done for non-carbon materials. But in the case of carbon, you call this process as pyrolysis and this kind of carbon is known as pyrolytic carbon. The carbon that you get from your pyrolysis of a polymer or pitch is also called pyrolytic carbon because pyrolysis is the fundamental process that is happening, it is the process of thermochemical decomposition of an organic molecule.

Now, what is very interesting is that, when you deposit the layers of carbon; what kind of carbon do you think you will get? I mean when we were learning about graphite and all, we talked about that whenever there is atomic deposition of carbon you get graphite or you get at least graphite-like carbon.

So, carbon tends to make hexagonal sheets, because that is the most stable form of carbon. Here also in this case if you have an entire film of, for example, copper, you will get some sort of carbon film and that film, however, does not have a 3D crystal structure. It has this random organization of sheets and those sheets also call graphene sheets.

If you have graphene sheets then they will contain a lot of defects, their sizes may not be uniform throughout. And if you control the CVD parameters to some extent; you can get if not single, maybe bilayer graphene's. It is like two layers of this entire material because you want to make the film as thin as possible.

But in that case, you may also get more defects; because some of the you have this dendritic growth or the film growth right and in some cases then the film is not properly grown or it has a lot of still, a lot of defects, then you stop the process. So, in that case you can get thinner layers; but then the quality of the graphene may not be so good.

But this is a process actually commercially used for making graphene flakes. Also what you can do is, if you change the catalyst then if instead of having a catalytic film like if you have catalytic nanoparticles, then you can only grow your carbon structures around that nanoparticle.

Now, if you also can change the shape of your nanoparticle, like you can have them spherical or polyhedron kind of structures, because that depends on also what metal do you want to use, typically you would use iron. Now, if you have these nanoparticles, then what happens? Then your carbon one-layer deposits and then the second one and the third one and so on and you may end up getting tubes or fibers.

This is what our carbon nanotube is. So, both carbon nanotubes, and as well as your graphene flakes are fabricated or synthesized using this CVD process. However, in today's lecture, we will talk about the graphene. And we will have more detailed lectures on carbon nanotubes.

Our goal is to make graphite now what do I have? I have a large sheet of copper and I have some of these graphene sheets deposited on top of that; however, they are randomly oriented, this is called turbostratic arrangement, this random orientation of graphene flakes on top of each other. Now, we have turbostratic graphene and we want to get graphite. How do you do that?

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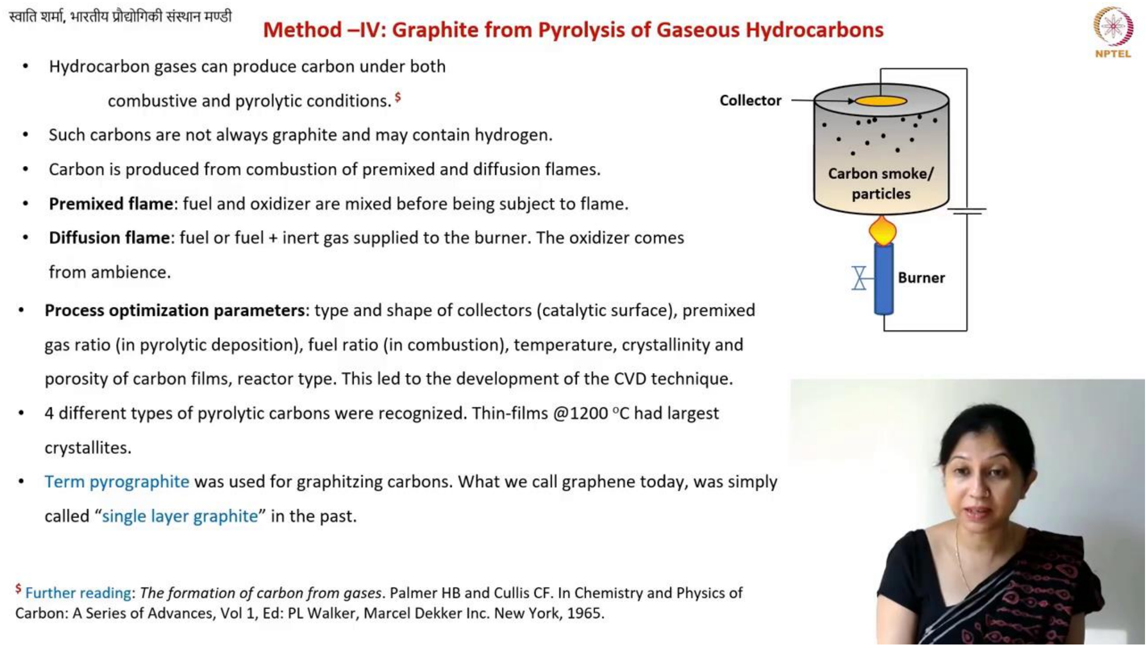

