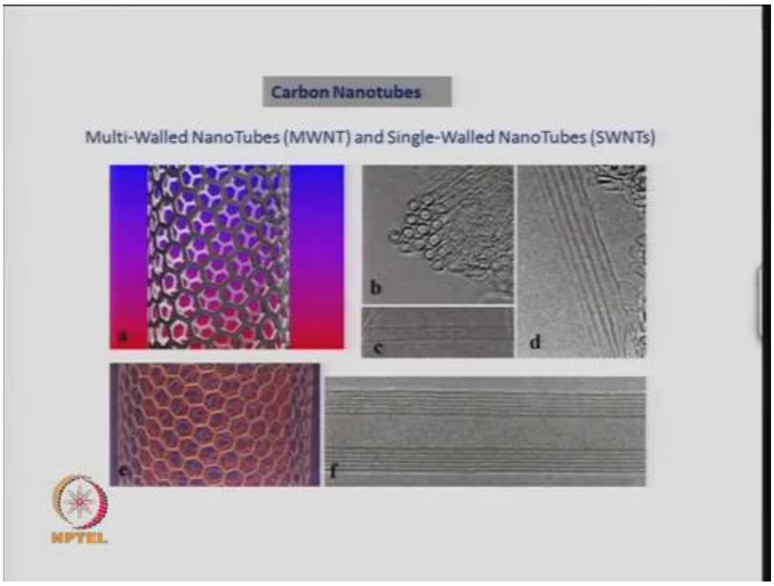
Nano structured Materials-Synthesis, Properties Self Assembly and Applications
Prof. Ashok. K. Ganguli
Department of Chemistry
Indian Institute of Technology, Delhi

Module - 3
Lecture - 17
Fullerences and Carbon Nanotubes – III

Welcome back to this course on nanostructured materials synthesis properties self assembly and applications. We are into the module 3, and today we will be discussing the third lecture of module 3. We started our module 3 with carbon nanotubes and we have finished two lectures on fullerenes and carbon nanotubes, and today is the third lecture which is the, which will complete the section on carbon nanotubes and fullerenes.

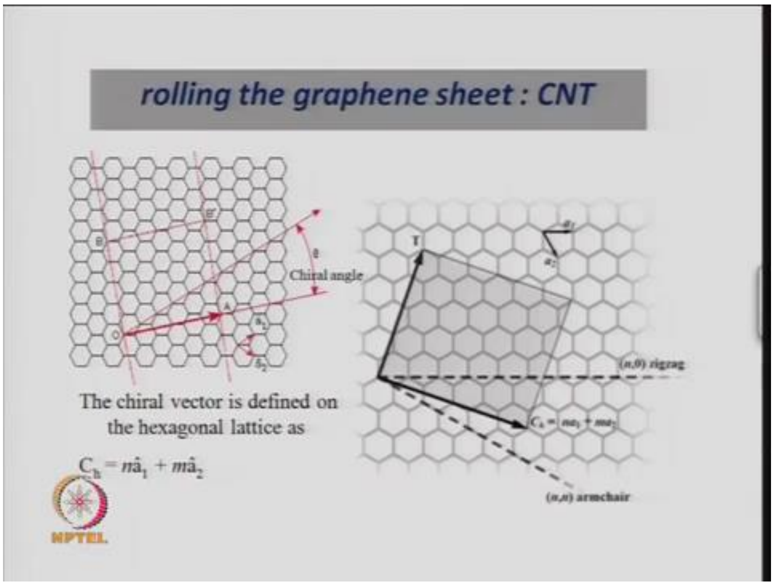
(Refer Slide Time: 01:02)



So what we discussed briefly was about different types of nanotubes, both multi walled nanotubes and single walled nanotubes. And these nanotubes as you see are made up of hexagons of carbon, and when these nanotubes the cylindrical part has to closed, they have to have pentagons and heptagons.

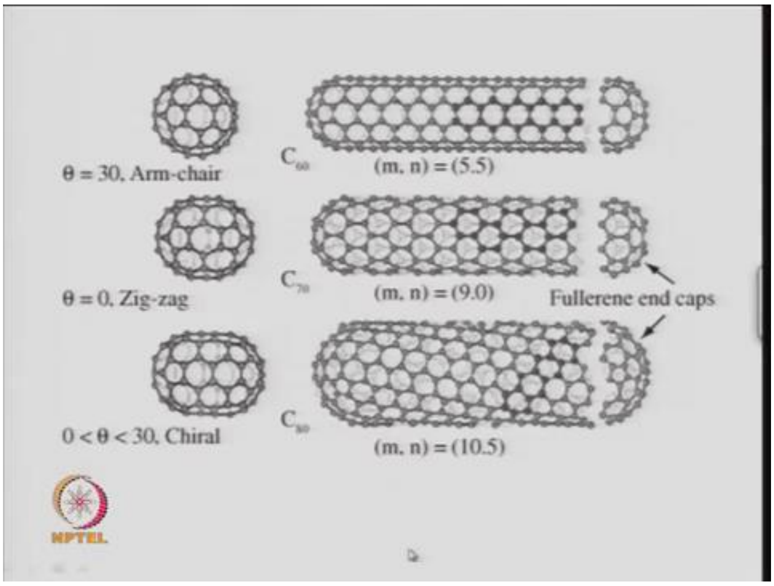
Now, these nanotubes in a microscope look like this. So you can see these nanotubes, this is a schematic pictures and this how it looks in the electron microscope. So, where you can see the ends of the carbon nanotubes which are single walled. And these single walled nanotubes make an aggregate through under walled interaction through their walls and form these bundles of carbon nanotubes. You can have multi walled nanotubes as shown here where you can count 1, 2, 3, 4, 5, 6 or 7 layers of carbons. And this actually each layer made up of a graphene type of layer.

(Refer Slide Time: 02:20)



And which we discussed in our earlier lecture, how you roll a graphene layer? So, this is a single graphene layer shown schematically made up of hexagon. And if you roll them using different chiral angles, you get different nanotubes and we discussed how you define the chiral vector using two unit vectors a 1, a 2, where a 1 and a 2 can be defined like this. And based on that, you can generate n 0 types of nanotubes which are called the zig zag nanotubes or an n nanotubes which are the arm chaired nanotubes.

(Refer Slide Time: 03:05)

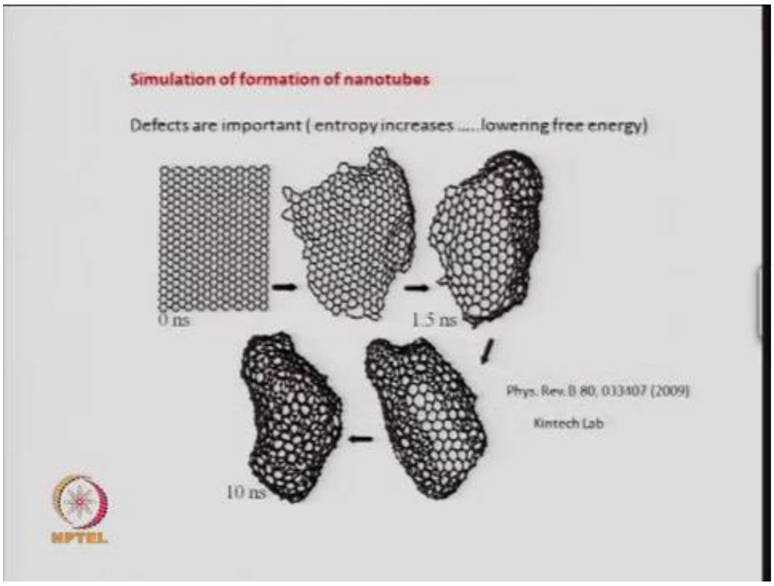


And this nanotube which is like a zig zag nanotube, where the chiral angle is 0. If you look at this cylindrical part is looks different then what you would have for a nanotube whose chiral angle is not 0, is here 30 degrees and you get arm chair type of nanotubes. And the ends of this nanotubes if you need to close, you either close for this type of arm chair nanotube with part of the C 60 molecule. Whereas if you have a zig zag nanotube, it has to be closed by a cap and the cap will be of a C 70 type of nano fullerene. So, C 60 fullerene can cap an arm chair nanotube while C 70 type of fullerene can found to be capping the zig zag nanotube.

If you are neither having a chiral angle of 0 or 30, but in between any angle then, those are chiral nanotubes and then they will be having different types of molecules at to cap this nanotube. This is basically half the part of the unit of C 80 fullerene. So, depending on what kind of nanotube you have to end the nanotube. If you want to close the nanotube, then you need a fullerene of a particular kind and which varies with the type of the nanotube you have, where m and n are the indices which define the type of nanotube.

And these are the basically the coefficient of the two vectors in the hexagonal ring of a graphene layer. So, these are different types of nano tubes which we discussed earlier and we looked at the concept of chirality and the importance of chirality in bringing about different types of carbon nanotubes.

(Refer Slide Time: 05:16)

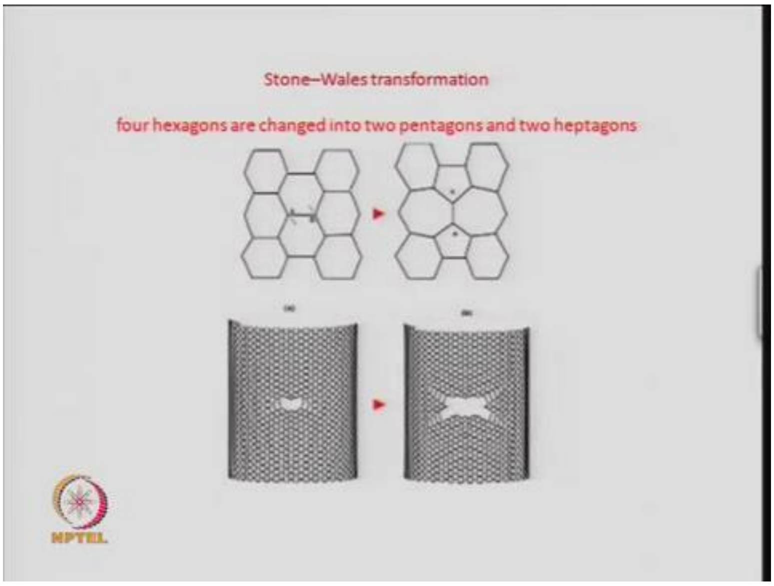


Now, how do these nanotubes form? So, what is the mechanism of nanotube? Though the mechanism is not exactly understood, but it is known that defects are very important for formation of nanotubes. So, people have done computer simulations and other studies, where if you take a single graphene layer and run the simulation, then with time you see that this single graphene layer will generate defects which are not hexagonal.

