Materials Chemistry
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Module - 5
Lecture - 6
The New Carbon Family I - Fullerenes and Nanotubes

In module 5, we have discussed many of the materials, which show interesting properties both from electrical resistivity point of view, and also how some of these materials hold key to electronic properties based on the magnetic response. So, in the first few lectures we have discussed about colossal magneto resistance, it is mainly to do with oxides, where the resistivity is basically fine tuned by the magnetic transition.

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A New Carbon family

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And we have also looked at two other applications namely GMR and TMR, those are actually not the materials intrinsic property, but those are extrinsic property dependent on the interface of the multilayered structure. And how this magnetic alignment of these layers across the interface can define the electrical property, and those are specially rich features, because they affect the applications yet to a larger extent. And we have also seen another extremely illustrious candidate that is a high temperature superconductor in the form of oxides.

How they have shown unusual properties, mainly coming from defect chemistry, and the class of superconductors that we have seen are mainly highlighting the importance of what can happen within one unit cell, which can affect a bulk phenomena, such as metallicity in metal oxides. Today, I am going to attempt on a larger issue of carbon family, because in the last 15 years the number of publications that has been generated, because of the new adventures that have gone through in this carbon family has almost overtaken any other field.

And this carbon family has also is another very important interface, which is brought biologist, physicist, chemist, and engineers together, this is one of the another important milestone, other than the high temperature superconductivity and colossal magneto resistance which has brought inter disciplinary approach into our modern research. So, I would like to place all this issues on record, because if we really look at some distinctive innovations or discoveries, which has come, which has almost shaken our research activities across the world.

I would say that this is the most important and third most important milestone in the last 25 years. The first slide also sums up the complexity, because it is not possible to just represent one structure to define what is carbon family? New carbon family is. As you would see here, it is all about a black stuff that is coming and that black stuff can be anything it could be in the form of a ball, which we call it is fullerene; or it could be in terms of a wire, which we call it as carbon nanotube or it could be as a sheet which we call this as graphene.

Now, to just bring to your focus, what is hidden here it is not just the shape, but it is the dimension that has progressively changed and to understand all this three new allotropes of carbon is absolutely impossible to cover in just one lecture. So, in this lecture I will try my best to bring essential features of each class, and try to see whether we can get some comprehensive picture of all the three discoveries that has come through in the last 10 years.

And this is just a few milligrams of carbon, which is actually carbon nanotube which a person is holding and this little amount of carbon can actually cost you several hundred thousands of rupees or dollars. So, it is so expensive, so important and the we will see in the next few slides, what are the rich chemistry that is hidden in this compounds.

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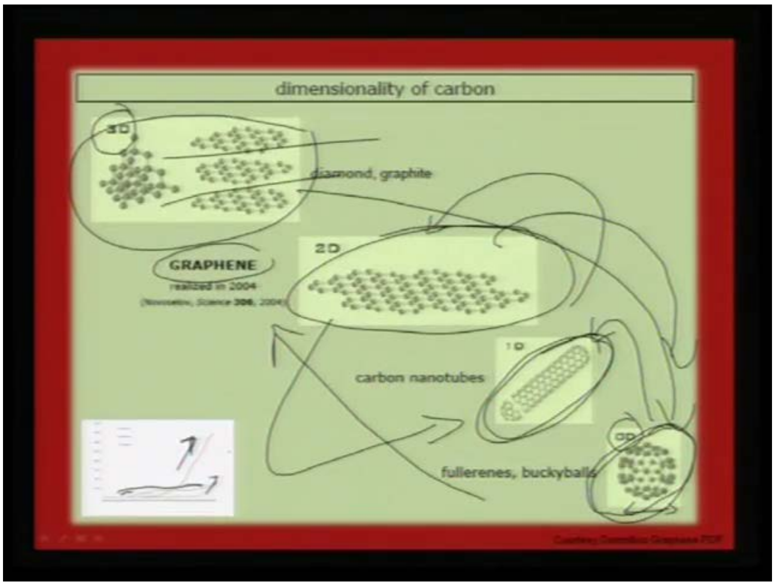

dimensionality of carbon

3D

diamond, graphite

GRAPHENE

realized in 2004

(Novoselov, Science 306, 2004)

2D

1D

carbon nanotubes

0D

fullerenes, buckyballs

Just to highlight, how much we have transcended in this research in terms of dimensionality, all we know is the most familiar three dimensional carbon that is graphite and diamond, both the chemistry of it and the practical applications of it we know. So, I do not want to highlight dwell more into it, but after 3D we have immediately come across the zero dimension carbon that is nothing but fullerenes or buckyballs they are actually form of a football.

And if you look at the symmetry if you take a icosahedron and then try to chop of the apical carbons, then you would be able to get this buckyball ar the fullerene. And therefore, if you look at the, this is of a higher symmetry icosahedron has the highest symmetry, and in this symmetry you call this as a zero dimension and the also the confinement of this size is very few nanometer.

So, from 3D actually we have transcended to zero dimension, and in terms of the history of the invention from zero dimension we have transcended to one dimension, that is single wall carbon nanotube or multi wall carbon nanotube. And from one dimensional carbon recent discovery, holds lot of promise on the two dimensional carbon that is grapheme, this is realized in 2004.

And now, you would see on a comparative scale graphene is actually going to take over the whole industrial applications, because of it is rich physical properties, now what we need to understand. As, we go from a zero dimension to two dimension these are the new manifestation of carbon until recently, even in the school text books it was written as the third allotrope of carbon, which is grapheme.

But, now if somebody has to write or history makers have to re correct that we now have at least five manifestation of carbon including the two dimensional graphene and one dimensional carbon nanotube. But, basically I want to bring another essential feature if you really look at the structure of how this fullerene or this one dimensional carbon nanotube evolves, you would understand that it is basically made of the two dimensional graphene sheet.

So, you can build up on a single wall carbon nanotube or a one dimensional carbon nanotube, basically understanding how to roll this carbon graphene sheet or if by some means you can scroll it up into a buckyball. The basic unit then happens to be that of a two dimensional graphic graphene or graphite sheet, and as you know graphene is nothing but graphite only thing it is actually sliced.

So, when you slice these layers, then you result in a graphene sheet, so it is as simple as that, but then the technology was not to the to, it is maturity that such two dimension layers could not be achieved, but now we have a way to do that and we will also look at the chemistry begin how to make this graphene sheet. So, this is the paradigm shift that we see in this carbon research and therefore, we can very confidently call this as a new family of carbon.

So, in this lecture I will highlight to you starting from a zero dimension fullerene and I will dwell little bit more on one dimensional carbon nanotube, and then I will look at some of the details of two dimensional graphenes. Just to highlight one more point this curve which is shooting up is actually, the amount of publication that has gone through in the recent past on carbon nanotubes, compared to the fullerenes.

The fullerenes is here, and then you can see a sudden up search here for the graphene, graphene is just hit the news and therefore, graphene is going to really transcend, but overall the major focus among all these three has been carbon nanotubes, because it has been well established now even in terms of applications. So, just to give you idea about how the global research is positioned, now you have lot of activities mostly on carbon nanotubes compared to fullerenes.

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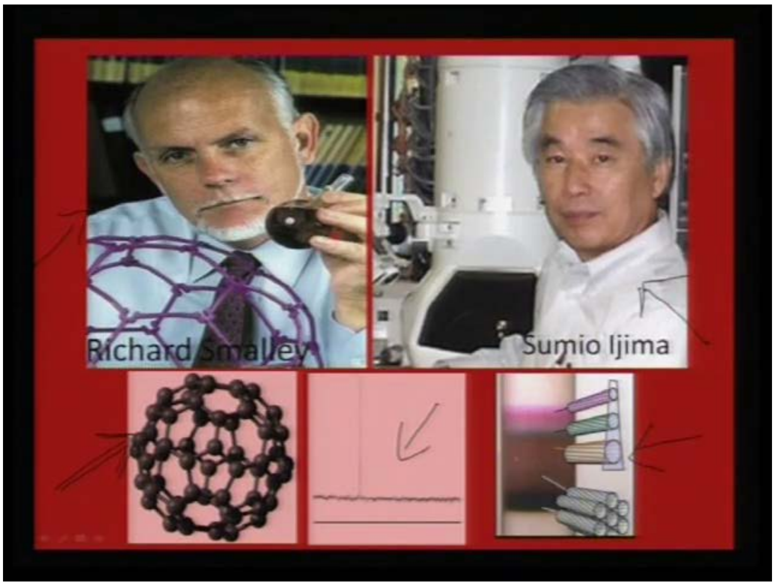

I cannot resist by introduce these two people, who actually have been involved along with them professor Kroto also is given the distinction of being one of the noble laureate, but first person who really hit the news is doctor Richard Smalley from the rice university. But, with profound sadness I should also say that he succumbed to cancer few years back, so he is no more, but he was the person who really found this buckminsterfullerene he isolated it along with professor Kroto.

And this is the picture of the buckyball, that they isolated from rice university at houston in texas and here is another person, he is actually a electron microscopists, and he was not a synthetic person though he is basically electron microscopists. All he did was a very careful investigation of the fullerene, which was made and during his electron microscopy studies he found some images, which became very prominent.

And that was the cause for the discovery, but what really brought the fullerene to focus is this simple cartoon, which otherwise would have missed the whole lot of discovering. One day just emphasize the curiosity, that we need to have in doing research and in this case what is what you see here is a mass spectra. Mass spectra which gives just one single m by e peak ratio for this fullerene which does not come in 0 to 100 m e, it is beyond 500 m e, which usually we might be tempted to ignore.

Specially, when you talk about carbon clusters you would not like to look at a higher m by e ratio, and this is m by e ratio comes beyond 500 m mass and this single peak actually, brought the discovery of fullerene into focus otherwise there was no way they could map it. So, every characterization tool in material synthesis is of a great importance and therefore, I would like to stress how this discovery in the first place was made, and then because of the curiosity that was generated in fullerene chemistry, the single walled carbon nanotube was found.

And as you see from this cartoon below that there are different layers that or different layers with different color purity, you can see, but each of this layer actually is a composition of carbon nanotube, but with different wall diameter. So, this wall diameter tells the intensity or the different carbon nanotubes that you can separate, and thanks to chemistry that it is possible to really purify this different carbon nanotubes when they are suspended into common solvent.

