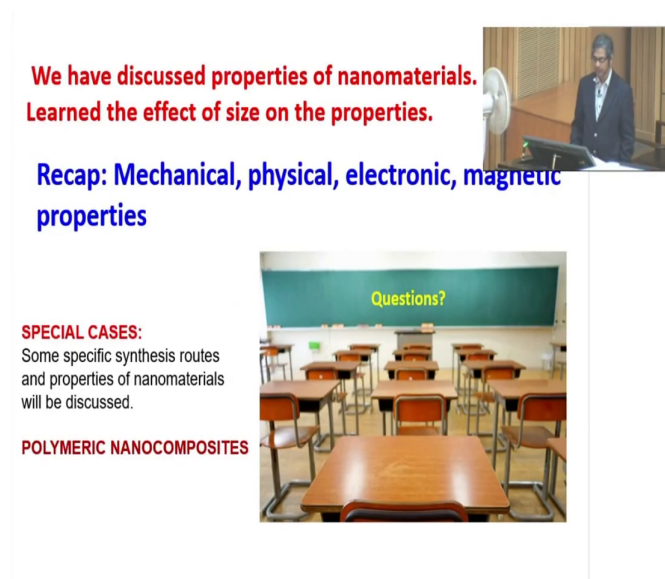


Nanomaterials and their Properties
Prof. Krishanu Biswas
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 28
Special Cases: Carbon-Based Nanomaterials

Today we are going to talk about something new and this is lecture number 28. So, far we have discussed lots of things about nanomaterials, their properties, correlation between structure, size with the properties and you know we are at the fag end of this course. So, what we should do now is to rather discuss with you some specific special cases and next two lectures I am going to do that. So, before that let me just tell you few things.

(Refer Slide Time: 00:57)



We have discussed properties of nanomaterials.
Learned the effect of size on the properties.

Recap: Mechanical, physical, electronic, magnetic properties

SPECIAL CASES:
Some specific synthesis routes and properties of nanomaterials will be discussed.

POLYMERIC NANOCOMPOSITES

Questions?

So, we have discussed a lot on the properties of nano materials. We discussed about mechanical properties, physical, electronics, electrical, magnetic, optical properties. You must be thinking what about acoustic properties. Well, you know materials do interact with radiations, we have seen in our discussions.

Now, you know this interaction depends on the wavelength of the material, which should be comparable with the internal structure or dimensions. Therefore, in case of nanomaterials for which the characteristic, structural or even dimensional length scale is in nanometers that is

between 1 to 100 nanometers. So, hence the wide range of electromagnetic radiations will interact with the nanomaterials like UV, visible lights, X-rays everything.

On the other hand, if you look at acoustic waves their wavelengths are much higher right. The wavelengths varies from microns to kilometers. So, it is expected that acoustic waves will not interact much with the nanomaterials and but what is surprising is that we have discussed about uses of ultrasonic waves for the preparation of nanomaterials. What does it mean? We have shown you that sono-chemical routes can be used effectively to produce different kind of nanomaterials.

In addition, this is done show by using certain kind of devices like ultrasonic devices, which will produce ultrasonic waves inside the solution. And during this process because of the interaction of the ultrasonic waves with the solution we will have small cavities produced. These cavities are basically produced because of collapse of the bubbles and in these cavities you can then prepare or synthesise nanomaterials.

So, other than that there is not much interactions of the acoustic waves with the nanomaterials. So, hence we have not discussed much we are not going to discuss much about the interaction of the acoustic waves with the nanomaterials or rather on the acoustic properties. So, what and then we should do in the next couple of lecture is as follows. We are going to show some specific synthesis routes and the properties of nanomaterials.

And I am going to take here the examples of carbon-based nanomaterials at the beginning. Carbon-based nanomaterial means I will talk about carbon nanotubes, I will talk about graphenes, and even I will talk about some other 2D materials in this lecture. So, if I have to recap the whole thing, so, we have seen that the properties of nanomaterials are affected very strongly by the size and dimension of the nanomaterial.

In the case of mechanical property, you have seen the grain size of the material do affect the elastic strength or the plastic strength or even the dislocation activities, and especially we have seen the yield strength of the material scales $1/\sqrt{d}$ Where d is the grain diameter of a nanomaterial and this is known as a classical Hall-Petch equation, but it is evident this equation also breaks down at grain size below certain value for a specific material.

And that is mainly because this particular equation is based on the concept that the strengthening due to grain boundaries is basically because of the pileup of dislocations in the grain. So, when the grain size become very small this pile up of dislocations of the defects inside the grain is no longer possible because in order to pile up the dislocations you need to maintain a minimum distance between the two dislocations.

