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Module - 02 Defects, and reaction kinetics of non - metallic materials Lecture - 11 Carbonaceous materials

Welcome to the course of Non-metallic Materials. So, we are in module number 2 Defects and Reaction Kinetics of Non-metallic Materials where I will be taking you through Carbonaceous material.

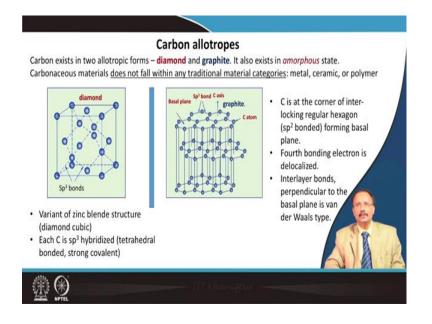
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Now, the lecture basically will describe different carbon allotropes which is diamond is one of them, synthetic diamond and polycrystalline diamond, its manmade diamond, graphite, carbon fiber is the basic carbon allotropes.

Nowadays, the nanocarbon lot of research is going on in nanocarbon and you might have heard the name of fullerenes; we will be showing that what exactly it is. Then carbon nanotube various types of carbon nanotubes and the exotic material which is a single layer of grapheme, we call single layer of graphite which called graphene types of different types of graphene this is ultimate material its very heavy high elastic constant. And various other exotic properties so we will be talking on this graphene based material.

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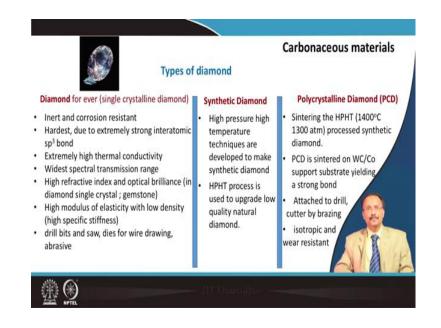
So, diamond you know the diamond is forever. So, diamond is having a zinc blende kind of structure, although exclusively I have not taken the structure, but I assume that you know the basics of the crystal structure.

So, zinc blende structure is something where the sulphur is in the fcc position and the tetrahedral voids which are shown in this view graph this is occupied by zinc cation in case of carbon it is all carbon. So, it is a variant of zinc blende structure and we call it is a diamond cubic structure.

And here the carbon-carbon bond they are all sp 3 hybridized bond and they are very strongly covalent bond. So, diamond is very strong material as you all know. So, one variation of diamond is graphite, where the basal plane is hexagonal as you can see that the basal plane is hexagonal. Carbon is at the corner of this inter locking hexagonal structure and here it is sp 2 kind of bonding is there to form this basal plane.

Now, the fourth bonding electron that is delocalized. So, if it is delocalized it will aid to the electronic conduction and interlayer bonds which is perpendicular to the basal plane this is van der Waals type. So, it is very strong to break in this direction because sp 2 bonding is there covalent, but it its having a flaky structure flaky kind of structure where you can just have a little bit of force then the flak will come out, just like the graphite is having this kind of structure.

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So, the listed the properties and the properties as you can see for the diamond they are all good, it is inert corrosion resistant it is a very hard material hardest material we know on the earth extremely high thermal conductivity wide spectral range is there. So, it has the vibrance color. So, starting from visible to infrared refractive index is also very high very high modulus of elasticity. So, this is a good material and usually the drill bit that is covered by this diamond and which is a very strong material.

Now, natural diamond is very expensive. So, people try to use synthetic synthesize synthetic diamond and high pressure and high temperature is required to develop the synthetic diamond and this process itself called HPHT High Pressure High Temperature. And this process is also utilized to upgrade the natural diamond which is not very good quality. So, you apply this high temperature and high pressure and make it precious.

There are small particle of this HPHT kind of diamond which is sintered at temperature typically 13 to 1400 degree Celsius and this sintering is done on a plate of tungsten, carbide and cobalt, composite. And cobalt goes inside this diamond. So, this substrate gives a strong bond with the top layer of diamond and this total thing can be bridged on a drill bit or on a cutter. So, it can cut very hard brittle material can be cut by this diamond

well. And this is isotropic and they are very very wear resistant material this polycrystalline diamond which is abbreviated as PCD.