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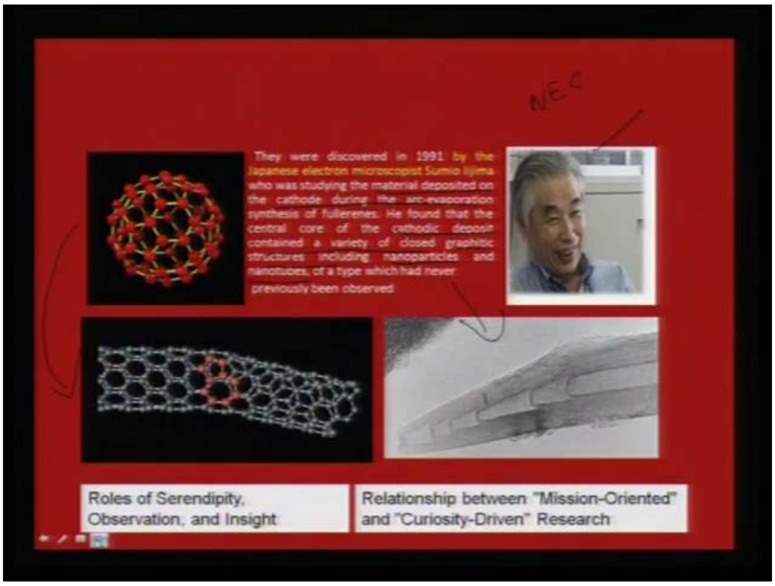

They were discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes, of a type which had never previously been observed

Roles of Serendipity, Observation, and Insight

Relationship between "Mission-Oriented" and "Curiosity-Driven" Research

So, this is how it is isolated and little bit more into the discovery of carbon nanotube, the whole transition from fullerene to carbon nanotube came, because of this microscopists doctor Sumio Iijima from Japan. He is in the NEC center and this is how it was to be when he was studying the material deposited on cathode during the arc evaporation of synthesis fullerenes, he found that the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubues.

So, this is a simple curiosity and this is the mapping of such discovery, and what you see here these are all closed walled nanotubes, carbon nanotubes and they are also multi volt and this brought the curiosity about the discovery of a carbon nanotubes. So, to start with make two observations, because this issues need to be told that there is a role of serendipity that is sudden discoveries, which has played a very heavily in this new family of carbon, and observation and insight along with relationship between mission oriented and curiosity driven research.

So, each one is a classic example of the statements that I have made mission oriented research, and being very careful when you stumble at a discovery, because that might actually transcend you to another discovery. If you are only concerned about that one single peak corresponding to fullerene, we could have just missed out on whole rich chemistry of carbon nanotubes. So, this is a curiosity driven research therefore, every single image that we record every single spectra that we record is actually very, very important.

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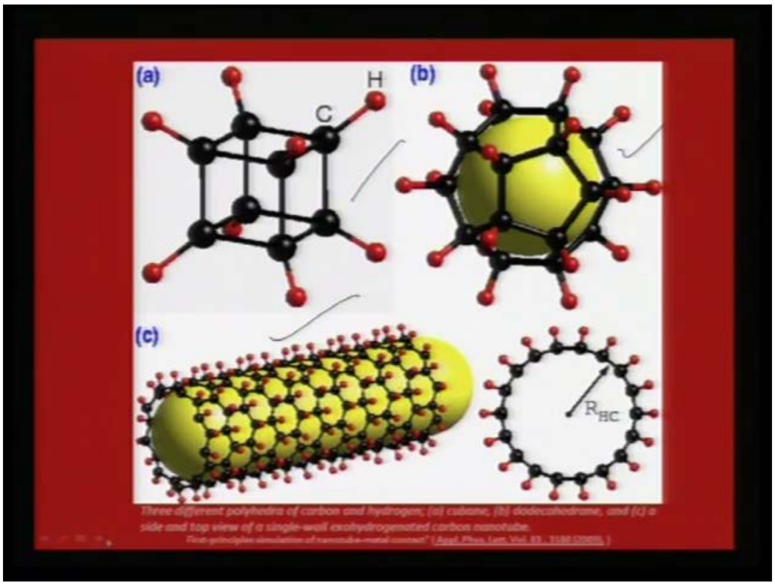

Three different polyhedra of carbon and hydrogen; (a) cubane, (b) dodecahedrane, and (c) a side and top view of a single-wall exohydrogenated carbon nanotube.

"First-principles simulation of nanotube-metal contact" (Appl. Phys. Lett. Vol. 83 , 3180 (2003).)

Now, this is a cartoon which is actually a simulation, but this shows the different polyhedras that the carbon can generate, and in this case you can see the three different polyhedra of carbon and hydrogen. One is a cubane type, another one is dodecahedron, and the other one is the carbon nanotube, this is exohydrogenated carbon nanotube, so this is out of a simulation that we have done developed just to show that there are three different polyhedras that the carbon can exhibit.

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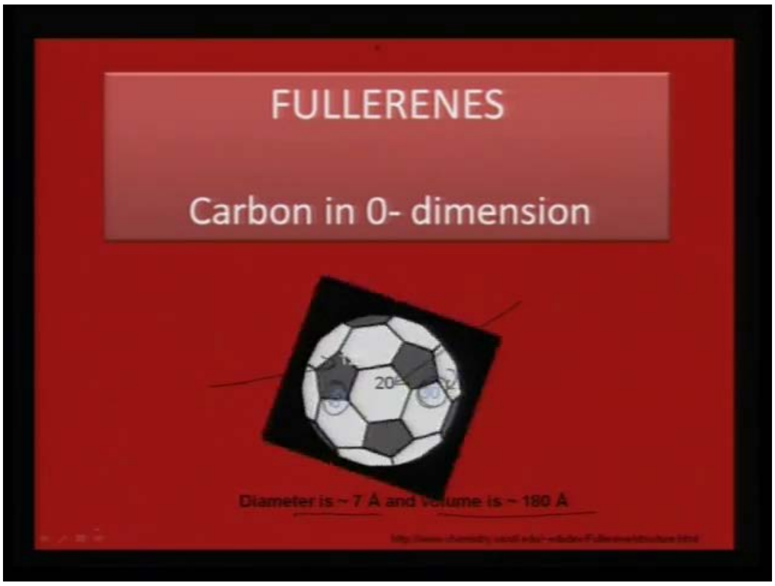

FULLERENES

Carbon in 0- dimension

Diameter is ~ 7 Å and volume is ~ 180 Å

So, let us take for in the first place the discovery of fullerene and what it really means as I told you in the previous slides, this is a carbon with higher symmetry and therefore, we call it zero dimension. And the numbers that we need to remember here are there are twelve carbons with 5 membered ring, and there are 20 carbons with 6 membered ring in this buckyball, and out of which if you look at the edge sharing between the 5 membered ring and the 6 membered ring. There are 30 such edges and there are 60 such edges between a 6 membered and a 6 membered and a 6 such edges between a 5 membered and a 6 membered ring.

These are the features of this carbon, why I am telling that is because when we tried to bring out different chemistry or some new chemistry out of this fullerene, we need to understand in perspective, where to attack which carbon atom to attack. Therefore, it is important for us to know some of this co ordinates, and this fullerene C 60 is typically of the order of seven angstrom that is 0.7 nanometer and therefore, the volume is around 180 angstrom.

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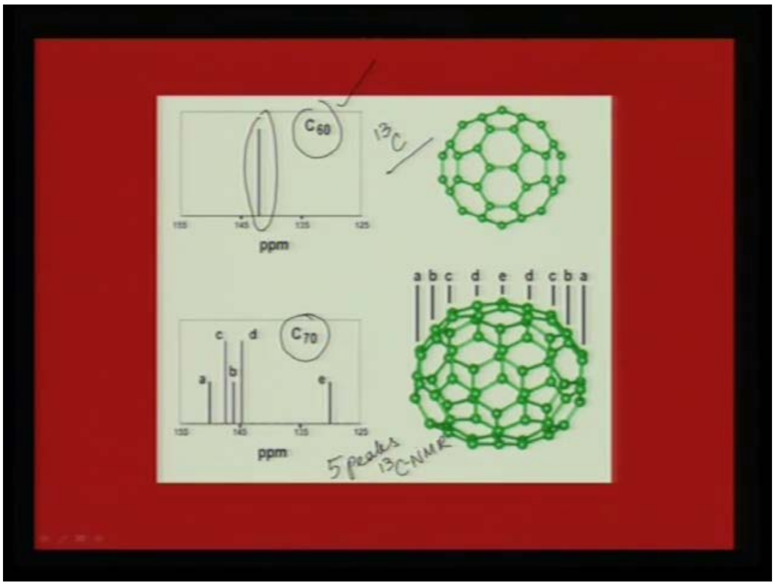

So, these are the numbers that we need to have in perspective, and how do we isolate, because whenever a fullerene is made you actually get a range of a carbon suite, which can have different fragments or different C carbon clusters. So, the chief of this is nothing but C 60, but it is also observed that C 20 C 30 C 70 are all fragments that can be observed along with C 60, which is the major product or which is called as the fullerene.

So, one of the useful way to identify whether you have a very clean C 60 or not is to use NMR, and here is a NMR of C 13, which is recorded for fullerene that is C 60 and C 60 will actually give you only one C 13 NMR peak, and that is between 140 to 145 ppm it is a very characteristic peak coming from a C 13. So, if you have just one peak in C 13; that means, you have got a clean C 60, but if you are going to have C 70 then you would actually have 5 peaks coming in the same range.

Therefore, it is very easy for us to map whether we have C 60 or C 70 as a mixture, and in C 70 you do not have the same sort of symmetry therefore, there are 5 different carbon centers in C 70. As, a result you would actually find 5 peaks in C 13 NMR, so therefore, it becomes very easy for us to map whether it is a pure compound or not.

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Solvent	Solubility
1-chloronaphthalene	51 mg/mL
1-methylnaphthalene	33 mg/mL
1,2-dichlorobenzene	24 mg/mL
1,2,4-trimethylbenzene	18 mg/mL
tetrahydronaphthalene	16 mg/mL
carbon disulfide	8 mg/mL
1,2,3-tribromopropane	8 mg/mL
xylene	5 mg/mL

Hydrated fullerene

And one of the best things that can happen in this whole chemistry is the solubility, because it is otherwise very difficult to isolate carbon and fortunately carbon 60 can dissolve in a variety of solvents. And as you see here I have listed very few of several common solvents have been explored organic solvents, but these are some unusual solvents in which carbon 60 is soluble. And therefore, I have recorded it reason is in most of the common organic solvents like ethanol, methanol, dichloromethane, DMF or DMSO.

