Electrochemical Energy Storage

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Module - 09
Li - Air batteries
Lecture - 44
State of the art Li - Air Batteries: Carbonaceous Materials

Welcome to my course Electrochemical Energy Storage and this is module number 9; we are discussing about Lithium Air batteries. And this is lecture number 44, where we are talking about lithium air batteries.

And specially for this lecture, we will introduce various carbonaceous materials, which is not relevant only for lithium air batteries; but we have used it in lithium ion batteries, we have used it in bat cap carbonaceous material we are also used in super capacitative materials, sodium ion batteries. So, I thought some discussion on carbonaceous material would be appropriate.

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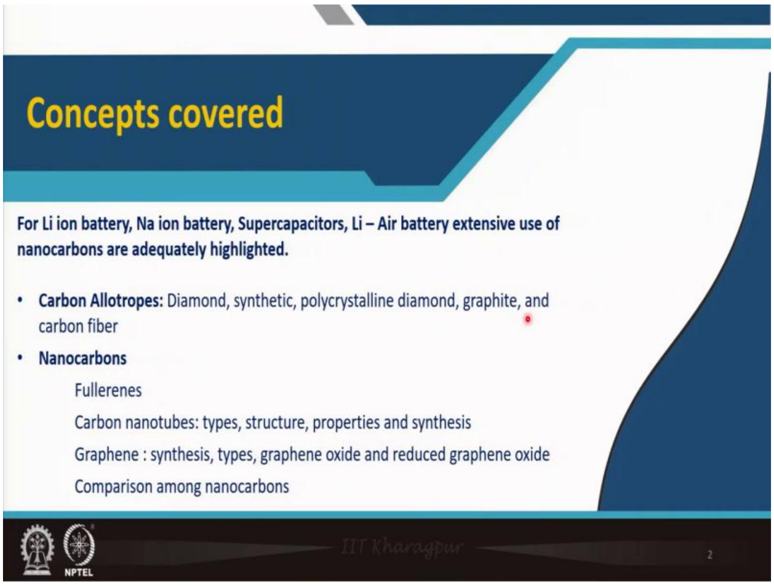

Concepts covered

For Li ion battery, Na ion battery, Supercapacitors, Li – Air battery extensive use of nanocarbons are adequately highlighted.

- **Carbon Allotropes:** Diamond, synthetic, polycrystalline diamond, graphite, and carbon fiber
- **Nanocarbons**
    - Fullerenes
    - Carbon nanotubes: types, structure, properties and synthesis
    - Graphene : synthesis, types, graphene oxide and reduced graphene oxide
    - Comparison among nanocarbons

So, as I was telling that for lithium ion batteries, we have already seen use of carbon nanotubes, graphene base material; sodium ion battery also they use. And in fact they use hard carbon as one of their negative electrode materials. Super capacitor already we have discussed and lithium air batteries, extensive use of nano carbons they need to be highlighted. So, first we will talk about carbon allotropes, you know diamond is one of them; both natural diamond and synthetic diamond, then we will talk about polycrystalline diamond, graphite and carbon fibers.

Now, this nano carbons which include fullerenes, carbon nanotube, their types of carbon nanotubes, their properties, synthesis of carbon nanotubes will be covered. Then subsequently I will be talking about grapheme, the synthesis part, their types from graphene oxide, how it is reduced to form reduced graphene oxides and used in the electrochemical energy storage materials and different comparison among this nano carbons that will be introduced.

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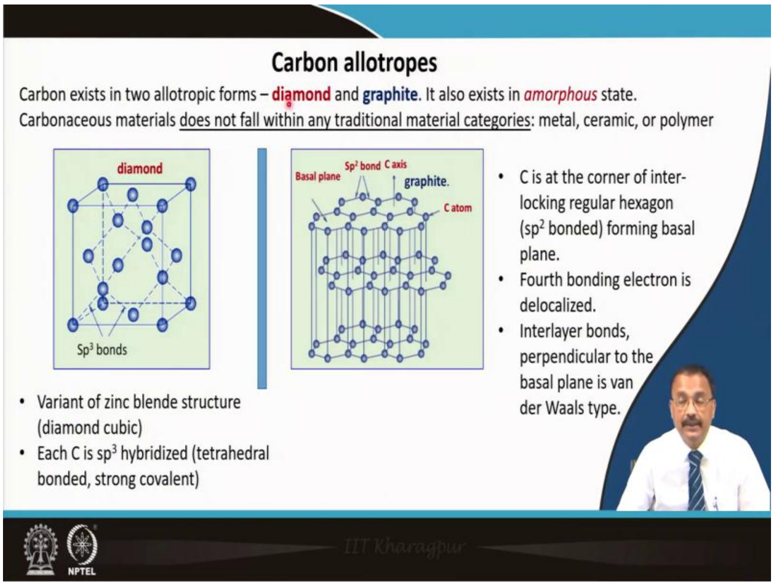

Carbon allotropes

Carbon exists in two allotropic forms – **diamond** and **graphite**. It also exists in *amorphous* state.

Carbonaceous materials does not fall within any traditional material categories: metal, ceramic, or polymer

- Variant of zinc blende structure (diamond cubic)
- Each C is sp^3 hybridized (tetrahedral bonded, strong covalent)

- C is at the corner of inter-locking regular hexagon (sp^2 bonded) forming basal plane.
- Fourth bonding electron is delocalized.
- Interlayer bonds, perpendicular to the basal plane is van der Waals type.

Now, you know that carbon it has two allotropic forms; so composition remain same, so diamond is one of them and graphite. And apart from that, apart from this crystalline counterpart, we have also the presence of carbon in amorphous state. So, this carbonaceous material whatever I am talking about, they actually do not fall to any of this traditional material category, which is usually either metal or ceramic or polymer. So, it is categorized as a different types of material.

So, in case of diamond, it is although I have not taking taken the crystallography exclusively; but you should know that, that it is a variant of so called zinc blend structure and we also call it diamond cubic. Now, in case of this zinc blend structure, that is zinc sulphide; the sulphur atoms they actually occupy this face centred position and the tetrahedral positions they are occupied by zinc. But in diamond, these are all carbon.

So, everywhere you can see carbon and the bonding between them is typical s p 3 kind of bonding. So, each carbon they are hybridized s p 3 and that is tetrahedrally bonded; you can see that this is tetrahedrally bonded with this one, this one, this one and this one which is out of the plane.

So, they are very strong in nature and if you look at the graphite structure; then you can see that the carbon they are at the corner of an otherwise interlocking regular type of hexagon. And in this case, this hexagons, they in the carbon they are s p 2 bonded.

So, they form some kind of basal plane like this right, this is the basal plane. Now, the fourth bonding electron they are in fact delocalized. So, they are delocalized, they can travel. So, this interlayer bond which are perpendicular to the basal plane. So, this is the basal plane and this is the interlayer bonds which is holding between this and this. So, which are perpendicular to this basal plane, they are having a van der Waals type of bonding, they are not very strong.

So, it is easy for you to cleave the graphite plane and graphite you know we have used it in lithium ion battery as negative electrode material. So, you can cleave it along with this, but it is very strong to bond along with this; I mean it is difficult to break along this, but it is relatively easier to break along this one, because of their structural configuration.