Carbonaceous materials Graphite Carbon fiber-Turbostratic carbon graphene sheets Highly anisotropic: Parallel to basal plane randomly folded resistivity if $10^{-5}\Omega$ -m , perpendicular $10^{-2}\Omega$ -m (delocalized electron) · Basal plane slide past one another, excellent lubrication Soft and flaky. Significantly smaller modulus of elasticity than diamond. In plane electrical conductivity is significantly higher than diamond. Thermal conductivity is approximately same. · Thermal expansion value in plane is small and Hybrid graphitic - turbostratic carbon negative, plane perpendicular is positive and fiber. large. Strength and elastic modulus greater Crucible, Li ion battery anode, machinable parallel to longitudinal direction

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Now, the graphite as you understand that the flake structure is easily identifiable because of the basal plane and with van der Waals bond in between. So, it is highly anisotropic parallel to basal plane the resistivity if it is 10 to the power minus 5 ohm meter perpendicular it is much low 10 to the power minus 2 ohm meter because of the delocalized electron which I have talked about.

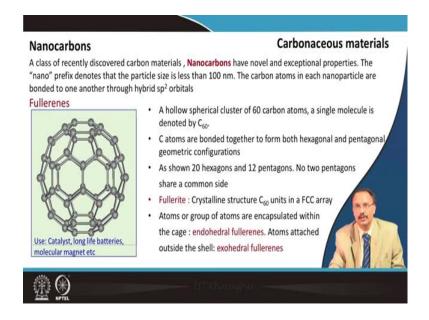
And basal plane they slide past to one another, so that gives a lubrication property of the graphite powder, they are soft and flaky. And in plane conductivity electrical conductivity is significantly higher than diamond for this delocalization of electron. And thermal conductivity between these two is almost same and thermal expansion is another important parameter in plane, it is small and even negatives and plane perpendicular to it is positive and very large.

And usually one can make the graphite crucible which of course, inside the furnace you will have to use an inert ambient otherwise you cannot use it. And also the exotic use is anode material for lithium ion battery. In fact, Sony started their lithium ion battery by using graphite as anode material and it is machineable also.

Now, once carbon fiber is prepared it has this graphitic component, it is basically a hybrid kind of thing. So, each fiber the cross section if you can see that in this region you have the flakes of carbon and in this region we call this is turbostratic carbon.

So, this turbostratic region it is basically the graphene sheet, you know that each single layer of graphite is graphene they are randomly folded. So, this is not that much good alignment is there. So, it is trembled in this region which I have defined as turbostratic carbon carbonaceous region. And this is a typical example of carbon fiber micro structure and strength and elastic modulus is greater parallel to the longitudinal direction for this material.

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Now, these are natural carbonaceous material it was well known to us, but very recently although two decades are passed in 1990 it started through the formation of this nanocarbon.

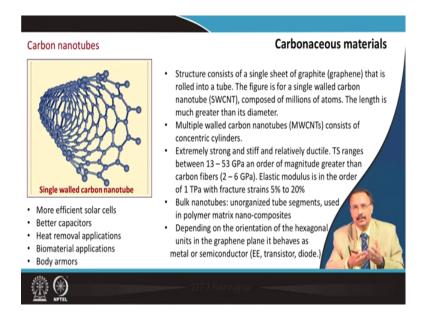
And, this nano prefix that determines the particle size is less than 10 nanometre. although there is no strict guideline 2 nanometre is also nano and 10 nanometre is also nano, it depends on whether this nano size is changing the properties or not, but usually 100 nanometre and less dimension, we call it nano. And the carbon atoms in this nano particles are bonded to one to each other as you can see by sp 2 hybrid orbital bonding.

So, it form some kind of hollow structure with 60 carbon atoms and a single molecule of fullerene is basically represented by C 60 which denote 60 carbon atoms are there. And they are bonded such that it forms a hexagon and it forms a pentagon pentagonal geometrical consideration.

So, if you count it you will find 20 hexagons are there and 12 pentagons are there, but no 2 pentagons they have a common side. So, if you have a hexagon and pentagon it is always 2 pentagons are separated by hexagon. So, it gives a football like structure when you form a crystalline material out of this.

