INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

NPTEL

NPTEL ONLINE CERTIFICATION COURSE

Biomedical Nanotechnology

Lec - 10
Carbon Nanotubes and its Bio-Applications

Dr. Arup Kumar Das
Department of Mechanical and Industrial Engineering
Indian Institute of Technology Roorkee

Hello everyone I welcome you all to the 10th lecture of this course. The 10 lecture is on carbon nano tube and needs bio applications, so in lecture we are going to learn what is carbon nano tube.

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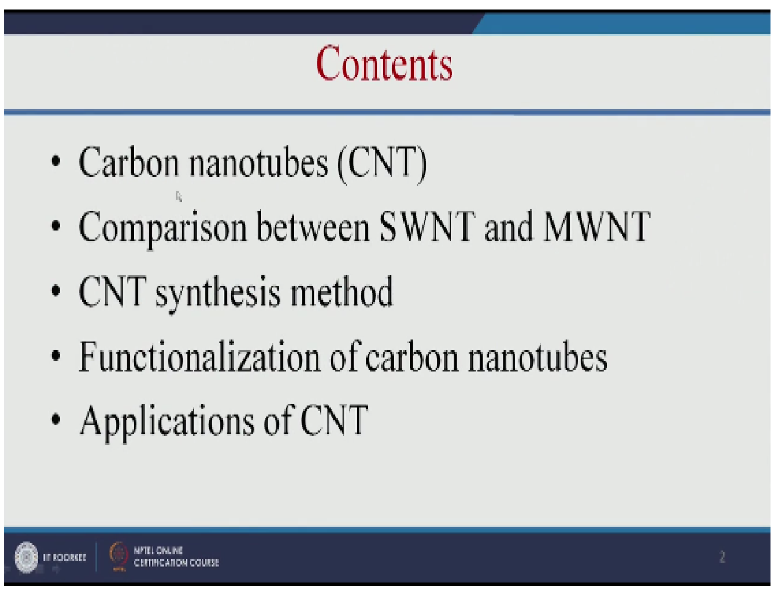

And what is a difference between single wall nano tube and multi wall tube and we are going to learn how to synthesis this carbon nano tubes and also we are going to learn how to functionalize this carbon nano tube the various applications of carbon nano tube and also there are various applications of carbon nano tube.

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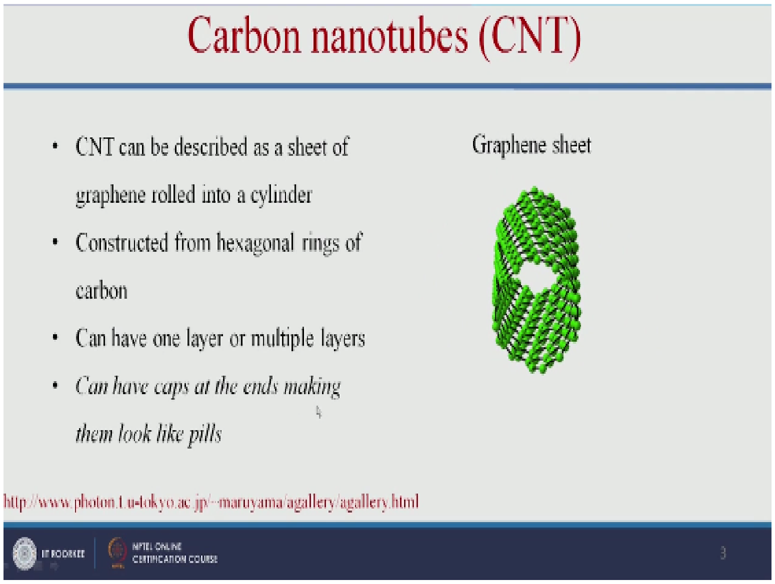

So let us see what is carbon nano tube the carbon nano tube can be described as a sheet of graphene rolled into a cylinder so here you can see this animation this is a graphene sheet it is rolled into cylindrical shape this is called as carbon nano tube and this graphing it is mainly made up of hexagonal rings of carbon and this carbon nano tubes can have 1 layer or multiple layer of graphene sheet if it is having 1 layer that is single wall carbon nano tube if it is having multiple layer that is called as multi wall carbon nano tubes.

And this carbon nano tube can have caps at the ends okay so we can have caps at the ends of this tube so that we can load any therapeutic molecule are we can load any anti cancer drugs inside the carbon nano tubes and we can use it for various therapeutic application.

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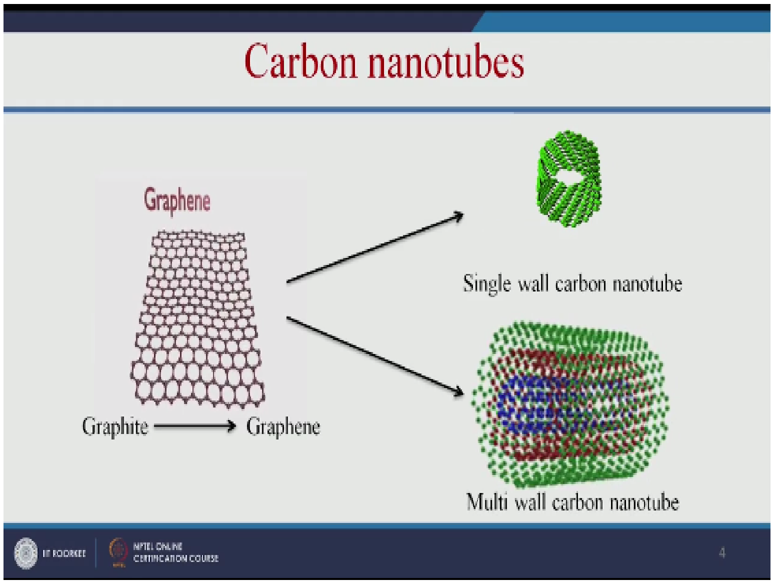

So form where we get this graphene so we get the graphene from the graphite okay so the single layer of graphene if it is rolled into tubular form that is called as single wall carbon nano tube and if you are using multi layers of graphene that is called as multi wall carbon nano tubes.

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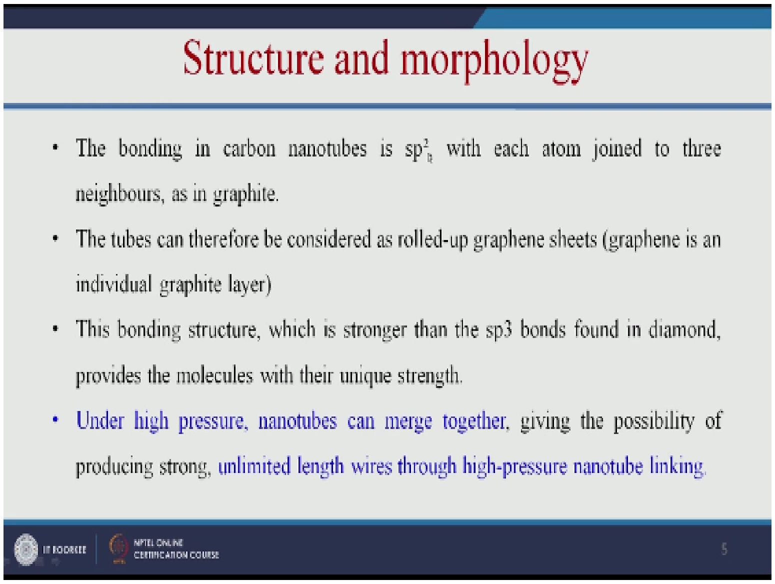

Let us see the structure and morphology of carbon nano tubes so the bonding in the carbon nano tubes is sp^2 with each atom joined to 3 neighbors as in graphite okay, so that tubes can therefore be considered as rolled up graphene sheets and this bonding structure which is stronger than the sp^3 bonds found in diamond and also under high pressure this nano tubes can join together and form a nano wires.

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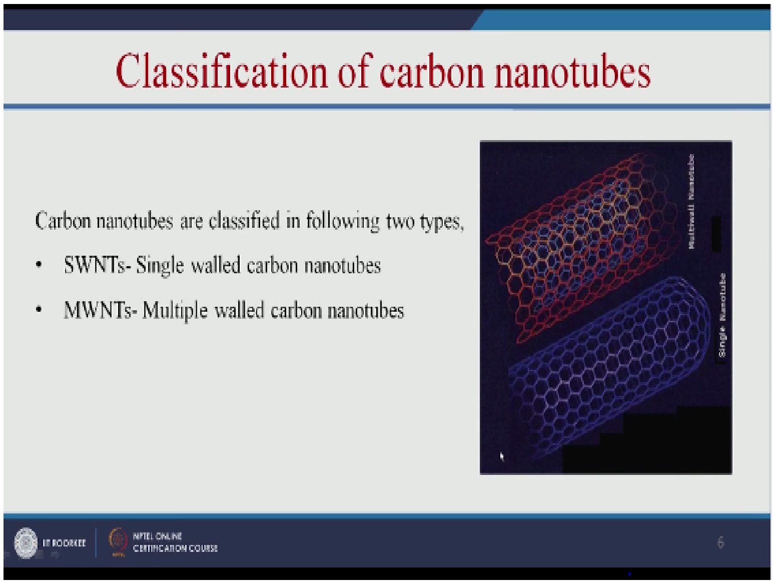

So let us see the different between the single wall carbon nano tubes and multi wall carbon nano tubes.

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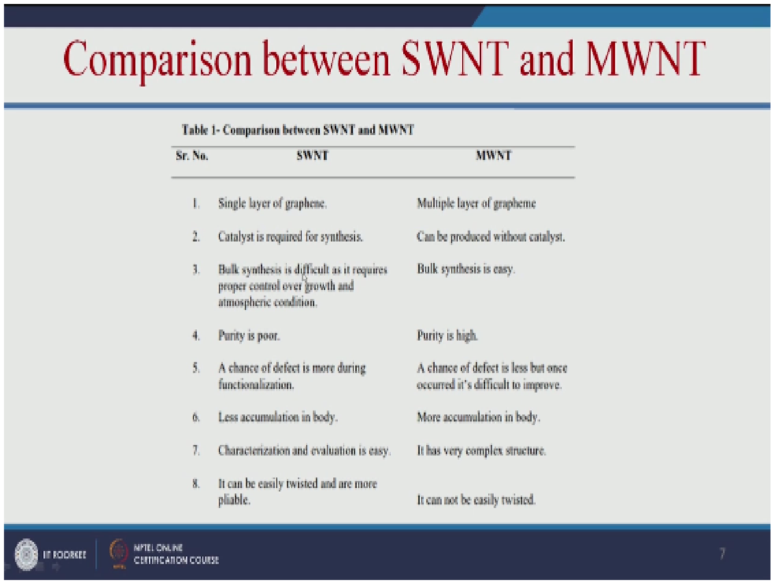

Sr. No.	SWNT	MWNT
1.	Single layer of graphene.	Multiple layer of grapheme
2.	Catalyst is required for synthesis.	Can be produced without catalyst.
3.	Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition.	Bulk synthesis is easy.
4.	Purity is poor.	Purity is high.
5.	A chance of defect is more during functionalization.	A chance of defect is less but once occurred it's difficult to improve.
6.	Less accumulation in body.	More accumulation in body.
7.	Characterization and evaluation is easy.	It has very complex structure.
8.	It can be easily twisted and are more pliable.	It can not be easily twisted.

As I told you earlier single wall is single layer of graphing and multi wall is multiple layer of graphing and for synthesis it need catalyst and here we can but it without the catalyst also and here the bulk syntheses is difficult but here bulk syntheses is easy and the purity is poor here and purity is high so the main important point is less accumulation of the body single wall nano tubes it will accumulation less in the body and multi wall nano tubes it accumulate more in the body.