So, here in the ideal graphene layer, you have only hexagonal rings of carbon, but as you run the simulation, you will see that you will start having 7 membered rings or 5 membered rings which are like defects. And these defects are important and as you see that with time this layered structure of graphene starts to curl and ultimately it tries to close itself. So, it can only do that from the defects which results.

So, defects are very important and thermodynamically speaking, as you increase defects the entropy increases which brings about a lowering in the free energy. And so this is the a kind of mechanism which is proposed for the formation of carbon nanotubes from a graphene based layer.

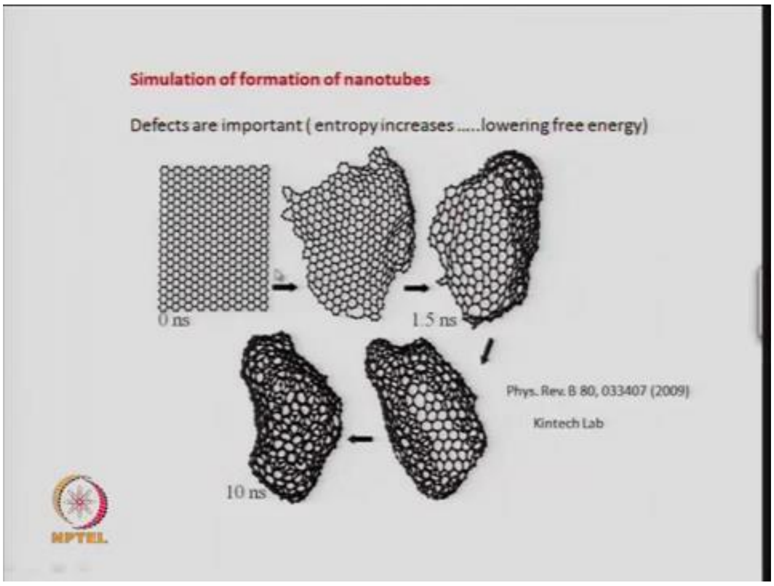
(Refer Slide Time: 06:50)



Now, here one of the defects which is very important in carbon nanotubes or most of the carbon structures is that, if you consider 4 hexagonal rings next to each other, so if you look at 4 hexagon rings in the graphene layer, you have all, the entire plan is made up of these hexagonal rings.

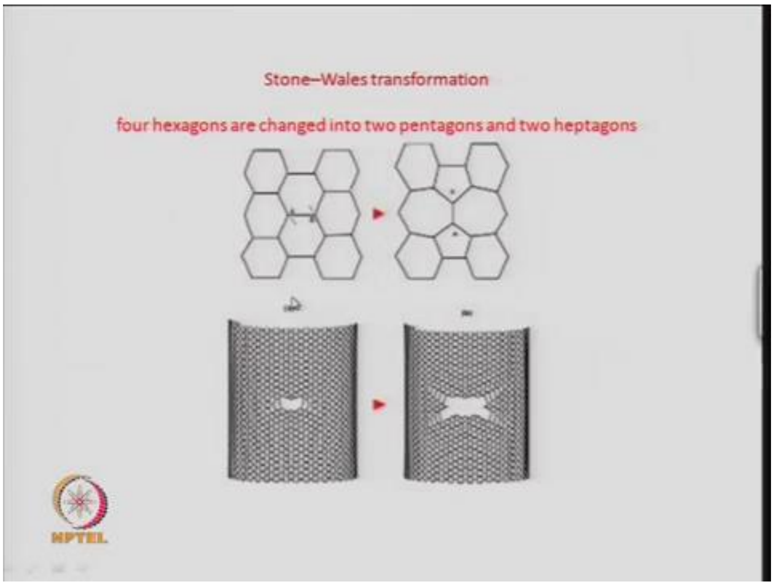
But just focus your attention on these 1, 2, 3, 4 hexagonal rings and by changing them to heptagons and pentagons. So from 4 hexagon if you can you generate 2 heptagons and 2 pentagons and you get a defect, this is called a stone wales transformation and these are also called stone wales defects, and these defects can be seen in the carbon nanotubes. And ideally these defects are present whereever the tube wants to curl and especially at the edges of the carbon nanotube. If you want to close the tube the stone wales defects are very helpful in making the tubes curl, the graphene sheet curl or close and such defects are important as shown in the previous mechanism.

(Refer Slide Time: 08:13)



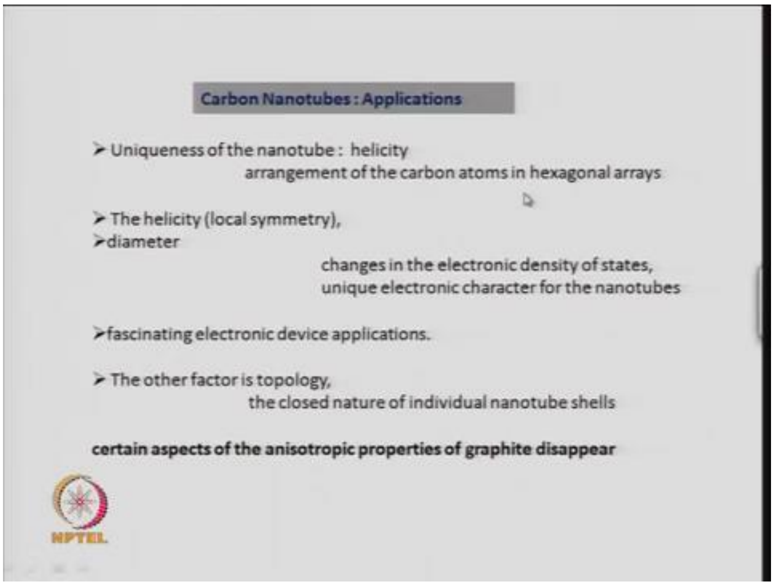
So there can be many types of defects.

(Refer Slide Time: 08:17)



But here we discuss one of the important defects or an important transformation of how ideal hexagonal layer can generate instead of hexagons, pentagons and heptagons and which lead to curling of the graphene layer.

(Refer Slide Time: 08:41)



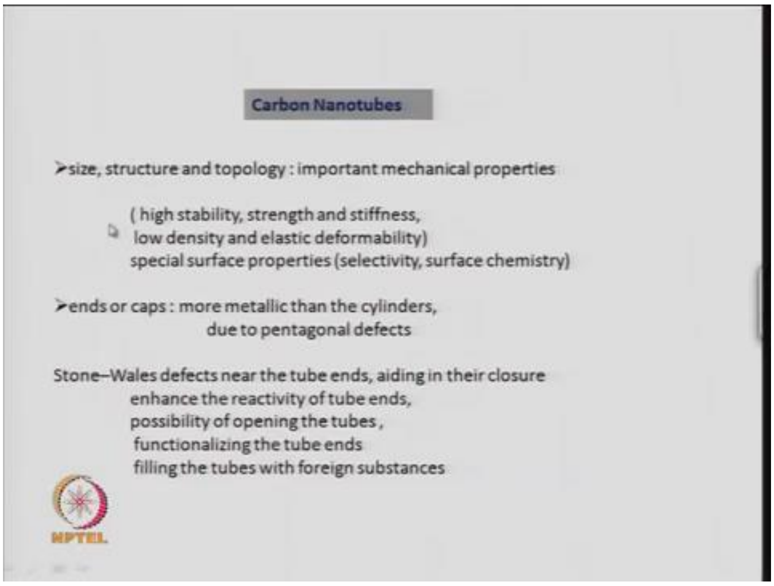
Now, coming to applications, carbon nanotubes have a variety of applications. And what is the reason for such a material which has got, so many applications? One of the unique features of these nanotubes is its helicity or the chirality, and the arrangement of the carbon atoms in the hexagonal layers will define this chirality, which is what we just discuss that is how the two vectors a 1 and a 2 in the graphene layer will give rise to a resultant chiral vector depending on the coefficients of those two unit vectors.

So, the helicity which is guided by the local cemetery is very important. The other important fact other than the helicity or chirality is the diameter of the nanotubes. Since, it has a very small diameter, this brings about a very interesting change in the electronic density of states. So, from the planer graphene layer which has a particular type of density of states and electronic properties, there will be certain changes in the electronic density of states due to the helicity and due to this small diameter of these carbon nanotubes.

And such changes in the electronic density of states which means how many electrons you have per unit energy at different energy levels. So, what is the electronic density of states with respect to energy? And these lead to fascinating electronic device applications. Another very important fact is that, these nanotubes is, there is a topological effect in these nanotubes. This closed nature of the individual nanotube shells is very important and gives it a unique properties compared to its parent graphene layer or the graphite sheets.

So, if you want to identify three points which are important for carbon nanotubes unique properties, they are the helicity, the small diameter and the topological nature of the carbon nanotubes. And hence there are several properties of graphite which are anisotropic and such properties are not found in carbon nanotubes.

(Refer Slide Time: 11:25)

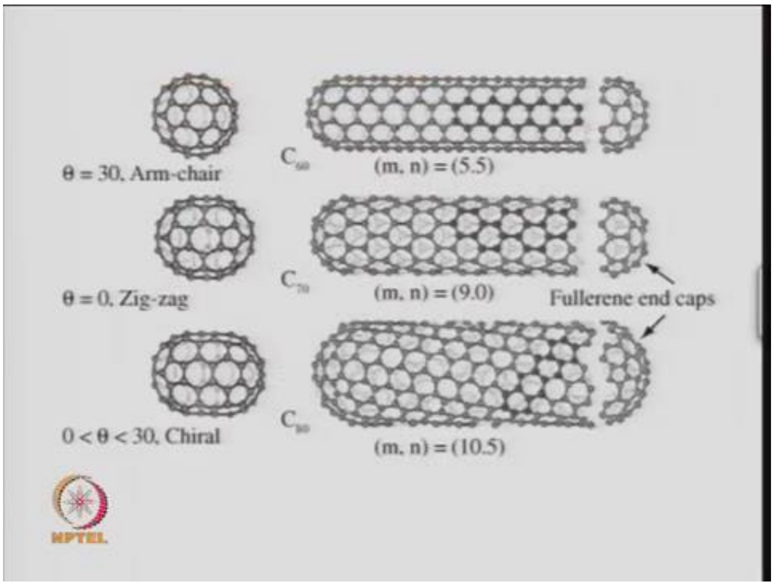


Now, we mention that size, structure and topology are important for the properties of carbon nanotubes. Not only the electronic properties, but also the mechanical properties. So, the mechanical properties are also guided by the size, structure and topology. And they have very high stability or strength and stiffness compared to any other material which is known today. And will come to the numbers soon. So, it has low density and it has a flexibility or elastic deformability. So, all these properties are good or positive for materials to be used for applications.