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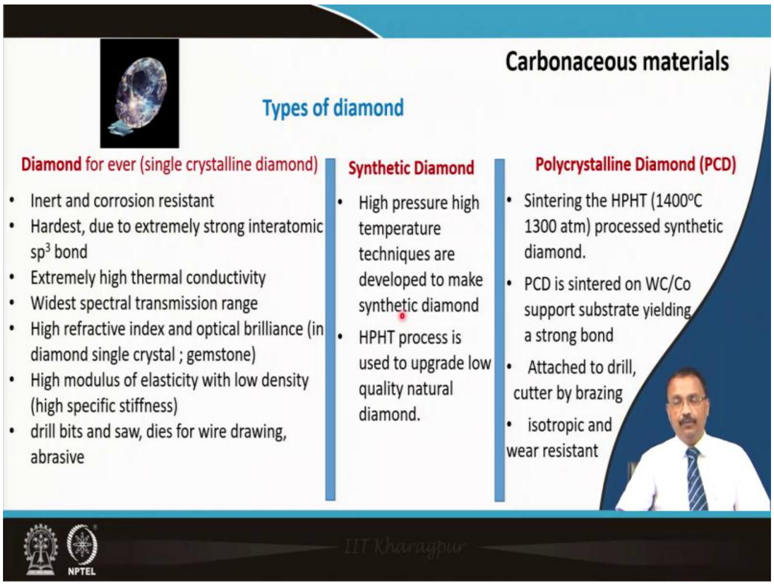

Carbonaceous materials

Types of diamond

Diamond for ever (single crystalline diamond)
- Inert and corrosion resistant
- Hardest, due to extremely strong interatomic sp^3 bond
- Extremely high thermal conductivity
- Widest spectral transmission range
- High refractive index and optical brilliance (in diamond single crystal ; gemstone)
- High modulus of elasticity with low density (high specific stiffness)
- drill bits and saw, dies for wire drawing, abrasive

Synthetic Diamond
- High pressure high temperature techniques are developed to make synthetic diamond
- HPHT process is used to upgrade low quality natural diamond.

Polycrystalline Diamond (PCD)
- Sintering the HPHT (1400°C 1300 atm) processed synthetic diamond.
- PCD is sintered on WC/Co support substrate yielding a strong bond
- Attached to drill, cutter by brazing
- isotropic and wear resistant

So, diamond mostly we know that, this is a single crystalline form, which is used as a gem. And apart from this gem, they have several other use; first and foremost they are hardest material ever known and that is due to their s p 3 bonding.

And they have extremely good thermal conductivity and wide spectral range they can transmit, so that gives the vibrancy. Along with that it is having high refractive index and that actually gives the optical brilliance and therefore, this diamond is used as gemstone.

If you consider their mechanical property, they have very high modulus of elasticity; you know the stress and strain ratio that is in the elastic region, that is modulus of elasticity and it is having relatively low density.

So, if you calculate the stiffness, it is having one of the highest stiff material. So, you know the drill bits, then diamond saw they are used apart from there are used as a gemstone and they are very inert in nature and they are corrosion resistant. So, naturally they are available.

Synthetically also you can prepare. So, you need to apply a very high pressure as well as temperature to make this synthetic diamond and therefore, this process called high pressure, high temperature process. And sometimes a low grade naturally obtained diamond that also you can have this kind of process; you can take it through this kind of process, HPHT process to make what we call artificial diamond. And the quality of the otherwise natural, either you can make it or the quality of the so called natural diamond, which is not that good that can be improved.

The third category is polycrystalline diamond. So, we abbreviate it as PCD. So, this is actually done by sintering this high pressure, high temperature processed diamond and you can see the temperature is about 1400 degree Celsius and pressure is 1300 atmosphere. And you can imagine, because the natural diamond with the with the time, millions of years maybe it is required to transfer the carbonaceous material in the form of diamond.

So, this polycrystalline diamond, they are basically sintered on a tungsten carbide and cobalt support as a substrate and that yields a very strong bond. So, that is used in the drill cutter.

So, you can braise this tungsten carbide and cobalt support and PCD, poly crystalline diamond which are sintered on top of it and by brazing, you can attach it to the drill cutter. And this is used for cutting the brittle materials; in our laboratory, we use we have diamond cutter, diamond saw, where it is coated with polycrystalline diamond.

And at very slow speed, you can nicely cut the brittle material. They are actually isotropic and needless to say they are wear resistant.

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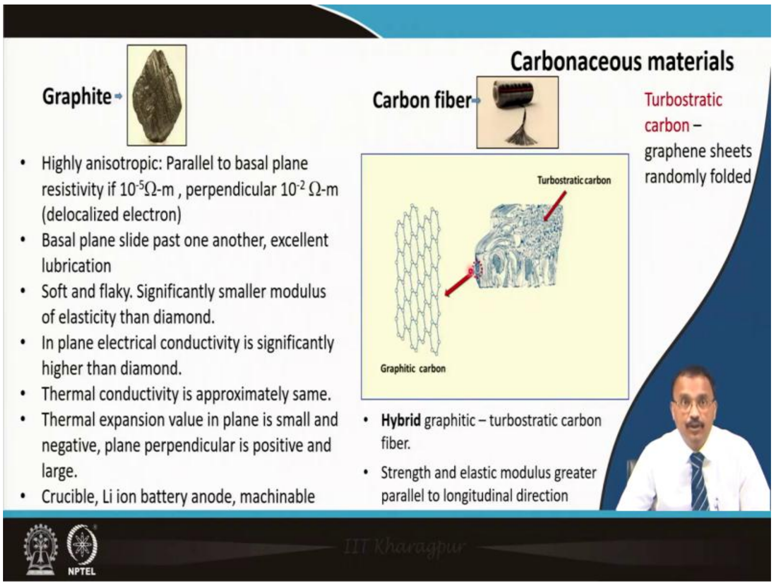

Carbonaceous materials

Graphite

- Highly anisotropic: Parallel to basal plane 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 negative, plane perpendicular is positive and large.
- Crucible, Li ion battery anode, machinable

Carbon fiber

Turbostratic carbon – graphene sheets randomly folded

- **Hybrid** graphitic – turbostratic carbon fiber.
- Strength and elastic modulus greater parallel to longitudinal direction

So, graphite you know, we have used graphite as a negative electrode material, in fact it was commercialized by Sony. So, this is highly anisotropic. So, as I have explained that parallel to the so called basal plane; if you measure the resistivity, it is 10 raise to minus 5 ohm meter.

But if you take it perpendicular, it is a 7 order magnitude you can gain. And why this is happening; because the delocalized electron that I talked about which are free to move, so that is something like a free electron and that will raise the resistivity, in fact one by resistivity as you know is conductivity.

So, you get very high conductivity, electronic conductivity in graphite. And since they are attached with van der Waals bond, so this basal plane can pass over one another and that will give you the property like lubrication; for as a lubricant, the graphite powders are used. And as you can understand by seeing at this that, they are soft in nature and they are flaky. So, you can easily flak it, you can just break it along with parallel to the basal plane and suddenly it has significantly smaller modulus of elasticity.