So, crystalline structure is having FCC array and you have certain other atoms or group which is attached to this carbon atom, when it is inside the cage we term this one as endohedral fullerenes and when the atoms are attached bellow or outside the shell, then we call it exohedral fullerenes.

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Now, one variation of the single layer of graphite which we call graphene is the formation of a tube tubular structure. So, as if a single layer you can roll it to form a structure like this, whatever I have shown. So, it is a single walled carbon nanotube, so only one wall is there.

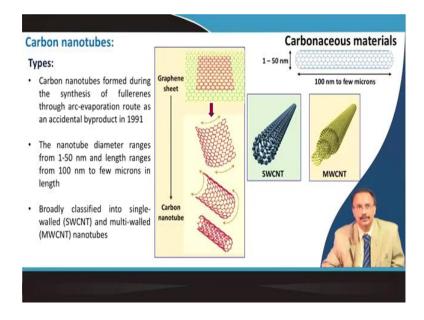
And there are many uses nowadays they are proposing, it can be a more efficient solar cell it will be a better capacitative application heat removal application because of its

thermal conductivity, several biomaterial application drug delivery system and also in body armour because we are very strong. So, body armour also can be used.

So, this is a typical example of a single walled carbon nanotube and millions of carbon atom it constitutes and as you can see the length is much larger than the diameter. So, the diameter actually defines its nano size. Similarly, we can explain in the later part of the lecture that multiple walled carbon nanotube is also there and the properties are very very exotic the tensile strength is somewhere in between 13 to 53 giga Pascal.

And, this is an order of magnitude more than the carbon fiber you know the carbon fiber is used as a reinforcement in polymer matrix. So, if we use carbon nanotube they are each much stronger elastic modulus is in the order of 1 tera Pascal and fracture strain is 50 to 20 percent, normal ceramic 0.1 percent strain is sufficient for brittle fracture to take place. So, they are very exotic material. And bulk nanotube one can have their unorganized tube segment entangle to each other.

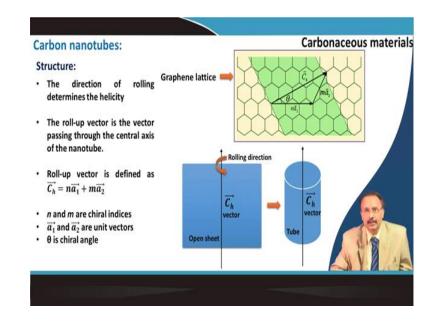
So, that is used in polymer matrix to form nano composites and depending on the orientation of these hexagonal unit in the graphene plane, that behaves as a metal or semiconductor in a movement I will describe the thing to you.



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So, there are various types of carbon nanotube as you can see a single layer grapheme, you can just role it to form a single wall carbon nanotube abbreviated as SWCNT. And

the concentric this kind of feature is also possible you can make it, we call it say multiwalled carbon nanotube see the length is quite large 100 nanometre to few microns it can go, but the diameter is much low it signifies a tube. So, that it is 1 to 50 nanometre.



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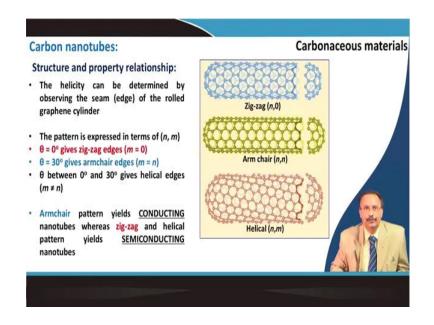
So, if you go in to the depth of the structure of the nanotube your graphene sheet is something like this and you have a axis and with this axis you can just roll it right. So, this roller vector passing through a central axis of the nanotube, which is shown here ok.

So, basically this is a graphene lattice and then you have a this is although a arbitrarily kind of axis I have chosen. So, this axis is the chiral axis and you can roll the graphene sheet across it. So, there are two unit vector that is there, which is denoted by a 1 and a 2 and this term m and n they are chiral indices right.

So, they define the type of the carbon nanotube and theta is the angle between these chiral vector and this unit vector a 1, so that is theta. So, theta can assume any angle from 0 degree, when it is 0 degree, then this axis false on the unit vector and there is no existence of this second vector right.