Apart from high strength and stiffness and such mechanical properties, it also has unique surface properties, and you can do lot of surface chemistry with some selectivity towards certain reactions. Now, in the carbon nanotubes, you have a part of the nanotubes is like a cylinder, which is the middle part of the nanotube. If you go towards the end of the nanotube then you have these caps; that is the cap may be like half of the C 60 molecule.

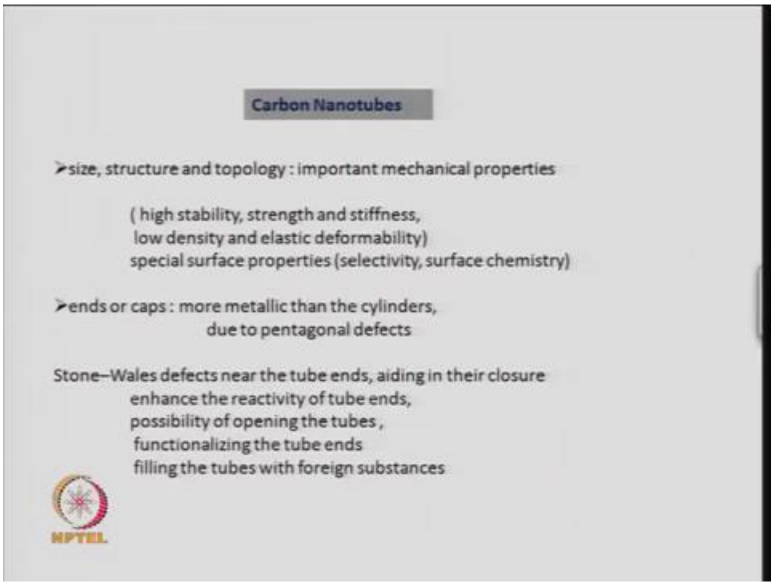
So, if you take a C 60 molecule, and you divide it in the middle, so you get a hemisphere. So, if this hemisphere is acting as a cap on an carbon nanotube that will of course, depend on the chirality of the tube. So C 60 can be capping only certain kinds of carbon nanotubes with a particular chiral angle.

(Refer Slide Time: 13:12)



And this, that angle as we discussed earlier is a for theta is equal to 30 which is chiral angle, you can cap with a C 60 molecule. But of course, if these this cylindrical part is made up of a chiral angle which is different like if theta is 0, then you have C 70.

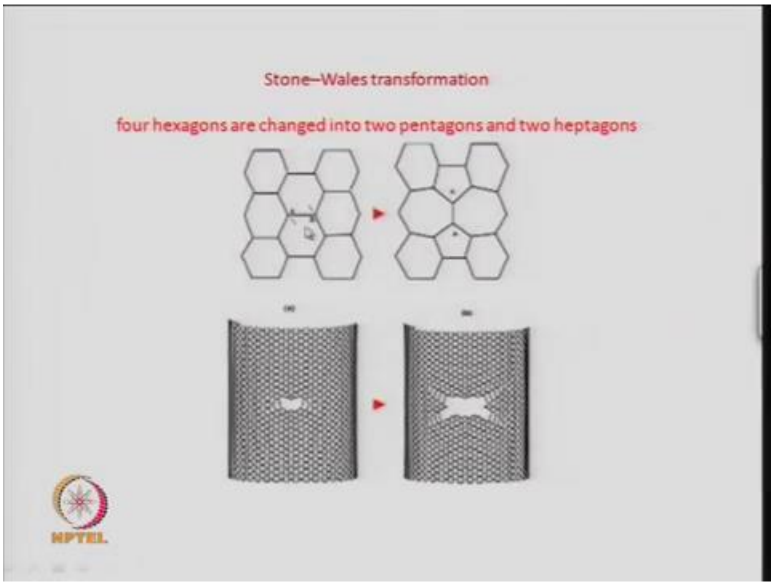
(Refer Slide Time: 13:34)



So, you will have these caps, which are different compare to the cylindrical part which has mainly 6 membered rings of carbon. So, you have 6 membered ring of carbon in the cylindrical part, whereas the caps which are part of the C 60 or C 70 or C 80 molecules will certainly have some pentagons. So, towards the end of the nanotube, you will have these pentagons or heptagons, which is necessary for the curvature of the nanotube.

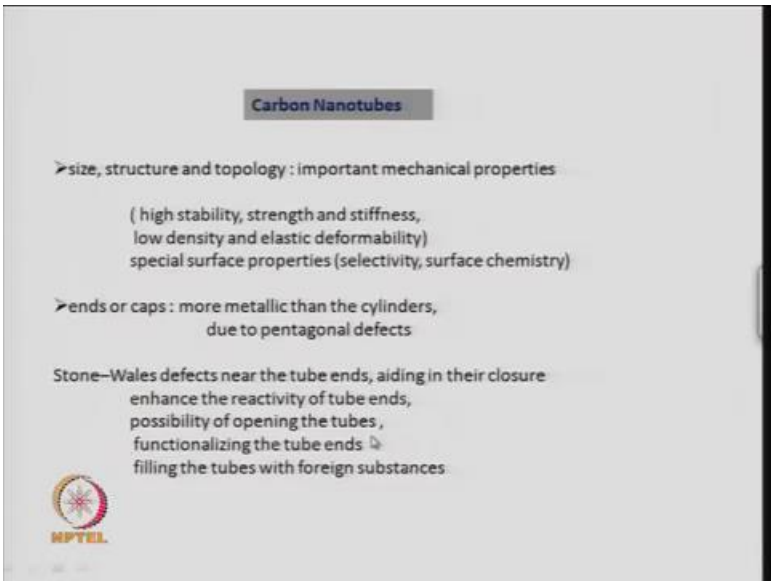
And these ends will be more metallic than the cylindrical part which is at the centre because of these pentagons. So, always if the metallicity of the carbon nanotube is less in the cylindrical part and more towards the end, that is where you have the C 60 kind of molecule or C 70 kind of molecule. Apart from that, you will have the stone wales defects, which is the 6, the 5 membered ring and the 7 membered ring which were generated. They are also found where the tube ends, because that is where the curvature is required, that is where the defects are required.

(Refer Slide Time: 14:54)



So, these stone wales defects, they will be found more towards the ends of the nanotubes where the curvature is there.

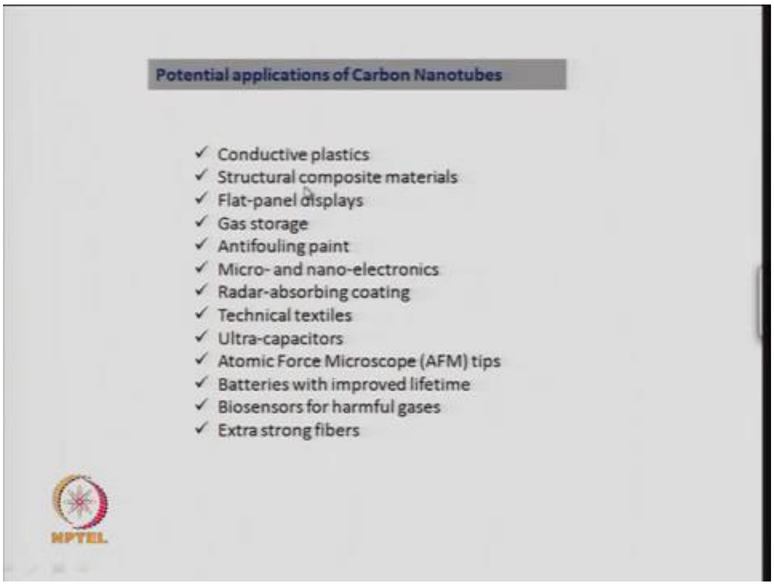
(Refer Slide Time: 15:02)



And that enhances the reactivity of the tube ends. So, the tube ends are more reactive and it is much more easy to open the tube ends, whereas it is more difficult if you want to rupture the nanotube at the center of the tube, that is where the cylindrical part is there. So, because of this 5 membered rings or defects likes the stone wales defects, the reactivity at the end of the tube is higher and it is possible to open the tubes towards the end much more easily than you can open the carbon nanotubes at the middle of the cylinder.

Now, you can also fill these tubes with foreign substances, that is with new material, and you can functionalize the tube ends. Because the tube ends are more reactive, so the functionalization by of the carbon nanotube is more easy at the end of the tube where the curvature is there, where the defects are there, where the 5 fold and the 7 fold rings may be there. So, there activity is more there functionalization is much more easy there.

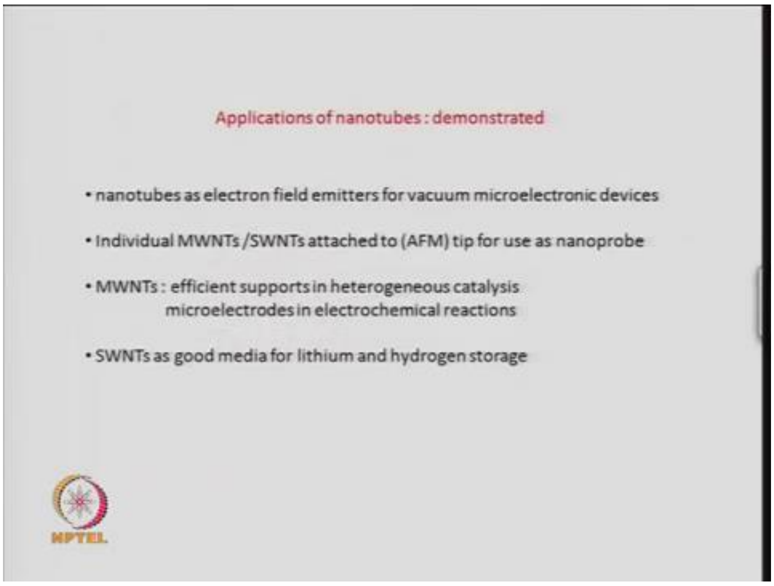
(Refer Slide Time: 16:22)



Now, a large number of applications I have listed here in industry. So, starting from conductive plastics, structural materials, because these are very mechanically strong. Flat panel displays, this comes from the unique electronic properties of a carbon nanotubes. Then, we will discuss about gas storage and several other properties, using tips made from the carbon nanotubes in AFM.