In plane electrical conductivity is significantly higher than the diamond and that is the reason I just explained. If you talk about the thermal conductivity, they are more or less same. Now, you talk about the thermal expansion value; in plane it is small and sometimes it is negative, but in the plane parallel perpendicular, it is positive, thermal expansion is positive with temperature.

So, for making the crucible and as I said lithium ion battery anode, they are used and also they are machinable; so we can figure out that how to make shapes out of this graphite. So, making the crucible etcetera is important, where in inert ambient you can, it can withstand very high temperature. But you will have to maintain the inert ambient, so that you can use it as a crucible.

Carbon fibers, mostly they are used for composite. So, once you are talking about the fiber, then it is having a composite kind of structure. So, that is why it is called hybrid graphitic and it has a turbostratic carbon fiber.

So, this turbostratic carbon fiber, you can see that there are two types of region. So, one region is this graphitic planes. So, you can just keep one plane apart, that is graphene and also you have this region, where this graphene sheets are randomly folded and this one is called turbostratic region.

So, the strength and the elastic modulus greater parallel to the longitudinal direction because of their characteristics in the microstructure.

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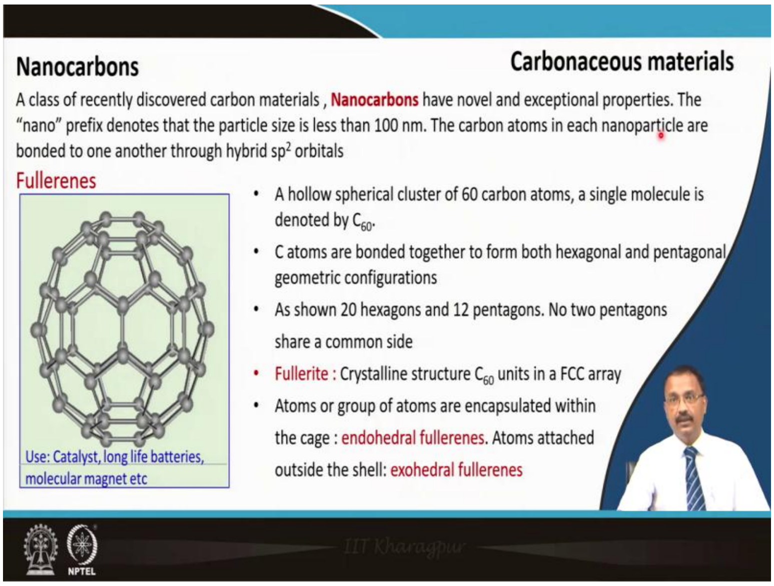

Nanocarbons

Carbonaceous materials

A class of recently discovered carbon materials , **Nanocarbons** have novel and exceptional properties. The "nano" prefix denotes that the particle size is less than 100 nm. The carbon atoms in each nanoparticle are bonded to one another through hybrid sp^2 orbitals

Fullerenes

Use: Catalyst, long life batteries, molecular magnet etc

- A hollow spherical cluster of 60 carbon atoms, a single molecule is denoted by C_{60}.
- C atoms are bonded together to form both hexagonal and pentagonal geometric configurations
- As shown 20 hexagons and 12 pentagons. No two pentagons share a common side
- Fullerite : Crystalline structure C_{60} units in a FCC array
- Atoms or group of atoms are encapsulated within the cage : endohedral fullerenes. Atoms attached outside the shell: exohedral fullerenes

So, they are mostly the bulk carbonaceous material, now mostly we will be following the nano carbons. So, this nano carbons is a class of relatively recently discovered carbon material, we call it nano carbon. So, they have many novel and exceptional properties. So, the term nano it denotes the particle size is less than 100 nanometer, this is the characteristic length. And this carbon atom as you can see here, they are in each of this nanoparticle; they are bonded to another through a hybrid s p 2 type of bonding.

So, for catalyst and for long life batteries, molecular magnet this type of structure which is professionally known as fullerene, the football kind of structure. So, as you can see the structure is a hollow in nature.

So, this is basically a cluster of 60 carbon atoms and they form a single molecule and therefore, it is termed as C 60, C 60 fullerene. So, you can see that they are bonded both in hexagonal type of structure and pentagonal kind of structure. So, there are if you count it 20 hexagons and 12 pentagons and one interesting part is that, no two pentagon they can share a common site.

So, you can just check it out. So, no two pentagons they have a common side and this forms actually the fullerene. Now, another structure that is known as fullerite, that is also crystalline C 60. Now, the crystal structure here is an FCC array. So, various atoms or sometimes group of atoms they can be encapsulated within this cage. So, when it happens, when you have encapsulation; then we call it endohedral fullerenes. And when the atoms or group of atoms they are attached outside the cell, then we call is exohedral fullerenes.

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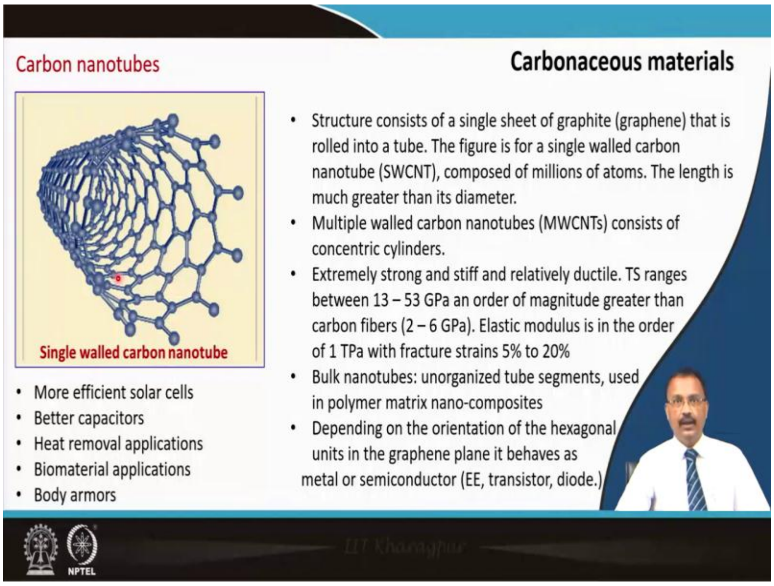

Carbonaceous materials

Carbon nanotubes

- More efficient solar cells
- Better capacitors
- Heat removal applications
- Biomaterial applications
- Body armors

- Structure consists of a single sheet of graphite (graphene) that is rolled into a tube. The figure is for a single walled carbon nanotube (SWCNT), composed of millions of atoms. The length is much greater than its diameter.
- Multiple walled carbon nanotubes (MWCNTs) consists of concentric cylinders.
- Extremely strong and stiff and relatively ductile. TS ranges between 13 – 53 GPa an order of magnitude greater than carbon fibers (2 – 6 GPa). Elastic modulus is in the order of 1 TPa with fracture strains 5% to 20%
- Bulk nanotubes: unorganized tube segments, used in polymer matrix nano-composites
- Depending on the orientation of the hexagonal units in the graphene plane it behaves as metal or semiconductor (EE, transistor, diode.)