The solubility is very, very negligible of the order of sometimes one gram or less than one milligram per ml, therefore the most important one is one chlorine naphthalene where up to fifty one milligram you can dissolve in 1 ml. And as you can see here you get a very good purplish color of solution, which is a devoid of any suspension therefore, it is possible for us to even make a film out of it and this can be used for variety of other operations.

And therefore, the solvents that we need to use whenever we get a carbon suite, goes in this order naphthalene based solvents or as you see here dichlorobenzene, trimethylbenzene, xylene, carbon disulfide all this shows a very good solvent property for this carbon nanotube. One more thing that you need to understand in perspective is there is another cartoon which clearly gives another possibility, that if you oxidize the fullerene then this can actually, become if you hydrate this fullerene then it can become a hydrated fullerene as a result you can make this even water soluble.

So, this is a example of a hydrated fullerene, which can improve on water based chemistry, which is environmentally also more preferred therefore, hydrated fullerenes are also possible when you try to carefully hydrate this fullerene molecule.

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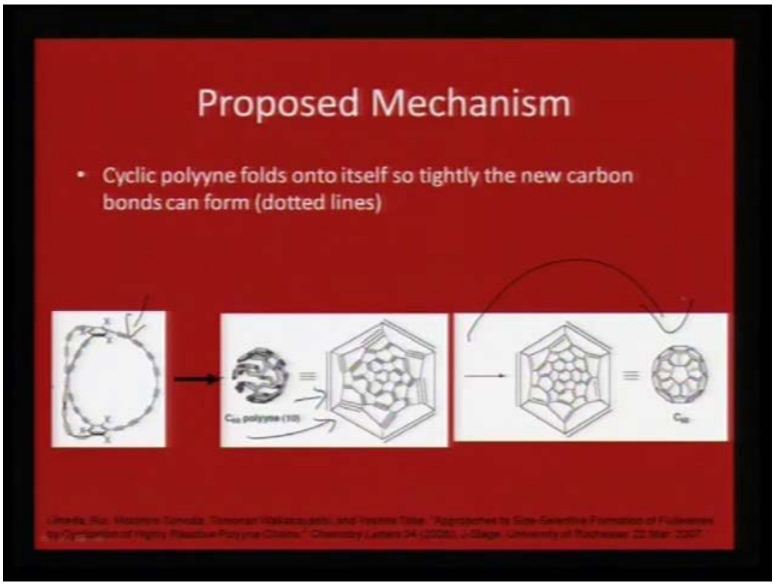

Proposed Mechanism

- Cyclic polyyne folds onto itself so tightly the new carbon bonds can form (dotted lines)

Now, how does this fullerene come, because when you try to synthesize fullerene as you know you try to use a arc plasma method, by which you try to get a sudden deposit of carbon from graphitic rods. And how it all happens the proposed mechanism is as follows cyclic polyynes what you see here they can hold onto itself, so tightly that the new carbon bonds can form which is actually shown in the dot dotted lines.

So, these are all C 60 polyyne actually can be bundled into this fashion where new bonds come up and they curl up to give a C 60 molecule. Other than that because it such a flash process there is no way that we can generate or simulate how the bond making happens for this to happen, but this is the proposed mechanism for how the new carbon bonds can be formed.

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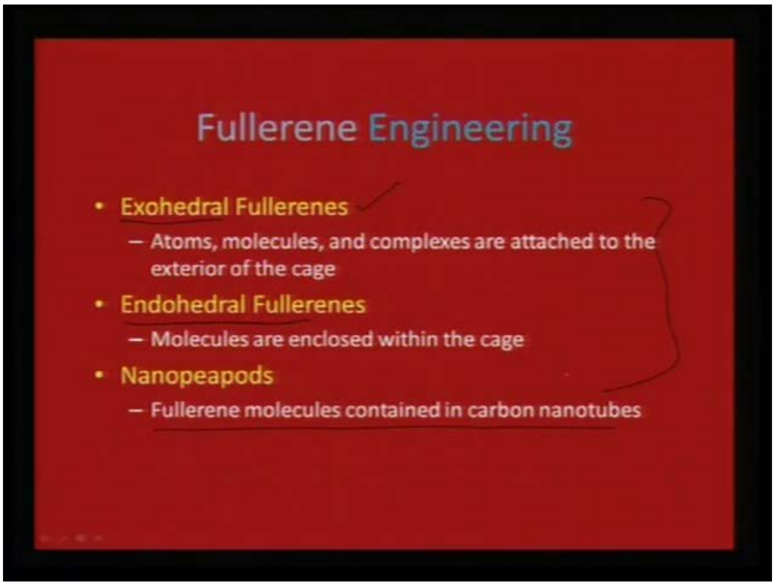

Fullerene Engineering

- Exohedral Fullerenes
  - Atoms, molecules, and complexes are attached to the exterior of the cage
- Endohedral Fullerenes
  - Molecules are enclosed within the cage
- Nanopeapods
  - Fullerene molecules contained in carbon nanotubes

Now, what do we do with this fullerene and where is the chemistry lie in this buckyballs? Actually fullerene can be modified and that is where the chemistry comes into picture, you just do not look at it. And simply appreciate, but then you try to put lot of molecules or take out some atoms out of it and try to create rich chemistry in that, so the substitution of this fullerenes actually can be viewed in 3 ways one is exohedral fullerenes, where you try to put atoms molecules or complexes on the top and the surface of the buckyball or the fullerene, so you call it exo.

Another thing we can do we can try to push some atoms or molecules in a preferred way which can go and they can be held through a real charge transfer process, it is not simple physical existence, but there is a chemical phenomena happening between the molecules which are caged inside. And therefore, those are called as endohedral fullerenes and another thing is it is not just the fullerene playing a host lattice, where it can either do a exo or endo it can also be a guest it not only a host. And in that case fullerene molecules can actually be pushed into carbon nanotubes, so it can actually play a guest role also as much as it is a good host.

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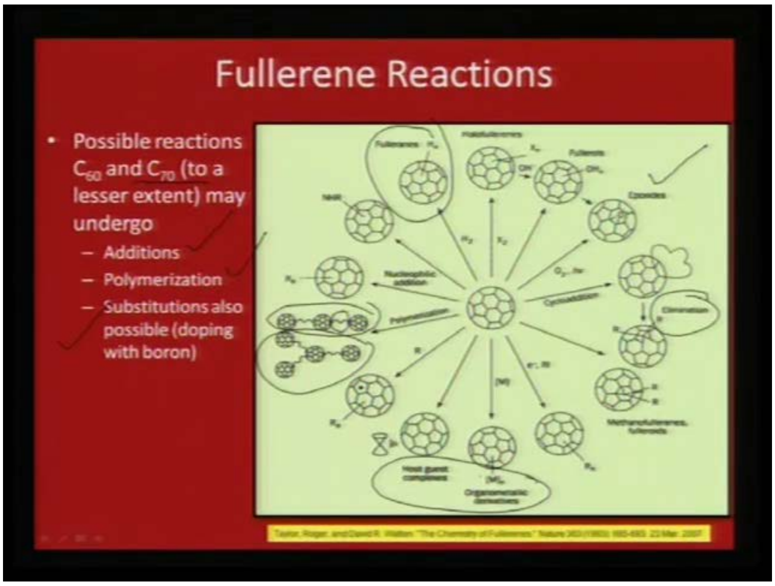

Fullerene Reactions

- Possible reactions C_{60} and C_{70} (to a lesser extent) may undergo
  - Additions
  - Polymerization
  - Substitutions also possible (doping with boron)

Taylor, Roger, and David R. Walton "The Chemistry of Fullerenes" Nature 363 (1993) 685-693 23 Mar 2007

So, based on these three divisions a several examples can be generated, this cartoon gives you an idea all the fullerene reactions that are possible, specially C 60 molecules undergo most of the reactions that we have listed here. Also, C 70 to a lesser extent may undergo addition type of reactions polymerization type or substitution types of reaction specially with the boron.

So, just I would like to pull out few examples one is this buckyballs can be polymerized in this fashion, this can become very interesting, so simple polymerization of this through extended linkages like this is possible. So, you make a polymer which can be dendrimeric or it can be linear therefore, polymerization of this is possible. And then I will take few examples to discuss it is impossible to go through all the cycle one is hydrogenation to fullerenes you can completely hydrogenated, because there are double bonds in it.

And then you can also make epoxides this is a very reactive reaction, where you try to treat it with oxygen in the presence of light or we can actually do cycloaddition in this fashion or we can actually have lot of host guest complexes organometallic derivatives which can be generated on the top of the buckyball.

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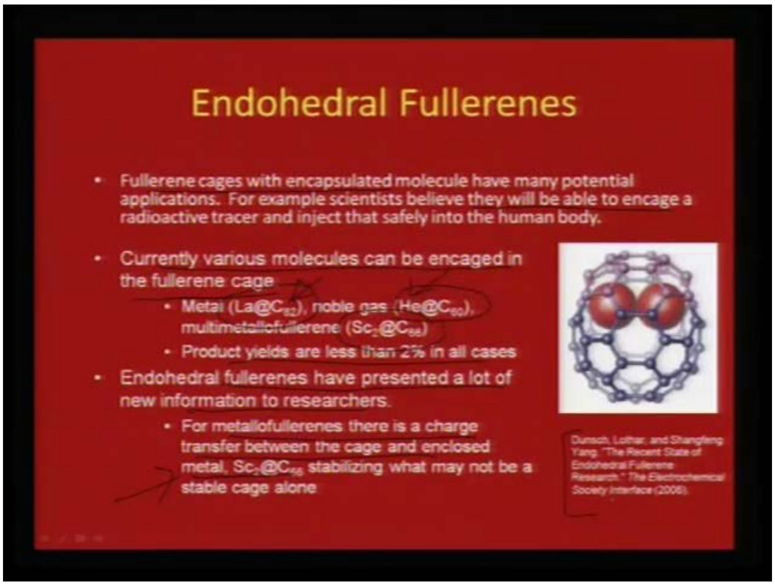

Endohedral Fullerenes

- Fullerene cages with encapsulated molecule have many potential applications. For example scientists believe they will be able to encage a radioactive tracer and inject that safely into the human body.
- Currently various molecules can be encaged in the fullerene cage
  - Metal ($La@C_{82}$), noble gas ($He@C_{60}$), multimetallofullerene ($Sc_2@C_{66}$)
  - Product yields are less than 2% in all cases
- Endohedral fullerenes have presented a lot of new information to researchers.
  - For metallofullerenes there is a charge transfer between the cage and enclosed metal, $Sc_2@C_{66}$ stabilizing what may not be a stable cage alone

Dunsch, Lothar, and Shangfeng Yang. "The Recent State of Endohedral Fullerene Research." *The Electrochemical Society Interface* (2006).

