# Carbon Materials and Manufacturing

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## Lecture - 58
## Micro and Nano Scale Applications of Carbon Materials: Rigid and flexible carbon devices

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Hello everyone. Now, we are going to talk about some Micro and Nano-Scale Carbon Structures and Devices. We have already discussed the large-scale carbon materials, we have talked about making electrodes using graphite and glass like carbons. We have also talked about catalytic beds using activated carbons and so on.

Now, let us talk about some micro nano scale devices. So, if you remember from our micro nano fabrication class, that we discussed the scale at which we are talking about. So, 1 μm equals $10^{-6}$ m and 1 nm equals $10^{-9}$ m. For a device to be called a microdevice, the functional element should be smaller than 100 μm. And in the case of nano scale device, the functional element should be smaller than 100 nm. So, you can imagine that there are difficulties in making these devices. Now more than the material properties, the manufacturing becomes complicated.

Why? Well, because for large-scale manufacturing, first of all we already have a lot of techniques available. And also, whenever there is something that you can touch with your hands, slightly larger than that even that is possible. When you can operate things with your hands and when you can see the material or see the structure with your eyes naked eyes, in that case, it is much more convenient for us to make something.

But, if our material itself or the structure itself is in the nanoscale, there is no possibility of looking at that material without using a very high-end microscope. You can definitely not pick that material using a tweezer or you cannot hold it with your hands.

In that case, even though the fundamental principles might be simple photolithography or various other similar techniques. The fact that these materials are so small; it is not very intuitive how you handle them, how you hold them, how you deal with them. So, in that case, the manufacturing processes become a little bit different.

So, when we talk about micro nano scale devices, what carbon materials come to your mind first? So, first you think of carbon nanomaterials because they are of nanoscale. So, we can also make nano-scale devices using them which is correct.

You can also use them at larger scale, but you can also definitely make nano and microscale devices for sure, using carbon nanomaterials like graphene and carbon nanotubes and fullerenes and there are also some other materials that I have not discussed in this course, for example, graphite whiskers.

So, there are materials that you can use and then also you have fullerenes and that are embedded inside a carbon nanotube, these are called pea pod structures. There are still many structures that we did not discuss. We have discussed some primary structures. So, what else can be used at micro-scale if not nano, glass-like carbon.

So, glass-like carbon this is what we learned in our photolithography sections, that actually certain phenol formaldehyde resins can be photo patterned. And well, using the same principles as we did for the bulk, we could convert them into carbon and get our carbon devices, carbon structures.

Now, structure and device, you understand the difference. Structures are not functional but devices are functional. So, well glass-like carbon can be used for this purpose similarly activated carbon also. See in the case of carbon, we are using some polymer, patterning it and converting it into carbon; that is what we did also for large-scale structures. For graphite, we used needle coke or other precursors to carbon.

The idea is that use some precursor; give it a shape, that is what we do also in the case of carbon fibres. So why not in the case of micro nano scale. In fact, it is very easy to translate our carbon materials or to make micro nano scale devices using carbon materials. Because of the fact that a lot of lithographic techniques or micro nano fabrication techniques are compatible with polymers and polymers are our precursors; organic materials have been our precursors.

In fact, that is the reason it is indeed easy to convert. I was saying about activated carbons. So, if there is a precursor which give activated carbon instead of glass-like carbon. So, it goes through the charring process rather than the cooking process. In that case, that can also be used and we can use porous carbons also in the case of even small scale structures.

So, this is what we are going to discuss. Again, I would say like in the previous lecture that I am not going to give you too many examples because it is also not possible for me to cover all the examples in one place. But, we are going to at least compare different techniques and different carbon materials that can be used at micro nano scales. Here I have mentioned some more names graphene, carbon nanotubes, vapor grown carbon fibers again fullerenes and so on.

Now, let us come to the device fabrication aspects. So, the title of this slide says that these are going to be top-down approaches that we are going to discuss in this lecture. Top-down approach is your photolithography followed by carbonization or any lithography followed by carbonization.

Another, top-down technique if you can think of; well if you can use carbon fibers in your micro nano scale devices; well in the case of composite materials, they are used at a large scale. they are used definitely as CFRP and CFRCs.

They are used for making very large structures, but at the same time, you can directly use these carbon fibers for making micro nano scale devices especially different kinds of sensors and membranes; even electrodes because they are high surface area structures.