Then, you can have batteries like you have lithium batteries made with carbon nanotubes, which have very good lifetime. Then, you can do lot of sensing properties using carbon nanotubes. Extra strong carbon nanotubes can be made much stronger than steel by because of its very important mechanical properties.

(Refer Slide Time: 17:18)

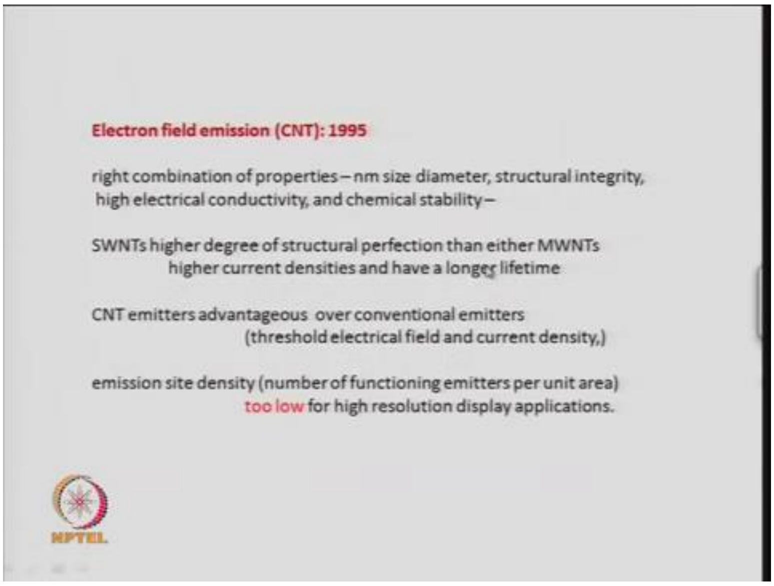


Now, some of the properties we are mentioning have already been demonstrated and they have been made. For example, nano, carbon nanotubes have been used as electron field emitters.

That means, you apply electric field to carbon nanotubes and they emit electrons. And these have been utilized for vaccum microelectronic devices. Then, a very important application is in AFM tip, many single walled nanotubes or multi walled nano tubes you can take, you can attach 1 single carbon nanotube or you can attach several nanotubes like a brush to AFM tip, and then you can use that as a nanoprobe. And it can be much more sensitive than any metallic tips which are used, which we will show in our subsequent slides.

So, very important property of individual nanotubes being used as tips in AFMs for as nanoprobes. Then, multi walled carbon nanotubes are efficient supports in heterogeneous catalysis. They can be functionalized and then used for other purposes. They have been used as microelectrodes in electrochemical reactions especially in sensing in biosensing. Then, as we mentioned that that single walled nanotubes is a very good medium for lithium and hydrogen storage. So, there are these applications have already been shown and they are highly successful.

(Refer Slide Time: 19:10)



Now, taking about field emission which we just mentioned. Electron field emission in carbon nanotube that means, you apply a electric field and electrons are emitted was shown way back in 1995. And why is carbon nanotube an excellent field emitter? Because of its combination of properties, these are very thin so you have these nanometer size diameter tubes, and you need this thin tubes, width tips, fine tips for good field emission. And the other thing is they are structural integrity, but most important is their high electrical conductivity. So, their narrowness and their high electrical conductivity are two very important factors for any good field emitter. Apart from that of course, you must have structural integrity and chemical stability for use over long period of time.

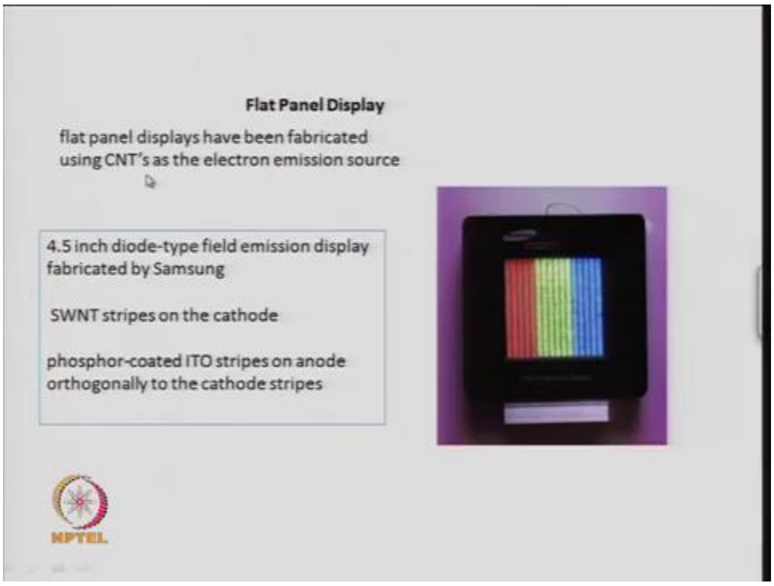
Now, the single walled nanotubes have a higher degree of perfection than multi walled nanotubes. And hence, they show much higher current densities and have a longer life time. But making single wall nanotubes is more difficult than multi walled nanotubes. So, overall if you want to use single walled nanotubes in your application, they are more efficient, but they would be more expensive because synthesis and purification of single walled nanotubes would be more expensive job in bulk quantities compared to multi wall nano tubes.

But, property wise they are much better than multi wall nanotubes, and they show much higher current densities. Now, see this carbon nanotube field emitters are advantageous over conventional emitters. That means, those emitters which are already known earlier before carbon nanotubes were discovered. For example, certain metals like tungsten is used as the field emitter, then borides like hexaborides, like lanthanum hexaborides or cerium hexaborides have been used as field emitters.

But carbon nanotube emitters have much more advantages over such a conventional emitters. Since, they have a low threshold electric field and very high current density. So, these factors make them much better than what was being used a earlier like tungsten or lanthanum hexaboride. Now, the emission side density, this is a probably a one thing which is not so good for carbon nanotube that is the number of functioning emitters per unit area is low for very high resolution display applications.

So, these field emitters as you know are used in display applications and such carbon nanotube based field emitters will have low resolution. It is because the number of emitters per unit area is low and so for high resolution applications they may not be efficient.

(Refer Slide Time: 22:33)

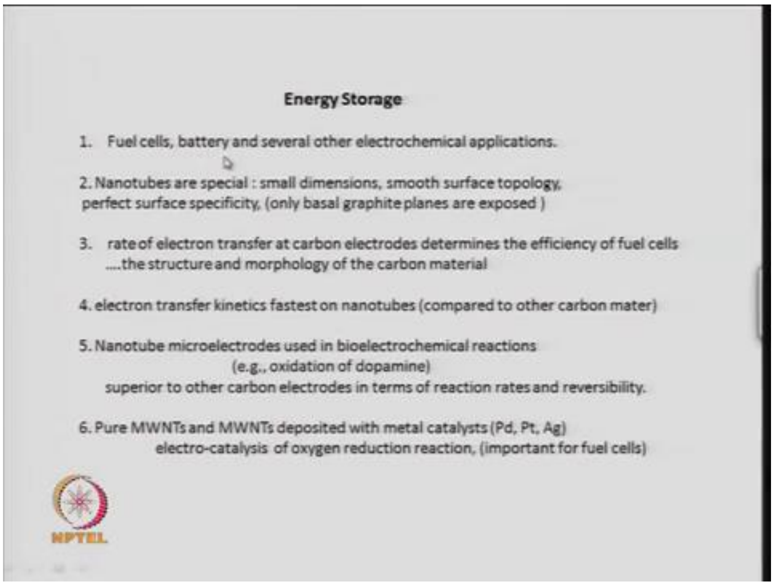


But, people have made flat panel displays. For example, using carbon nanotube as the electron emission source, people have made a 4.5 inch diode type field emission display this was fabricated by samsung.

And you have single wall nanotubes or stripes on the surface and then, you have got phosphor coated ITO stripes on anode. So, the single walled a nanotubes are on the cathode whereas, you have phosphor cotes ITO stripes on the anode which is perpendicular to the cathode. So, if you have the nanotubes in this direction then, you have the cathode perpendicular to it which is on ITO which is indium tin oxide, it is a conducting glass. And so you have a phosphor coated conducting glass like ITO which is indium tin oxide, indium doped tin oxide.

And that acts as anode and the single walled carbon nanotube acts as a cathode, and you can generate this kind of display which has been shown by samsung earlier. Now, coming from field emission or from displays to energy storage, it is known that we need to store a energy to make the electric vehicles run for a long distance. So, if you need batteries for cars etcetera, you need to have energy stored in the batteries to a much larger extent.

(Refer Slide Time: 24:10)



So, fuel cells, battery and several other electrochemical applications, where energy has to be store there also carbon nano tubes have found their importance. These nanotubes, why they are so special? Because in energy storage, why they are so important, because they have small dimensions, they have a smooth surface topology, and they have very good surface specificity.

That means, the surface has only one particular plane. So, if you know that the graphite planes, that is the basal graphite planes which are like the hexagon rings, they are only exposed. And hence, they have a very a perfect surface specificity which is important for a many applications. Now, the rate of electron transfer at the carbon electrodes, where the carbon nanotube is there determines the efficiency of the fuel cells, and the structure and morphology of the carbon material will dictate this rate of electron transfer. And that will be ultimately which will be determining the efficiency of the fuel cell.