Now, if you consider a single layer of the graphite sheet and then you can have a role of it; then what you call, what you end up is a single walled carbon nanotube. There are various uses and more effectively they are used in solar cell in the capacitor, already we have talked about to remove the heat from a heat source. There are several bio material applications and they are strong enough; you can make composite and make the body armor light wet. So, body armor also can be made out of it.

So, as I said, the structure is basically a single sheet of graphite and this is called grapheme. And this basically is rolled here and this is the typical structure of a single wall carbon nanotube. And this is abbreviated as SWCNT. So, as you can understand, it contains millions of atoms and the length of this kind of nanotube, they are much larger than the diameter.

Similarly, you can have multiple wall carbon nanotube and they basically have concentric circle like this; they are extremely strong, stiff and thermal, sorry tensile strength is very high about 13 to 53 giga pascal.

And carbon fiber if you compare, the carbon fiber is only 2 to 6 giga pascal and elastic modulus in order of 1 tera pascal extremely high value, fracture strains is also 5 to 20 percent. Normal ceramic brittle material even 0.1 percent strain is sufficient to break it.

So, you can understand that it can use, it can be used as a buffer to shock the strain shocker, it can be used. So, in case of a bulk nano tube, this kind of segments they are unorganized and we use it in polymer matrix to form some kind of nano composite, which are light weight and that can be used as body armor. And depending on this orientation, I will commit come in a minute; this hexagonal units, this orientation it behaves like a metal, sometimes it behaves like a semiconductor.

So, they are used in transistor diodes, electron emitters; so various types of views are possible for this carbon nanotube.

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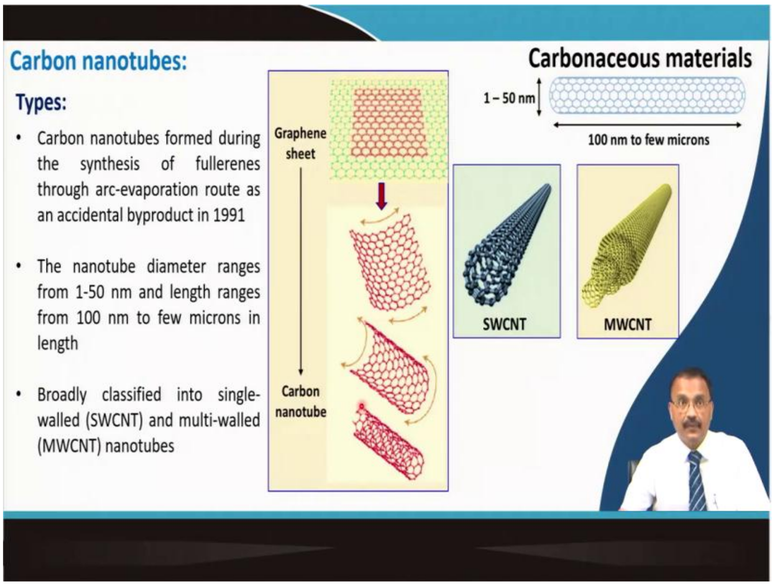

Carbonaceous materials

Carbon nanotubes:

Types:

- Carbon nanotubes formed during the synthesis of fullerenes through arc-evaporation route as an accidental byproduct in 1991
- The nanotube diameter ranges from 1-50 nm and length ranges from 100 nm to few microns in length
- Broadly classified into single-walled (SWCNT) and multi-walled (MWCNT) nanotubes

So, if you see the types, carbon nanotubes form during the synthesis of fullerene; when fullerene was discovered, carbon nanotube they were simultaneously discovered in 1991. The diameter as I said that is 1 to 50 nanometer, but the length sometimes it is in few microns. So, when I called this is nano carbon, it means that at least one of the dimensions they are falling in the nano range.

So, they can be either single walled carbon nano tube and as I mentioned, it could be multi walled carbon nano tube, where the coin centric carbon nano tubes one inside other and it forms this kind of multi walled carbon nanotube.

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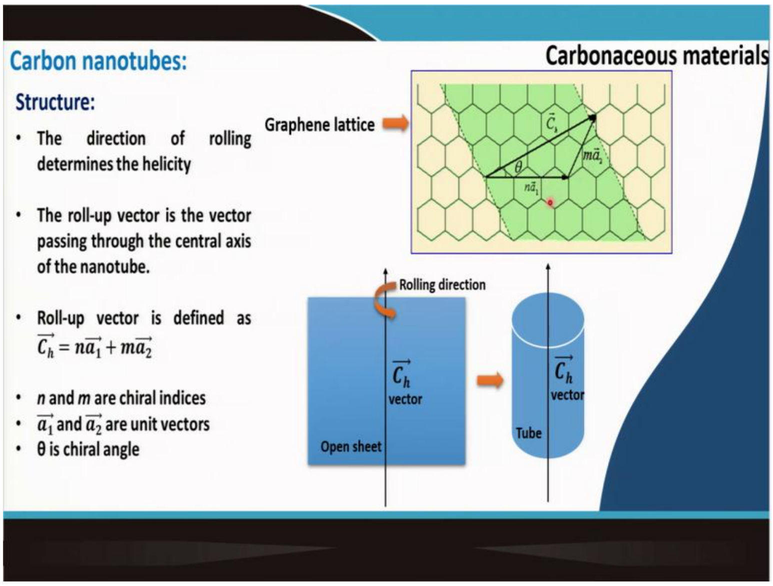

Carbon nanotubes:

Carbonaceous materials

Structure:

- The direction of rolling determines the helicity
- The roll-up vector is the vector passing through the central axis of the nanotube.
- Roll-up vector is defined as $\overrightarrow{C_h} = n\overrightarrow{a_1} + m\overrightarrow{a_2}$
- *n* and *m* are chiral indices
- $\overrightarrow{a_1}$ and $\overrightarrow{a_2}$ are unit vectors
- θ is chiral angle

Now, if you look at the structure, the structure is something like a planar graphene sheet. So, here the direction of the rolling; because as you can understand if you have this sheet, then you have a vector which is demarked by C h vector and you can roll this. So, this open sheet like this can be rolled to form a tube.

So, this roll up vector that is passing through the axis of this plane sheet. So, that is an important parameter and this rolling vector as you can see here that, basically can be defined by this two vectors right; these two vectors can define this rolling vector.

So, these two vectors is a 1 and a 2 and n or m, this is termed as chiral indices and the vector a 1 and a 2 they are termed as units vector. And the angle between them this theta, this is termed as chiral angle. So, based on this concept, you can understand different types of carbon nanotube.