So, several reactions are possible in this form and we will take one or few two examples, to see how this can be done endohedral fullerenes, these are fullerene cages with encapsulated molecules, which have many potential applications. It is constitute that that scientist will be able to engage a radioactive tracer and inject that safely into human body for mapping or for any spectroscopic investigation, for any radiation therapy.

It is possible that we can actually use radioactive tracers to be injected into human body in a very safe mode, and that way fullerene is compared to be a very safe carrier, because you can put that inside and you can transfer it into the body. Another thing is currently various molecules can be engaged in fullerene for example, lanthanum can be put inside carbon cage, which is a C 82 cage. And helium which is a monatomic gas can be put inside C 60, therefore even putting preferred metal ions depends on the cage that you are looking for.

See for example, lanthanum cannot be easily put into C 60, because of it is dimension and other physical properties that may become intricate therefore, it is also to some extent selective and similarly you can put scandium in C 66 cage. So, it is possible, but in those cases the product yields are actually less than 2 percent and in endohedral fullerenes there are lot of information that we can get. For example, metallofullerenes there is a charge transfer between the cage and the enclosed metal as in the case of scandium that is put inside C 66.

So, many rich chemistry can be verified as to what really is the interaction it is not just a bound pair, but something unusually happens to this endohedral fullerenes, and for a review actually we can go through article by professor dunsch.

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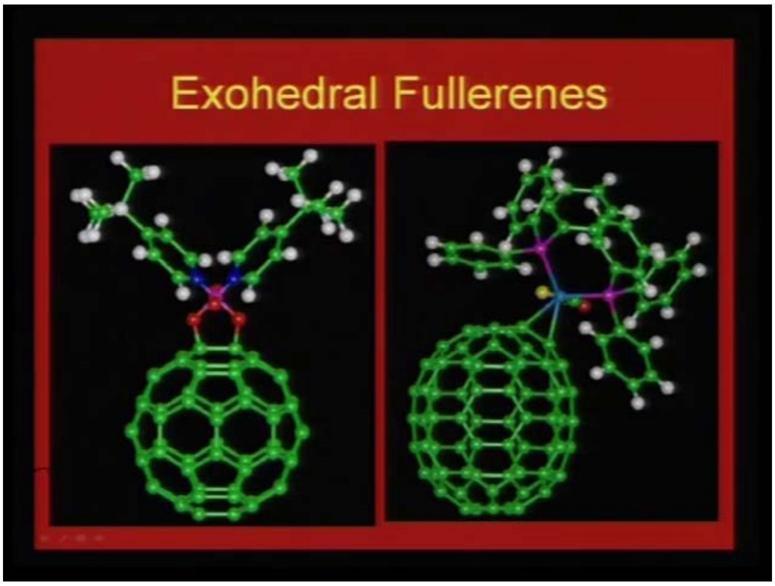

Exohedral Fullerenes

These are again two examples of exohedral fullerene and this is from a C 60 molecule which is actually kept to osmium metal here, and this osmium metal is bound to two pyridine rings. So, you can actually get a exohedral fullerene using osmium and this can be put in this apical position here or we can actually use iridium metal center also and iridium carbonyl, this is a carbonyl moiety and chlorine attached to it with the other aromatic rings, so this sort of exohedral fullerenes have also been attempted.

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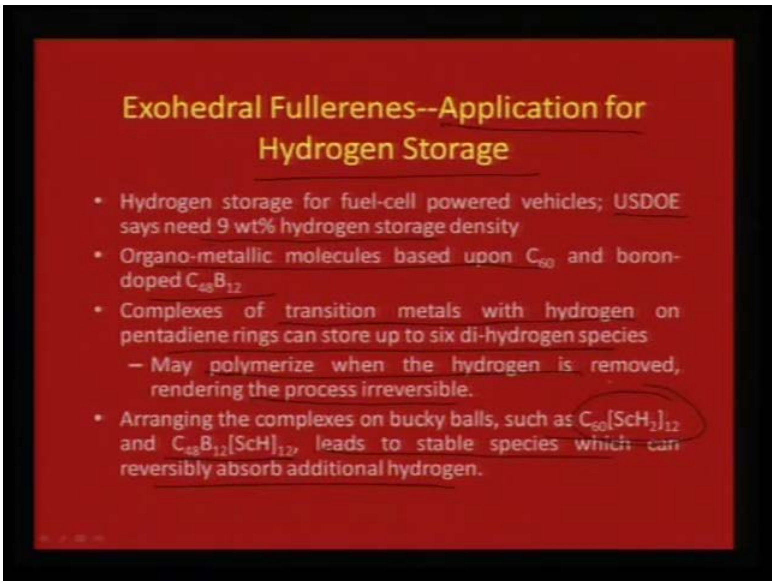

Exohedral Fullerenes--Application for Hydrogen Storage

- Hydrogen storage for fuel-cell powered vehicles; USDOE says need 9 wt% hydrogen storage density
- Organo-metallic molecules based upon C_{60} and boron-doped $C_{48}B_{12}$
- Complexes of transition metals with hydrogen on pentadiene rings can store up to six di-hydrogen species
  - May polymerize when the hydrogen is removed, rendering the process irreversible.
- Arranging the complexes on bucky balls, such as $C_{60}[ScH_2]_{12}$ and $C_{48}B_{12}[ScH]_{12}$, leads to stable species which can reversibly absorb additional hydrogen.

And if you find out this exohedral fullerenes actually has a very potential application as hydrogen carriers and therefore, it is being explode very richly for application into hydrogen storage because this osmium or iridium this metal centers can actually bind dihedral dihydrogen species. And they have a special tendency to exchange this dihydrogen give it give up and also to retake and therefore, when it becomes a reversible process then it is a very useful material for hydrogen storage.

And what US department of energy forecast is they just need a 9 weight percent hydrogen storage density in any material, and 9 percent is enough to drive any automotive vehicles. So, it is found that organo metallic molecules based upon C 60 and boron, which is doped seem to have special affinity to dihydrogen species that is molecular hydrogen. So, you can try to take it. Complexes of transition metals with hydrogen they also can take only thing these transition metal complexes, they actually polymerize the dihydrogen species is removed.

As, a result it is a irreversible one and that is not the chemistry behind hydrogen storage, so if you want a hydrogen storage material then you need to be able to liberate the hydrogen and also selectively take it back. Otherwise, this cannot be a useful candidate and in such cases scandium hydrogen species which is attached to C 60 has been found to be a very good complex, this leads to stable species which can reversibly absorb additional hydrogen, so this is one of the candidate which is being explode for hydrogen storage applications.

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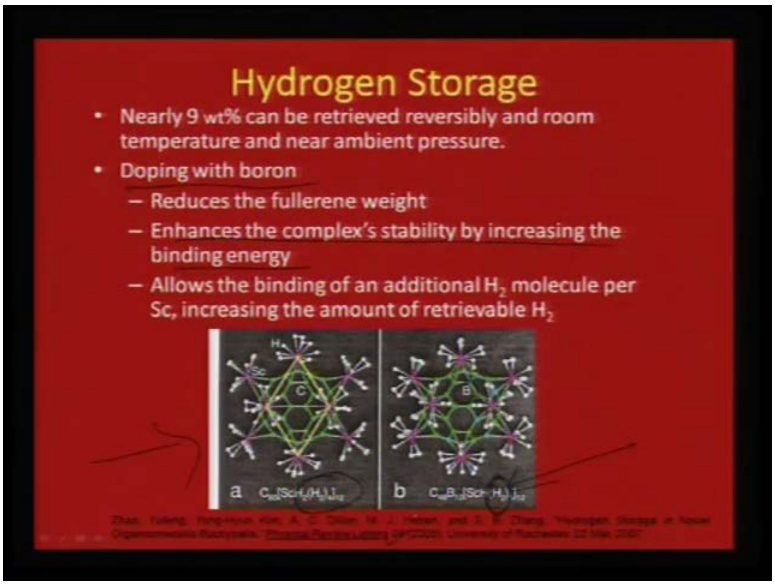

Hydrogen Storage

- Nearly 9 wt% can be retrieved reversibly and room temperature and near ambient pressure.
- Doping with boron
  - Reduces the fullerene weight
  - Enhances the complex's stability by increasing the binding energy
  - Allows the binding of an additional H_2 molecule per Sc, increasing the amount of retrievable H_2

And same I have tried to show you through this view graph you can see here scandium metal center, which is able to bind rich amount of molecular hydrogen species here, and this can become reversible, so we can put it and take it back doping with boron becomes very important in this case. So, this enhances the complex stability by increasing the binding energy and this allows the binding of an additional hydrogen molecule per scandium increasing the amount of retrievable hydrogen, and this is actually a paper found in physical review letters in 2005.