So, in that case, another technique that you can think of is electro-spinning. So, you can make something using electron spinning, it is a top-down technique; you are making fibers you are pulling fibres. And then we are removing the non-carbon atoms from it. So, it is subtractive.

Carbonization is actually always subtractive. So, these are the top-down approaches for making carbon-based structure devices. Here are some nice pictures that I have shown. This particular AFM tip is made of carbon. First, we made it using some acrylic polymer and this was fabricated using nanoscale 3D printing.

Now, you also have phenol formaldehyde resins. So, what are the precursors? The same precursors that you have for large-scale glass-like carbons can be used at micro nano scale. The only difference is that your heat treatment temperatures are relatively lower. So, you may not have the exact same properties as you have for large-scale glass-like carbons but you will have properties reasonably close to it.

Well, you can use not just phenol formaldehyde resins, also furan resins acrylic polymers and maybe some other polymer will give you a good carbon. There are certain hydrogels which give you a good quality carbon and whether or not it is glass-like carbon that is something you have to see.you have to perform certain experiments to see what is happening to your structures, whether they are getting deformed because of the coking process or not.

So, these kinds of experiments you can do and then figure out. But, definitely many high carbon containing organic polymers can serve as a precursor. You can get these kinds of structures. So, this is some lithographically pattern structure which then you convert into carbon via heat treatment. Heat treatment temperatures are relatively low and there is one more little challenge here, the fact that whenever you are performing lithography, you have a certain silicon wafer.

You have a substrate, on top of that you are doing your spin coating; you know the fabrication that you are performing is substrate-bound which means you need to place the substrate also inside your furnace when you are performing the heat treatment and that is why the heat treatment temperatures are also limited by the substrate, another problem is that you also have non-isometric shrinkage.

What does that mean? Typically, if you have something in space or a free-standing structure; it will shrink from all sides. But, in the case of surface-bound structures then you have one side does not shrink as good as the other sides, we had discussed this in the past anyway. So, these are the challenges that you have to think of. One interesting thing is that now we can use carbonization as a tool for converting micro-scale structures into nanoscale.

So, if our fabrication technique, can only give us micro-scale structures but now because we can here utilize the dimensional shrinkage and we can actually convert micro-scale structures into nanoscale. Why would we do that? To further increase its sensitivity or further increase the surface area.

Often, you would also use a combination of different techniques. So, for example, you can use electro-spinning with lithography. Here is an image that I have shown. You have two contact pads on top of that you see there is a fibre. now, the fiber was made using electron spinning and in such a way that you got only one single fiber. We do not need to go into the details of that and the other the electrode structures are made using photolithography.

And then you carbonize everything altogether. When you carbonize everything together, then you also have it is like a monolithic structure; monolithic means everything is made of the same material. There are no joints, there are no junctions, there are no additional contact pads. Carbon is electrically conductive, so you can also utilize all of these properties and you can also use a combination of different fabrication techniques.

There are also several cell culture scaffolds is one example where carbon also happens to be biocompatible especially this polymer-derived carbon, something that is similar to glass-like carbon. So, these kinds of materials can then be used for making cell culture scaffolds and substrates.

So, there are a variety of materials or variety of applications that are possible with micro nano scale carbon structures. You can also use the combination with other materials, for example, ceramics and metals in silicon and whatever you can also; because at micro nano scale often you are using multiple materials.

So, if you want to make a large-scale graphite electrode that is probably; just a cylinder of graphite. It will have some connections but you will typically fabricate just the graphite cylinder.

But, in the case of micro nano devices when you are making something typically you would like to make a complete device which means that you have to work with not just carbon but also various different materials which also leads to certain problems that we are going to discuss soon.