So, hence if I have a very small grain size then it is no longer possible to do that and therefore, instead of hardening effect or instead of strengthening effect by the grain boundaries we observe softening effect. On the other hand, that means we also see below a certain grain size the yield strength decreases instead of going keep on going increasing.

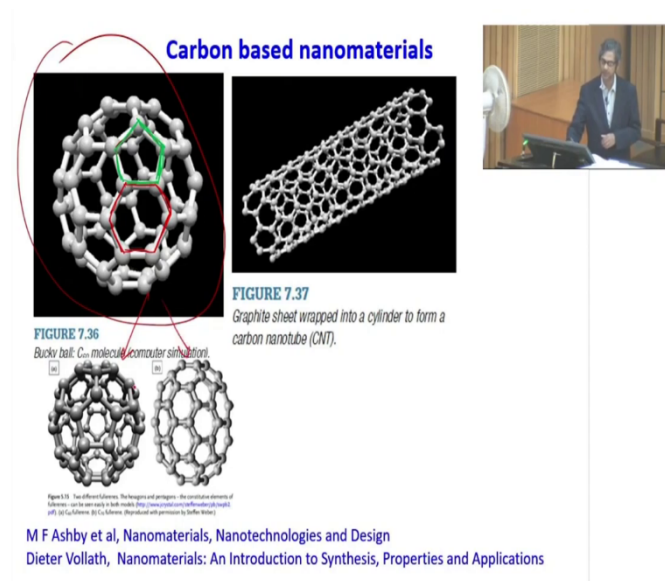
This is a very very typical feature, which has been observed in varieties of materials metallic ceramics, and we have discussed about it. Then we have discussed about lot of things about electronic properties, how electronic structure can get modified because of the size and dimensionality. We can have band structure getting modified ok, where this will affect significantly the electronic properties, thermal properties ok.

We have discussed lot about thermal property thermal transport right. Banded properties are affected strongly by the size because the magnetic domains or domain walls they are significantly affected by these. We have seen the super paramagnetic effect below a certain size and finally, we do discussed a lot about the optical properties right.

And we have shown you very different new kinds of defects in the sense of optical properties. What is the defect we discussed about it, do you remember that? Do not remember. So, the effects which we discussed about this is the, what is the name of the defect, can you remember it or you do not remember it? Well, let me tell you what the defect is. So, defect is known, as it is lowness.

So, sometimes also instructor needs to look at the book ok and this is what is important, the presence of both the hole and the electrons together ok and this is something exciting, yes. We have discussed about excitement for the optical properties. The excitement their nature how they are affected we have discussed a lot about it. So, that is the recap. Now we are going to discuss something new right.

(Refer Slide Time: 07:24)



Well, not something new, I have already discussed a part of it in some of the lectures. You know carbon based nano materials have become very important of flat and their very recent discoveries maybe 20 to 30 years, yes 30 years is maximum. So, as you if you, this whole thing is taken from the book of Michael Ashby et.al's as well also by Dieter Vollath.

I acknowledge these pictures, which I have used from them. Now, if you look at carefully these structures, what I am showing you is basically a buckyball or C_{60} molecules and a graphene right. So, carbon nanotubes they are discovered in 1991 by Sumio Iijima, you know in Japan. In addition, he was looking at the shoot from the electrical discharge between two carbon electrodes under transmission electron microscope.

That is why he discovered and discovery is obviously, serendipity or accidental. But you know before him studying before him there are lot of people who studied this about this material mostly Harold Kroto and Richard Smalley during 1970s. Kroto and Smalley found that under the right experimental conditions, what you can have is basically carbon atoms can basically self assemble and this self assembly into a molecule of specific shape such as C_{60} which is shown here.

You can see the C_{60} molecule here, this is the one right. So, what do you see here? The C carbon atoms have self assemble under certain condition experimental conditions ok when

experiments are done. And you can see there are two types of element, one is hexagonal element here which is very routine in case of benzene rings and also you see some element like pentagonal. Can you see that?

So, let me just put a different color to make you believe that that is a pentagon; 1, 2, 3, 4 and 5 and hexagon anyway I have already done that ok. What is that? This is the one, which is hexagon. So, a combinations of hexagons and pentagons can together be used to self assemble carbon atoms just like a ball and this is what is call a buckyball ok. This name comes from you know structure in Great Britain.

So, therefore, however, Iijima has shown that under different experimental conditions this can produce this ball can open and then could produce a tubular structure and that is what is known as the basically this produces cylindrical structure. So, now as you know the buckyballs can have different kinds of shapes as what is shown here.