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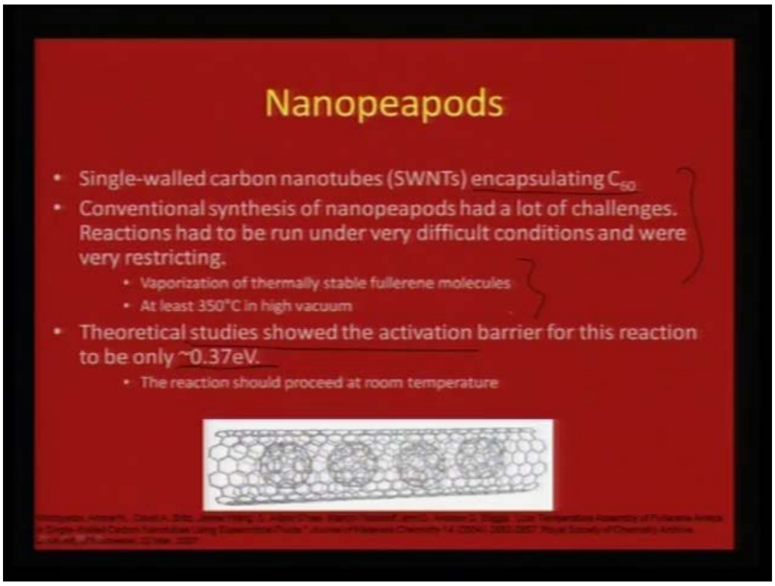

Nanopeapods

- Single-walled carbon nanotubes (SWNTs) encapsulating C_{60}
- Conventional synthesis of nanopeapods had a lot of challenges. Reactions had to be run under very difficult conditions and were very restricting.
  - Vaporization of thermally stable fullerene molecules
  - At least 350°C in high vacuum
- Theoretical studies showed the activation barrier for this reaction to be only ~0.37eV.
  - The reaction should proceed at room temperature

Now, the other chemistry that can happen from fullerene is that you can get into the carbon nanotubes and therefore, fullerene when it is endohedral fullerene they can actually serve as a carrier which can be filled into open sided carbon nanotubes. So, single walled carbon nanotubes encapsulating C 60 is also there only thing achieving this is a very tricky thing, although theoretical studies they show that to put fullerene into carbon nanotube. It takes only 0.37 electron volt which means it should actually happen at room temperature, but so far studies have not been successful where people have tried it up to 350 degrees in vacuum.

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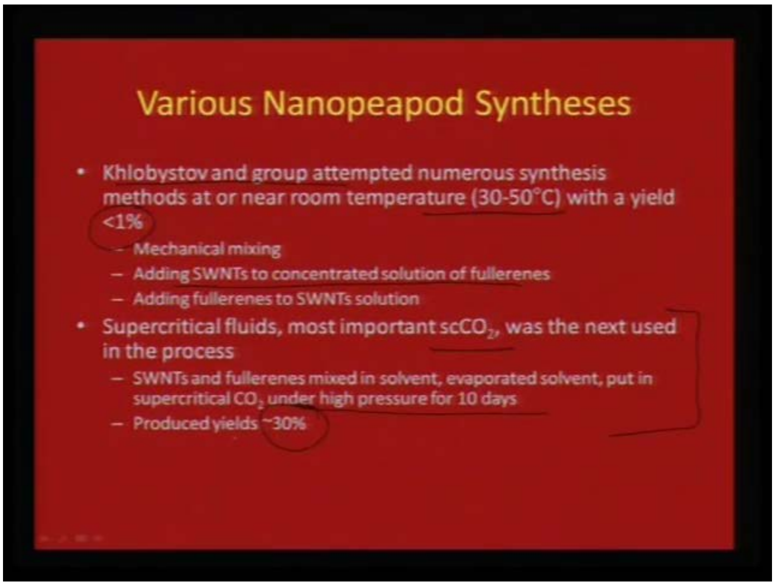

Various Nanopeapod Syntheses

- Khlobystov and group attempted numerous synthesis methods at or near room temperature (30-50°C) with a yield <1%
  - Mechanical mixing
  - Adding SWNTs to concentrated solution of fullerenes
  - Adding fullerenes to SWNTs solution
- Supercritical fluids, most important $scCO_2$, was the next used in the process
  - SWNTs and fullerenes mixed in solvent, evaporated solvent, put in supercritical CO_2 under high pressure for 10 days
  - Produced yields ~30%

So, here is an another example where the Russian group they have tried to attempt at room temperature, only thing the yield is one less than one percent adding single wall carbon nanotubes to a saturated solution of fluorine has been attempted, and vice versa. Taking fullerene into a saturated solution of single wall has been attempted and one approach, which has given dividends is it is almost like a brute force, where you try to use high pressure.

So, here is super critical carbon dioxide which is used and using this under high pressure for 10 days they were able to dope successfully, fullerene into carbon nanotubes to the order of 30 percent. So, it appears that with the more of high pressure it is possible to do this nano peapods sort of synthesis, so this is also been attempted in the recent past.

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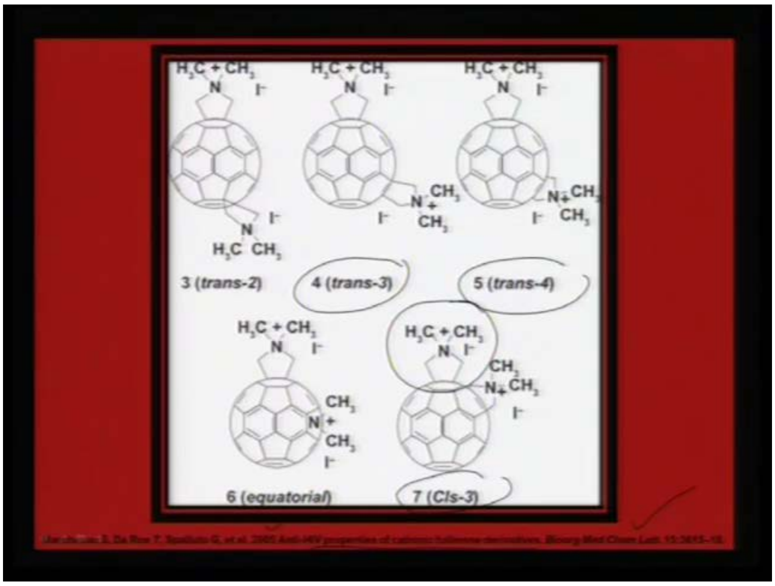

3 (*trans-2*) 4 (*trans-3*) 5 (*trans-4*)

6 (*equatorial*) 7 (*Cis-3*)

Marchesan S, Da Ros T, Spalluto G, et al. 2005 Anti-HIV properties of cationic fullerene derivatives. Bioorg Med Chem Lett 15:3615–18.

These are some of the examples of how different derivatized fullerenes can be made and these are specially candidates for HIV properties, and this has appeared in bioorganic medical letters, chemistry letters and this has come out in the year 2005, where they have found specially the geometrical ones the trans and cis isomers they have a very selective response to HIV virus.

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Brettreich M, Hirsch A. 1998. A highly water-soluble dendro[60]fullerene. Tetrahedron Lett. 39:2731–34.

So, these exohedral fullerenes are specially candidates which can have specific activity, and here is another example, where we can try to make dendrimers out of fullerene. So, you have the fullerene moiety here, but you can actually attach such first generation dendrimers. So, as a result you can actually get a very microscopic molecule and this is especially useful because it turns out to be totally water soluble, so this has specific applications therefore, such molecules also have been prepared in the recent past

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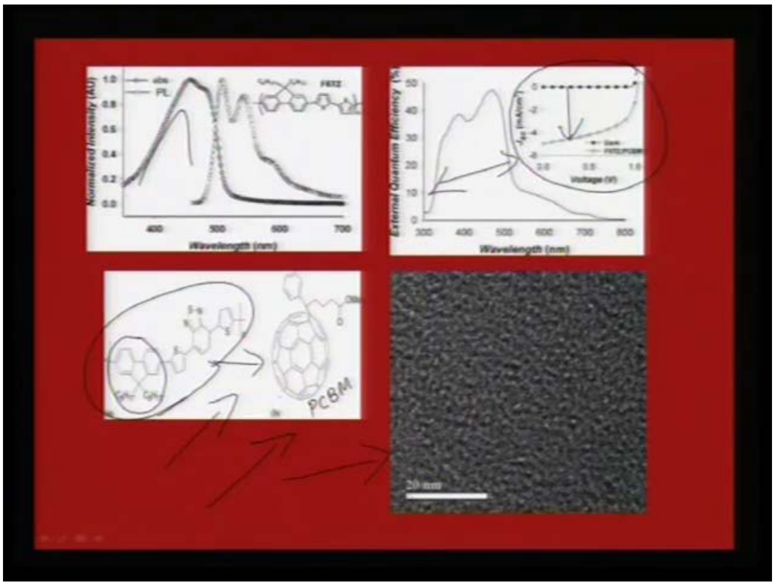

And lastly on fullerenes I would like to mention that fullerene is not just about a substitution, but fullerenes with doping with potassium ions have shown a extraordinary property of super conductivity. So, this is a superconducting potassium doped C 60 K 3 C 60 which actually shows a t C somewhere at 19 K, but what you would see here, if you try to replace the small cation potassium with rubidium or then rubidium you can put an translate it with caesium.

You can see that the lattice parameter of the C 60 is changing from 14.2 to 14.6 and as there is a expansion you also in the crystal lattice you also see that the T C is varying, so this has been attempted and this is one of the extraordinary response of fullerene in terms of it is electrical property. So, just carefully dope it with the monovalent ion potassium rubidium caesium anything you can translat it and these are not just a fluke method it has been characterized very clearly that it seems to have a very definite dependence on carrier density.

So, depending on the carrier density the T C can be altered, so fullerene has specially hit the super conductivity map mainly, because of it substitutions around the carbon cage. Apart, from this phenomena of super conductivity that is seen in fullerene, another important application is also in the area of photovoltaics, as you would see here this is called as PCBM, which is a very well known candidate of C 60 which is now a day’s used as a blend along with a fluorine fluorine polymer.

This is the fluorine based with the different substitution in this case it is with the benzothiazole and with such molecules it is possible for us to make a blend, where you actually get a donor and a acceptor fullerene as a acceptor and the fluorine as the donor. So, you can actually make a heterojunction polymer and this is the view SEM view graph of how a polymer blend will look like you can see that you get a very continuous spread of a amorphous polymer film, and what you can clearly see is that.

This is the PL this is the absorption and PL of the fluorine moiety, where you can see the fluorine absorption is somewhere around 500 maximum at 500, but once you make the blend you can see that it is actually blue shifted, which means it is sifted to higher energy. Therefore, this will become a very efficient blend for photo photovoltaic application and this is the view graph at the in the inset, which gives you approximate clue to how this sort of heterojunction can behave.

And this is in dark and this is the I V curve in light, and you can see that the open circuit voltage OC and the film factor is quite decent here and carries a good amount of current density. So, the latest application of fullerene although it is not being talked about as much as carbon nanotube, but it actually playing a very, very silent role in terms of becoming a very useful electron acceptor in photovoltaic devices.