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Method –IV: Graphite from Pyrolysis of Gaseous Hydrocarbons

- Hydrocarbon gases can produce carbon under both combustive and pyrolytic conditions.[$]
- Such carbons are not always graphite and may contain hydrogen.
- Carbon is produced from combustion of premixed and diffusion flames.
- **Premixed flame**: fuel and oxidizer are mixed before being subject to flame.
- **Diffusion flame**: fuel or fuel + inert gas supplied to the burner. The oxidizer comes from ambience.
- **Process optimization parameters**: type and shape of collectors (catalytic surface), premixed gas ratio (in pyrolytic deposition), fuel ratio (in combustion), temperature, crystallinity and porosity of carbon films, reactor type. This led to the development of the CVD technique.
- 4 different types of pyrolytic carbons were recognized. Thin-films @1200 °C had largest crystallites.
- Term pyrographite was used for graphitzing carbons. What we call graphene today, was simply called "single layer graphite" in the past.

[$] Further reading: *The formation of carbon from gases*. Palmer HB and Cullis CF. In Chemistry and Physics of Carbon: A Series of Advances, Vol 1, Ed: PL Walker, Marcel Dekker Inc. New York, 1965.

How do you do that? You need to provide some sort of energy, some sort of heat, which will force your graphene sheets to get into a more stable form, which is graphite. Before we talk about that, here I will tell you a little bit of history of this pyrolytic carbon preparation.

It is not like it is a very new process. Often people think graphene is a very new material and it is advanced materials. Yes you can call it. But new is not really correct, because different forms of similar materials were always there. It's just people did not use them for technological applications. People did not think of it as a useful material, in fact for a long time.

Whatever you prepare by CVD that was just called carbon. People did not really directly use this pyrolytic carbon but now we do that in the form of graphene. What people did in the past is, they always tried to prepare graphite out of it because that was the goal. Graphite is like the better quality, best quality industrial carbon.

Hhowever, this pyrolysis process was very much studied and understood and scientists also tried to understand that will all organic materials give you carbon? And if yes, then what kind of carbon and what are the conditions? This whole optimization which led to the current day CVD of carbon materials.

So, how did it all start? Well, it is known that all the hydrocarbon gases will produce some sort of pyrolytic carbon; but there will also be some combustive carbon. What is combustive carbon? When you burn the any material as I said that there may be some oxygen always present also in the organic molecule. So, there will be always some combustive carbon and some pyrolytic carbon. We should clearly have these two things separated in our mind that they are not the same. Pyrolysis definitely is purely thermo chemical, but if there is some oxygen whether it is supplied from outside or whether it is from the polymer itself, there will be some combustion or some burning as well.

So, what you will get is combustive carbon. Combustion carbon is what you also get from your car exhaust, that is combustive carbon. So, you will have both types of carbons. Of course, this combustive carbon especially in that case, will have impurities primarily hydrogen. In the case of pyrolytic carbon, sometimes you will have some hydrogen impurity as well and which you need to remove at a later stage.