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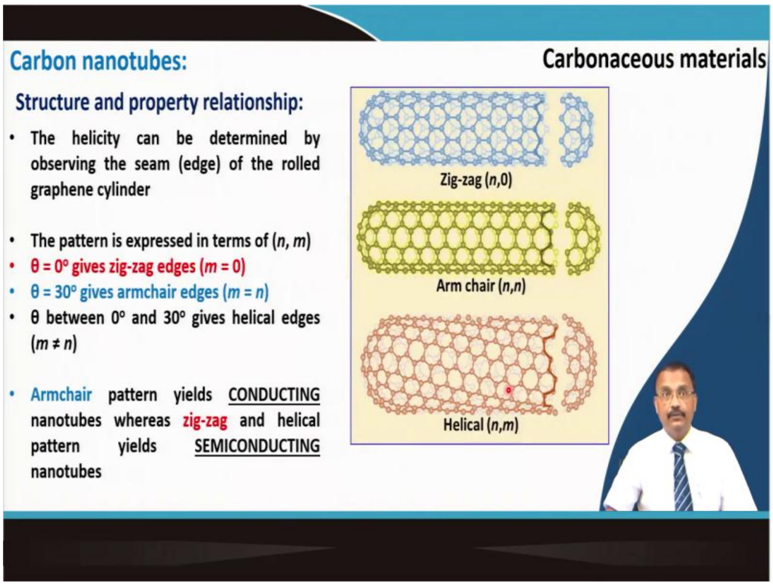
Carbon nanotubes:

Carbonaceous materials

Structure and property relationship:

- The helicity can be determined by observing the seam (edge) of the rolled graphene cylinder
- The pattern is expressed in terms of (n, m)
- $\theta = 0°$ gives zig-zag edges ($m = 0$)
- $\theta = 30°$ gives armchair edges ($m = n$)
- θ between 0° and 30° gives helical edges ($m \neq n$)
- Armchair pattern yields CONDUCTING nanotubes whereas zig-zag and helical pattern yields SEMICONDUCTING nanotubes

So, here I have shown it that, once you understand the concept of helicity of this carbon nanotube; then you can think of that in what way it acts like a conductor or it acts like a semiconductor. Now, how to define it? So, this helicity can be defined by observing the seam at the edge; you cut this carbon nanotube and see how this edge is formed. So, this is the seam, that is the edge, right.

So, the pattern that I explained earlier, in fact you can define this as these two chiral indices n and m. So, this n and m as well as theta, this angle between this; angle between this rolling vector and one of this chiral indices. So, here you can see when theta equal to 0; that means one vector is does not exist. So, when theta equal to 0, then that gives this zig zag pattern; there the m vector that is not existing the same indices, in fact a 2 vector, a 2 unit vector that is not existing.

So, this n and 0 when this configuration is there when m equal to 0; then we call theta is 0 and we call it is a zig zag kind of pattern. So, this is zig zag edge. Similarly when theta is 30, then what we get is some kind of this type of armchair kind of configuration and the name is also armchair type, where n and m they are equal. So, n is equal to m. And when theta is in between 0 and 30 degree; so that gives a helical kind of pattern. So, here m is not equal to m. So, this gives a helical kind of seam.

So, this is called a helical, helical kind of carbon nanotube. So, actually the armchair pattern they gives you the conducting nanotubes; whereas if it is zig zag and helical, either this one or this one, then usually they exhibit semiconducting behaviour. This is how easily you can transport the electron, so that will decide whether it is conducting; armchair is conducting or it is semiconducting in nature.

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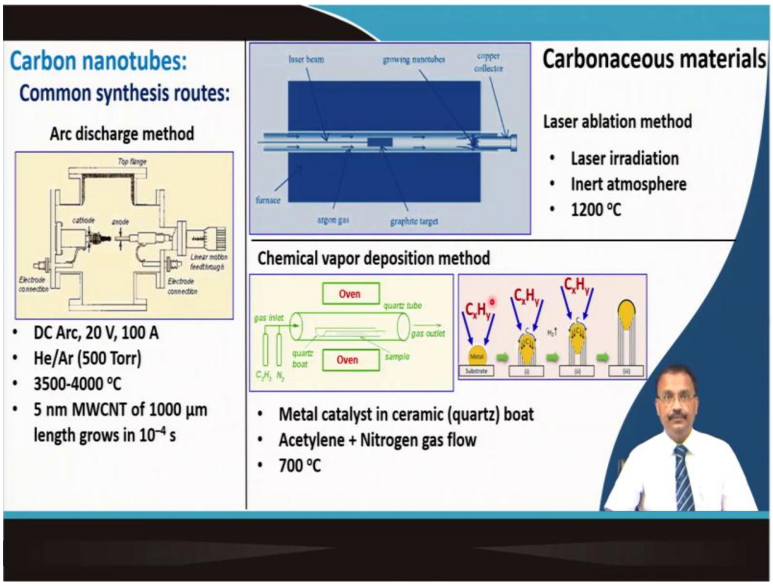

Carbon nanotubes:

Common synthesis routes:

Arc discharge method

- DC Arc, 20 V, 100 A
- He/Ar (500 Torr)
- 3500-4000 °C
- 5 nm MWCNT of 1000 µm length grows in 10^{-4} s

Carbonaceous materials

Laser ablation method

- Laser irradiation
- Inert atmosphere
- 1200 °C

Chemical vapor deposition method

- Metal catalyst in ceramic (quartz) boat
- Acetylene + Nitrogen gas flow
- 700 °C

Carbon nanotube they can be synthesized by DC arc discharge method. So, typically huge current, a power supply is required and these are the two electrode. So, a spark is generated, one of them is of course made out of carbon. And the ambient is maintained either helium or argon and typical 500 Torr that is the pressure that is used; temperature is used 3500 to 4000 degree Celsius.

And in this process, one can grow from 5 nanometer usually it is multi wall carbon nanotube or it can be large enough about 100 micrometer lengths; that can grow in very fast time, I mean 10 raise to minus 4 second within no time you can get the carbon nanotube. The other process is laser ablation process.

So, in one end, laser is irradiated and a graphite target is there. So, inert ambient is maintained and there is a cooled place, this copper correct collector; here you will find that the carbon nanotube is grown, typically temperature is 1200 degree Celsius.

The third process is chemical vapor deposition process, where metal catalyst is used in a ceramic quartz boat, you can see it is here. So, that is inside a furnace and you use a gas like acetylene and nitrogen, nitrogen is a carrier gas. So, that is passed through this. And you will find that this metal catalyst and this is the substrate, which is kept on the quartz tube.

So, carbon nanotubes starts to grow here, because of the dissociation of this acetylene; temperature is pretty low as compared to this one and this one. And finally, you get the carbon nanotube grown over the chemical vapor deposition system and the catalyst basically dissociate this acetylene gas and nitrogen is a carrier gas.

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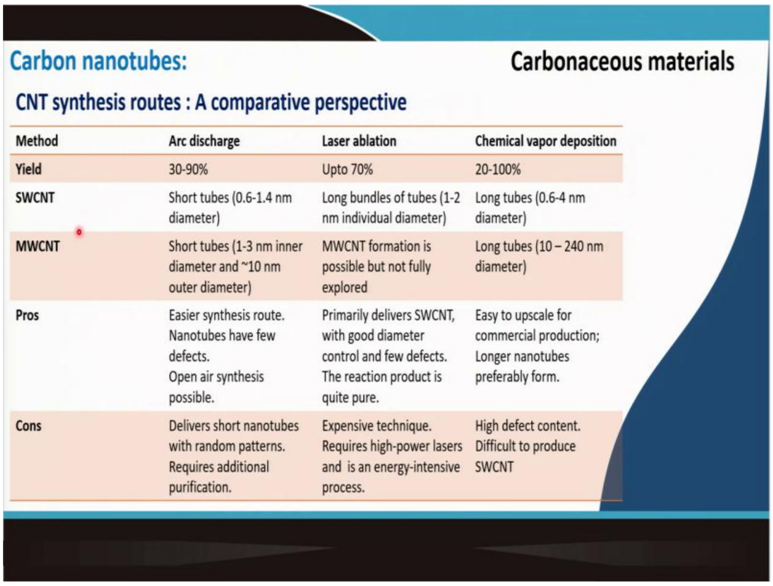

Carbon nanotubes:

Carbonaceous materials

CNT synthesis 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, there is a comparison between this three process, I am not going line by line; but as you can see the yield here, chemical vapor deposition sometimes it is pretty large, single wall carbon nanotube they are short tubes. And usually for chemical and laser, they are long nanotubes are grown; whether it is easier to grow, so this is a easy process, your arc discharge as well as CVD, usually the CVD, this arc discharge process that delivers relatively shorter nanotubes as compared to laser.