This is this one and you can also have a completely sorry this is yeah this is this no this is this one actually, yes. Let me just and then the new one in which you can see that other combinations are present

(Refer Slide Time: 10:59)

Carbon based nanomaterials

Fullerenes

Figure 5.14: Five hexagons surrounding a pentagon. Closing the gaps between the hexagons leads to a three-dimensional structure -- the basic element of fullerenes.

Figure 5.15: Two different fullerenes. The hexagons and pentagons -- the constitutive elements of fullerenes -- can be seen easily in both models (<http://www.crystal.com/staff/wuwei/jh/zwq02.pdf>). (a) C₆₀ fullerene, (b) C₇₀ fullerene. (Reproduced with permission by Stefan Wörner)

M F Ashby et al, Nanomaterials, Nanotechnologies and Design
Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

So, now, the question is in these structures the basic unit which is present is the graphene it is the graphite state. So, before I come into that picture let me just take a few moments. Suppose

if I take a hexagon sorry if I take a pentagon and if I want to arrange you know hexagons around it around each of the sides of the pentagon you will see I will leave behind certain free spaces like this.

So, structural arrangement will not be possible. You know this will lead to some kind of a voids or something. So, therefore, you need a combination of hexagon and pentagons to have this kind of structures. So, there are you can see here I am showing you two different kinds of fullerenes ok.

One with hexagons other one is pentagons ok right. This is completely with hexagon, you can see that 1, 2, 3, 4, 5, 6; 1, 2, 3, 4, 5, 6 right this is what it is and this one has been two combinations of hexagon and pentagons. So, now, as you can see and you know this is easily available in this website crystal dot com and you know steffenweber website and this is C_{60} , this is C_{70} .

So, 70 carbon molecules are arranged if you produce such a kind of things. This as your football. So, the closing gap between this hexagon lead to three dimensional structure which is the basic thing about the fullerenes this closing gaps. So, what do you understand from this picture?

From this picture you clearly understand that under certain experimental conditions we can allow the carbon atom to self assemble and produce such kind of nice structures. And this was the discovery done long back by Harold Kroto and Smalley. They proposed this model and discover it.

(Refer Slide Time: 12:50)



Carbon based nanomaterials

MWCNT

SWCNT

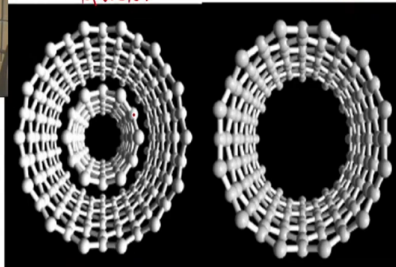


Table 7.2 Advantages and Disadvantages of Widely Used Techniques to Synthesize CNTs

Method	Type of Nanotubes	Diameter	Length	Advantages	Disadvantages
Laser vaporization	SWNT	1-2 nm	—	Few defects, good size control	Very expensive
Arc discharge	SWNT/MWNT	0.6-1.4 nm/10 nm	Short	Easy to produce, few defects	Random sizes, short length
CVD	SWNT/MWNT	0.6-4 nm/10-240 nm	Long	Easy to produce	Usually MWNT, defects

M F Ashby et al, *Nanomaterials, Nanotechnologies and Design*

Dieter Vollath, *Nanomaterials: An Introduction to Synthesis, Properties and Applications*

Now, as far as the carbon nanotubes are concerned because all of you must have heard about carbon nanotubes very widely known material and they are nanotubes; that means, they are nanoscale. So, in a nanotube as I have discussed in many previous lectures the length of a nano tube is pretty long. It maybe a micron or maybe millimeter size long but the diameter is basically in nanometric domain.

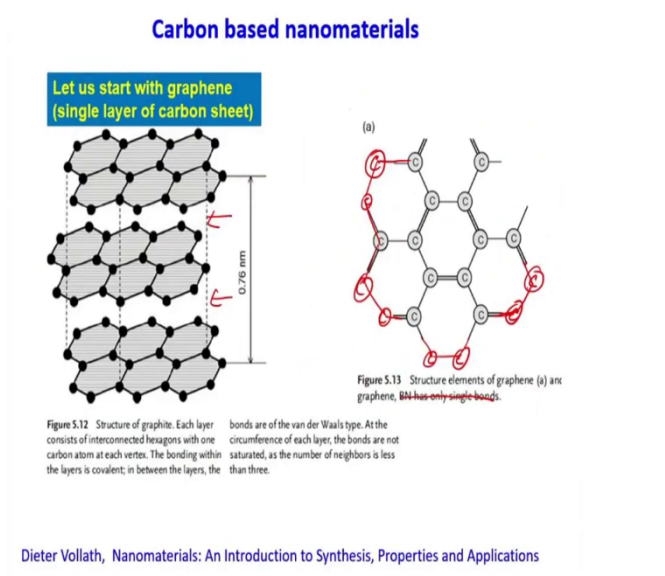
They are the nano dimensional in all the three x, y, z directions rather they are nano-dimensional along x and y directions not in the z directions ok. So, if you carefully look at this picture which is taken from Michael Ashby's book, you see this is the picture of a single walled carbon nanotubes and multi walled carbon atoms. So, this one is single walled carbon nanotube is single walled CNT and this is multi walled CNT. What do you see here?