There was one experiment done long time back. I have taken it from this book. This references here is from 1965, chemistry and physics of carbon volume 1. I read about this experiment, this is one of the very initial experiments discussed even the today’s version of CVD, where carbon was produced in the premixed flames and diffusion flames.

In case you do not know what is a pre mixed flame? You have a fuel let us say any petroleum product or any gas which is flammable and one oxidizer. It contains oxygen but let us say we have air, and they are mixed before being subjected to a flame. And what is a diffusion flame? Diffusion flame is where you have fuel plus inert gas, there is no oxidizer. So, that is the whole point; the oxidizer is not supplied from outside, but it may come from the ambiance.

These are the two types of flames and the experiment that was performed, it looked something like this; there is a burner and then on top of that you just have a chamber, where you have either a premixed flame or a diffusion flame, but in both cases you have a inorganic fuel and you will get these smoky particles.

You will say that you also can get these kinds of particles from the candle. Yes, but if this is done in a very controlled way and the particles are collected and their concentration is understood. And then you can also try to make a circuit out of it. Why do you do that? Because you also want to collect the particle; in order to collect the particles, there should be some sort of attractive force. So, then you make a proper collector and that is how you collect your carbon particles. Now, you try to optimize this process as I said. This setup is for optimizing the process and what are the parameters? You can try out different collectors. That is how we have come to the modern day's optimum collectors for graphene and carbon nanotubes because these kinds of experiments were performed, where a lot of different catalytic surfaces were tried out.

Of course, when you have the premixed flame, then you will change the ratio of the gases. Whatever is your fuel that is your that is the source of your pyrolytic deposition; so you will change the ratio of that.

You can also change the ratio of the carrier gas, you will change the temperature, you will optimize also what you achieve. Optimization means, every time you change the process parameter then you will see what kind of carbon we will get.

Now, what is the crystallinity of that kind of carbon and what is the porosity of that film and how long do I need to perform this experiment and at what temperature I need to perform that experiment? This electric circuitry that you see, that is also used for heating the substrate, the Joule heat.

You can also see what kind of temperatures you need, and this was the optimization that went on for developing the CVD and for developing the optimum pyrolysis condition for gaseous hydrocarbons. Now, in this kind of experiment, there were four types of pyrolytic carbons. They had different crystallinity. I've not given the details of all four types but the thin films that were deposited at 1200 °C that had the largest crystallites.

This kind of characterization is done by X-ray diffraction techniques, that we will learn in the characterization techniques. X-ray diffraction will basically tell you, what is the value of La and you can back calculate what is the value of Lc from there. By characterizing the material, this type of film was found the best quality film with the largest crystallites.

These kinds of the materials, at that time they were not called graphene. They were rather called either pyrolytic carbon and in some case pyrographite. When the material was more closer to graphite and when it had reasonably large crystallites then they were called pyrographite in the past. And the one that we now call graphene as I have mentioned multiple times that was just called single layer graphite.