So depends on your application you have to select weather you need single wall nano wall tube or multi wall nano tubes because in some cases we need less circulation and in some cases we need more accumulation.

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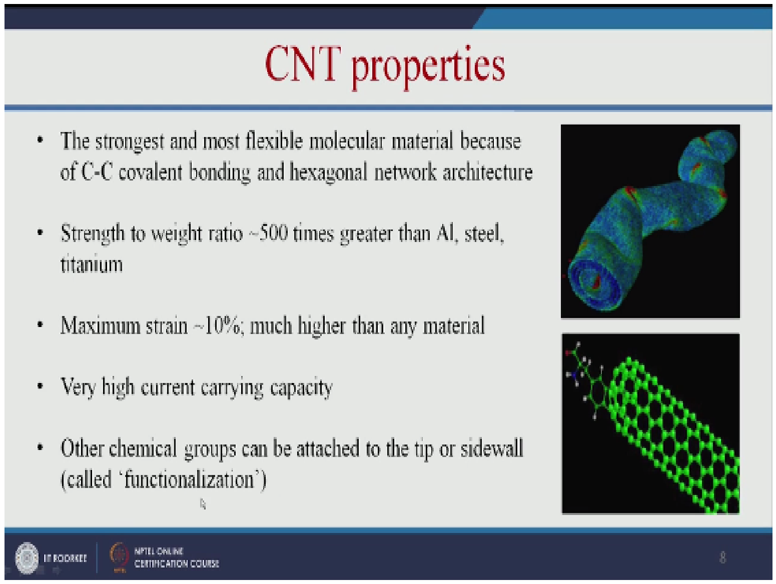

And let us see some of the properties of carbon nano tubes so this is a strongest and most flexible material because of CC covalent bonding okay and it is 500 times greater than the AL, steel and the maximum strain it can with stand is more than 10% which is higher than any material and it is having very high current carrying capacity and also we can adds any kind of functional group that is called as functionalization adding of functional group is called as functionalization.

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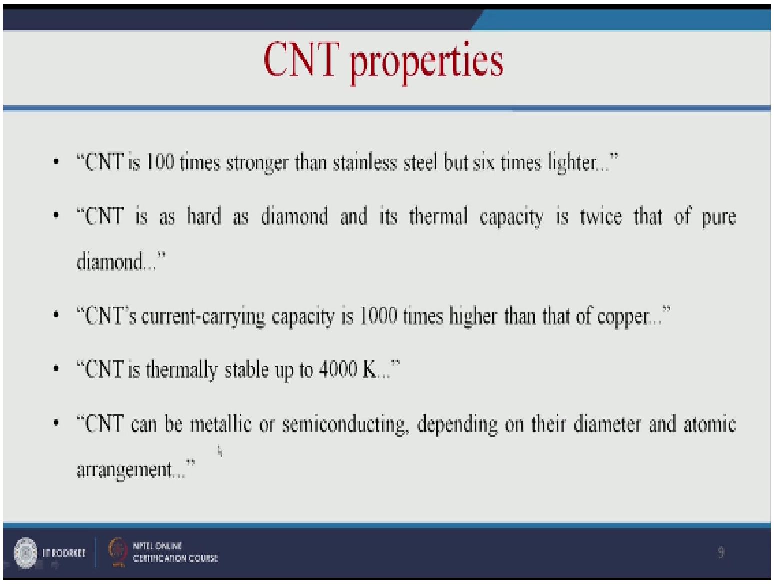

And it is 100 times stronger than stainless steel but it is six times lighter than the stainless steel and it is hard than the diamond okay and it is having high current carrying capacity and high thermal stability and depths on the arrangement of the atoms it can be metallic or semiconducting.

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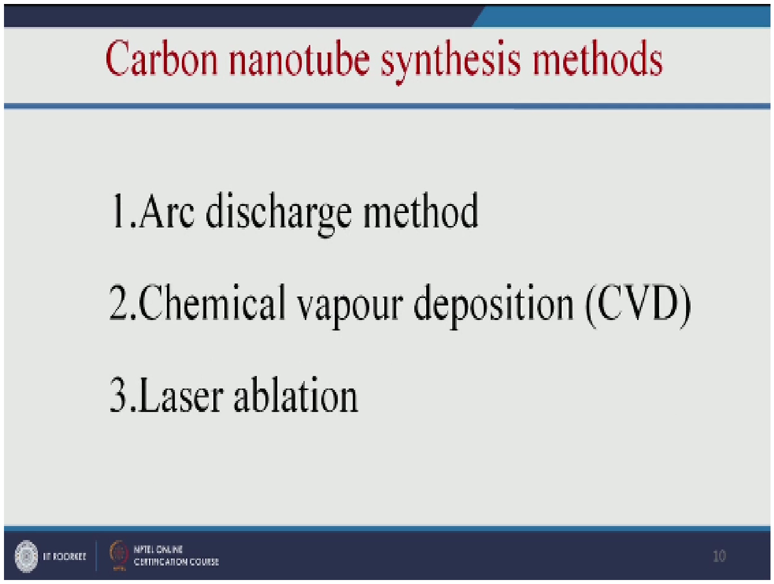

So let us see how to synthesis this carbon nano tube so these are 3 approaches available to make the carbon nano tubes that is arc discharge chemical vapour disposition and third one is laser ablation.

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Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Who	Ebbesen and Ajayan, NEC, Japan 1992 [13]	Endo, Shinshu University, Nagano, Japan [33]	Smalley, Rice, 1995[14]
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

So let us see how we can use this 3 methods ands make the carbon nano tube first one is arc discharge method and here you will connect two graphite rods to a power supply and place then a few millimeters apart okay so that will make the carbon nano tubes here the yield will be like 30 to 90% and you will get short tubes with diameter of 1.4 nano meter and the advantages are like it can easily produce single wall nano tubes and single wall nano tubes have few structural defects.

So that is good for functionalization and here we can make multi wall nano tubes without any catalysis okay and it is not a expensive method so the next method is chemical vapour disposition so place a substrate oven and heat to 600^0 C and slowly add carbon bearing gas such as methane as gas decomposes it is produce carbon nano tubes okay and here the yield will be like 20 to 100%

So here we can get the long tubes with the diameter of 10 to 240 nano meter and it is the easiest to scale up the industrial production and here the purity will be high and the next method is laser ablation so here we will be applying the laser light on the graphite and it will produce a carbon nano tubes here the yield will be lie 70% and the advantages are like primarily it is used for single wall nano tubes and it is a pure material so the reaction product is pure so we can used it for biological application but the problem is this is little bit costly technique.

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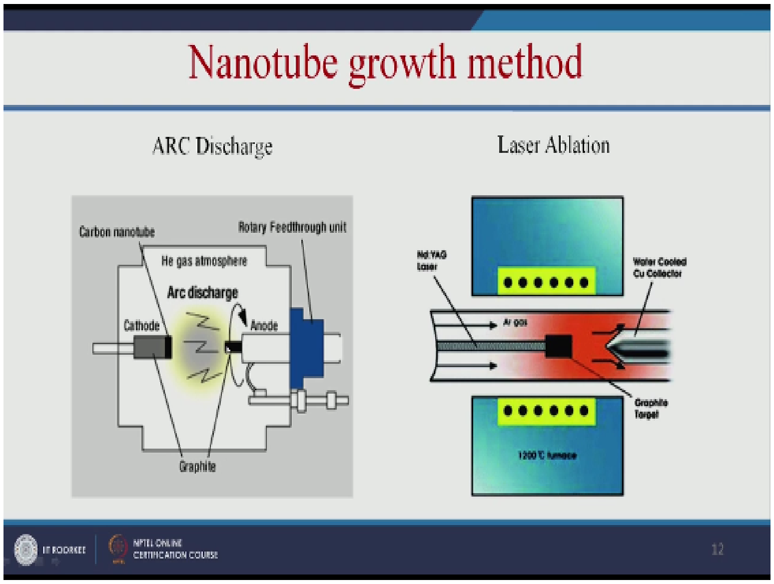

So when this arc discharge they will be having this graphite and cathode and anode will be connected and power will be applied and the all the carbon hands will be deposited in this, okay.

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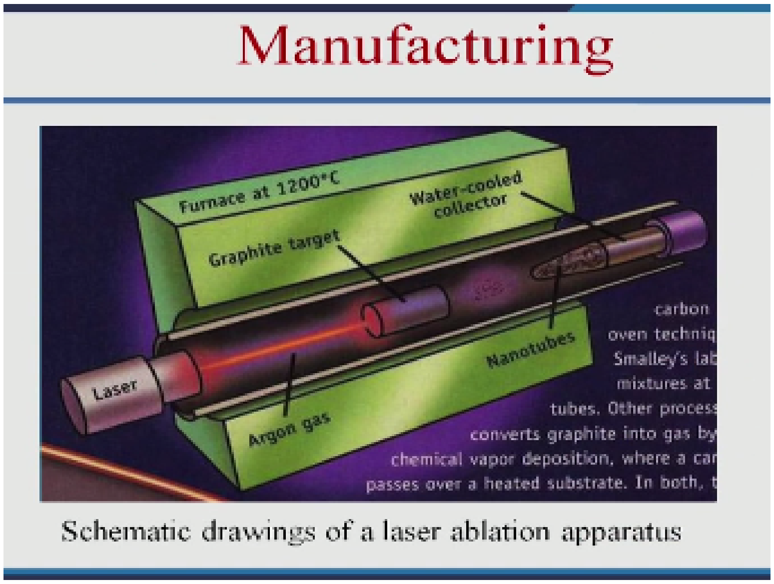

Schematic drawings of a laser ablation apparatus

And in this laser ablation so we will be applying the laser light to the graphite target, okay. And this is kept in the furnace, the furnace is at 1200^0 Celsius and in presence of argon gas so this laser light will vaporize to the graphite target and it will produce the carbon nano tubes so that will be collected in a water cooled collector.

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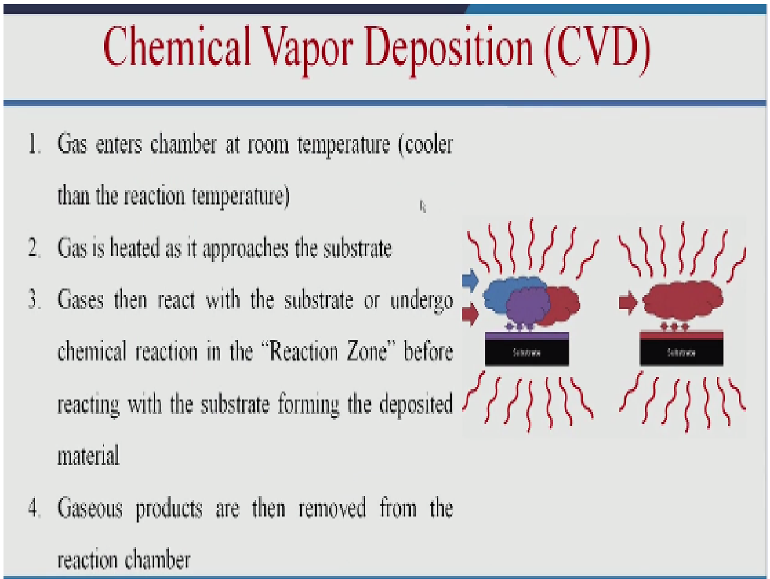

So next one is CVD that is chemical vapor deposition so here the gas enters the chamber at room temperature that means it is cooler than the reaction temperature and gas is heated as it approaches this substrate and gas then react with the substrate or undergo chemical reaction in the reaction zone, before reacting with the substrate forming the deposited material, here the gas is products are then removed from the reaction chamber, okay.