So, this is one case where it is 0 degree, similarly you have another case which is 30 degree. So, the terminology is important the roll up vector is defined at C h, n and m they are chiral indices, a 1 and a 2 they are unit vector and the theta whatever I have defined that is the chiral angle.

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Now, if you see the structure and property relationship in this carbon nanotube, we will have to understand the geneses of this kind of structure of the carbon nanotube. Now, we define a term which we call helicity, this is defined by looking at the seam that is the edge of this carbon nanotube.

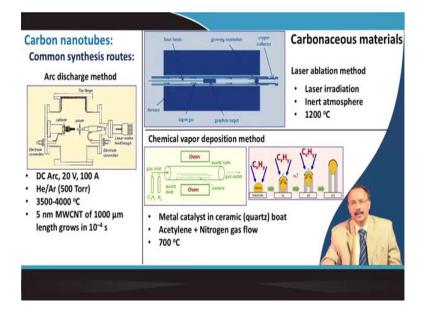
If you just break it then the edge you can see either it is marked by red pattern or it is marked by blue pattern or it is marked by the black pattern. So, each of this kind of pattern define the type of the nanotube; the first one we call it is a zig zag kind of thing, the second one it is a arm chair kind of thing and the third one this is a helical kind of thing. So, in case of the zig zag as I told that m vector is not there. So, therefore, only n is there and another one is 0. So, we call it is a zig zag vector.

So, the pattern is expressed in terms of n and m and also as I showed that when theta is 0 then n equal to 0. So, it forms this kind of zig zag pattern, when theta is equal to 30 degree m and n they are equal. Although, not very clearly understandable form this figure you will have to work it on I will try to set an assignment problem where you can actually work out that what is the interrelation between these two vector angle and the rotational axis to clarify these ideas.

So, when theta is equal to 30 degree we call this is a arm chair kind of a carbon nanotube and theta is between 0 to 30 degree anywhere, then this is a arbitrarily shape we call it's a helical shape. Now, as you can see in case of the arm chair this carbon this hexagonal

are very well coordinated. So, their electronic conduction is pretty good. So, that is why this armchair type of carbon nanotube they are electronically much more conducting as compared to the zig zag and helical because of their structural irregularities usually they exhibit semiconducting behaviour.

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Now, one can prepare the carbon nanotube using different synthesis route. One is the common synthesis is arc discharge method you have two electrode in close proximity and you apply small voltage, but large current 20 volt and 100 ampere huge power supply is required for that.

And ambient is maintained which is inert because otherwise your nanotube will get oxidised. Temperature here it is very large about 3500 to 4000 degree Celsius and usually 5 nanometre multiwalled carbon nanotube to 1000 micron length it can be grown by this technique within no time about less than a second much less than a second, lot of carbon nanotube you can form.

Other good way to make it is a laser ablation method. So, laser is directed to the graphite plate. So, it irradiates the graphite target and then inert ambient is of course, maintained. And then this there is a cold junction here typically 1200 degree Celsius is required for this purpose and you collect the carbon nanotube grown on the cold surface, this is the second technique.

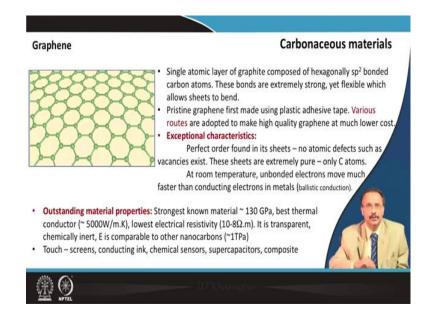
More lucrative technique is chemical vapour deposition where a gas basically is used and a metal catalyst is used. So, the gas typically is acetylene.

So, nitrogen is a carrier gas it passes through inside the furnace and then on the substrate you have a catalyst and this gas dissociates and carbon and hydrogen forms and carbon nanotube start to grow from the catalyst surface as you can see initially this is the state and then as time passes then the carbon nanotube grows and eventually you get the carbon nanotube grown by the CVD process.