A laser is an expensive technique and chemical vapor deposition, they have relatively higher defect contents and it is suddenly difficult to grow a single world carbon nanotube by this process.

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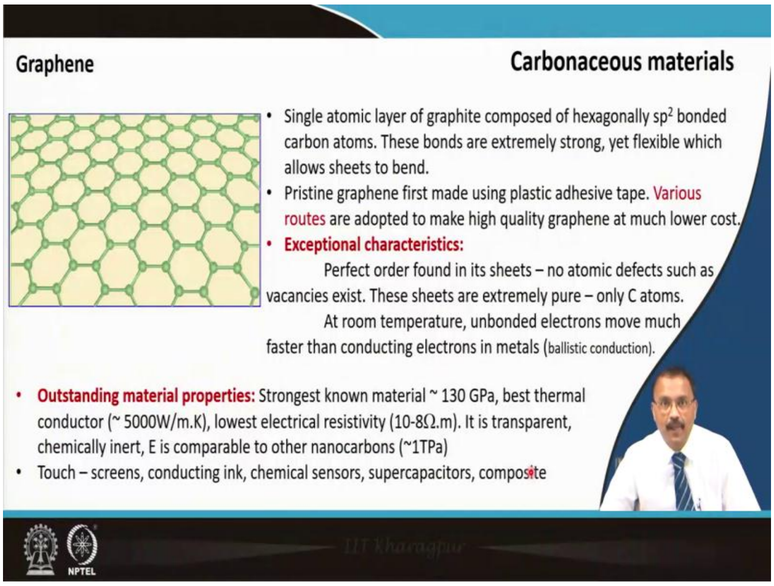

Graphene

Carbonaceous materials

- Single atomic layer of graphite composed of hexagonally sp^2 bonded carbon atoms. These bonds are extremely strong, yet flexible which allows sheets to bend.
- Pristine graphene first made using plastic adhesive tape. Various routes are adopted to make high quality graphene at much lower cost.
- **Exceptional characteristics:**

  Perfect order found in its sheets – no atomic defects such as vacancies exist. These sheets are extremely pure – only C atoms.

  At room temperature, unbonded electrons move much faster than conducting electrons in metals (ballistic conduction).

- **Outstanding material properties:** Strongest known material ~ 130 GPa, best thermal conductor (~ 5000W/m.K), lowest electrical resistivity (10-8Ω.m). It is transparent, chemically inert, E is comparable to other nanocarbons (~1TPa)
- Touch – screens, conducting ink, chemical sensors, supercapacitors, composite

Now, we will talk about graphene. So, graphene is having a single atomic layer of graphite. And as I have told that it is having hexagonally s p 2 type of bonded carbon atom and this s p 2 bonding, they are extremely strong and also very flexible, so that you can easily bend it, bend this kind of, in fact it will roll in the form of a single wall carbon nanotube.

So, very simple process initially was adopted. So, you take a graphite flake and with a scotch tip; you just keep on taking out layer by layer, because you can cleave it in the direction which is parallel to the basal plane. So, apart from that, there are various routes they have adopted to make a very high quality graphene. And cost wise one of the problem; but efforts have been made to make it cost effective.

And this is ultimate material, exceptional characteristics you can go through the properties, this is perfect in order. So, no atomic defects you can find; so there is no vacancy even and only carbon atom you will find. So, at room temperature, this unbonded electron which I was talking about; they move in a very fast way, we call it is a ballistic conduction. So, it is highly conducting electrons as compared to metal. So, it is highly conducting material.

So, certain outstanding material properties you can get. So, first and foremost it is a very strong material about 130 giga pascal strength, tensile strength you can get; good thermal conductor, it has lowest electrical resistivity that one can think of, this is 10 raised to minus 8 ohms meter. And it is a single layer, so it is transparent; chemically almost inert and the elastic modulus that is comparable to other nano carbons, whatever I have talked about 1 tera pascal.

So, they are used in various places and prominent among them is touch screen, conducting ink, super capacitor I have already talked about, various types of composite. And also you will see that in lithium air battery also graphene and its duped part in the next class I will be taking that, so they are being used.

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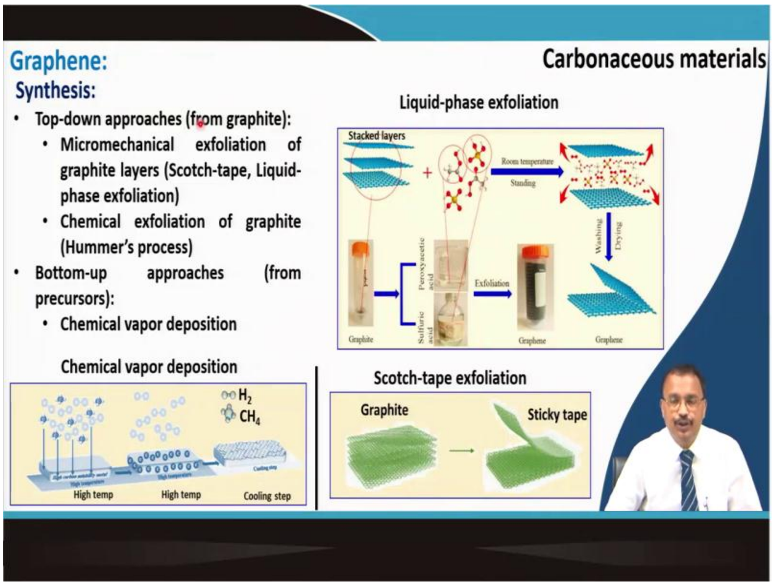

Carbonaceous materials

Graphene:

Synthesis:

- Top-down approaches (from graphite):
  - Micromechanical exfoliation of graphite layers (Scotch-tape, Liquid-phase exfoliation)
  - Chemical exfoliation of graphite (Hummer's process)
- Bottom-up approaches (from precursors):
  - Chemical vapor deposition

So, synthesis could be either top down approach, from graphite you take a scotch tape test and stick it and then layer by layer you can exfoliate it. You can do it by micro mechanical exfoliation of graphite layers. In this case it is using some liquid, so this liquid as you can see that these are the stacked layer in graphite.

And then you use the solution of sulphuric acid and peracetic acid and mix it together and then you exfoliate it to form the graphene layer. So, what happens, this molecules they actually go inside this layer and forcefully they separate the graphene sheet.