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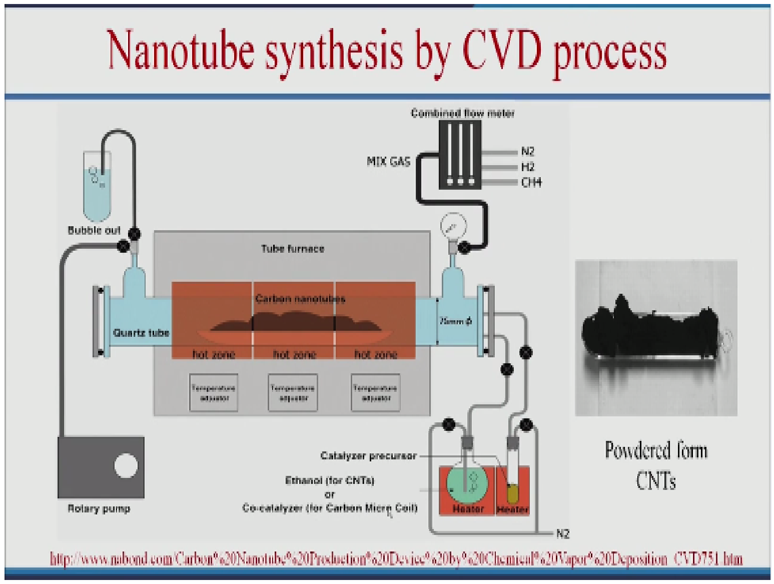

So this is a nano tune synthesis by CVD process set up okay. So you will get this kind of powered form of CNT.

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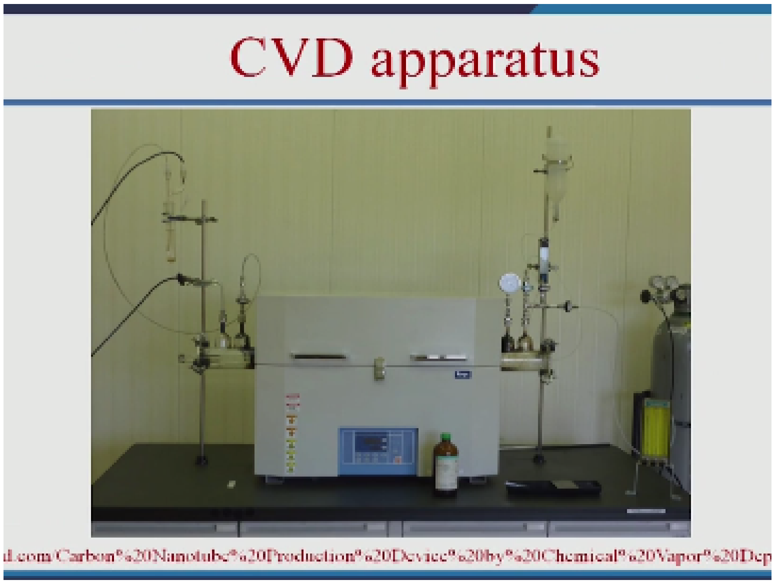

And this is the bend stop CVD apparatus.

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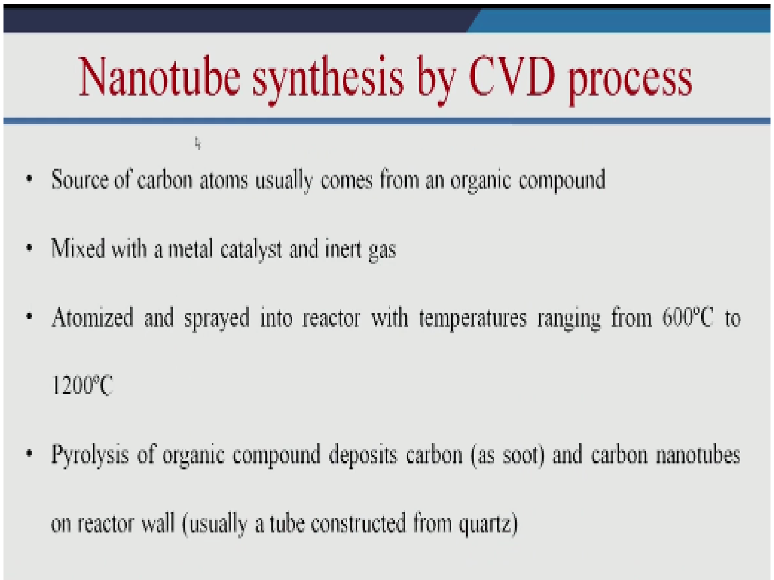

So here the source of carbon atoms usually comes from an organic compound, okay. So mix with a metal catalyst and inert gas and here it will be atomized and sprayed into reactor with temperatures ranging from 600 → 1200^{0}C. Here the pyrolysis of organic compound deposits carbon and carbon nano tubes on the reactor wall.

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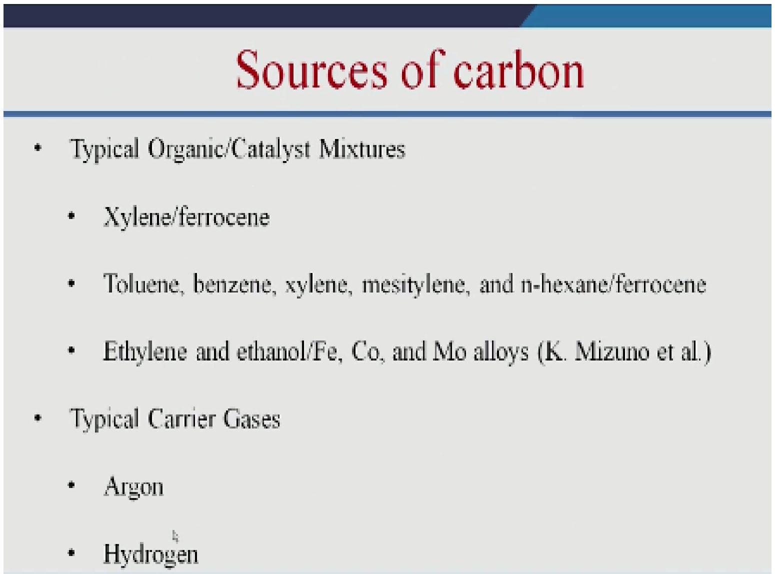

So these are the typical carbon sources Xylene or ferrocene and these are the typical carrier gases like argon and hydrogen can be used for making this CNT using CVD method.

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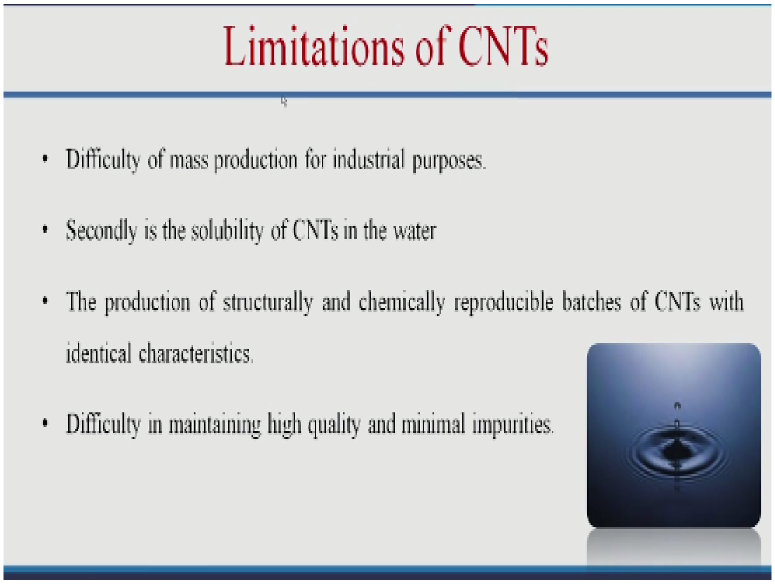

So the limitation of CNT, the first thing is difficulty for the mass production and second thing is the solubility of CNT in the water okay and also it is very difficult to produce the CNT uniform CNT batch wise, okay. And the fourth one is like difficulty in maintaining high quality and minimal impurities.

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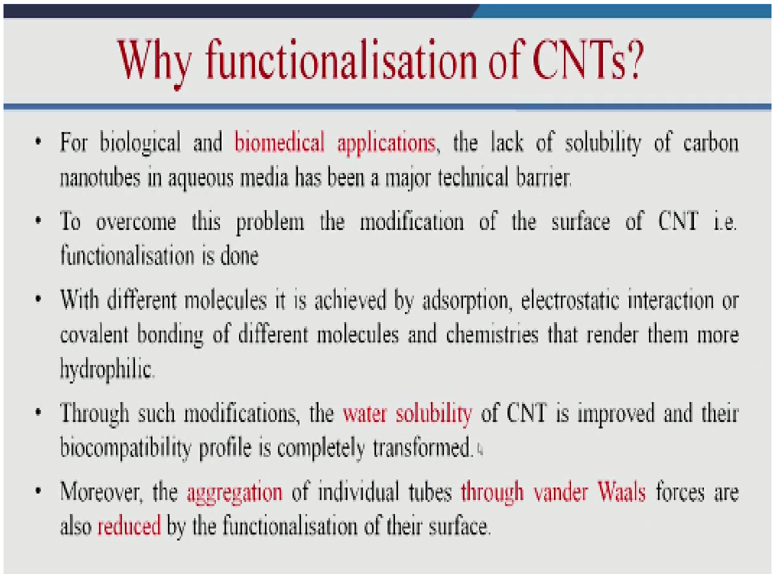

So to overcome those difficulties we have to functionalize this CNT, okay. For biological application biomedical applications so the lack of solubility of carbon atoms in of course media has been imagined technical barrier because this carbon atoms aggregate through Vander Wall forces, so we can overcome this aggregation by doing functionalisation and also it will increase the water solubility of CNT and it will also improve the bio comparability of your CNT.

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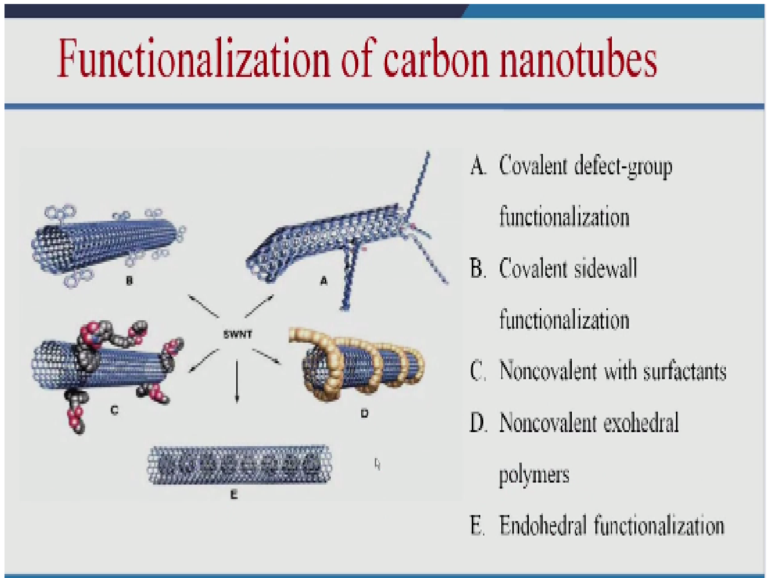

So how to functionalize the carbon nano tubes so these are the various approaches for making the carbon atoms functionless carbon atoms, the first one is covalent defect group and next one is covalent side wall, third one is non covalent with surfactants and fourth one is non covalent exohedral polymers and this one is endohedral functionalisation, so let us see one by one.