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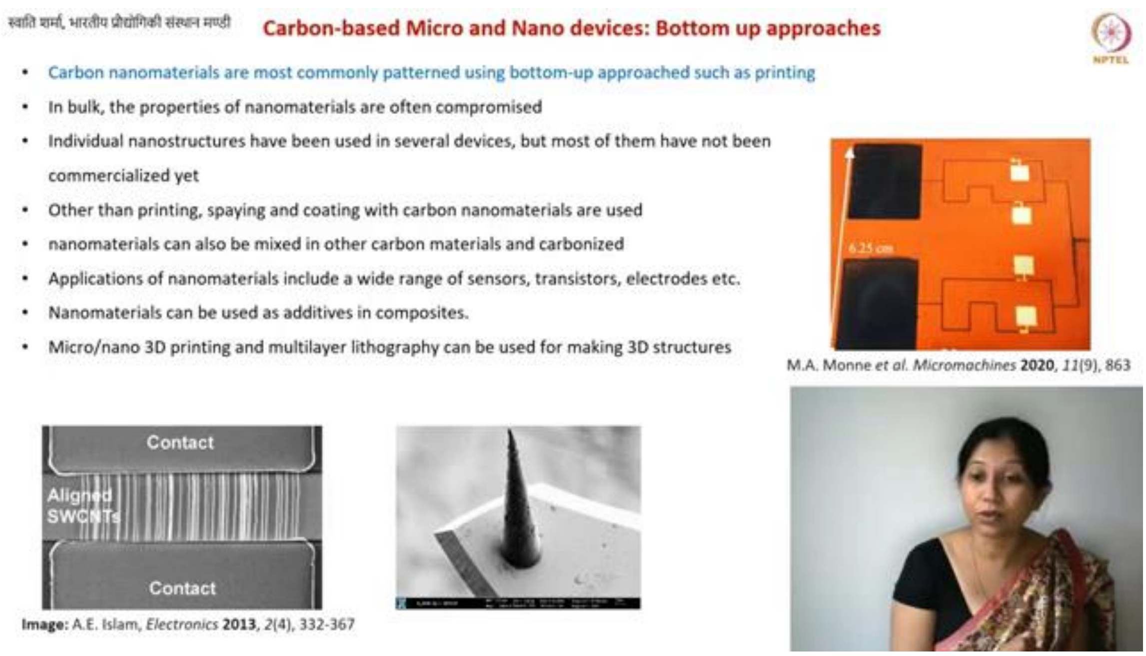



Now we are going to talk about the bottom-up approaches. Bottom-up means we want to build something up. So, what is the technique you can think of? Not lithography; lithography is top down. It is Printing, so if somebody asks you what is the most common technique for making carbon nano material-based devices. Well, that is printing. So, what you are actually doing is you are making ink; printing requires ink.

Now, this may not be your simple inkjet printing, but it may be some specialized type of printing, where the structure sizes are very small maybe micro-scale maybe even nanoscale. So, these kinds of printing techniques can use inks that are made of a certain pigment.

And that pigment is your graphene. You remember from the carbon black lecture that even 3000 years ago, people were using, especially in India, inks made of carbon; carbon was used as the pigment. So, this is something that is already well known. All you need to do is, to make sure that you have the right interface properties between your carbon nanomaterial and whatever is the binder or the medium that you have used.

So, the commonly used technique, one is this; you will see these two black patches in this image. This is an example of a graphene-based device. So, you can use graphene or carbon nanotubes or any other carbon material. You can make ink and then you can make large-scale patterns; also very small scale to large scale patterns can be made using these materials.

However, you know this, and also in all the nanomaterial lectures, I have mentioned this multiple times that when you are using a bulk carbon with nanomaterial in bulk, then you are often compromising the properties. So, you are not going to get the properties of single graphene sheets or single carbon nanotubes. When you are doing printing like this and when you are really making a bulk type of structure so, your properties will be definitely compromised; still you can get reasonable properties.

There have been examples also of single or a few carbon structures. For example, you see in this image, you have s two contact paths and between them, you have carbon nanotubes. So, you can actually also grow carbon nanotubes onto your contact. Especially, if it is a metal contact because you know that transition metals or at least some of them serve as a catalyst for carbon nanotube fabrication.

So, you can even mix these catalytic particles into your polymers or any other substrates for that matter, and then directly grow your carbon nanotube on top of it or you can use metal contact pads and then carbon nanotubes can be grown in an aligned fashion as well.

So, this is an example where you can use few carbon nanotubes. Also single nanotube and graphene-based devices have been fabricated, but none of them have been fabricated at a large scale, at least as on date. So, other than techniques that you can use for bulk material; also spraying and different kinds of coatings can be made using these kinds of carbon nanomaterials.