So, chemical exfoliation of graphite that is called the hummers process. And bottom up approach also you can undertake from the precursor you can use it, various precursor. Chemical vapor deposition is another way; it is almost similar to what I described in making the carbon nanotube. So, here also in high temperature, basically the gas is getting dissociated and then a layer of carbon single layer is deposited on a substrate up and cooling.

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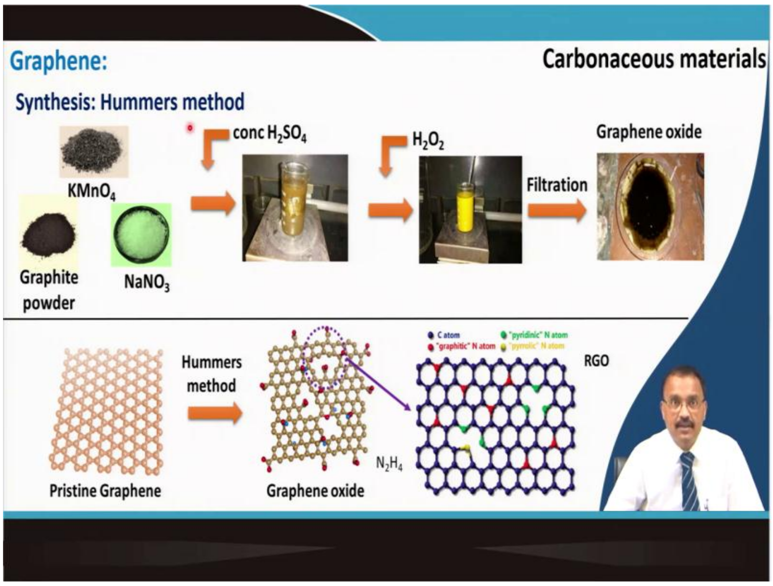

Carbonaceous materials

Graphene:

Synthesis: Hummers method

So, in the laboratory, we can synthesis the graphene by hummers method and sodium nitrate is used; graphite powder of course, you need and a strong oxidizing agent in the form of potassium permanganate. So, that you form a solution like that and then you put sulphuric acid and also hydrogen peroxide in it. And then basically what you are doing; using this highly oxidizing agent, you are oxidizing the graphite and up and filtration what you get is the graphene oxide.

So, this was your pristine graphene and by the hummers method, by adding this strong oxidant; you get graphene oxide, where you can see that there are lot of things they have been attached into it, it is not only the array of carbon atom. And finally, you reduce it by this chemical hydrazine into H 4. So, with that you again reduce it the oxidized part and then somewhere you will see it is not a real array of carbon; you can have some defects also and carbon atoms they are shown in this blue color.

And you have graphitic type N atom and depending on where exactly they are sitting; so they are sitting in a position of carbon, so it is graphitic N atom. And apart from that, there are two types of nitrogen dopant, which has been introduced in the reduced graphene oxide. And one position is pyridinic position and another one is pyloric position. So, it is no way similar to this type of pristine graphene; but by doing this, you could exfoliate the graphite powder and initially lot of garbage was there and then you get it reduced and you get this form of reduce graphene oxide.

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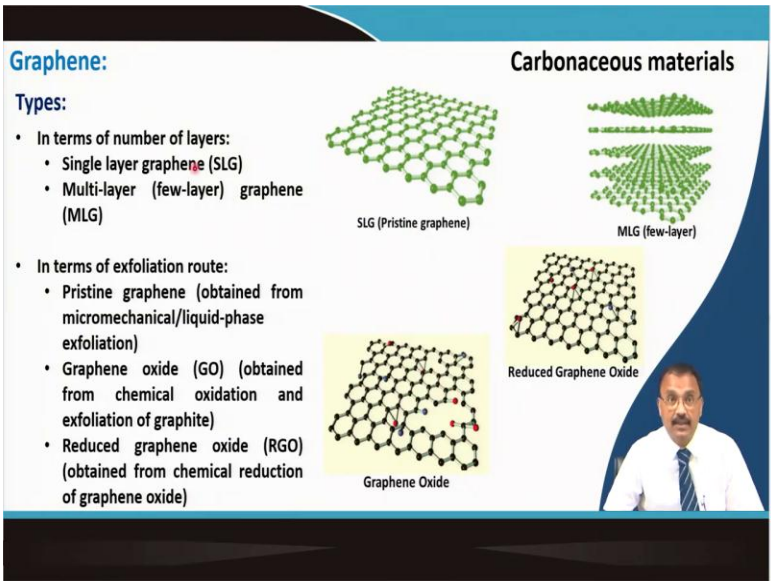

Graphene:

Carbonaceous materials

Types:

- In terms of number of layers:
  - Single layer graphene (SLG)
  - Multi-layer (few-layer) graphene (MLG)
- In terms of exfoliation route:
  - Pristine graphene (obtained from micromechanical/liquid-phase exfoliation)
  - Graphene oxide (GO) (obtained from chemical oxidation and exfoliation of graphite)
  - Reduced graphene oxide (RGO) (obtained from chemical reduction of graphene oxide)

So, there are various types, single layer type graphene this is called pristine graphene; you can have a multi-layer graphene and I am not sure that few layers means what whether it is 5, 10 or 2, but this is called abbreviated as multi-layer grapheme, so few layers there. And if you talk about exfoliation route, then pristine graphene that is obtained from this micro mechanical or liquid phase exfoliation that is one; the first one that I talked about, these two different types of chemicals were used here.

And one of them was sulphuric acid and then peroxyacetic acid and then you exfoliated it. So, this is one way to make the, from the pristine graphene you can make by exfoliation; the graphene you can make pristine graphene or graphene oxide, which is obtained from a chemical oxidation and also exfoliation of the graphite, which I just described.

And then you reduce that and obtain the chemical reduction of this graphene oxide. So, there also you get this reduced graphene oxide, where many of these things they are no longer there get reduced; but you have the nitrogen which is graphitic or pyridinic, so three different types of nitrogen doped graphene you can make.

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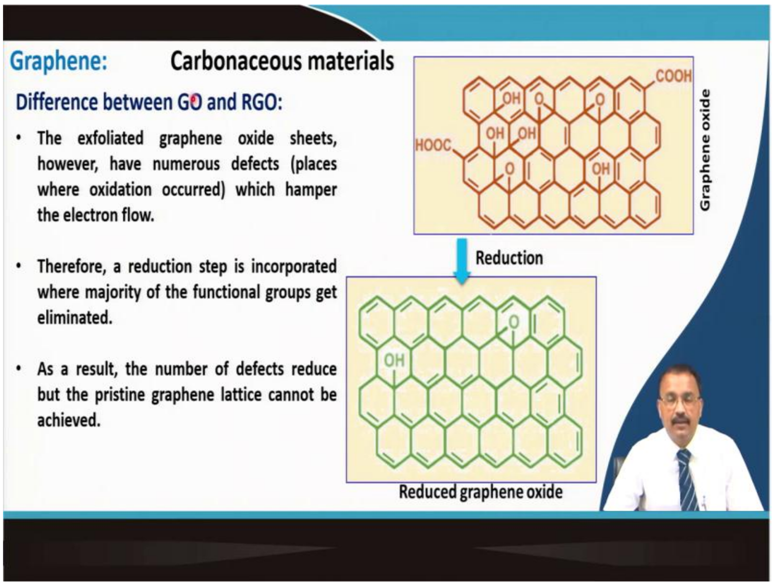

Graphene: **Carbonaceous materials**

Difference between GO and RGO:

- The exfoliated graphene oxide sheets, however, have numerous defects (places where oxidation occurred) which hamper the electron flow.
- Therefore, a reduction step is incorporated where majority of the functional groups get eliminated.
- As a result, the number of defects reduce but the pristine graphene lattice cannot be achieved.