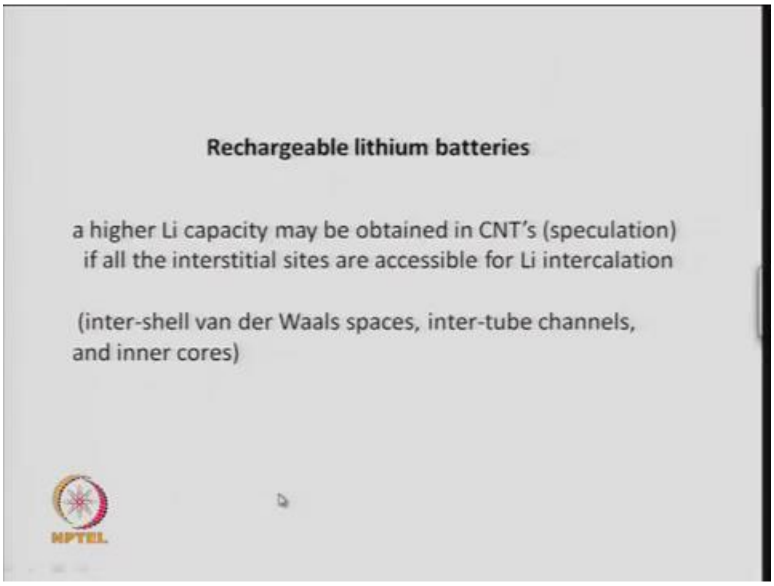
So, rate of electron transfer depends on the morphology of the carbon nanotube. Now, so that is one thing, and if you are look at the electron transfer kinetics compared to a planer material, the electron transfer kinetics is fastest on nanotubes compared to other carbon materials like graphite or diamond. So, electron transfer is very fast on the nanotubes, and hence the efficiency will be much higher. People have looked at these nanotubes as electrodes example in a oxidation of dopamine which is a electro chemical a reaction using a bio reagent.

So, you can study bio electrochemical reactions using nanotube micro electrodes, very fine electrodes made of carbon nanotubes, and you dip it in solution containing dopamine here. Here a particular dopamine is a kind of a drug and it is also secreted in the human body and you can study for example, the oxidation of dopamine and using micro electrodes of nanotubes, carbon based nanotubes. And this is much superior to other carbon nanotube for example, if you take graphite, it can also act as an electrodes, but the nanotubes are much more superior in terms of the fast electron transfer kinetics.

And the reversibility which is possible when you switch current in the opposite direction. So, these efficient electron transfer and the reversibility using carbon nanotubes is much better than other electrode materials including other carbon based electrode materials like graphite. Now, pure multi walled nanotubes and nanotubes deposited with metal catalysts are also very important. And if this particularly has been seen where metal deposited catalyst carbon nanotube has been used for oxygen reduction reaction.

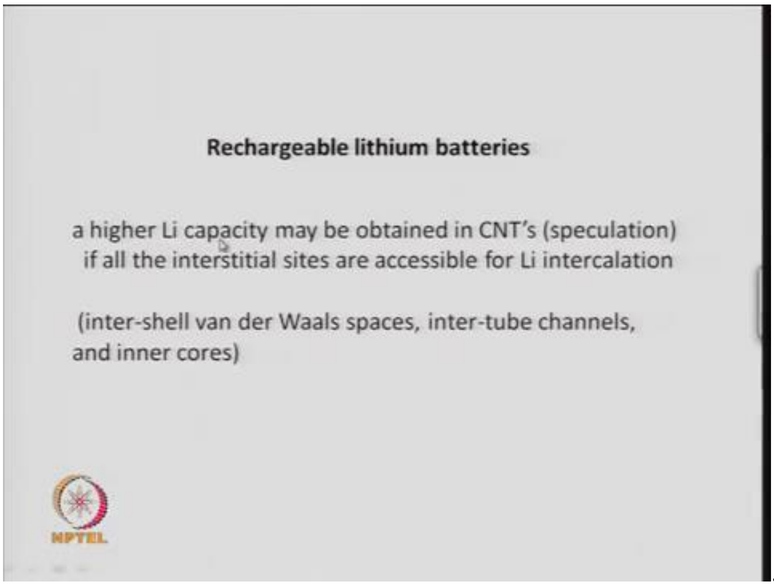
And this oxygen reduction reaction is important for fuel cells because in fuel cells you have oxygen coming into one electrodes and hydrogen coming in from the other electrode and then, you generate energy and water is liberated. So, at one of the electrodes you need to reduce the oxygen which is being passed at that electrodes, and for this reaction in the fuel cell multi walled nanotubes especially doped with metal catalysts have very good, very high efficiency. And so there are several applications in energy, energy related applications of carbon nanotubes.

(Refer Slide Time: 28:27)



Now, coming to another application, again in energy if you look at lithium batteries, lithium batteries are used everywhere and these lithium batteries require a host material. So, there are several host materials like metal oxides, metal sulfides, etcetera, where lithium can be intercalated and can be deintercalated. So, we call the charge discharge cycles. Now, if you change that material, the basic oxide material or the sulfide material with carbon nanotube, a higher lithium capacity can be obtained.

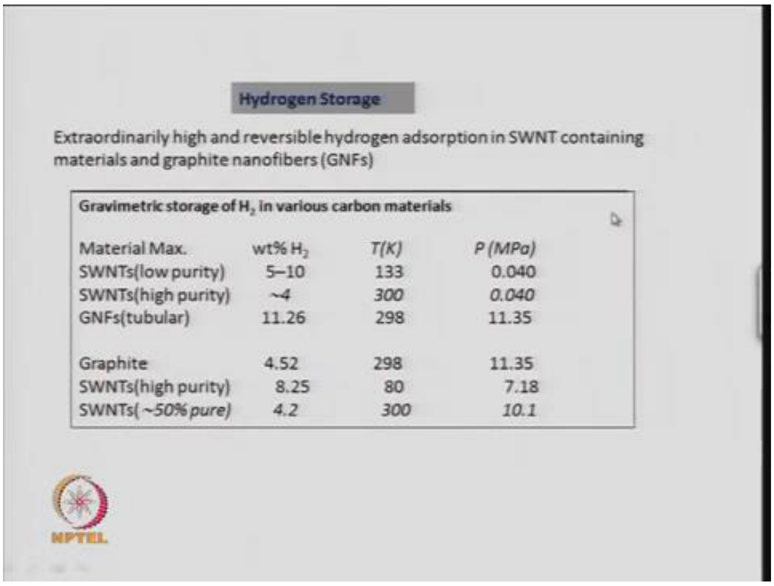
(Refer Slide Time: 29:06)



So, you can insert more lithium compared to other materials which are known, which are being used in the market in lithium batteries where for example, a manganese dioxide or a some oxides of nickel or some oxides of cobalt are used for reachable lithium batteries. It has been seen to some extent that lithium capacity can be much higher in carbon based nanotubes if all the interstitial sites are accessible by the lithium. So, if you can somehow put all the lithium in the interstitial sites which are available in these carbon nanotubes then, the lithium capacity can be taken to very high values.

And here the inter shell van der waals spaces, the inner tube channels and inner cores. These are the places where the lithium can be intercalated. So, there are several spaces where the lithium can intercalate into the carbon nanotube and lot of possibilities are there for enhancing the lithium capacity. Depending on how much lithium you can take in or take out will result in how many electrons per gram you can recycle, and that will lead to a very high capacity of the batteries.

(Refer Slide Time: 30:42)



Now, coming to hydrogen storage, which is also of importance in many applications where you are going to use hydrogen as a fuel. Hydrogen can also be used as a fuel as you know it is a important material, but how to store that hydrogen is of a matter of concern. And which material can store hydrogen to a large extent.

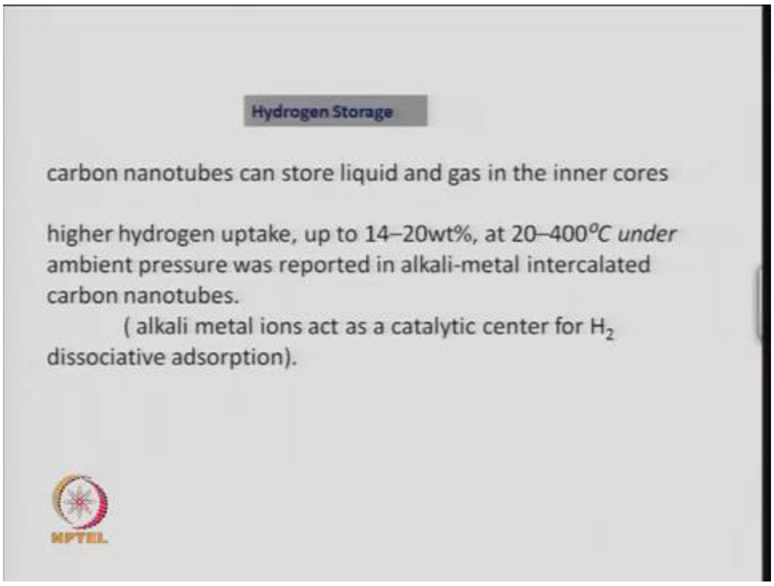
So, hydrogen storage in carbon base materials is shown here in a table. So, you can see that a single walled nanotubes can store 5 to 10 percent, weight percent of hydrogen at a particular temperature is 133, which is low temperature because 273 kelvin is 0 degrees or 300 degrees Kelvin, 300 kelvin is around 27 celsius. So, at room temperature around 27 celsius single walled nanotube, which are highly pure can store around 4 weight percent of hydrogen.

So, extraordinary high and reversible hydrogen absorption in SWNT single walled nanotubes can be stored. So, high purity nanotubes store 4 weight percent at 300 K whereas, low purity nanotubes can store 5 to 10 percent, but at a much lower temperature. So, at much lower temperature means, it is not so good for applications, you need to store at room temperature and because if you store at low temperature that means, you are going to spend money to refrigerate etcetera.

So, high purity nanotubes therefore are better than low purity nanotube. Of course, if you compare with other nanotubes like these are graphite nano fibers or graphite, these numbers are high. So, carbon nanotubes still has lower hydrogen storage capacity than graphite and, but there are applications where it can be used. So, there basically carbon base materials have hydrogen storage capability. Carbon nanotubes have around 5 to 10 weight percent, whereas graphite has around 4.5 weight percent at room temperature.

So, this is important. The room temperature storage is more important than storing at low temperature which cost you more money. So, you would like to store as much hydrogen at room temperature.