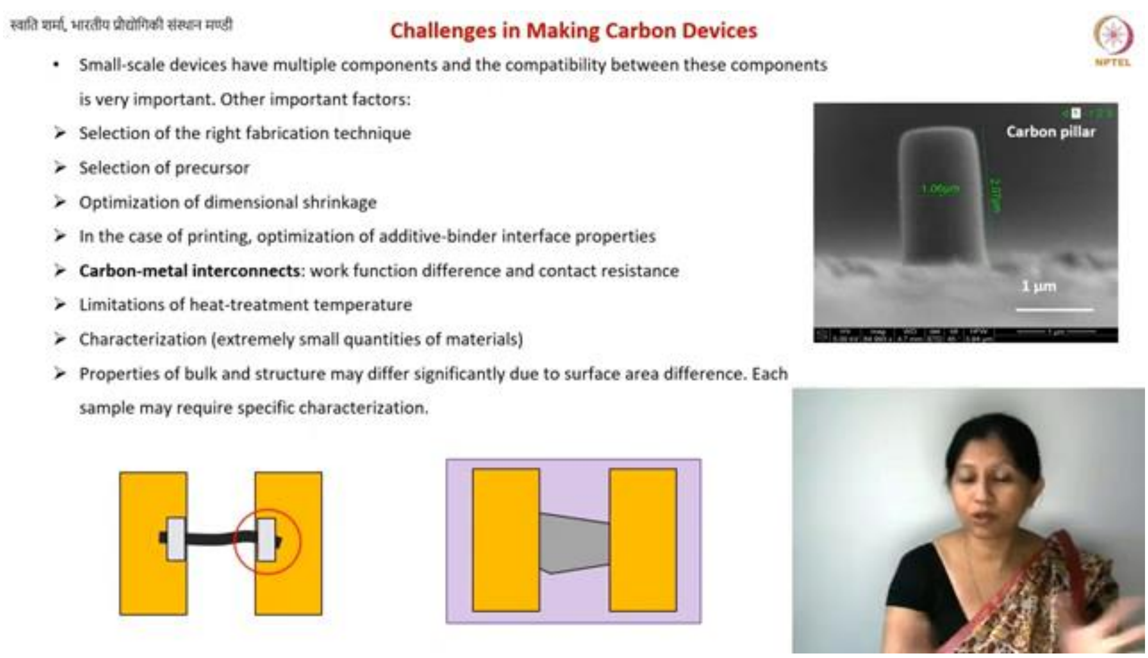
They can also be mixed in other carbon materials and then further carbonized; similar to how we make composites. The application areas are way too many. You can make transistors, you can make electrodes of various kinds; when I say electrodes they can be electrodes for sensors and again sensors. There are a lot of sensors biosensors, chemical sensors, optical sensors and surface sensors.

You can make a lot of things with carbon structures. Basically, what you have is a nicely conductive and mechanically strong nanoscale material that can be synthesized. In many cases, you can even purchase them. So, one application of carbon nanomaterials is also as an additive in the composite materials and there are many techniques.

Here again, I have shown an example of nano-scale 3D printing. In this case, you can use similar inks that you use for 2D printing; if 2D printing is possible then 3D is also possible. All you need to do is slightly change the viscosity properties of the ink, for example, in the case of two-photon lithography.

This is also a kind of 3D printing at nanoscale but you are cross-linking your polymer using a raised laser. A lot of techniques that are available at nanoscale are suitable for making polymer structures and polymer structures can be converted into carbon that is number 1. And number 2; you can also mix your nanomaterial into polymers and then further use these techniques, then you can also carbonize.

So, using a good combination of bottom-up, top-down; all kinds of techniques. Because often this happens in the nanoscale devices that you use a combination of various techniques. (Refer Slide Time: 17:20)



Now let us talk about some primary challenges when it comes to carbon-based micro nano scale devices. Not just for carbon but for all small-scale devices often it happens that since you are using multiple components in a very small area; the footprint is very small. So, you are using some metal contact pads, you are also using a silicon substrate and then you are using certain types of maybe glue; binder because you need to attach one material on top of another and everything needs to be done at micro nano scale under microscopes and many things are automated, but some things are done by hand.

Working with multiple materials, in itself is a challenge at micro nano scale. And definitely, that is also important for carbon materials a little bit more because carbon materials are very light. So, dealing with carbon nanomaterial is extremely difficult and that is why I would again like to mention think about health safety when you are working with carbon nanomaterials.

Because we do not know too much about the long-term effects of the presence of carbon nanomaterials inside your body, those studies are still ongoing. So, think about it but anyway, the point is that if you are wearing proper masks and everything then it is alright to work with these materials. But, they are so light that it is very difficult to handle them and also they get electrostatic charge.