So, if you compare this graphene oxide and reduce graphene oxide, you can understand that this exfoliated graphene oxide sheets; as I told they have numerous defects where exactly the oxidation has occurred, so defect regions are generated. And this will basically hamper the constant electron flow.

So, it will not be conducting in nature; but once you reduce it, then most of this groups like C double O H group or hydroxyl group they are grossly reduced, they are not completely eliminated.

So, this reduction step, majority of the functional groups they will get eliminated and number of defects will be grossly reduced. And although the pristine graphene types of material cannot be achieved; but this is also reduced graphene is almost equivalent to pure graphene sheet.

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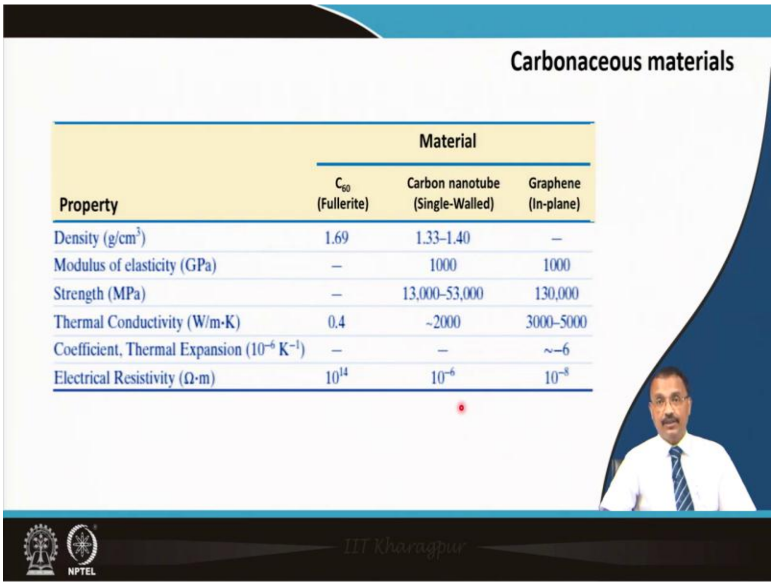

Carbonaceous materials

Property	Material		
	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)	10^{14}	10^{-6}	10^{-8}

So, if you compare the different nano carbons, starting from fullerite, then carbon nanotube which is single walled and graphene which is in plane. So, you can see they are very light wet, modulus of elasticity is quite large, strength is extremely large for carbon nanotube as well as graphene based material; thermal conductivity also reasonably large as compared to fullerene.

Thermal expansion is you can have a negative thermal expansion coefficient for graphene and electrical resistivity they are also very high in case of, sorry very small in case of graphene and carbon nanotube and as compared to the fullerite and we have made use of it in the electrical chemical storage material.

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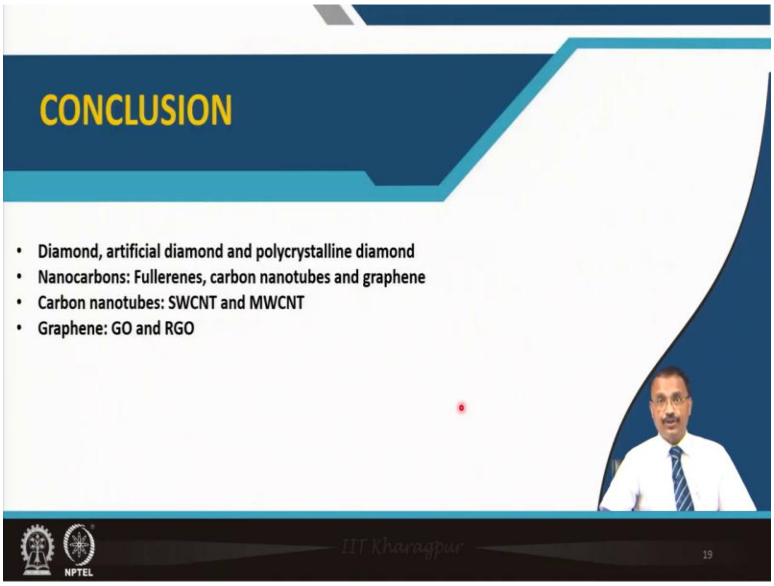

CONCLUSION

- Diamond, artificial diamond and polycrystalline diamond
- Nanocarbons: Fullerenes, carbon nanotubes and graphene
- Carbon nanotubes: SWCNT and MWCNT
- Graphene: GO and RGO

So, in this particular talk, we talked about diamond, artificial diamond, then polycrystalline diamond. Then we talked about the nano carbons and we introduced fullerenes carbon nanotube and grapheme; how the carbon nanotubes are made and how the graphene is made and what are their properties. And I will be using this carbonaceous material as a last lecture for lithium air batteries. So, now you have a basic idea about this carbonaceous material.

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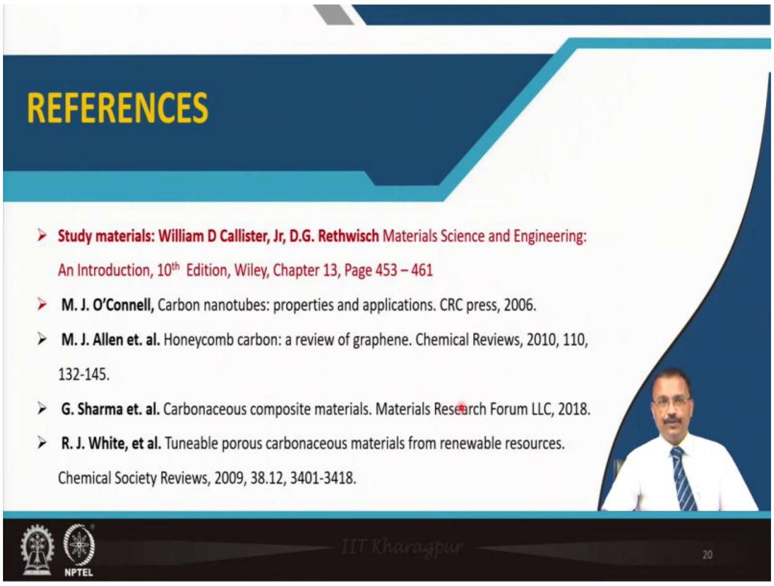

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There are many sources you can use; the study material is will be a book by William D Callister, Material Science and Engineering, this is chapter number 13. So, they have a decent description and if you want to get details about this types of carbonaceous material, please go through the reference material that I have talked about.

Thank you for your attention.