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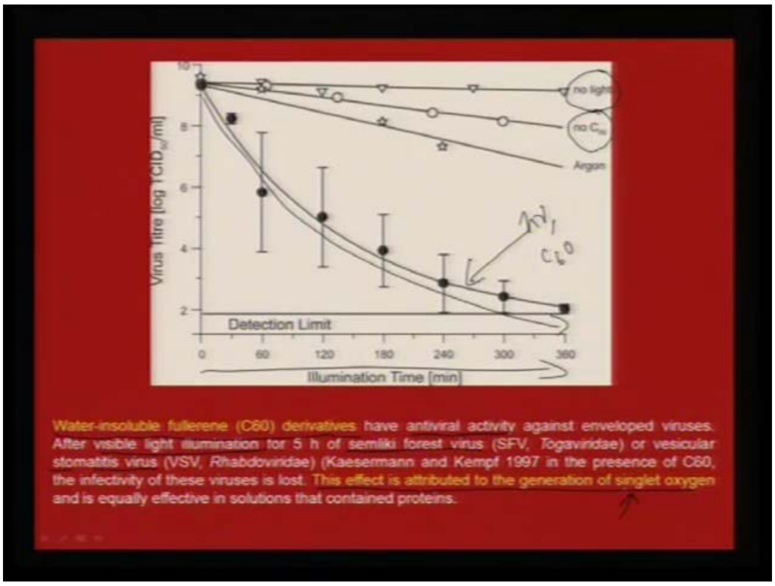

Water-insoluble fullerene (C60) derivatives have antiviral activity against enveloped viruses. After visible light illumination for 5 h of semliki forest virus (SFV, *Togaviridae*) or vesicular stomatitis virus (VSV, *Rhabdoviridae*) (Kaesermann and Kempf 1997 in the presence of C60, the infectivity of these viruses is lost. This effect is attributed to the generation of singlet oxygen and is equally effective in solutions that contained proteins.

One last example before I finish on fullerene is the water soluble fullerene derivatives, which has been found to have antiviral activity and specially in terms of treating with the this sort of virus, forest virus or stomatitis virus. What has been found out is if these viruses are blended with water soluble fullerene, and if there is a visible light illumination, with respect to the illumination time you can see that the virus level is rapidly coming down.

And this is with addition of C 60 and without the addition of C 60 you can see the response, and without light you can see the response and with light with C 60 you can see a tremendous influence on the antiviral activity. So, carbon 60 or fullerene seems to have a very peculiar response to biological applications also, the chemistry there is this effect is attributed to the generation of singlet oxygen, which actually will impair the viral activity, so it is the singlet oxygen that is generated which is responsible for this antiviral property.

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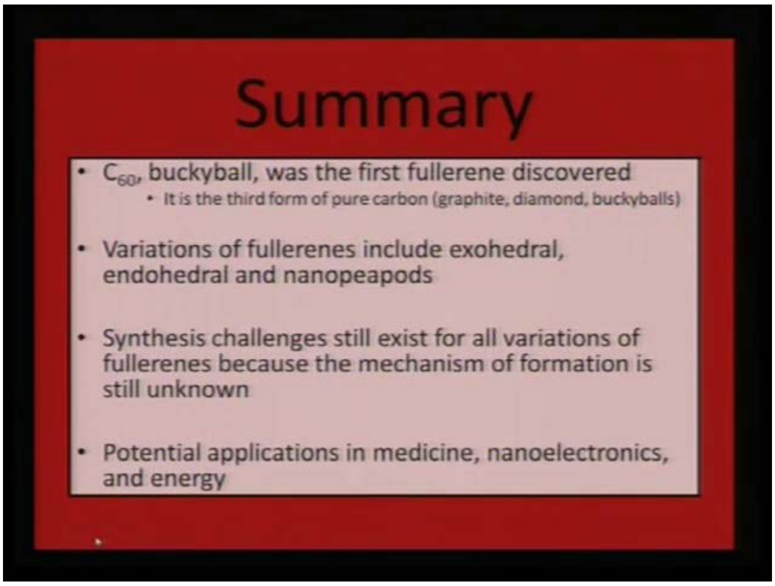

Summary

- C_{60}, buckyball, was the first fullerene discovered
  - It is the third form of pure carbon (graphite, diamond, buckyballs)
- Variations of fullerenes include exohedral, endohedral and nanopeapods
- Synthesis challenges still exist for all variations of fullerenes because the mechanism of formation is still unknown
- Potential applications in medicine, nanoelectronics, and energy

So, in summary of C 60 we can say C 60 buckyball was the first fullerene that is discovered, and it is the third form of pure carbon which is next to graphite and diamond, but this summary is inconclusive, because we have the other new ones which have come in to picture. Variations of fullerene include exohedral andohedral and nanopeapods, and synthesis challenges still exists for all the variations of fullerenes, because the mechanism of formation is still unknown.

And potential applications are now envisaged in the field of medicine nanoelectronics and in energy of which I have given a representative example. Now, having said this I have to confess that this is a very limited scope in which I have tried to tell about the chemistry of fullerene, but there are several literatures in the web sites. There are several useful links which can give us tremendous information about the chemistry of fullerenes, which I will be listing in the slides at the end of the lecture therefore, I encourage that the readers can go through that.

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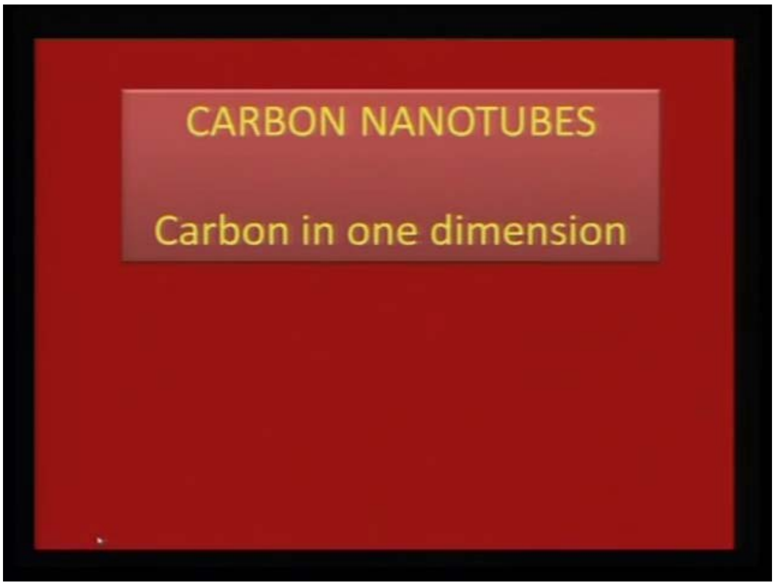

CARBON NANOTUBES

Carbon in one dimension

Now, we will focus our attention on carbon nanotubes, and this carbon nanotube is one dimension carbon nanotube, and we can see how this carbon nanotube evolved from the basic structure.

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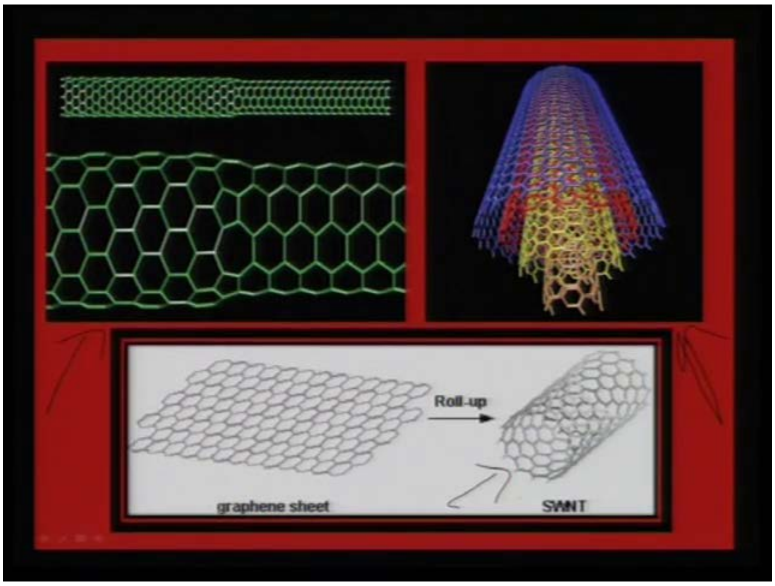

As, you would see here there are two cartoons which I have projected here, one on the left side on the top is a single wall carbon nanotube, which you can easily map it around, and this is just a picture of graphene which is actually rolled up. So, that is the easiest way to visualize, how a carbon nanotube is evolving and then on the right side you see the, this is a multi-walled carbon nanotubes.

So, several walls are there which means one small carbon nanotube got fixed to the other and then to the other therefore, you can actually go for several walls, so it is called multi wall nanotubes, and there can be just 2, there can be even 7, there can be 4, depending on the process that you adopt to make this compounds. So, as you see here the way the single wall nanotube can be easily envisaged is that you take a two dimensional grapheme sheet, which is nothing but a single layer of graphite chopped laterally. And let you just try to roll it, and as you roll it you will come across a single wall nanotube, but the point is the way you try to rollup the single wall nanotube will end up in different electrical properties of this single wall nanotube, which I will try to list it.

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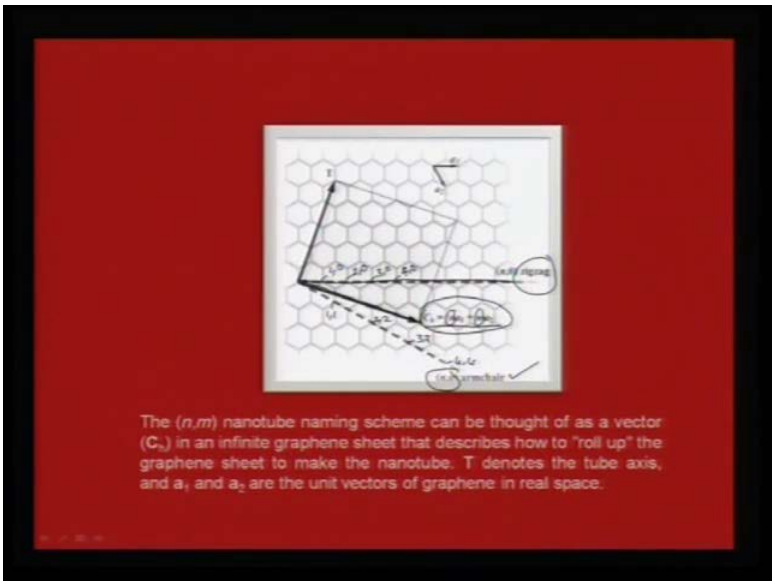

The (*n*,*m*) nanotube naming scheme can be thought of as a vector (C_h) in an infinite graphene sheet that describes how to "roll up" the graphene sheet to make the nanotube. T denotes the tube axis, and a_1 and a_2 are the unit vectors of graphene in real space.