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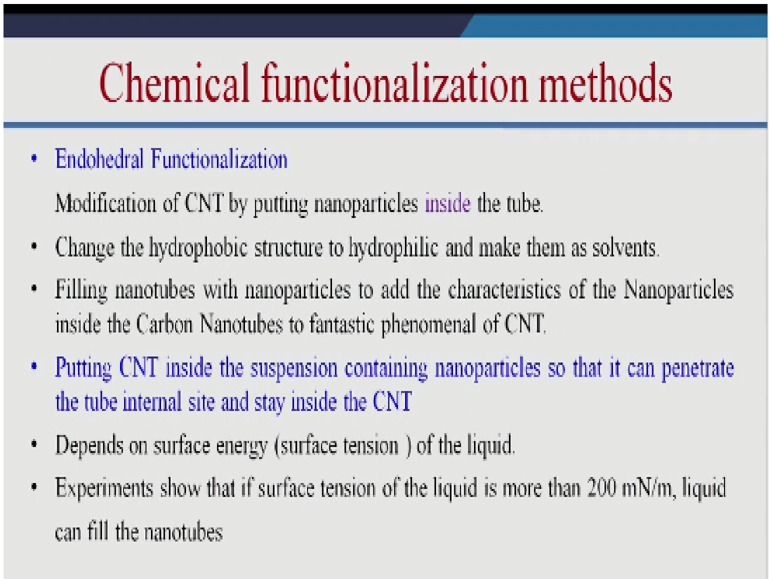

So let us see endohedral functionalisation, so here modification CNT by putting nano particles inside the tube, okay. So we have to incubate the CNT inside this suspension of solution which containing nano particles so that it can penetrate the tube internal side and stay inside the tube, okay. And here the endohedral functionalisation depends on this surface tension of the liquid and if the surface tension off the liquid is more than 200 the liquid can fill the nano tubes.

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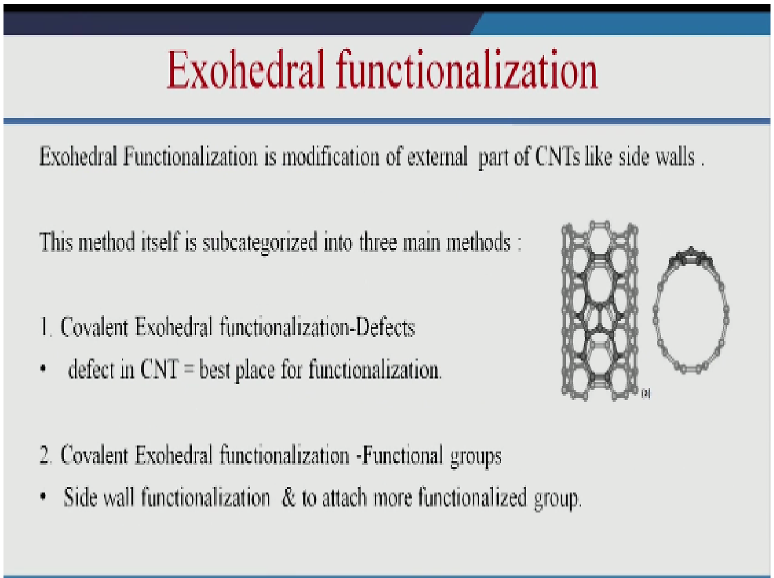

And again this exohedral functionalisation is sub categories into three main methods the first one is covalent exohedral functionalisation that means when you make the carbon atoms there will be some defects, so this defect in this CNT's is the best place for functionalisation, next one is covalent exohedral functionalisation so here we can add the functional group to the side walls of the carbon nano tubes.

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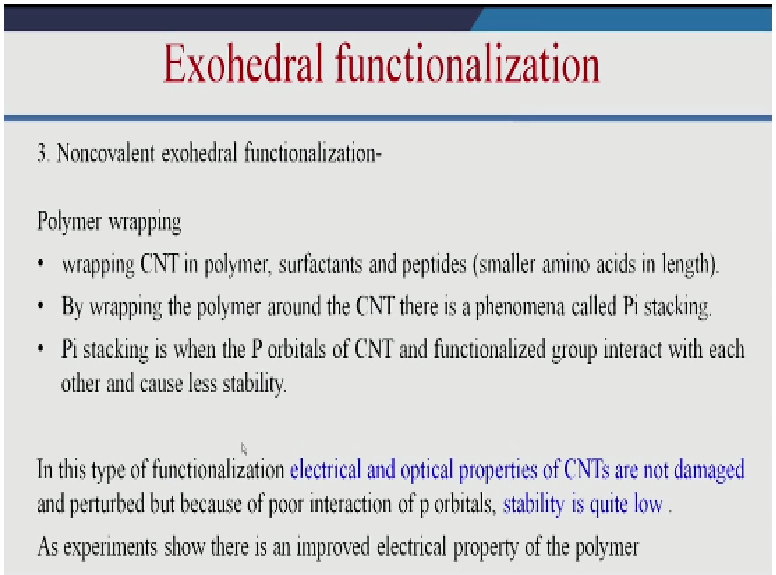

And third one is non covalent exohedral functionalization here you will be adding the polymer or surfactants so which will be wrapping this CNT okay, so by wrapping the polymer around this CNT there is a phenomena called Pi stacking, so what is Pi stacking? It is when the P orbital's of CNT and functionalized group interact with each other and cause less stability, okay. So in this type of functionalization the electrical and the optical properties of CNT's are not damaged. But the stability is quite low, okay.

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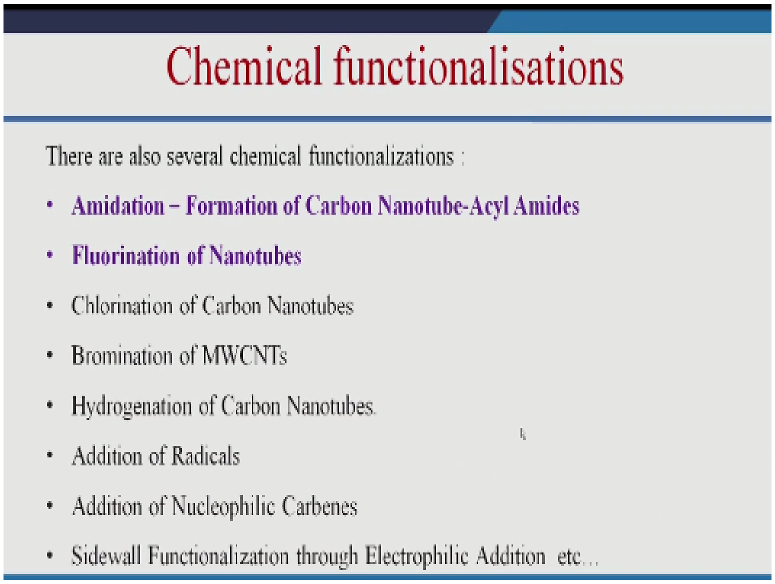

And these are the saw the other types of chemical functionalization but in this we are going to discuss only A midation and Fluorination.

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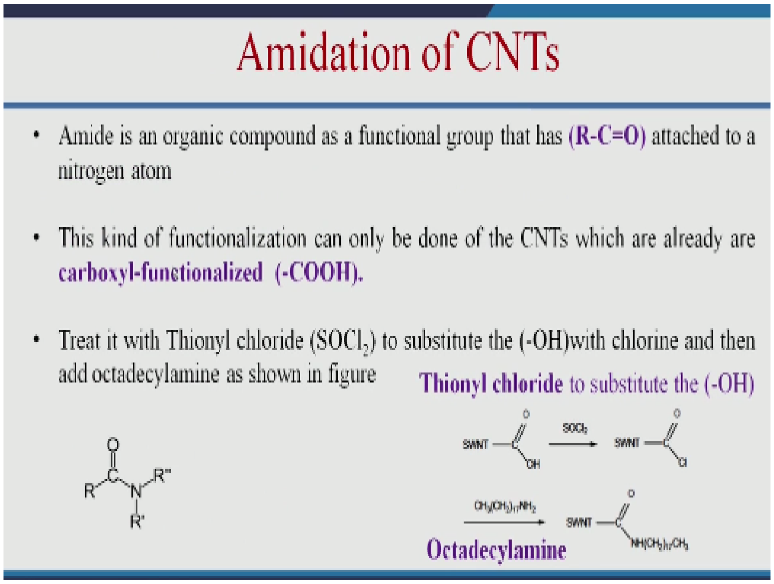

So amidation means addition of amide group but we cannot add the amide group directly the first we have to functionalize the carbon atoms with COOH and followed by that we can add the amide group.

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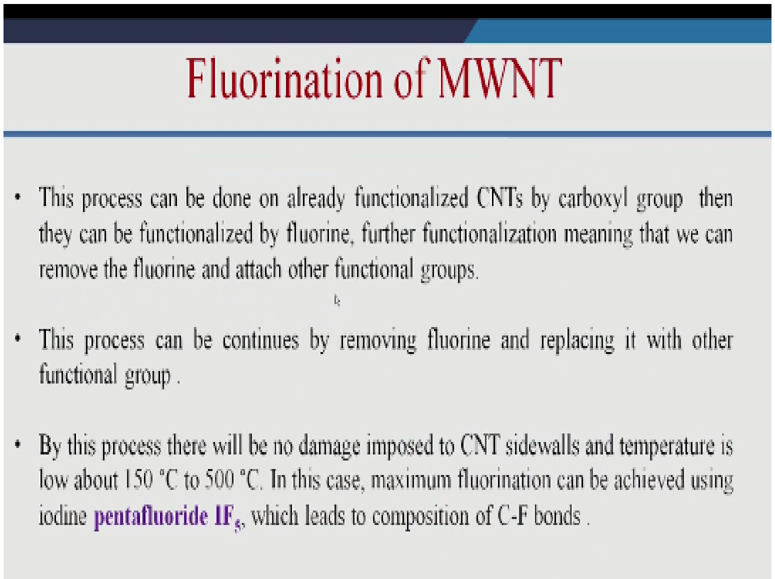

Similarly we can also add the fluorine group using Pentafluoride IF_5 okay.

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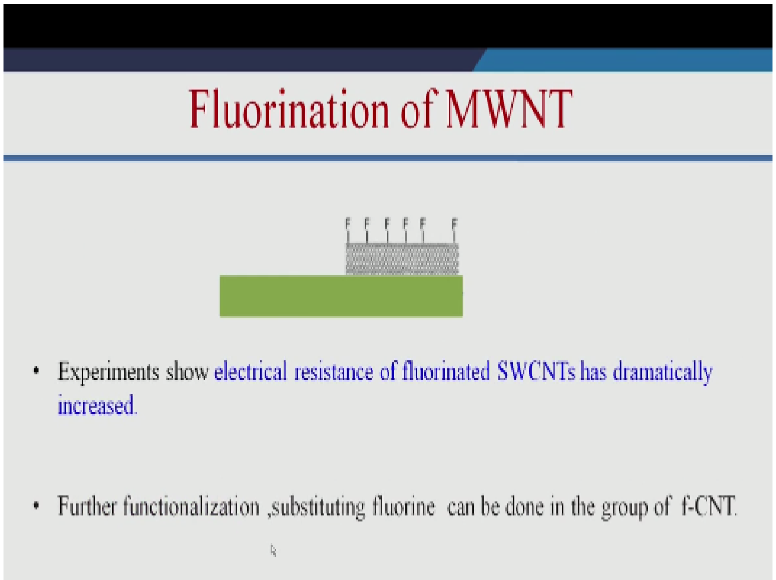

So this will also add the fluorine group so when you add the fluorine group so it is increasing the electrical resistance and also we can substitute the fluorine with some other chemical group and use if for various application.