So, it is very difficult to place them somewhere and to handle them. So, handling is also a little bit of an issue with carbon nanomaterials. Other than that what are the important factors? So, I have listed a few here, first of all, you need to select the right fabrication technique which could be a combination of two fabrication techniques. So, that you understand.

Selection of precursor; especially in the case of the top-down type processes because even though we have many polymers, but the selection rules are still the same that we had for large scale materials. So, you may not get good quality carbon because either the carbon content is too low in the polymer or you have too much oxygen in the polymer.

You know it takes a lot of carbon away. So, you do not get good quality carbon. The coking and charring mechanism, all the fundamentals of what gives you good carbon is also valid in the case of micro nano devices. So, the selection of precursors is very important.

Optimization of dimensional shrinkage. Also, in the large-scale structures that is the problem, but here the only additional factor is that you have a substrate. So, in 1 dimension you do not have the same shrinkage as in the other directions. But you can optimize it, you can do shape optimization even using a lot of CAD software. You can do this and then you can further accordingly make your polymer structure.

In the case of printing, one very important thing is the interface. So, it is like all the composite materials whenever you are mixing one carbon material with some polymer or any other material even water for that matter, but typically you will use the organic inks, organic binders and inks. In that case, the interface properties are very important otherwise your structures will peel off, or also you will definitely not get the same properties as you expect.

One very important thing is, what is known as the contact resistance or the interconnects between. Whenever there is one carbon material and then you have a metal contact pad. Why would you have metal contact pads? Because you need to complete your circuit, because ultimately you need to get some readout from your device. It is measuring some property and giving you some signal, but you need to have a circuit in order to receive that signal and to somehow convert it into the right format of the readout.

But to make these circuits, now you will need some contact pads. In the large scale, you will have wires and cables; in the small scale, you may often have these flat electrodes or even the wires are then printed like on top of your credit card like printed thin films of metals.

So, you will often have them in combination with the carbon materials and there what you have is something known as the work function; difference between carbon and metal. Work function basically means the energy or the thermodynamic work that is required to pull one electron out of material.

So, pulling one electron out of carbon and pulling one electron out of metal require different types of energies and that is why when there is a flow when there is a transport of electrons; where you do this is the interface? Again with between metal and the carbon material. There it may offer a lot of electrical resistance or not, but significant and something that does interfere with your signal.

Maybe if you have a sensor which already gives you very small reading and then you have contact resistance, in that case, it can often become a challenge and so this is one issue that needs to be solved. What you typically do is? Let us say here I have a metal or any substrate and then I have a carbon nanotube; somehow I was able to place it on top of that single carbon nanotubes.

But somehow, let us say under the microscope using certain specialized techniques I was able to place this carbon nanotube across this contact pad. But now, I need some other sort of glue or that glue could be another metal; it can be platinum, you can use ion beam deposition of this platinum.

But, you need to hold your nanotube there; this is where I am talking about the contact resistance. Because now you have multiple these structures and at that scale, you do not know if the region is good or not. So, in that case, what we can also do is take a silicon oxide substrate.

So, silicon oxide looks like this. At least it gives the impression of this purple-pink color because of the refraction of light, but that is why a lot of graphene pictures that you will see, look purple, but graphene is not purple; it is the substrate that is your silicon oxide substrate.

Let us say you have a graphene flake on top of silicon oxide and now what you can do is, from on top of that, you can then sputter your metal contact pads. But, in this case, you will see I have made much larger contact pads compared to what we had in the case of carbon nanotubes. So, you may have to play with these fabrication parameters a little, in order to get your optimum performance from your device and reproducible.

Altogether we have other limitations such as the heat treatment temperature that you already know that we cannot go above in principle 1400°C because if you are using a silicon substrate and 1400°C is the melting point of silicon. But, even you will not go to 1400°C because sometimes at lower temperatures also you can have thermal fatigue if you are performing very slowly heat-treatment process.

Generally, you will not go above 900-1000°C; in the case of micro nano scale devices and this is what I am talking about silicon substrates. Of course, if you use a substrate that can go to very high temperatures maybe you can use slightly higher temperatures. So, this is one limitation for sure.