Now, the way we can try to roll up this depends on the unit cell or the way we map it, for example let us take in the case of this axis if you try to draw a line and this is a C H vector. Now, in this we can express C H as n a 1 plus m a 2, where a 1 and a 2 are unit vectors of graphene in real space, so the way we mix this numbers n and m will matter what sort of carbon nanotubes we can get.

For example, in the case of n 0 what you see here n 0 this relates to a zigzag carbon nanotube, if it is going to be along n m and it is called a armchair nanotube. So, what does this means here this is going to be 1 0 and this is going to be 2 0 that is what we mean by n 0 and this is going to be 3 0 and so on, so if you are axis or you are vector is going to lie on n 0, then you would actually get a zigzag nanotube. And if it is going to be for example, here in this case this is 1 1 and in this case this is 2 2, and in this case this is 3 3, and here this would be somewhere around 4 4, then we are talking about a n n armchair.

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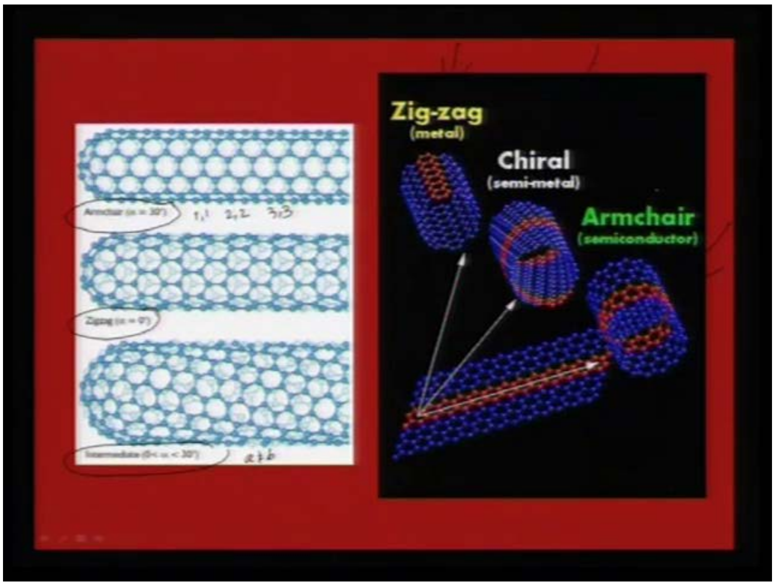

So, the way you roll it up matters with respect to this C H vector, and that will determine what sort of nanotube you get and the corresponding electrical property and that is what we see here in this cartoon. So, if you have a armchair which is nothing but your 1 1 2 2 3 3 and so on, then the alpha that you generate with respect to this alpha is going to be 30 degrees. And in that case actually you would end up with your armchair configuration and if it is going to be 0, which we saw in the previous cartoon that is your 1 0 0 2 0 sorry 1 0 2 0 3 0 4 0.

Then you get across a zigzag which is alpha is equal to 0 degree or it can be also a intermediate one where your a is not equal to b in that case the angle can vary between 0 to 30 degrees and you end up with other configuration. So, based on the way you scroll your graphene sheet, you can either get a zigzag one which is metallic in it is nature or it is a armchair which is semiconductor in it is nature or it can be a chiral one, which is semi-metal in nature.

So, carbon nanotube itself brings about lot more complexity by the way it is arranged, so it can result in different dimensions it can result in different configuration, it can result in different property. Different dimension I mean it can be single walled it can be multi walled and it can it can have the diameter which is different, and as you see here the way you roll it you can also expand the of your nanotube, and this also affects the electrical conductivity. So, you can also get a metal you can also get a semiconductor depending on this, so the whole issue of carbon nanotube revolves around which one you selectively get, and how what is the method that you use for getting such selective ones.

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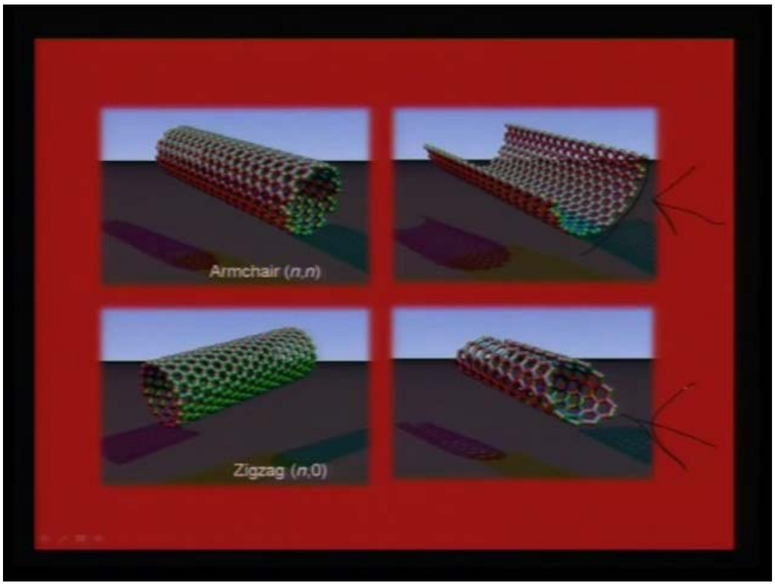

And as, you see here this is another cartoon, just tells you if you are going for a armchair then you look at the edges how they reflect, and if you are going for n 0 you can look at the edges how they transform to be. So, just by looking at the way it is scrolled you can decide on their configuration.

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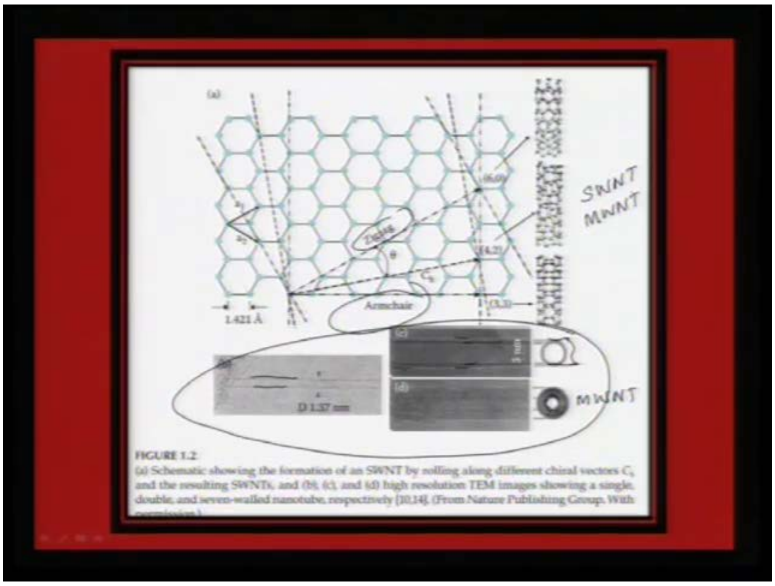

FIGURE 1.2
(a) Schematic showing the formation of an SWNT by rolling along different chiral vectors C_h and the resulting SWNTs, and (b), (c), and (d) high resolution TEM images showing a single, double, and seven-walled nanotube, respectively [10,14]. (From Nature Publishing Group. With permission.)

And depending on whether it is a zigzag or whether it is armchair, it is also possible for you to get a different sort of dimension of your carbon nanotube, and in this case you can see the t m microscopy, which clearly shows the t m image shows this sort of structure; that means, this is a single walled carbon nanotube which has a dia of 1.37. And here you have another one which is called a double walled, this is one wall and this is the outer wall, so we call this as a double wall.

So, this double wall stuff is also possible or you can see this a T M image which actually has more than 4, so this is a multi walled nanotube. So, in essence when you look at the literature, you can actually see this abbreviation quite a bit SWNT or MWNT both are referred to as single wall and multi wall nanotubes.

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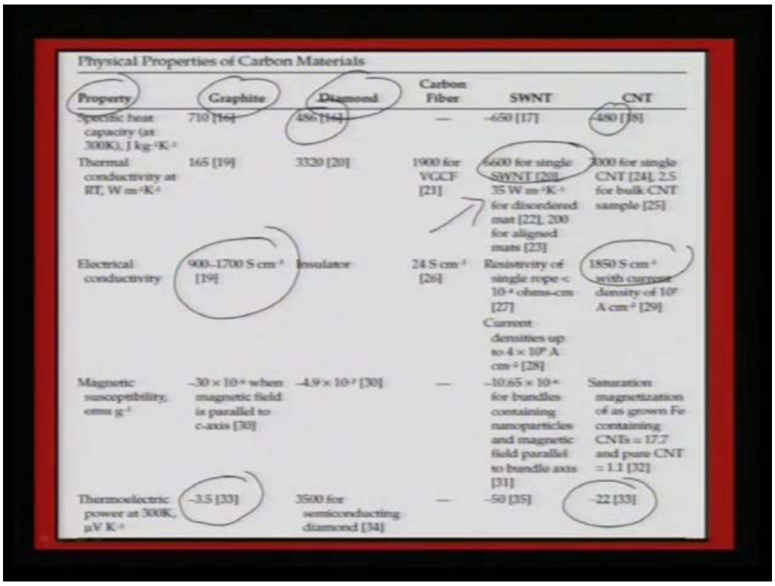

Physical Properties of Carbon Materials

Property	Graphite	Diamond	Carbon Fiber	SWNT	CNT
Specific heat capacity (at 300K), J $kg^{-1}K^{-1}$	710 [16]	486 [16]	—	–650 [17]	–480 [18]
Thermal conductivity at RT, W $m^{-1}K^{-1}$	165 [19]	3320 [20]	1900 for VGCF [21]	6600 for single SWNT [20], 35 W $m^{-1}K^{-1}$ for disordered mat [22], 200 for aligned mats [23]	3000 for single CNT [24], 2.5 for bulk CNT sample [25]
Electrical conductivity	900–1700 S cm^{-1} [19]	Insulator	24 S cm^{-1} [26]	Resistivity of single rope < 10^{-4} ohms-cm [27] Current densities up to 4×10^{9} A cm^{-2} [28]	1850 S cm^{-1} with current density of 10^{7} A cm^{-2} [29]
Magnetic susceptibility, emu g^{-1}	-30×10^{-6} when magnetic field is parallel to c-axis [30]	-4.9×10^{-7} [30]	—	-10.65×10^{-6} for bundles containing nanoparticles and magnetic field parallel to bundle axis [31]	Saturation magnetization of as grown Fe containing CNTs = 17.7 and pure CNT = 1.1 [32]
Thermoelectric power at 300K, $\mu V K^{-1}$	–3.5 [33]	3500 for semiconducting diamond [34]	—	–50 [35]	–22 [33]

For certain applications multi wall is more than enough, but for certain preferred applications you always desire to get a single wall nanotube which is a challenge. Just to draw your attention to the electrical properties and why so many literature outputs have come on carbon nanotubes, let us just make a lighter comparison between the different forms of carbon, then we will get to know why this research is still very intense activity.