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CNT synthes	is routes : A comparative	perspective		
Method	Arc discharge	Laser ablation	Chemical vapor deposition	
Yield	30-90%	Upto 70%	20-100%	
SWCNT	Short tubes (0.6-1.4 nm diameter)	Long bundles of tubes (1-2 nm individual diameter)	Long tubes (0.6-4 nm diameter)	
MWCNT	Short tubes (1-3 nm inner diameter and ~10 nm outer diameter)	MWCNT formation is possible but not fully explored	Long tubes (10 – 240 nm diameter)	/
Pros	Easier synthesis route. Nanotubes have few defects. Open air synthesis possible.	Primarily delivers SWCNT, with good diameter control and few defects. The reaction product is quite pure.	Easy to upscale for commercial production; Longer nanotubes preferably form.	
Cons	Delivers short nanotubes with random patterns. Requires additional purification.	Expensive technique. Requires high-power lasers and is an energy-intensive process.	High defect content. Difficult to produce SWCNT	

So, these are the three prominent technique. And here I have compared the pros and cons of different technique I am not going in to the details line by line you can read that it is in terms of the yield chemical vapor deposition sometimes they are having very large yield. The plus point and minus point formation of single volt or multi volt carbon nanotube, it depends on lot of factors and this is a good comparative table among this.



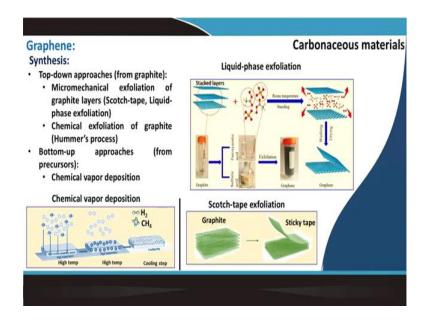
The second thing is graphene and this is the ultimate material as you can see it is a single atomic layer of graphite composed of hexagonal sp 2 bonded carbon atoms and these bonds are extremely strong, but flexible enough which allows the sheet to bend to form the carbon nanotube.

And first pristine graphene was made by scotch tape test a graphite flake put a scotch tape and then you keep on separating the layer till you get a single layer. This is still one of the best method of making graphene, but it is very expensive and graphene is having exceptional characteristics this is a perfect order that you can find in the sheet.

So, no atomic defect we talked about defect different types of point defect, but in graphene it is extremely pure only carbon atoms are there. And at room temperature this unbonded electron move much faster. So, this we call a ballistic conduction. So, it is very high electronic conductivity that you can think off.

So, it is outstanding material properties that they are strongest ever known material about 130 giga Pascal the strength that you can have best thermal conductor, lowest electrical resistivity it can have, it is transparent chemically inert, the elastic constant is comparative to the other nanocarbons which I have talked about and several use is projected like touch screen, conducting ink, chemical sensor, supercapacitor various types of composite it is a very exotic material.

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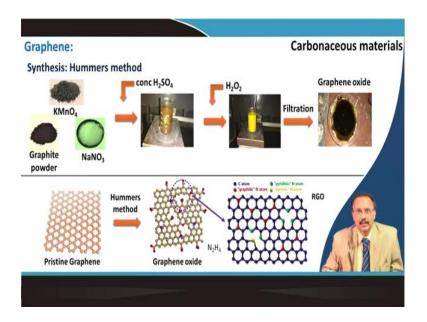


Now, if you see the synthesis of the graphene you have two approach; one is top down approach from the graphite you can just take out each layer still you get a single graphite layer, which we call graphene or second is a bottom up approach from the precursor also you can make the graphene by chemical vapor deposition.

So, chemical vapor deposition already I have described as you have seen in the last view graph you have carbon nanotube it is grown, but now if you ask it to grow on a flat surface not a circular metal catalyst. But, on a flat surface then a single layer graphene is possible by dissociation of the gas or you can use start up with the graphite and then you add a liquid specific liquid sulfuric acid and some kind of other acid and then you ultrasonic at it.

So, exfoliation will take place, this layer will get separated because the liquid molecule will just go in and they will force this to single layer graphene and then you wash it to get rid of the liquid and dry it you get the graphene single layer graphene or the well known scotch tape exfoliation you just take it out layer by layer.

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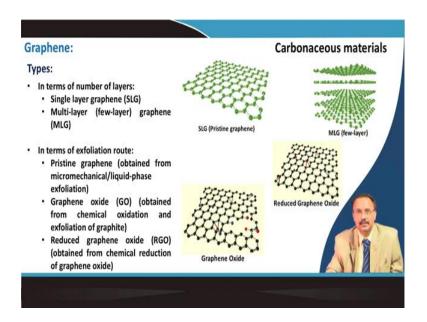


Now, usually the graphene one can make by Hummers method, from the graphite powder we add $KMnO_4$ its a strong oxidizing agent and sodium nitrate in concentrated H_2SO_4 . So, you can see all are oxidizing agent.