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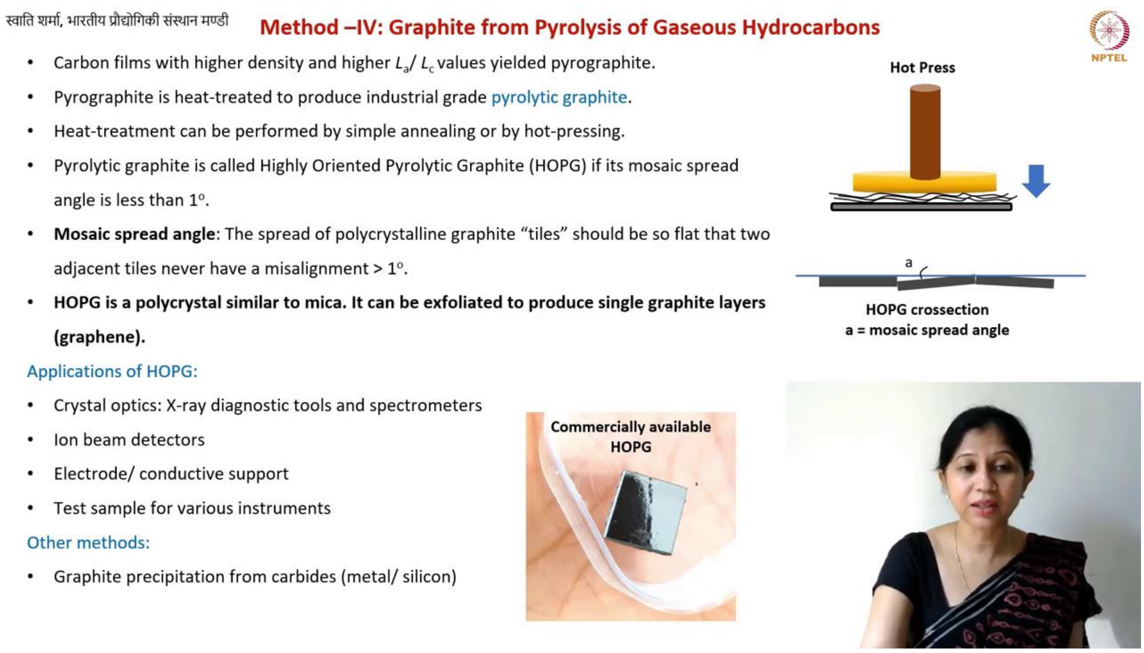

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Method –IV: Graphite from Pyrolysis of Gaseous Hydrocarbons

- Carbon films with higher density and higher L_a/L_c values yielded pyrographite.
- Pyrographite is heat-treated to produce industrial grade pyrolytic graphite.
- Heat-treatment can be performed by simple annealing or by hot-pressing.
- Pyrolytic graphite is called Highly Oriented Pyrolytic Graphite (HOPG) if its mosaic spread angle is less than 1°.
- **Mosaic spread angle**: The spread of polycrystalline graphite "tiles" should be so flat that two adjacent tiles never have a misalignment > 1°.
- **HOPG is a polycrystal similar to mica. It can be exfoliated to produce single graphite layers (graphene).**

Applications of HOPG:

- Crystal optics: X-ray diagnostic tools and spectrometers
- Ion beam detectors
- Electrode/ conductive support
- Test sample for various instruments

Other methods:

- Graphite precipitation from carbides (metal/ silicon)

Now we come to the method of making graphite from this pyrolytic carbon or pyrographite. If it has a very poor density and poor crystallinity, we will just call it pyrolytic carbon but if it has a reasonable La and Lc value, then you will call it pyrographite.

How do you make industrial pyrolytic carbon or industrial pyrolytic graphite from this material? Number one, you will choose the carbon films with high density and larger La and Lc. Why high density? Now, high density may not be a requirement for some of the graphene related applications nowadays.

But now here we want to make graphite. So, whenever we want to make graphite, we need to have a less porosity and high density of your film. And now this what can you do as I mentioned, you can provide it certain heat in order to get into a more stable form and in order for the defects to anneal out. What are the defects? Non six membered rings and also the organization.

So, you perform heat treatment of this kind of a pyrographite and then what you get is known as pyrolytic graphite. Now, how do you perform the heat treatment? Well, for a film the best option is to do it by hot pressing because that also provides certain force and certain pressure to your film. When you provide certain pressure, you will get flatter films and at the same time you are also providing it sufficient heat. So, it gets organized AB AB A fashion. Hot pressing of this kind of pyrolytic graphite films is done for getting the industrial scale pyrolytic graphite.

Now, this pyrolytic graphite material after the organization of your crystallites and when it has less than 1° of mosaic spread, then it is known as highly oriented pyrolytic graphite or HOPG. This is a very common material, you can actually buy HOPG and then you will use it for a large number of graphite related applications.