One more interesting thing is that the characterization. So, whatever we have talked about XRD, Raman spectrum; they require a reasonable amount of your material, at least a few micrograms, in some cases even milligrams. So, that is very difficult. The electron microscopy is easy for nano scale material especially transmission electron microscope. In fact, it is more convenient compared to bulk materials because your sample is already very small nano scale.

You know the challenge of making TEM sample is relatively less. But, on the other hand for XRD that is a very important technique for us. The sample sizes are often very small and the problem is also that; here I have shown one carbon pillar which is 2 nm in height and 1 μm in diameter.

When you have a structure of that dimension; that means, it has a very high surface to area; that means, it will carbonize fast. And maybe at lower temperatures, it has more crystal energy than your bulk material will have because the defects can anneal out easily.

Now, what does that mean; that means, the properties of this pillar are not the same as the properties of bulk material which is prepared at the same temperature under the same conditions. So, I need to do specific characterization for that pillar; now if it is that small, it is really difficult to perform XRD and also it is substrate-bound.

So, these are some of the challenges that you need to deal with, maybe you can make an array of such pillars or maybe you can make a lot of them; somehow etch them out of your silicon. But, a lot of effort to have enough sample for using characterization techniques that can be used for large scale materials. You can also perform some modifications; perform single crystal XRD and so on, but all of them have their pros and cons.

I have written; the properties of bulk do differ from what you have in micro nano scale especially when it comes to something that is prepared by heat treatment.

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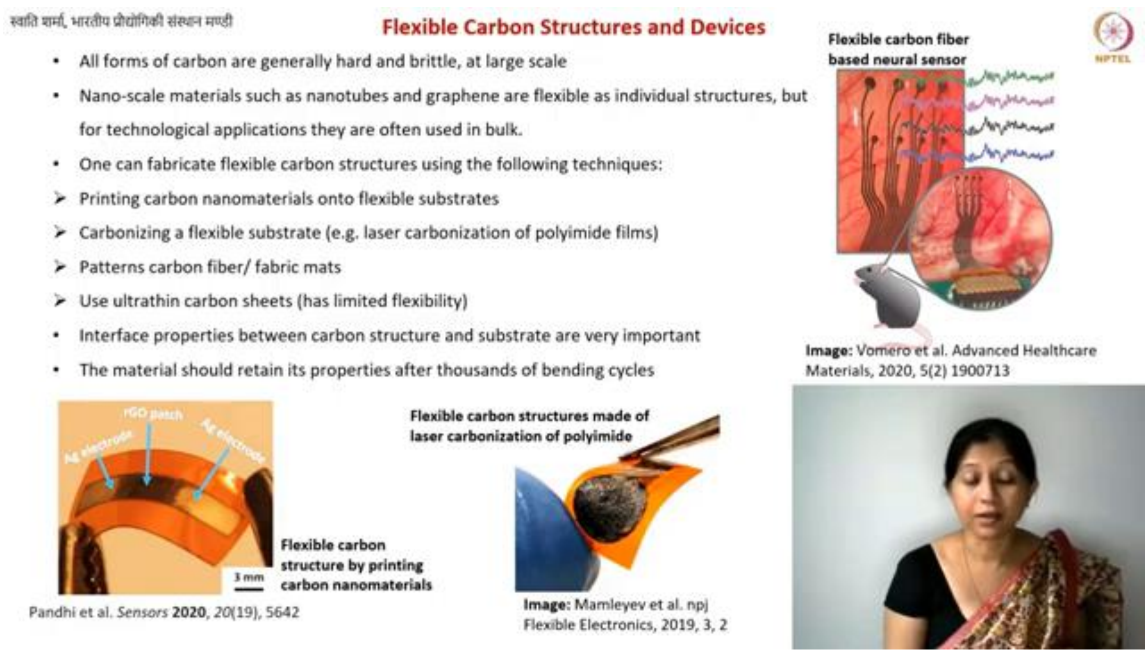


Finally, let us talk about some flexible carbon devices. So, this is actually not as complicated as you think, what is flexible? Flexible is anything, this thing is flexible, this is flexible. So, anything that is flexible and also wearable. Nowadays I see everybody wearing the watch which tells them how much do they walk; those kinds of devices. Those watches require a battery and their battery should also be flexible in principle, whatever electronics they have; some printed circuits should also be flexible only then you will have a perfectly flexible watch.