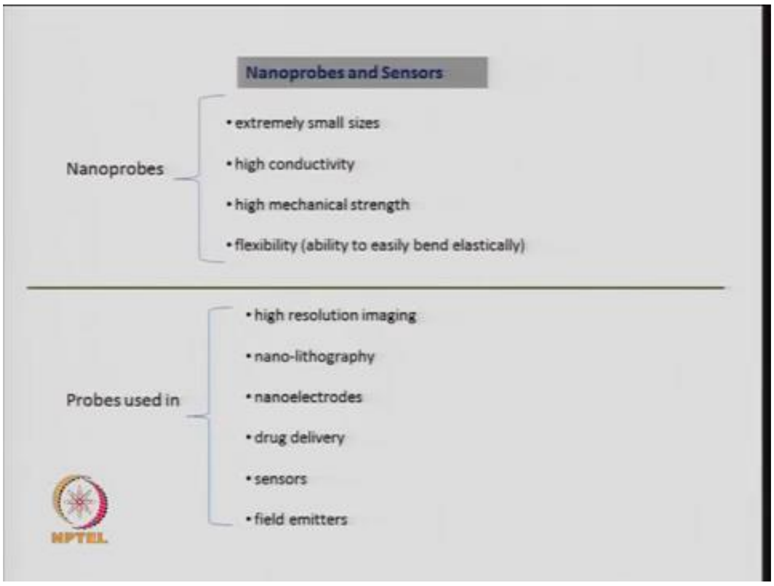
(Refer Slide Time: 33:28)



Now, you can also store liquid and gas in the inner cores, so you can store hydrogen as we discussed and you can also store liquids. So, higher hydrogen uptake up to 14 to 20 weight percent under ambient pressure is possible, if you have alkali metal intercalated in the carbon nano tubes. If you have just carbon nanotubes then, you can take around 4 to 5 weight percent of hydrogen.

But if you have alkali metals like sodium potassium, which are intercalated or lithium which has intercalated in the carbon nanotubes, then you can have much higher storage like up till around 20 weight percent can be stored in a temperature range of 20 to 400 degree Celsius, this alkali metal ions act as a catalytic center for the dissociative adsorption of hydrogen. So, the alkali metal helps H 2 to dissociate and get adsorbed as H in the carbon nanotubes. And hence, alkali metal intercalated carbon nanotubes have a much higher hydrogen adsorption capabilities.

(Refer Slide Time: 34:43)

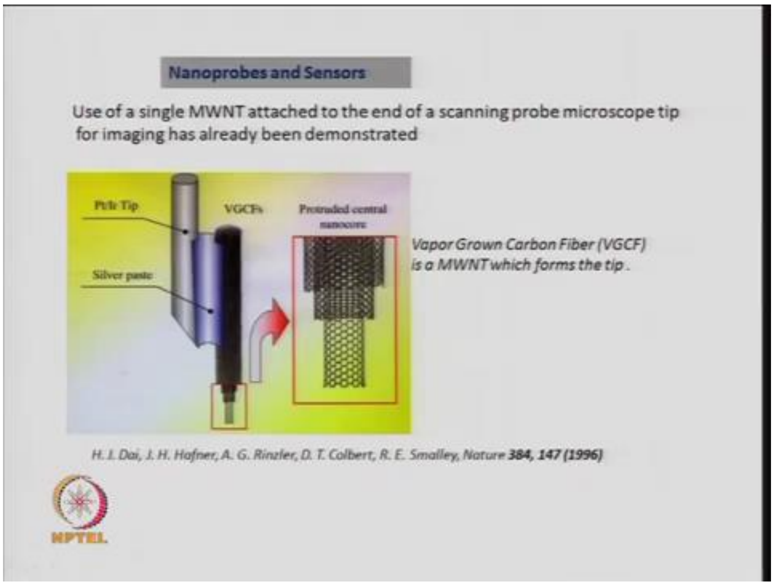


Now, moving from high energy what are the other applications carbon nanotubes? They can be used as probes, they can be use just nanoprobes because the diameters are in the nanometer size. And because of these extremely small size that is one reason then, they have high conductivity depending on what kind of nanotube it is, you can have metallic conductivity. And those metal conductivity can nanotubes can be used as nanoprobes, because you can generate an electrical signal and this electrical signal can be accessed very fast if the conductivity is high.

Apart from that, nanotubes have good mechanical strength, and they also have flexibility. So, your probe consider a nanotube like a wire, if that wire is brittle then it will break whenever it touches some material. So, whatever you are trying to probe, if your probe material is very brittle then it will break so whereas, carbon nanotubes are very flexible. So, it has mechanical strength, it is flexible and it has high conductivity that means, it can be a very good to send electrons or the signals, electrical signal very fast across the nanotubes.

So, hence they are very good nanoprobes. And where are these carbon nanotubes as probes or sensors being used? They are used in high resolution imaging, they are used in nano lithography as electrodes, nano electrodes, in drug delivery, in sensors and in field emitters. Some of these we just discussed before.

(Refer Slide Time: 36:35)

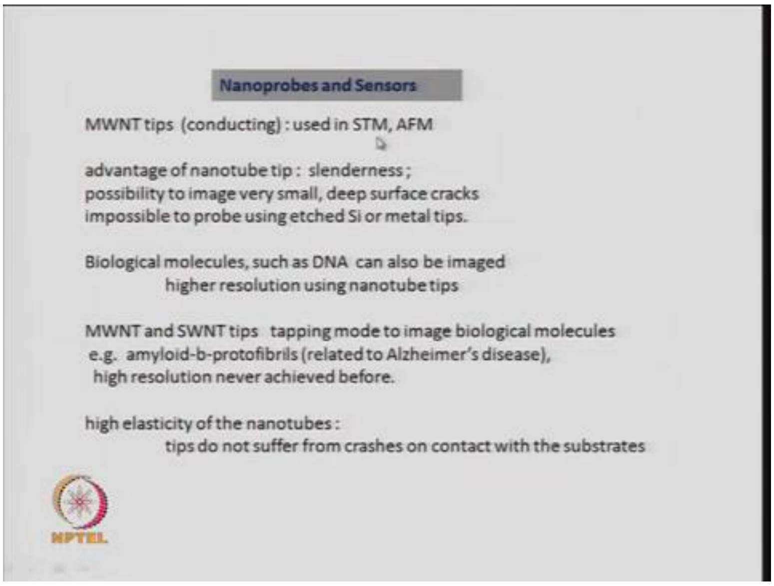


So, if you want to look at a nanoprobe of using a carbon nanotube, so you know there are a in all a scanning probe microscopes today, you have a tip and that tip can be made of many metals are used, like platinum or iridium. That is the tip which is found in most scanning probe micro scopes.

Now, if the diameter of this tape is a small, it is better for you because you will have much more higher resolution. So, if you use a carbon fiber at the nanotube, so say this is a nanotube, and instead of using this probe you attach this nanotube to this probe through some epoxy or some agent which can hold this together. Then, instead of using this as a probe to see the surface or wherever you are looking for the details, this will now be looking at the detail because this is very small, this is much smaller than the diameter of the original probe.

So, this can see much smaller things compared to your original tip. So, the use of a single multi walled nanotubes. So, this is a multi walled nanotube, this is the part highlighted in red which is shown here, and this is a multiwalled nanotube, and this will we probing the surface or the ridges wherever you want to study some property of that surface. And this is a vapour grown carbon fiber, and it is a multi walled nanotube. Of course, if you have the ability you can even attach a single word nanotube. In this case, a multi walled nanotube has been attach. And now, it is doing the job of the probe which this platinum or iridium tip is supposed to do.

(Refer Slide Time: 38:41)



So, using these multiwall nano tips, if they are conducting then you can use them in STM because you know in STM the surface is metallic and there is a tunneling from the surface to the tip and the tip has to be conducting in STM. And in AFM, you can use this kind of tips to study the changes in the atomic force.

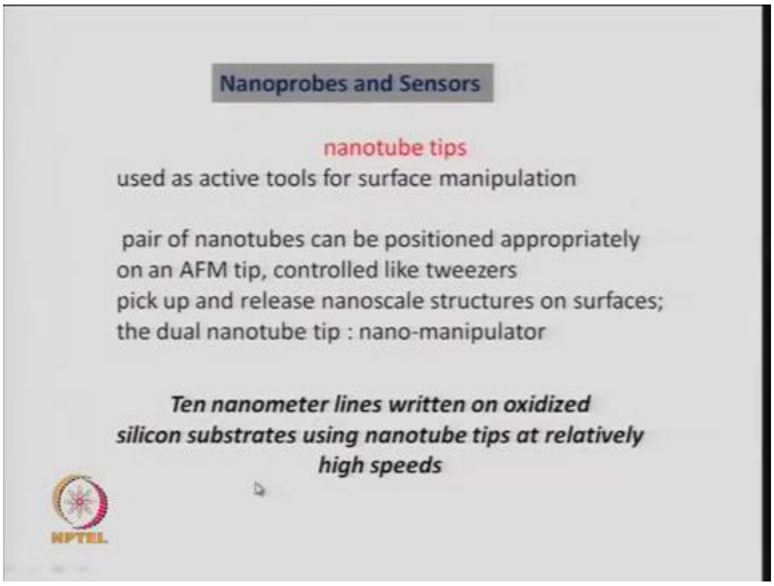
Now, the advantage of using a nanotubes tip is that it is very narrow, so it is very slender, and it is possible to image very small and deep cracks, which is not possible by standard metal tips like platinum, iridium which I showed or silicon which cannot be etched to such narrow dimensions. So, that is the advantage of this nanotube tip because it is very narrow, they can study much smaller details of a surface. Then, you can attach biological molecules such as DNA, you can image biological molecules like DNA using nanotube tips. So, DNA can have a diameter of say, has a turn of around of 2.5 angstrom.

And so if you want to see the details, you need very fine probes. So, such a probe can be made using carbon nanotube as a probe attached to a AFM and then, used as a tip to study biomolecules. And this has been shown in a molecule called the amyloid-b-protofibrils which is related to alzheimer's disease. This is an old age disease, where a person starts losing it is his or her memory. Then, you have alzheimer's disease and then you have these amyloid-b-protofibrils. And this was studied using a multi walled and single walled nanotube tips.