And, then this $KMnO_4$ to get rid of this $KMnO_4$ we use hydrogen peroxide also and basically then we get a graphene oxide we abbreviated as go because you are using a strong oxidizing agent. So, after Hummers method from a pristine graphite material, which is still graphite and then layers are oxidized and you get something like this which is a graphene oxide.

And in the graphene oxide you have several oxygen group, hydroxyl group that is attached with and then finally, you treat it with hydrazine. So, again you reduce it first you oxidize it and then reduce it to get rid of this oxygen. So, basically you are getting back the same graphene sheet you get back, but it is not as pure as your scotch tape kind of thing it is still very pure. So, this chemical route will not give you a very pure graphene, but something similar you will be getting.

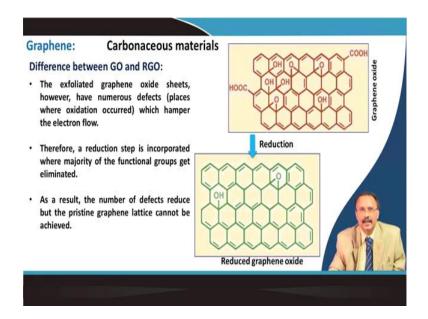
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So, depending on the characteristics of this thing; so, pristine graphene if you can make it is fantastic it is only a single layer or you can have a few layer; few layer graphene and this is not very well defined, what is this few layer, whether it is 2, 3, 10, 100, but it is defined as few layer this is multilayer graphene.

So, this is very common and graphene oxide as I mentioned that you have several other accessory group here which is attached and this again you get rid of by reduction. So, you get this kind of reduce graphene oxide.

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So, the difference lies here because this is still a graphene sheet and in graphene oxide you can see that hydroxyl group is there COOH group is there. And then when you treat it with hydrazine a strong reducing agent then it is they are not all gone, but some of them is still there oxygen is still there hydroxyl ion is still there, but you are getting a relatively pure form of graphene. So, this is we call a reduce graphene oxide.

		Material		
Property	C ₆₀ (Fullerite)	Carbon nanotube (Single-Walled)	Graphene (In-plane)	
Density (g/cm ³)	1.69	1.33-1.40	-	
Modulus of elasticity (GPa)	-	1000	1000	
Strength (MPa)	-	13,000-53,000	130,000	
Thermal Conductivity (W/m·K)	0.4	~2000	3000-5000	
Coefficient, Thermal Expansion (10 ⁻⁶ K ⁻¹)	-	-	~-6	
Electrical Resistivity (Ω·m)	1014	10-6	10 ⁻⁸	

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So, if you compare these three types of nanocarbon in terms of the density, you can see the density here for fullerene is quite low 1.69. So, this specific strength will be enormously high you have the carbon nanotube which is single walled and also graphene that you having.

This is the modulus of elasticity for both carbon nanotube and graphene is extremely high, strength is fantastic about 1,30,000 in plane strength tensile strength that you can get out of this material, they are highly thermally conducting thermally expansion, coefficient is also reasonable and electrical resistivity is very very low in case of graphene they are highly conducting materials.

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So, the study material for this particular lecture you can use the book by Callister its the 10th edition, the latest edition you will find the carbonaceous material. Mainly chapter 13 also part of chapter 12 you can consider.

There are good reference by O Connell, Carbon nanotube, then Honeycomb carbon, a review of graphene by M. J. Allen and carbonaceous composite material you will find from the book by G Sharma and tuneable porous carbonaceous material from renewable resource there is a good review paper that you can consider.

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So, in this particular lecture we talked about diamond artificial diamond and polycrystalline diamond, then we introduced the nanocarbons in terms of fullerenes, carbon nanotube and grapheme. Carbon nanotube could be single walled carbon nanotube or multi-walled their properties their synthesis procedure is defined. And finally, we talked about graphene and graphene oxide and reduced graphene oxide.

Thank you for your attention.