So, what is this mosaic spread first of all? You see this is the poly crystalline graphite material; you will get smaller crystallites. They will organize, but they will not be organized in a global way, they will be organized locally. Local organization you will call itis like a polycrystalline material. Here I have shown say three crystals; one is like this, the other one is slightly tilted, the other one is like that(refer to slides). So, it is a polycrystalline material.

Now, if you draw a line on the surface and then there is this angle where you have certain crystallites, which is not exactly parallel and the average of this angle throughout your surface is known the known as the mosaic spread angle.

So, this angle needs to be less than 1°; you can imagine 1° is so small and interestingly you can get graphite, the samples which are up to a couple of centimeters long in this way. It is poly crystalline type of graphite and the mosaic spread is less than 1°. So, that is what you call highly oriented pyrolytic graphite. You have these tile-like structures.

This is a picture of the sample; this is from my lab. You see this is the 1 cm*1 cm HOPG substrate that we purchase. This is how it looks like; you can see this is a very shiny and with very high purity and this particular the sample had 0.4° of mosaic spread,

Where did we start? We started from what is actually known as graphite CVD deposited graphene and then we converted this graphene by heat treatment into graphite crystal.

Now, what people also do is, they remove one layer of this this HOPG crystal to get a single layer of graphene. Single layer of graphene was otherwise very difficult from the

CVD. Of course, there are methods, we will talk about how you can get single layer or bilayer graphene from there.

But much easier method is to just purchase a HOPG sample and then by a tape or some other exfoliation methods, you can remove single layers of graphene from there. What is it? Exfoliation means removing something or some peeling something off.

This is one of the most common applications of HOPG nowadays, that it is used for exfoliation and for you know giving you graphene. But the actual industrial applications of HOPG are very much used in X-ray optics. Because I told you that the graphite is transparent to X-rays.

Now you can make a lot of diagnostic tools or little parts of the of your X-ray spectrometers that you can use but there you need good quality graphite and high purity with very small mosaic angle. So, HOPG is used a lot in X-ray optics.

You also use it for making ion beam detectors and various kinds of electrodes and conductive supports. You can see that this is the mica like material with layered structure and of course, this is also an interesting test sample for various instruments.

You have a lot of characterization instruments when you want to calibrate your instrument for example, for the angular spread, then you can use HOPG, because these samples have very small angles. So, if you want to make something very flat, you want to calibrate your certain parameters of your instrument; then you can also use HOPG, which is actually very frequently used for a as a test sample.

In general, HOPG is a very high quality graphite. You can get very nicely flat structures of relatively large sizes, which is otherwise difficult with other types of natural graphite. It is extremely difficult to get these kinds of samples and that is why this is one of the most sophisticated carbon materials.

So, this is also reasonably expensive, but this is one of the most important industrial graphite. I need to also mention that there are some other methods where you can get graphite, which is known as catalytic graphitization. When you are collecting these raffle sheets during CVD that has a catalytic support.

So, metal catalysts are always helping the growth of carbon materials or providing an orientation to the carbon materials. Now, in this case when you are making large scale graphite, you are not making a certain type of sample, but you are making bulk graphite; in that case when you are carbonizing a polymer or carbonizing any organic material, you can already add some metal nanoparticles into it or not nanoparticles, but even slightly larger particles, but you can add the powders of metals onto it. And on the surface of these metal particles; not just surface, but the area surrounding that surface, you have metal carbide forming. So, if it is iron, then you have our iron carbide forming around that surface.

And then this carbide further precipitates into graphite. And after you have done the heat treatment and you have now your bulk graphite material. Then you will leach out the material. So, you will get the metal. So, you will get rid of your catalyst afterwards.

This is one more method using metal carbides as well as silicon carbides, can precipitate graphite. We will not go into the details of this specific method, but these are all the methods of graphite preparation.