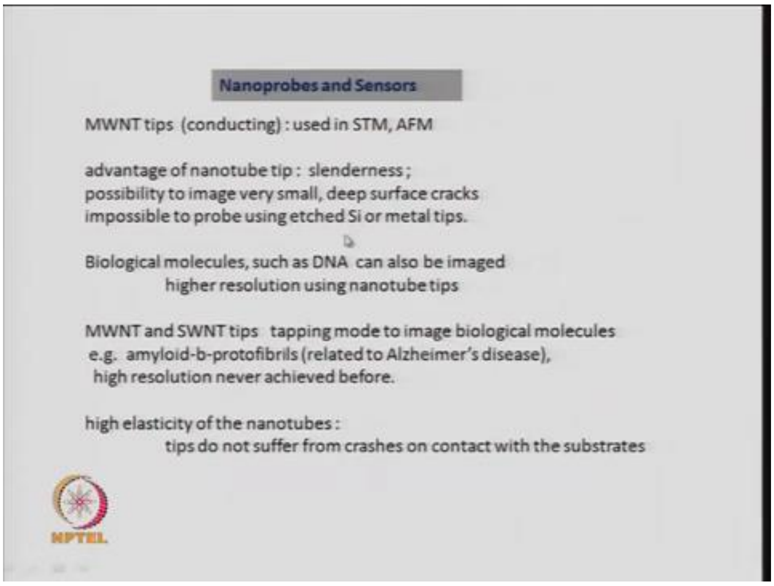
And it was used in the tapping mode, that is a particular type of methodology to study the AFM images where the tip is moving back and forth to the, on the surface of the molecules. So, it touches the surface and comes back then, again touches the surface. So, it is called the tapping mode, and it is also a sub class what is called the non contact mode because it is coming into contact for a very small amount of time. So, that tapping mode using a nanotube tip was used to study such molecules at a resolution which was never achieved before. So, this kind of very exiting work can be done using carbon nanotubes as tips.

Now, the high elasticity which I had said or the flexibility of the nanotubes leads to the fact that these tubes will break so easily. Whereas metal tips break quite often when they touch the surface, whereas carbon nanotubes do not suffer from these crashes on contact with the substrates because they are highly flexible. So, that is another important point because tips are expensive, and every time you break a tip you have to buy a new tip. So, the flexibility of the nanotube is very important.

(Refer Slide Time: 42:38)

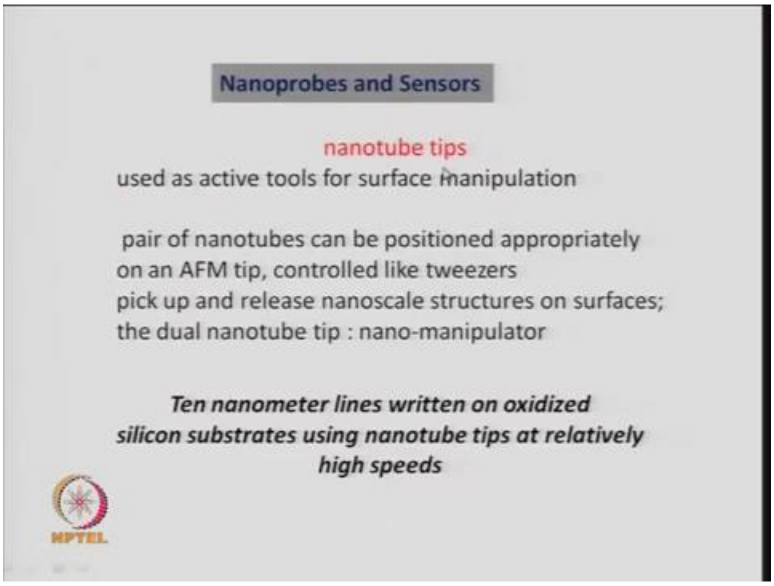


(Refer Slide Time: 42:43)



Now, these nanotubes tips can not only sense or image the surfaces or the cracks.

(Refer Slide Time: 42:53)



As we discussed or look at the surface of these biomolecules, but you can also use these nanotube tips for manipulation for surface manipulation, like a tweezer. So if you have instead of one nanotube, suppose you have a pair of nanotubes, two nanotubes which are placed appropriately on an AFM tip, then you can bring this pair of nanotubes very close to say a biomolecule or some nanoscale structure on a surface. And then you can hold that nanostructure with this pair of nanotubes, and you can pick it up and then release that structure at some other place.

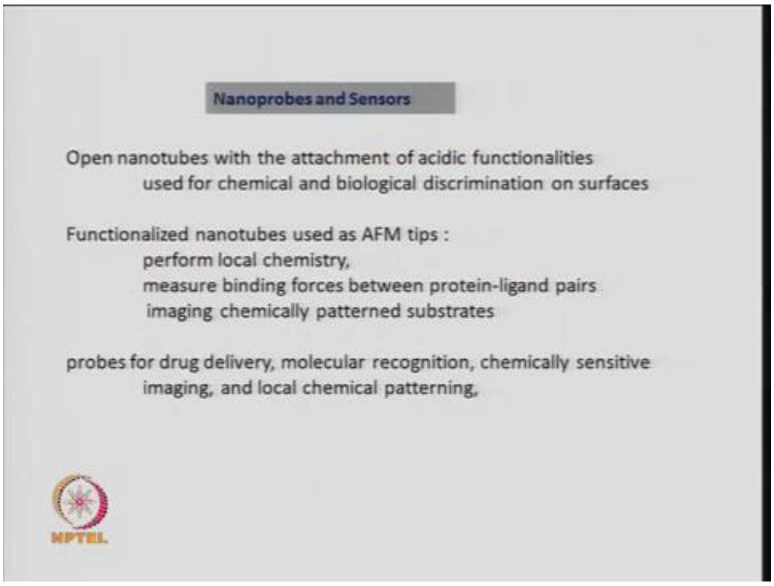
So, what you are doing is you are manipulating the molecule on the surface. So, this is called nano manipulation using carbon nanotubes as tips. So, you need at least a pair of nanotubes to act like you have this kind of a pair of you know scissors or something which are called tweezers or four steps which you have seen in the laboratory. And you can control them to pick up and release nanoscale structures at places where you want them to move.

So, this dual nanotube tip is what we call, like acts like a nano manipulator. So, a nano manipulator is something which can manipulate objects on a particular surface at very small or nanometer like movement. You have a nano structure, you are picking up a nanostructure, and you can move a nano dimensions and place it in a particular positions which is predesigned. So, this kind of application of a nano manipulator has been shown with carbon nanotubes.

For example, people have shown that you can write 10 nanometer lines that means, one line with the thickness of 10 nanometer can be drawn or written on an oxidized silicon substrate using nanotube tips. And you can write it very fast, so you can draw 1 line and then, draw another line very quickly compared to any other technique known today based on carbon nanotubes. So, this is very-very exiting research which is going to bring about very fantastic technology where you can draw fine lines.

Now, why are these lines required? These lines will be required, suppose you have to make a circuit with some particular design, and you want to make a very small chip then, you do need to draw very fine lines which can act as contacts so through which the current can pass. So 10 nanometer lines is one of a smallest type of dimensions that you can make and has been already shown using carbon nanotube tips, and you can draw because at what speed are you writing, because ultimately if you need to do mass production, you have to do these things very fast. You cannot take one hour to make a structure of few nanometers thick line then, you cannot have a very viable technology. So, this has to be done at a very fast speed and so that has been achieved in some cases using carbon nanotubes.

(Refer Slide Time: 46:36)



Now, as we discussed earlier, you can have open nanotubes. That means, nanotubes which may be you had closed and then, opened at the end where you have defects or where you have this pentagonal rings. And then, you have attached, you can attach functionalities, they can be acidic functionalities like carboxylic groups can be attached. And this has been shown and used for chemical and biological discrimination on surfaces.

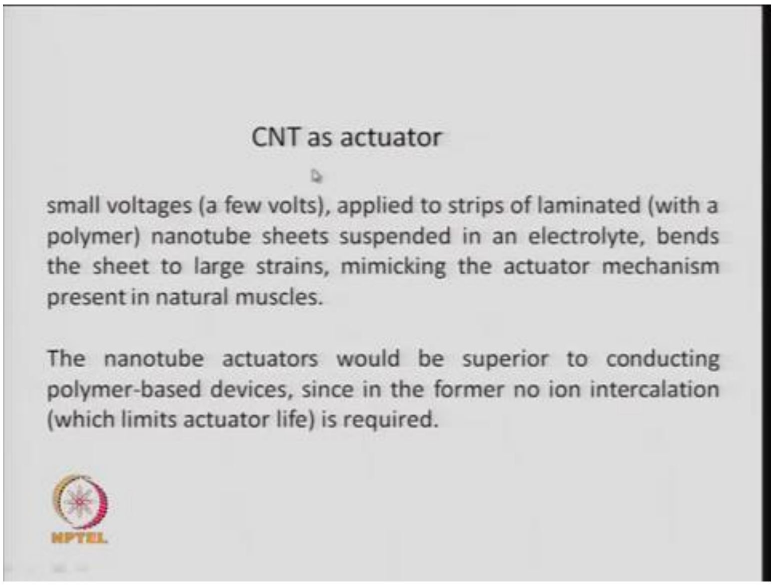
So, you have the various molecules and you have some functionalities which is, which can attack some particular molecules and hence, functionalize the surface of these open nanotubes. Now, these functionalized nanotubes have also been used as tips in atomic force microscopy. So, if you have a simple carbon nanotube and then, you have a functionality that means, you have a carboxylic group or amino group on the carbon nanotube tip. Now, when you move that tip in the AFM, then you can do some local chemistry that means, you can do some reaction in a very small region of the surface.

So, that is what we call you can do some local chemistry using AFM tips which have been functionalized with suitable molecules or suitable ligands. And that has been done. You can do measurements, like find out what is a binding force between a protein and a ligand. So, if you can measure the energy to pull apart a protein and a ligand using a carbon nanotube, you can find out then what was the binding force between this protein and ligand. Then, you can image chemically patterned substrates.

So, you have a substrates the substrate can be say silicon or something else, it may be glass. And then you have some molecules which patterned the surface. So, you have a molecules lined up like may be in a zig zag fashion, or as a cross. So, this pattern can be imaged by this kind of functionalized nanotubes, which will, which are acting as AFM tip. So, the tip is moving over the pattern and the functionalized part is kind of imaging those chemically patterned substrates.

So, that is possible using functionalized carbon nanotubes as AFM tips. Further they can be used for other things, like molecular recognition, drug delivery, and as we discussed doing chemical patterning. Now, other than carbon nanotubes acting as to image, to manipulate and then do patterning or imaging pattern surfaces.