So, those kinds of devices. Also nowadays, you hear of flexible electronics. You will have your computer screen which can be bent at a certain angle, your mobile phone can have some flexible structure; those kinds of structures devices are known as flexible devices structure, sometimes also called bendable.

Sometimes they are also called organic electronics; do not get confused basically any polymer is organic and often the material that you are using in these flexible. So, the flexible substrate instead of silicon for example, if I use a flexible substrate that substrate is most likely going to be a polymer. And since polymers are organic, so that is why they are called organic electronics.

But, organic does not mean biodegradable; organic does not mean anything, just think of it as flexible devices, you can also potentially make them using inorganic materials. In fact, when they are making; when we read about flexible solar cells photovoltaics. A lot of often there are thin films that are made of inorganic materials. So, it does not have to be organic electronics. So, it is better to call it flexible electronics. How do you make something flexible with carbon, which is hard and brittle. Most of the forms of carbon are hard and brittle unless you are taking a single carbon nanotube or single graphene sheet yes that is wavy and that is flexible, but that is single graphene sheet, you are hardly using it in devices.

If you are performing printing then you are using the entire thing in bulk. So, and if you are using any large-scale carbon material that is going to be hard and brittle. Even carbon fibers, if you think of the properties of the carbon; the carbon itself is hard and brittle. It is the structure that we give to it when we pull threads out of it, when we make tubes out of it.

So, it is the large-scale structure that we give, that we make; that is what can be flexible. Carbon itself by nature is not flexible, but we do have a lot of flexible devices using carbon.first of all you do this printing right with nano scale materials.

Printing with an ink can be done also on flexible substrates. So, that is one technique actually used in making a lot of flexible carbon devices. So, that is technique number 1. So, let me also tell you all the techniques; the first one is printing carbon nanomaterials onto a flexible substrate. This is an example, I have found this picture somewhere.

Here you have graphene oxides, it is also related material. You can have carbon nanotubes, you can have graphene itself, multilayer graphene. So, you can make up ink and then you can print these devices and typically this orange colour substrate that you see; these are polyimide sheets. But you can also use any other flexible polymer even PDMS; any flexible polymer if you want to make flexible devices. So, that is technique number 1.

What else can you do? We always carbonized polymers and you see this polyimide substrate here. So, don’t you feel like carbonizing it? Yes this is what we can do. We can use something like a laser to locally induce heat and carbonize the polymer substrate itself. So, then you are kind of writing using a laser. Here is an example.

However, the property of carbon, the quality of carbon is not going to be as good as any of the large-scale carbon materials, even if you induce very high temperatures. The reason is that the process is happening extremely fast. When you keep something inside the furnace then you anneal it out at very low very slow ramp rates. So, 5 degrees centigrade per minute or even lower than that.

So, there you are providing your material enough time, all the gases, by-product, whatever is coming out of it; you give it enough time to release. Also you have some nitrogen in your furnace which pushes these by-products out; that is not happening in the case of laser carbon.

Number 1 — the process is very rapid, so it leads to a lot of porosity. Number 2 — these kinds of carbons have a lot of impurities because some of the tars and byproducts they redeposit. But, you can get reasonable properties and also reasonable electrical conductivity. So, this is another method of making flexible devices using carbon.

What else? You can make carbon fiber mats that you know from electron spinning and also from melt spinning. So, you know carbon fiber mats you know carbon fabric. What you can do is you can pattern it. Now patterning it in micro nano scale is not easy, it can get very complex. You may have to mask your structures with certain metal masks even and then perform reactive ion etching; but it is possible.

Here is one example, where you can you take this carbon cloth like structure and pattern it in the micro scale and then make this very highly flexible device out of it. So, this is a neural sensor made using this kind of carbon fabric. So, this is another technique. What else? You can also use ultra thin carbon sheets, you can get glassy carbon sheets that are very thin.

And they are relatively flexible, but there you of course, have limited flexibility. So, whenever you are making certain device then you often need to test how many times it can bend before breaking; and not just bend but it should retain its properties and often you will do these kinds of bending tests; like thousands of times then you will say this is a stable flexible structure.

And even when you are performing printing, this film-like structure should not peel off. So, this peeling off from the substrate is also one of the challenges. When I am talking about interface it is about the interface between the substrate and the pattern structure.

So, this is an important thing and as I said thousands of bending cycles, you need to evaluate before you can think of using this material for a regular application.