Now, if you take the property and compare with the different carbon forms, you can see here specific heat this is comparable to diamond thermal conductivity, if you observe the thermal conductivity of single wall is much, much higher than diamond or graphite. Therefore, from thermal conductivity point of view single wall nanotubes are really most preferred electrical conductivity again, you can see for graphite it is 900 to 1700 seamans per centimeter whereas, in the case of carbon nanotubes it is almost comparable or even double then the graphitic form.

Therefore interms of electrical conductivity it holds a lot of promise, and then the same is true for thermoelectric also you can see the thermoelectric power at 300 k is around 3.5 for graphite, where as it is 22 for single wall nanotube. So, you name any physical property there is a very distinct difference between either graphite or carbon nanotubes are diamonds with carbon nanotubes therefore, there seems to be in essence some curiosity on almost every property that we are looking at.

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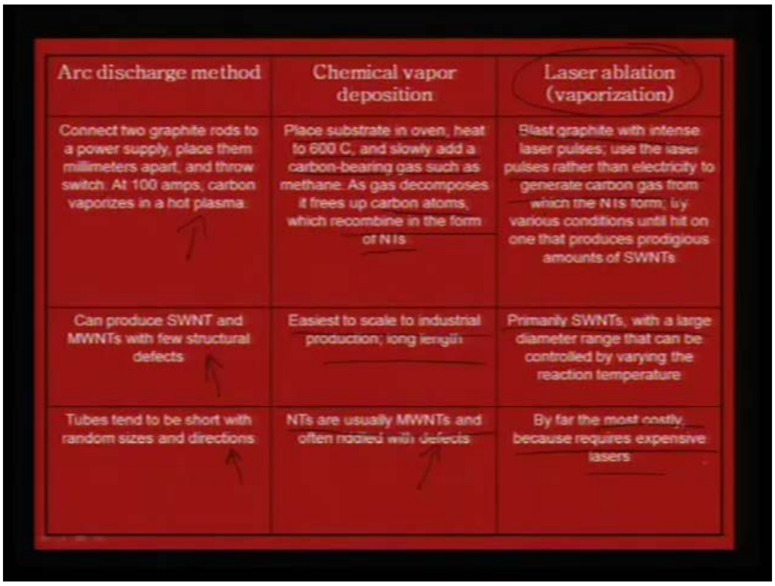

Arc discharge method	Chemical vapor deposition	Laser ablation (vaporization)
Connect two graphite rods to a power supply, place them millimeters apart, and throw switch. At 100 amps, carbon vaporizes in a hot plasma.	Place substrate in oven, heat to 600 C, and slowly add a carbon-bearing gas such as 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
Can produce SWNT and MWNTs with few structural defects	Easiest to scale to industrial production; long length	Primarily SWNTs, with a large diameter range that can be controlled by varying the reaction temperature
Tubes tend to be short with random sizes and directions	NTs are usually MWNTs and often riddled with defects	By far the most costly, because requires expensive lasers

Now, how do we make this carbon nanotubes 3 important methods are there which I would like to highlight, one is arc discharge method, another one is chemical vapor deposition, another one is laser ablation method, which is a vaporization method. So, in arc discharge you actually bring two graphitic rods, you apply very high voltage and a plasma generate then all the carbon suits are trapped in alkin, and then we can try to isolate different fragments of carbon nanotubes, so that is the way it is done.

And then we can actually produce a single wall and multi wall carbon nanotubes with the few structural defects, and then tubes tend to be shot with the random sizes and direction which is the limitation of your arc discharge method. Whereas, in chemical vapor deposition you place a substrate in oven, heat it to hundred degree and slowly add the carbon bearing gas, usually acetylene is sent.

And in that case it freeze up the carbon atoms which actually combine into carbon nanotubes, it is a easiest way to scale upto industrial production and the only problem with the chemical vapor deposition is it actually induces lot of defects. And then we can look for the most sophisticated one that is laser ablation blast the graphite and then try to trap the carbon that is coming, and it is various conditions primarily, this gives selective a single wall carbon nanotubes, but the problem is it is more expensive and it requires more sophisticated infrastructure.

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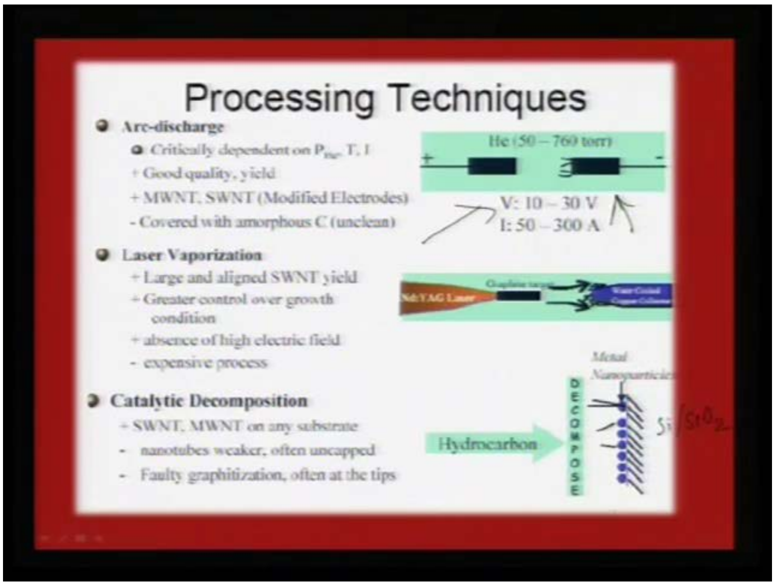

Processing Techniques

- **Arc-discharge**
  - Critically dependent on P_{He}, T, I
  - \+ Good quality, yield
  - \+ MWNT, SWNT (Modified Electrodes)
  - \- Covered with amorphous C (unclean)
- **Laser Vaporization**
  - \+ Large and aligned SWNT yield
  - \+ Greater control over growth condition
  - \+ absence of high electric field
  - \- expensive process
- **Catalytic Decomposition**
  - \+ SWNT, MWNT on any substrate
  - \- nanotubes weaker, often uncapped
  - \- Faulty graphitization, often at the tips

As a result people usually prefer either arc discharge or chemical vapor deposition which is much more versatile, and these I have included just to give you an idea about what this arc discharge, you have the two graphite rods. And this is actually kept in vacuum in helium atmosphere, then you get the discharge and trap the carbon suite or we can actually shine the laser to graphite rod.

And then we can trap the suit in a water cooled copper collector or we can actually take a silicon, silicon dioxide wafer, and try to put some nickel film on that, and then run it through hydrocarbon. And the when this is heated, then this would actually decompose the hydrocarbon to carbon nanotube on the nickel metal.

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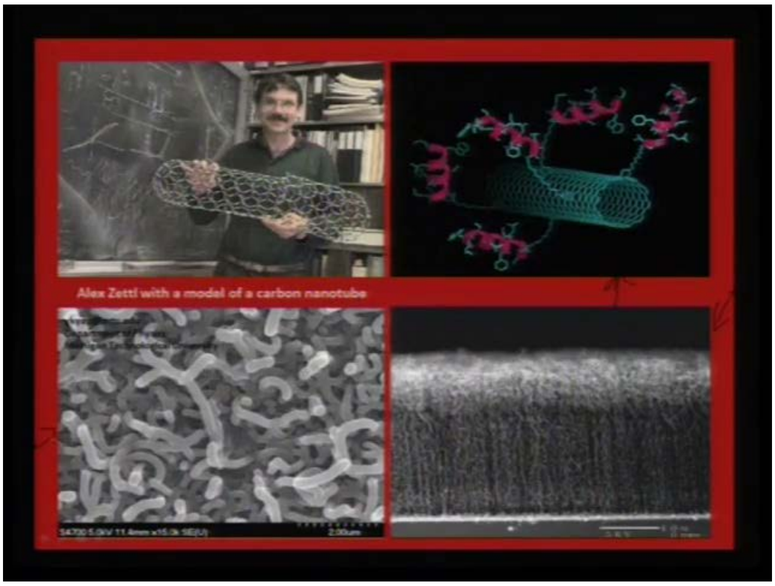

Alex Zettl with a model of a carbon nanotube

So, these are various ways of getting this single wall carbon nanotubes or multi wall carbon nanotubes, his one I have specially included just to show, how people have become obsessed with the carbon nanotubes. As, you can see for those who are really working on this it can become a obsession like a doll, and this person here is actually holding such a three dimensional model.

So, we can see how it can becomes, so close to your heart when you try to work on carbon nanotubes you can see the simulation pictures, which show how this carbon nanotubes can be tagged to something. And this is a another view graph, which shows about carbon nanotube forest look at the way latterly they are grown bundles of carbon nanotubes can be formed, and these are called as carbon nano worms.

You know, so the, so much of chemistry, which is rich and several groups are actually working into a probing the interesting aspects of carbon nanotube. So, I will stop here, and try to deal with this in the next lecture, especially on the chemical properties of graphene and also one single wall carbon nanotubes.