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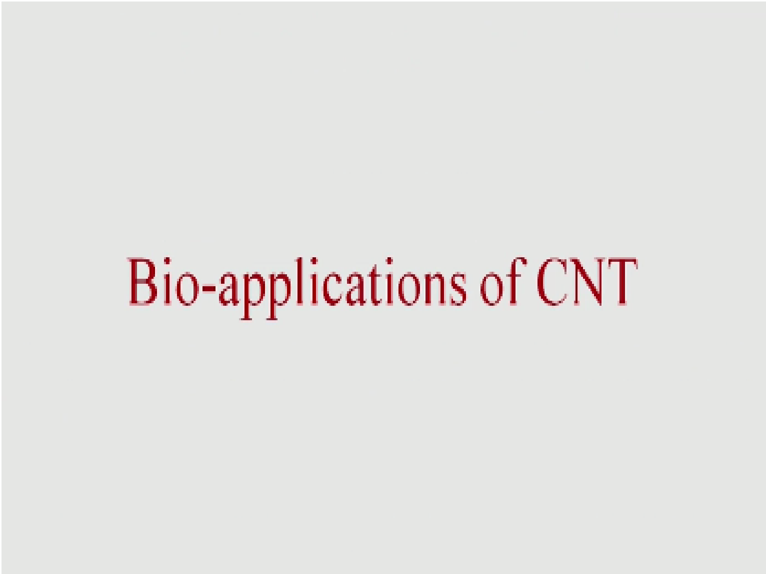

So let us see the various applications of carbon nano tube.

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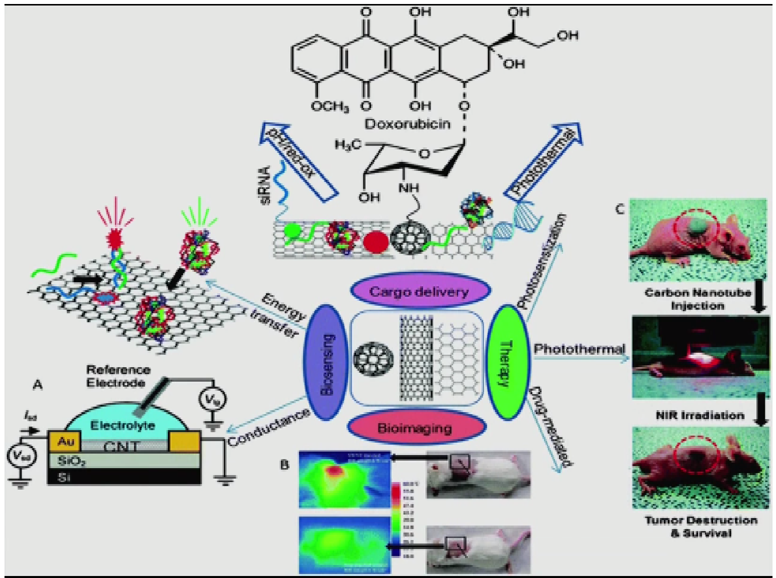

So this carbon nano tubes can be useful for bio imaging and also it could be useful for drug derive application and we can also use it for bio sensing and for therapeutic or therapist application so let us see one by one.

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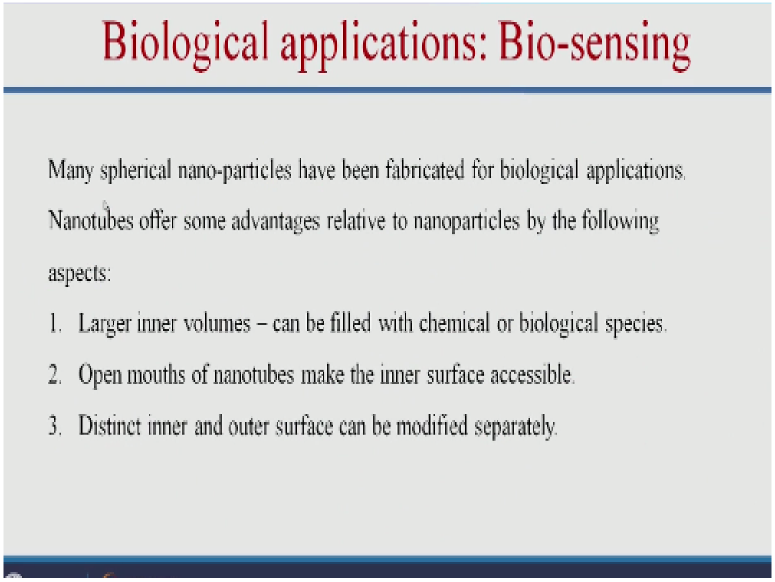

For biological applications so here the nano tube offer some advantages related to nano particles by the following aspects, the first thing is larger inner volumes so the larger inner volumes can be filled with chemical or biological species so it can be loaded with any kind of drug or any kind of imaging agent, so next one is the open mouths of nano tubes so make the inner surface accessible. And third one is distinct inner and outer surface so which can be modified separately.

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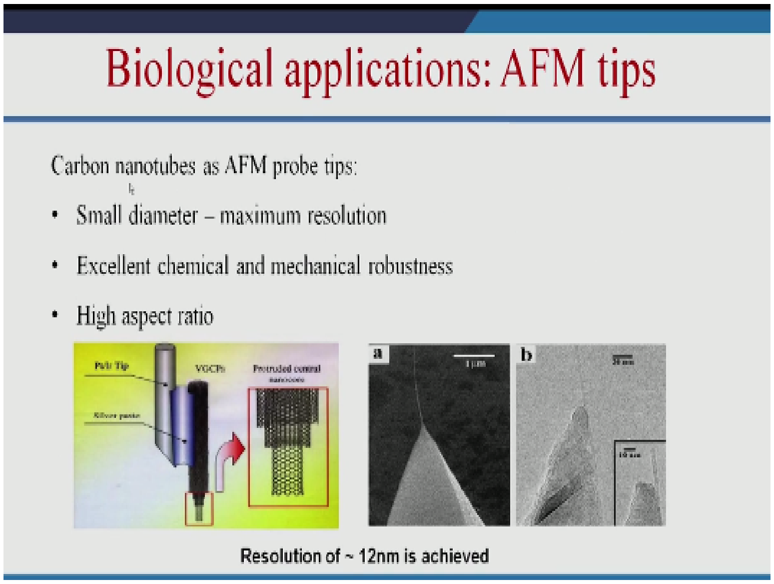

So let us see how we can use carbon nano tubes as a AFM probe tips so it is having small diameter and maximum resolution so it is a excellent chemical and mechanical robustness makes it suitable for AFM probe tips.

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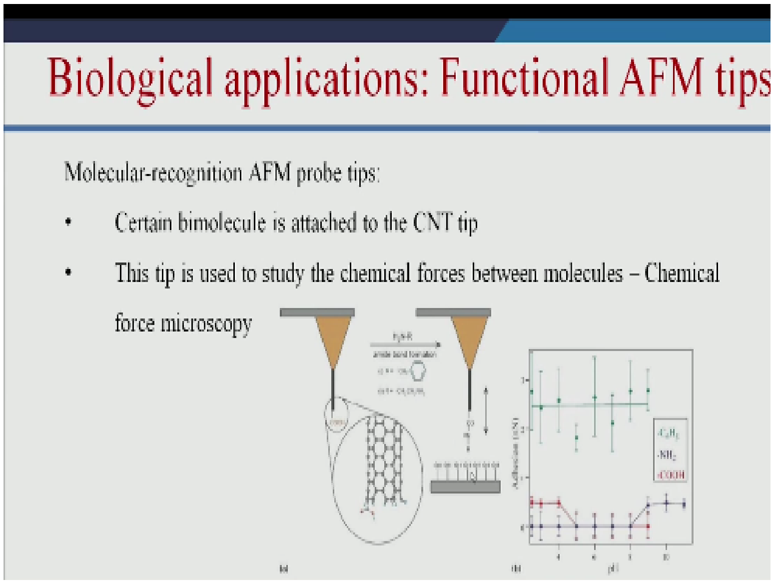

So let us see how to make functional AFM tips certain bio molecules can be attached to the CNT tip okay, so this tip is use to study the chemical forces between the molecules, so it is also called as chemical force microscopy6. So here you can see here that tip is having this some COH functional group suppose your sample is having NH2 so it can react and we can measure the force, so this is called as chemical force microscopy.

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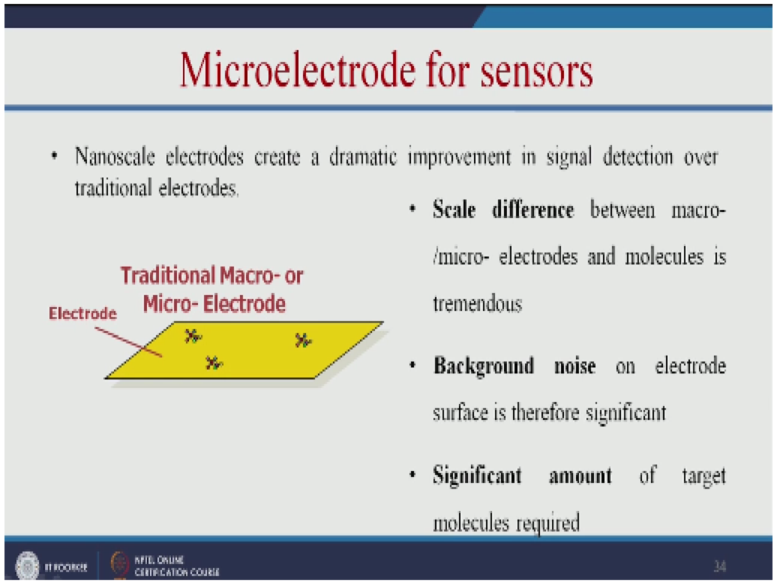

Let us say the comparison between the microelectrode and nano electrode for sensor application, in micro electrode the scale difference is very high because the molecules is in the range of nano scale and your electrode is in the range of micro scale, so the background noise will be very high and here we need more amount of target molecules for sensing the target molecule.

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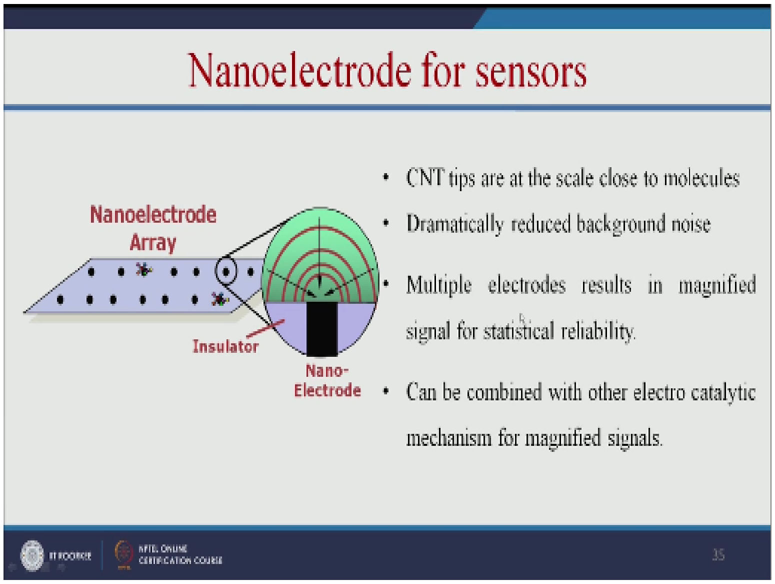

So but when we use CNT tips for making a nano electrode for sensing application it will reduce the background noise because the nano tubes is very, very small scale and it can match externally with your target molecule because that is also the range of nano scale okay, so based on that here the nano tips will be having high sensitivity.