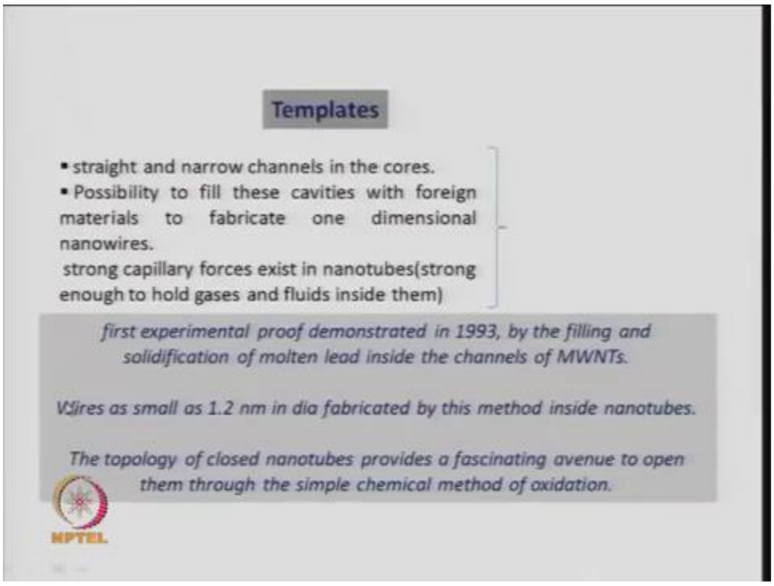
(Refer Slide Time: 49:44)



You can also use carbon nanotube as an actuator. An actuator means, something which will move of application of electricity. So, if you small voltages, a few volts applied to strips of a laminated nanotube sheets, so this is laminated with a polymer. So, you have nanotube sheets and you apply a small voltage, when it is suspended in an electrolyte. Now, this sheet bends due to large strains, and this mimics the actuator mechanism which is present in muscles. So, in muscles, in our muscles you know there are these nerve impulses and that triggers some electrical signal and our muscles act on that basis. Similarly, you have these strips of laminated nanotube sheets in an electrolyte and you apply a voltage, and this sheet bends in a particular direction and that mimics the actuator mechanism.

So, these nanotube actuators would be superior to conducting polymer based devices since, in this case you do not need any ion intercalation. Whereas in polymer based devices which have been used as actuators you need to add ions, and adding ions it limits the life of the actuator. Whereas carbon nanotube based actuators, you do not need to add these ions or intercalate these ions as you need to do in polymer based devices.

(Refer Slide Time: 51:26)



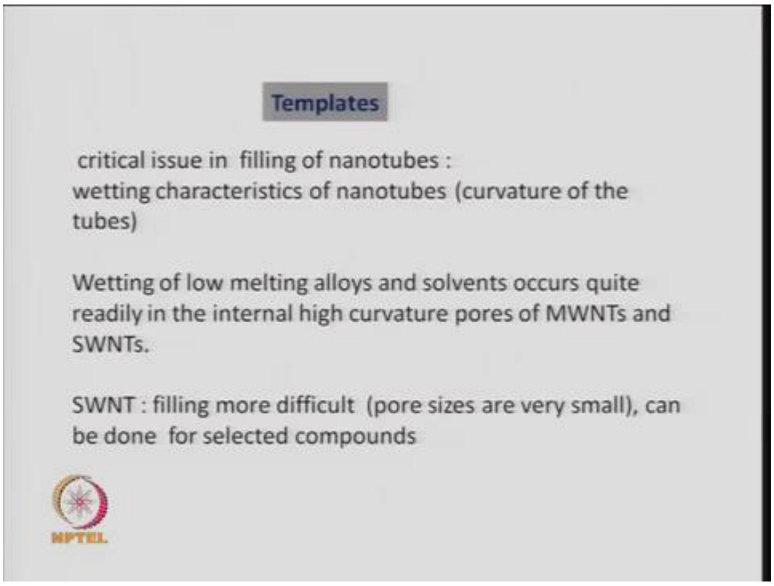
So, other than that, now nanotubes as you know if it is closed there is hollow space inside the nanotube. So, can it act as a template? That means, you have this hollow thing and then if I fill something, it will take the shape of the carbon nanotube.

So, carbon nanotube can act as templates because they are straight and narrow channels in the cores. It is possible to fill these pores or cavities this elongated cavities with foreign material. And then you remove the carbon nanotubes somehow to fabricate what is, what will be one dimensional nanowires. So, if you are able to put some copper inside the hollow carbon nanotube and then, if you remove or of the carbon then what will remain is a copper nanowire.

So, nanotubes can be used as templates. Now, there are strong capillary forces exists inside the nanotubes and which can, which actually help in holding the gases and the fluids inside them. Now, the first experiment was shown in 1993 where lead was molten lead was filled in the channels of multi walled nanotubes, and using that wires as thin as 1.2 nanometers in dia that is 12 angstroms in diameter were fabricated inside these nanotubes.

Now, these closed nanotubes hence provide a fascinating avenue to open them using oxidation. So, as you know the nanotubes which are closed can be oxidized at the ends because the ends are more active, more reactive because of the pentagon's. And so you can do several things not only fill the nanotubes, you can oxidize the ends of the nanotubes by simple chemical roots.

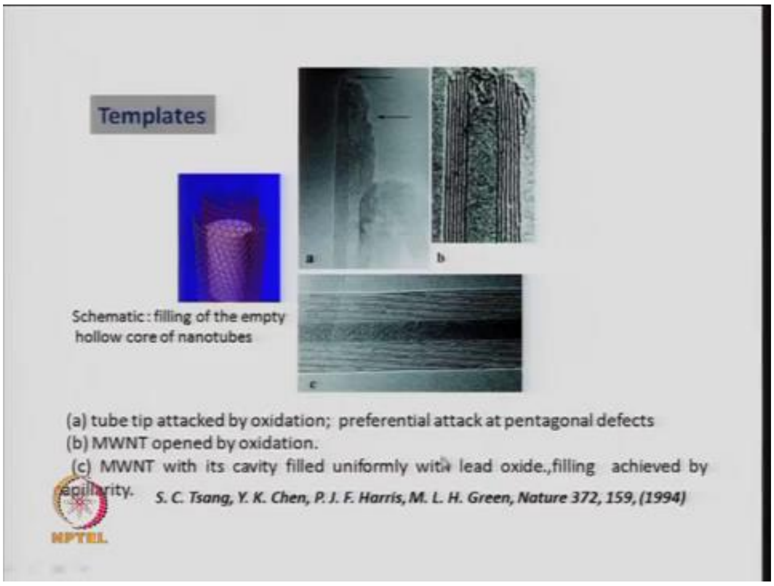
(Refer Slide Time: 53:39)



Now, the critical issue in filling the nanotube, when you fill nanotubes is the wetting characteristic of the nanotube. And that depend on the curvature of the nanotube. So, wetting of low melting alloys and solvents occurs quite readily in the multi walled nanotubes and single walled nanotubes.

However, if you compare them among multi walled nanotubes and single walled nanotubes, it is easier for to fill the multi walled nanotubes compared to single walled nanotubes. Because in the single walled nanotube, the pore size are very small, and only for some selected metals or compounds you can fill the single walled nanotubes easily, because the wetting characteristics of the single walled nanotubes do not permit the filling very easily.

(Refer Slide Time: 54:44)



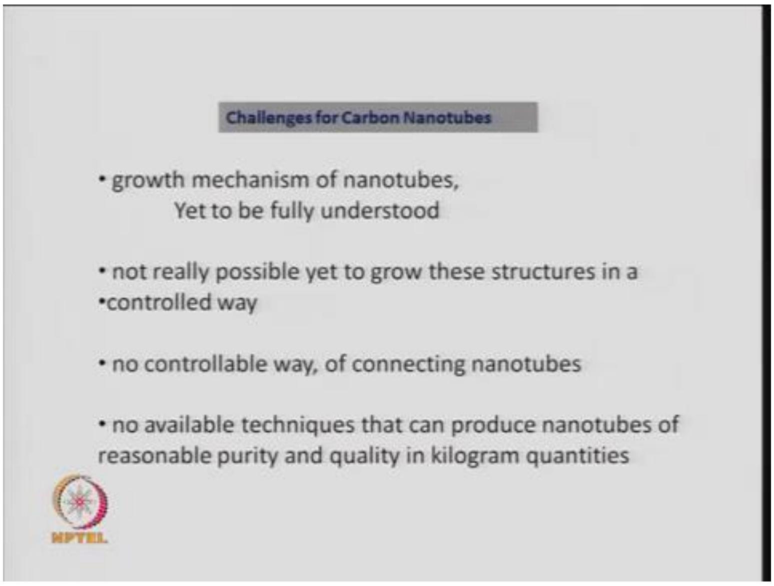
Now, if you look here this is a schematic diagram so you have these say 1 carbon nanotube and there is another wall of the carbon nanotube, so this may be called a double walled carbon nanotube and inside the hollow part you have filled with something.

So, this is filling of the empty hollow part of the nanotube. This is a schematic diagram. This is the real picture in electron microscopy, where you can see in the, in this picture you have a nanotube first which has been ruptured at the end. So, at the end where there are more pentagonal defects the nanotube has been broken. This is one particular tube which has been opened here by oxidation, and as you know oxidation is easier not at the sides of the nanotubes, but at the ends of the nanotubes so it has been affected by oxidation.

And here you see a multi walled nanotubes several walls are there and inside there a material which has been filled, and that is actually lead lead oxide and this was achieved using the capillarity, a capillary reaction of the nanotube. So, you can fill the nanotubes with different materials as has been shown here, and that leads to if you suppose you want this lead oxide nanowire of a particular diameter then, you choose a carbon nanotube of a similar diameter.

And then, after filling the nanotube, you can remove this carbon say burn off that carbon what will remain is only the material which is inside. So, you will have wires of this material. So, that is how carbon nanotubes can be used as templates.

(Refer Slide Time: 56:40)



So, there are several challenges for carbon nanotubes, alike the growth mechanism of nanotubes is yet to be understood. And these structures cannot be controlled in exactly the way you want. Then, connecting these nanotubes is also not easy and still there are requirements for producing these nanotubes in large quantities. So, we will save, we will stop here today and we, I hope that you got a good idea about carbon nanotubes and its properties and applications.

Thank you.