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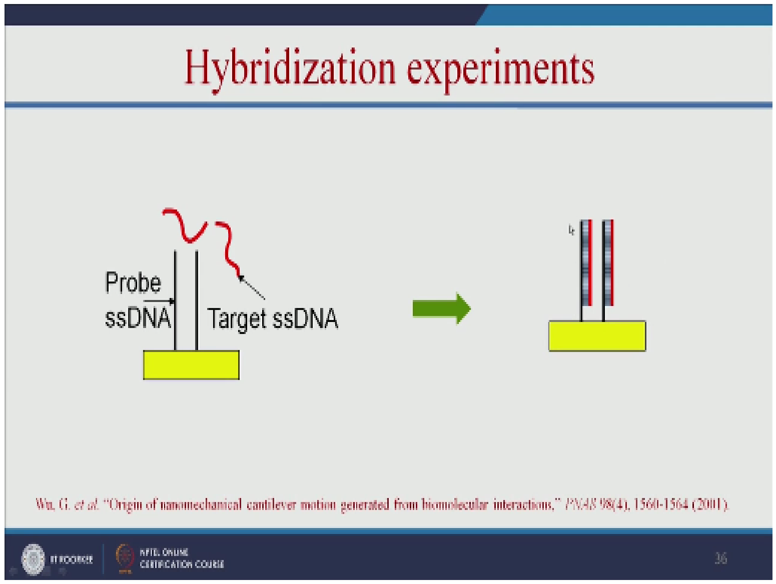

So let us see how we can use it hybridization experiments to make the CNT sensors, so here we will adding single sensor DNS to your cover and will take the target single sensor DNA, from your patients serum and when you put into this sensor this will combine in form this kind of bond that is your hybridization okay. So if the patients DNA is forming a bond with the probe DNA that means that person is having the particular disease.

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So you will be having a probe single standard DNA and another one is target DNA, for example so this DNA where taking from some patients serum so when it come and form a bond with this probe DNA by hybridization okay, so the electrical connectivity property of this CNT will be changed, so based on that we can detect the disease.

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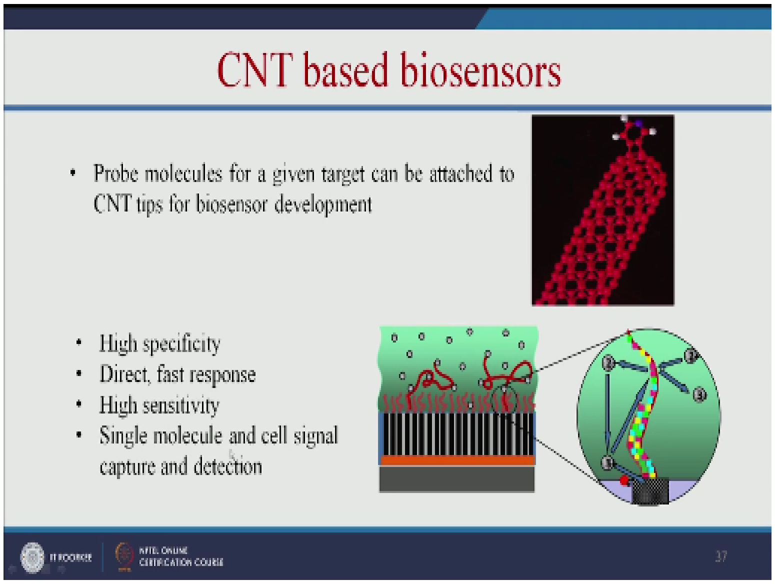

So as I told you earlier so this pro molecule for a given target can be attached to the CNT tips or making bio sensor just it has high specificity and it is very fast and direct response and it has high sensitivity even a single molecule can be also detected.

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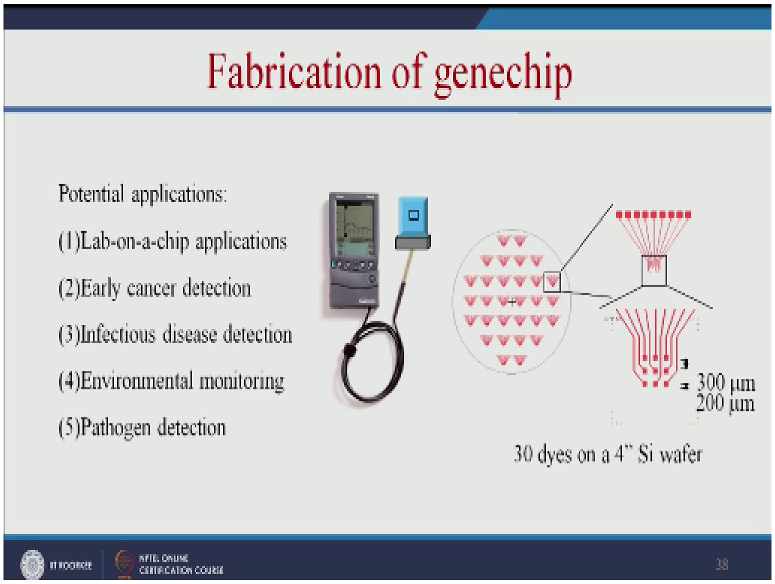

And based on that we can make a genechip or lab on a chip, so the lab on a chip is also the same principle for example.

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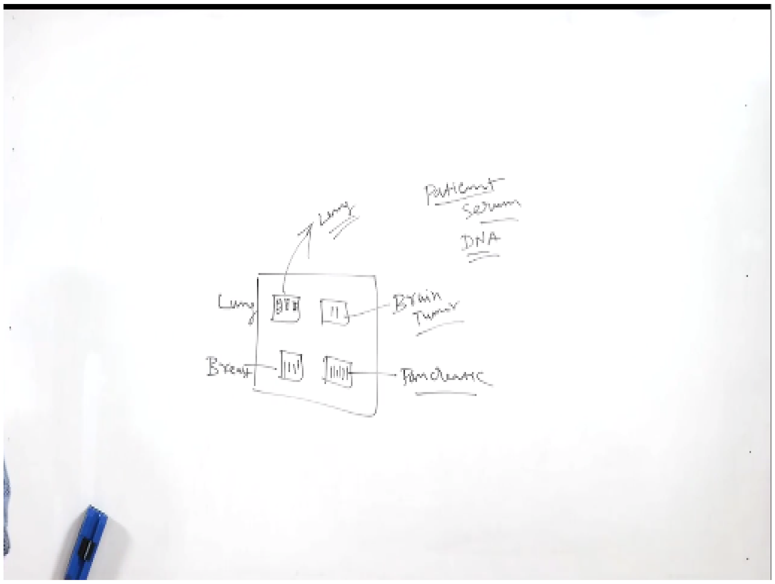

If a person is having some kind of cancer so you can make all the DNA probes for example the first box is for a lung cancer and this is for breast cancer so this is for pancreatic cancer okay and this can be for your brain tumor so we can have all the single standard DNA probe in the micro wave chips okay, and when you take the patient serum so we can take the DNA from the patient serum and you can harry to this and minute forms hybridization with the only lung cancer probe that means the person is affected by lung cancer okay.

So instead of going through all the reactions we can have all the things in a simple lab on a chip concept, so all the DNA will be here, so based on that we can easily identify what kind of cancer that particular patient is having and we can also increase the sensitivity and we can save lot of time okay so which will be useful for a Ellice cancer detection and also for various infection disease detection.

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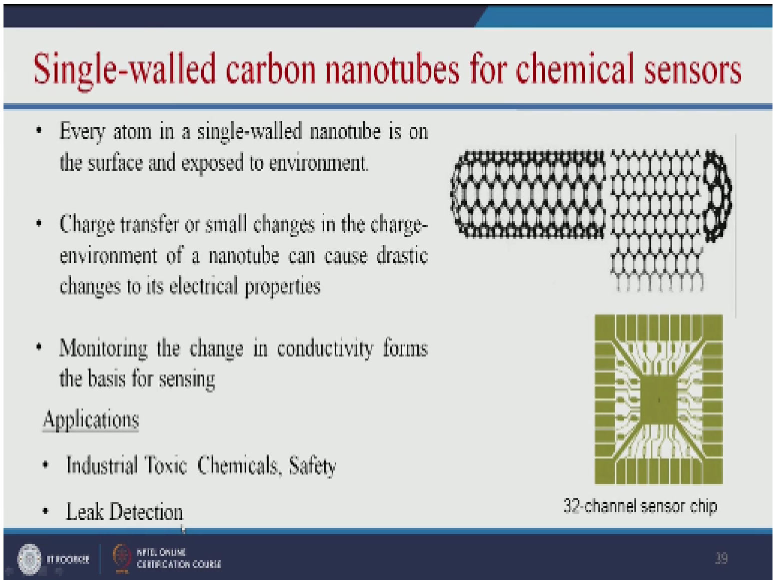

So let us see how we can use single wall carbon nanotubes for chemical sensor here every atom in a single wall nanotube is on the surface and exposed to environment okay, so charge transfer or small changes in the charge environment of a nanotube it can cause drastic changes to these electrical properties, so based on that we can make a chemical sensor which will be useful for lead direction and other application.

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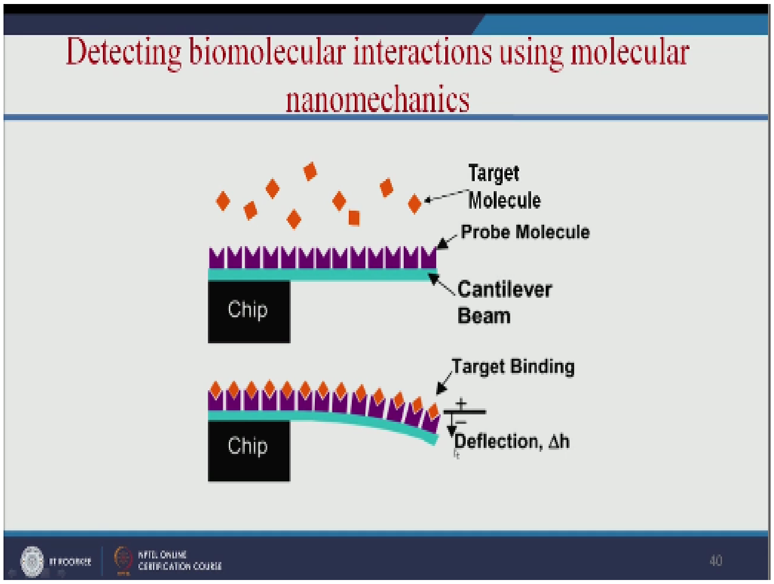

So let us see how we can use that cover nanotube base sensor for detecting the various diseases so we can have this kind of chip and it is a cantilever beam if the patient serum have more amount of particular antigen and if it is comes and bind depress the number of antigen there will be deflection, so we can measure the deflection and we can easily identify the disease.

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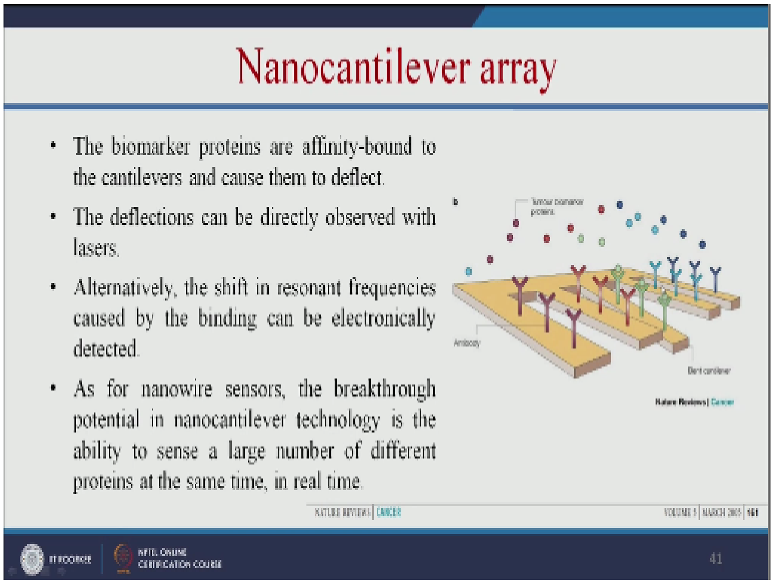

So with the patient serum having more amount of antigen there will be more amount of deflection so based on that we can make a nano cantilever based array for bio sensing application.

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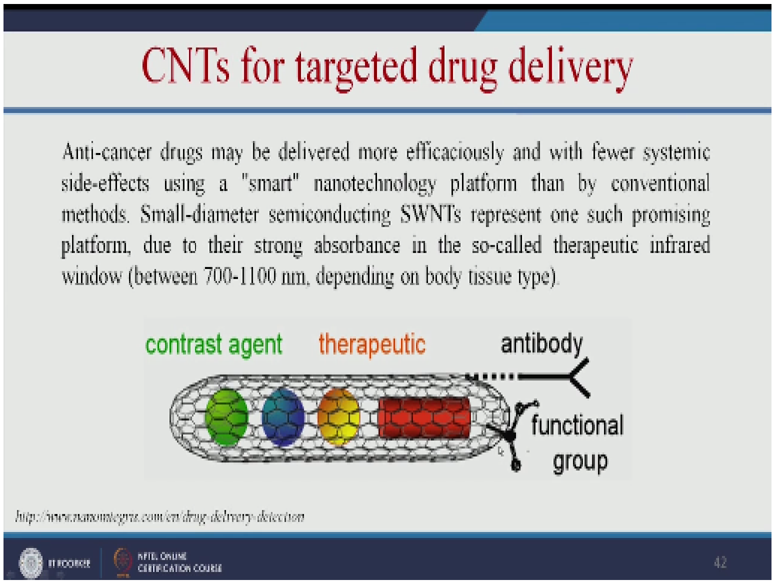

And we can also use cover nanotube for targeted drug delivery so here you can see here this carbon nanotube is loaded with contrast region, so this contrast region is for imaging application and therapeutic is for your it can be any antics drug for therapeutic application and antibodies for targeting your carbon anti body only to the cancers and we can also add functional group which will give the bio comparably to your carbon nanotubes and it will increase the circulation time so this is called as multi function nano particle or also called as theranostic nano particle because it is having both contrast stage and as well as the therapeutic agent.

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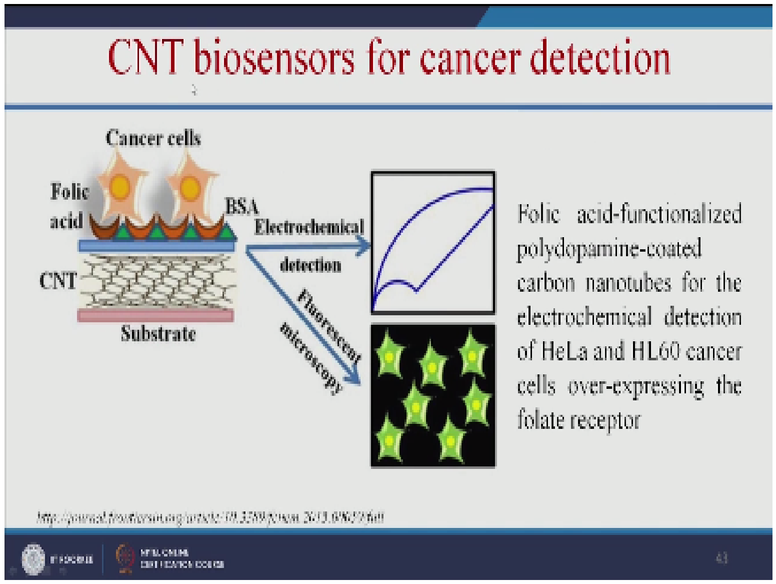

So let us see how to make CNT biosensors for cancer direction.

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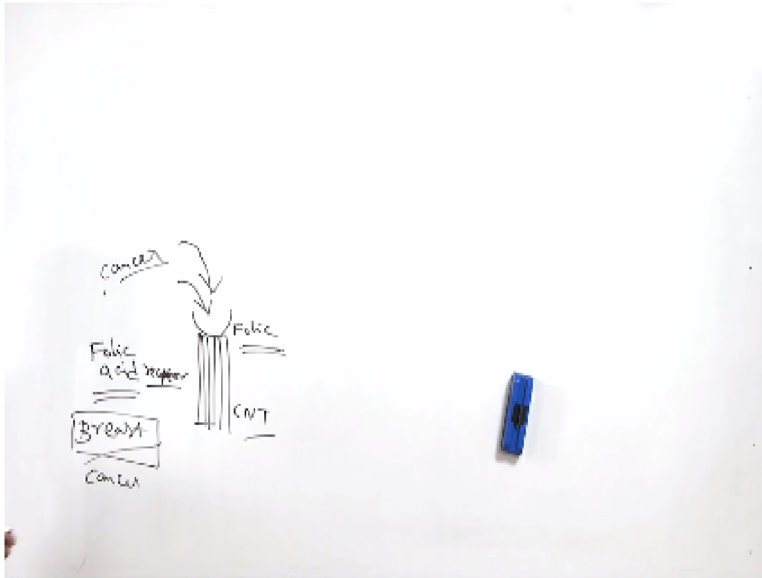

So some of cells will express receptor for folic acid, the some of the cancer cells like breast cancer it will express folic acid receptor so when you make the carbon atoms with the folic acid so this cells can come and bind to the folic acid, so it is not the single carbon atoms it will be a array of carbon nano tubes okay, so it is having folic acid and your cancer cell is having receptor for folic acid so your cancer cells can easily come and bind to the folic acid.

So based on that we can make a sensor for cancer detection so here you can see here this carbon atoms are coated with the folic acid so these are folic acid functionalized polydopamine coated carbon nano tubes and which could be useful for electrochemical detection of breast cancer cells or Hela cells okay, which we are expressing the floate receptor and we can also study the same sample under the fluorescent microscope and we can confirm it.

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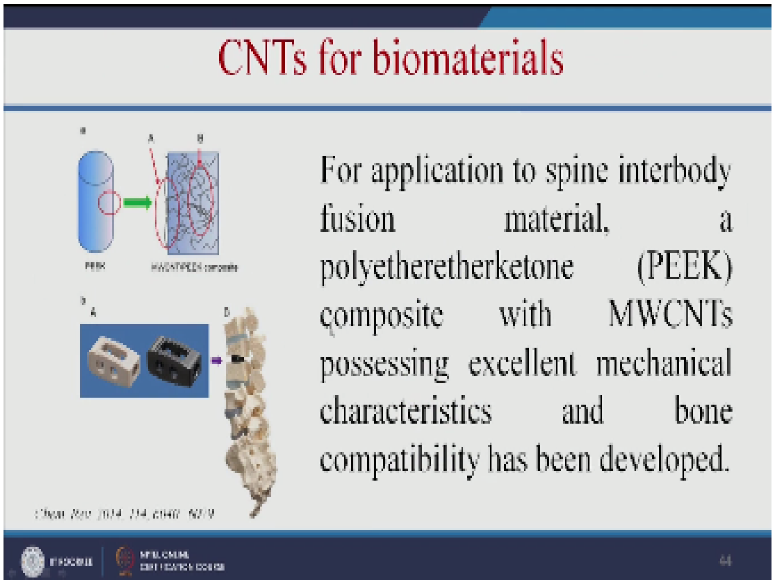

So next one is we can also use the carbon atoms for biomaterial applications, so for application to spine interbody fusion material a material call PEEK that is polytheretherketone so along with multi wall carbon atoms it is possessing excellent mechanical property as well as bone compatibility so which is useful for making a various bio compatibility materials for bone designing also.

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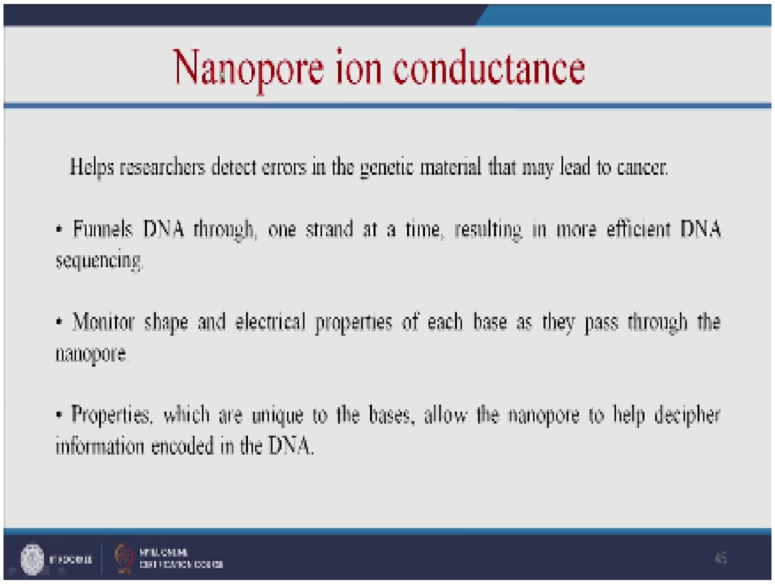

So let us see how we can use this nano pore ion conductance for DNA sequencing, so it will help the researchers to detect the errors in the genetic material that my lead to cancer.

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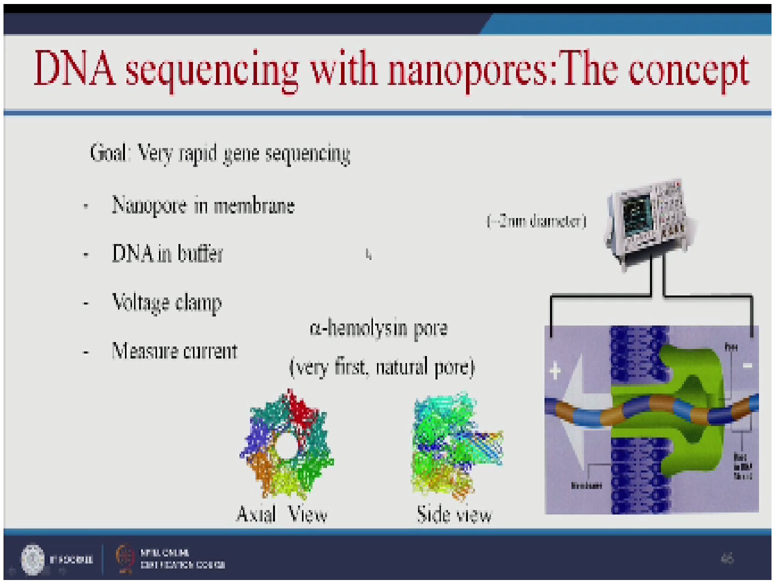

So here you will passing the DNA through this small pores and it will be like your DNA sequencing only and we can use the protein call α-hemolysin but the drawback is like it is toxic protein.

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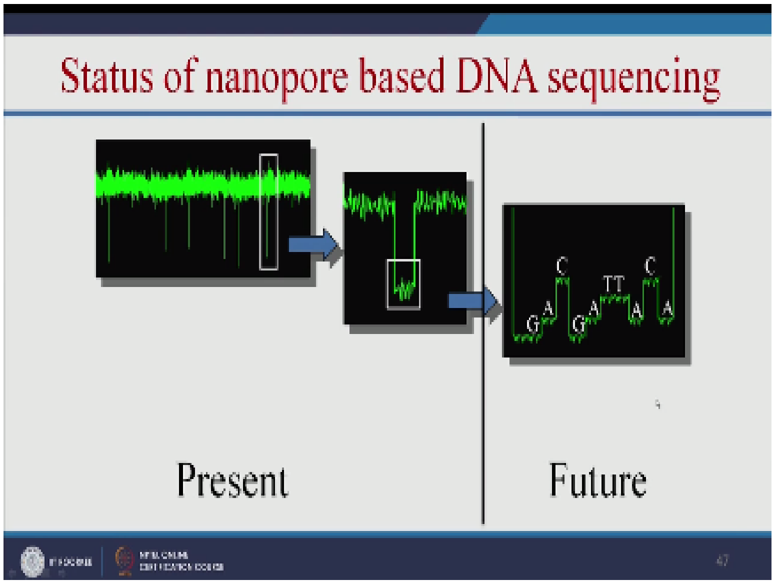

So we can use the carbon atoms for such kind of application so here you can sue the carbon atoms for the same application so when you pass the single standard DNA through the carbon atom there will be a decay in the current, this is the present scenario but in future researchers are trying to develop very specific sensor when the G pass through this carbon atoms it will have a different kind of current decay, and A and C. So we can easily sequence the DNA and it can be a like low cost DNA sequencing device.

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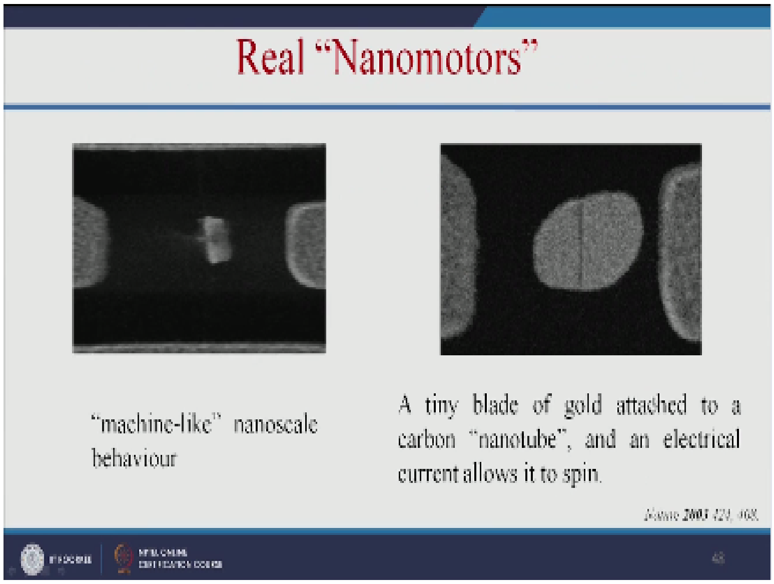

And we can also make carbon nano tube based nano motors you can see here it is like a nano scale motor and this is made up of like gold attached to carbon atom and due to electrical current it is spinning in this direction.

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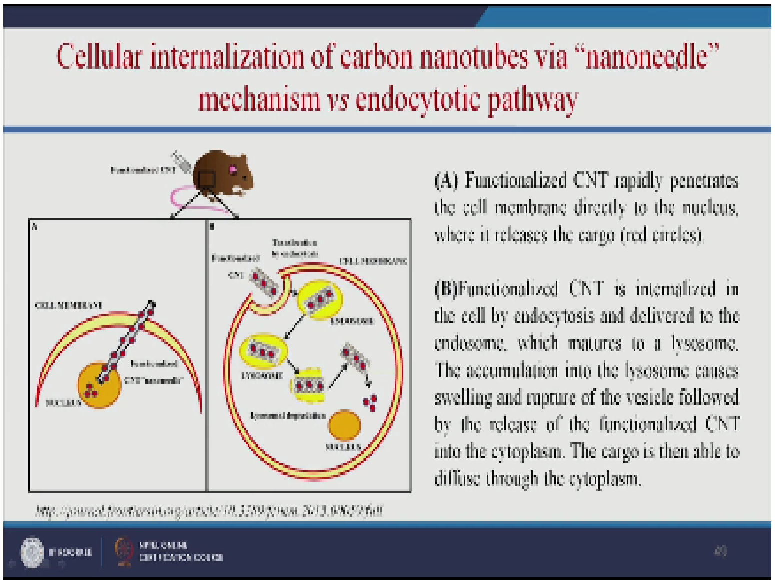

So let us see how this carbon atoms can be taken up by the cell, the one is nano needle mechanism the other is endocytotic pathway, so in this nano needle mechanism it will directly inject the cells and it will release the drug and the other one endocytotic pathway so here the CNT will be attached to the cell and endocytotics will happen and your CNT will be in endosome and this endosome will combine with the lysosome and it form the lysosome and it will degrade and it will release the drug molecules into the cytoplasm.

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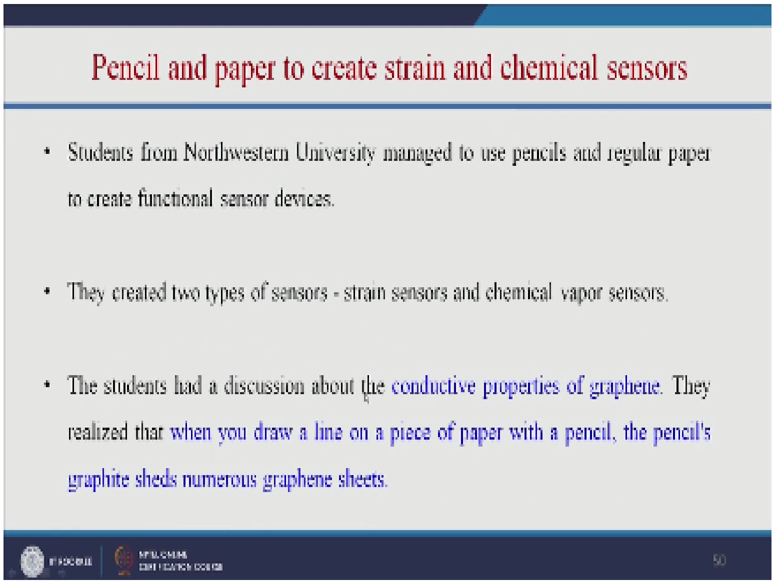

So let us see how to create a simple strain and chemical sensor using pencil and paper, so students from Northwestern University, so they used pencil and paper to create functional sensor devices. So the graphicness very good conductive property so when you draw a line on a piece of paper with the pencil, the pencil shades numerous grapheme sheets, okay.

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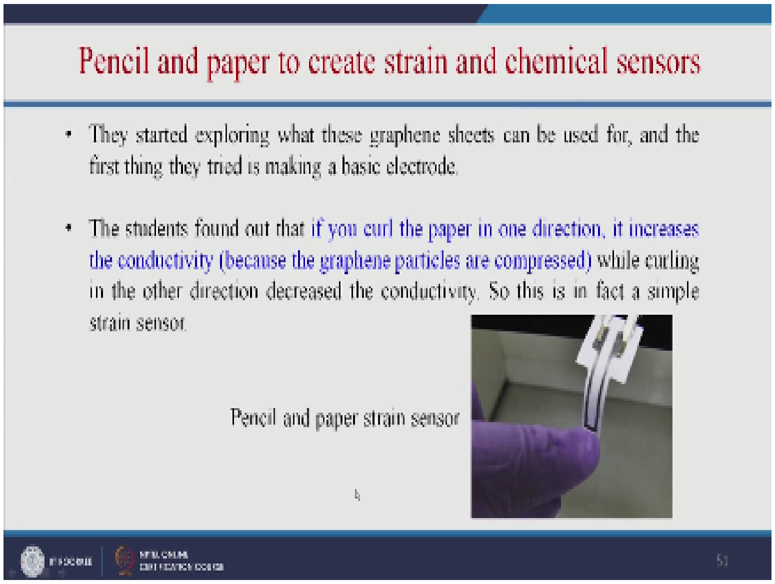

So based on that we can make a strain or chemical sensor, so if we make this kind of line on the paper and if you curl the paper in one direction it increases the conductivity, because the grapheme particles are compressed, okay. So while curling in the other direction it decrease the conductivity, so this is a simple strain sensor.

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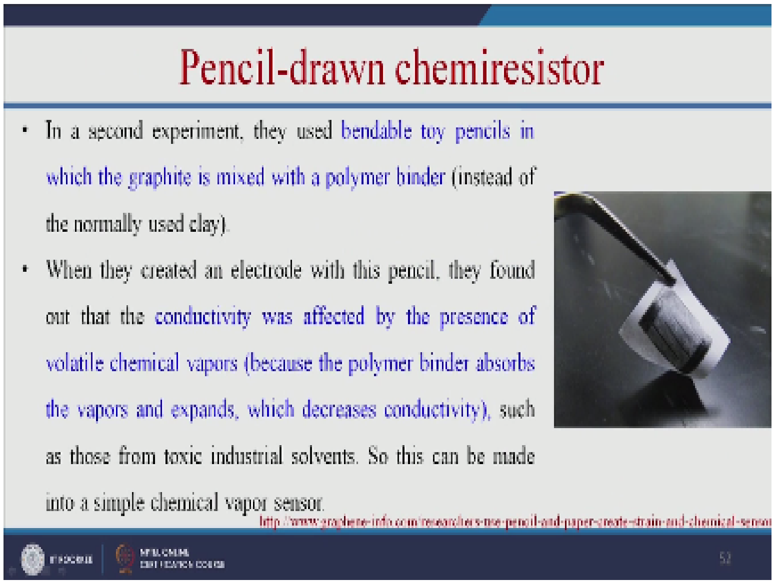

So in the second experiment they have shown that how we can use that bendable type pencil for making chemical sensor, so here they use bendable type pencil in which the graphite is mixed with a polymer binder okay, so when they create an electrode with this pencil they found out that conductivity was affected by the presence of volatile chemical vapours, because the polymer binder observe the vapour and expands and which decreases the conductivity, okay.

So we can use the simple paper and pencil for making chemical sensor as well as the strain sensor, so as a summary of this lecture so we have learnt what is carbon atoms and how to synthesis carbon atoms by various methods and also we have leant how to functionalized the carbon atoms and also various bio applications of this carbon atoms. So I will end my lecture here thank you all for listening, I will see you in another interesting lecture.

For Further Details Contact

Coordinator, Educational Technology Cell

Indian Institute of Technology Roorkee

Roorkee – 247667

E Mail: etcell.iitrke@gmail.com. etcell@iitr.ernet.in

Website: www.iitr.ac.in/centers/ETC, www.nptel.ac.in

Production Team	**Camera**
Sarath Koovery	Arun. S
Mohan Raj. S	
Jithin. K	**Online Editing**
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