Very clearly, you see that CNTs are parallel arrangements of these cylinders right. In case of multi walls, they are parallel element of cylinders. So, you must be thinking how one cylinder is put inside of the cylinder. Well you may have done some experiments in your childhood while you can put one cylinder into another one. There are forces exist in case of such a kind of species between them.

So, these are produced by laser vaporizations or arc discharge or CVD which we will discuss little later and you know diameters of the order of 1 to 2 nanometers lengths can very long short and it can have defects inside it. And you know most of the disadvantage is that single

nanotubes are very expensive ok because production is expensive. So, multiple nanotubes are more widely used.

(Refer Slide Time: 14:41)



Well to begin with as I said all these structures they are relying on the single layer of graphite. So, as you know graphite is a material in the carbon family with a lowest free energy. We have carbon, graphite, diamond and you know amorphous carbon and in fact, we have now CNTs, graphene, buckyballs. Out of all this material graphite has the lowest free energy and that is why it is, more you know widely available in the Mother Nature.

So, graphite structure well you know is a layered structure. Basically it has hexagonal closed packed structure these are layers. As you see each layer, the carbon atoms are arranged in a nice manner hexagonal manner and between the layers; there is Van der Waal forces. So, what one can do is simply one can take a device one can take a knife rather and blade to chop off these layers by cutting off this Van der Waal bonds here or there.

And once you cut off then you can produce the second structure right. Although this is shown you know like a graphene this is the one I have not shown you can see that the carbon atoms are coming like this and they are arranged in a very nicely. So, 1, 2, 3, 4, 5, 6 right, filling with C, I am completing it for your purpose. Similarly, 1, 2, 3, 4; so, 1, 2, 3, 4, 5; 1, 2, 3, 4, 6.

So, you can easily generate this way right, 1, 2, 3, 1, 2, 3, 4, 5, 6; right 1, 2, 3, 1, 2, 3, 4, 5, 6. Am I right? So, I can generate this network. So, this is the basic unit of the graphene single layer. So, now, if you go back to the earlier slides this one especially. So, if you carefully look at this, this is this tube is nothing but a graphene layer wrapped around a cylinder wrapped into a cylinder.

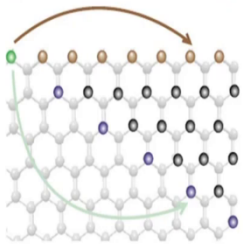
So, if I take a singular graphene and wrapped or you know bent it and wrap around I form a cylinder right. So, and then if you close the ends you will be able to form buckyballs carefully not like that because the units here hexagonal units and pentagon units both are present in the nanotubes. So, what do you understand? Although graphene does not have any pentagonal units these structures lead to formation of pentagonal units that is what you clearly, assume.

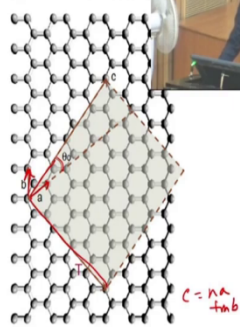
Now, CNTs are cylindrical molecules with diameter, which can vary from 1 nanometer to few nanometers, and lengths can be up to few micrometers and their structures is consisting of graphitic shape around the cylinder. Depending on the processing condition, CNT can be single wall or multi walls and in particular, CNT classified as classified by the chiral vectors ok. What is that?

(Refer Slide Time: 18:20)

Carbon based nanomaterials

Let us start with graphene
(single layer of carbon sheet)





$C = na + mb$




FIGURE 7.39
Graphene sheet rolled into a cylinder described by unit vectors a and b , chiral angle θ , chiral vector C , and translation vector T . The figure represents a (4,2) nanotube, where the shaded area is one unit cell. (Adapted from Barry J. Cox and James Hill)

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

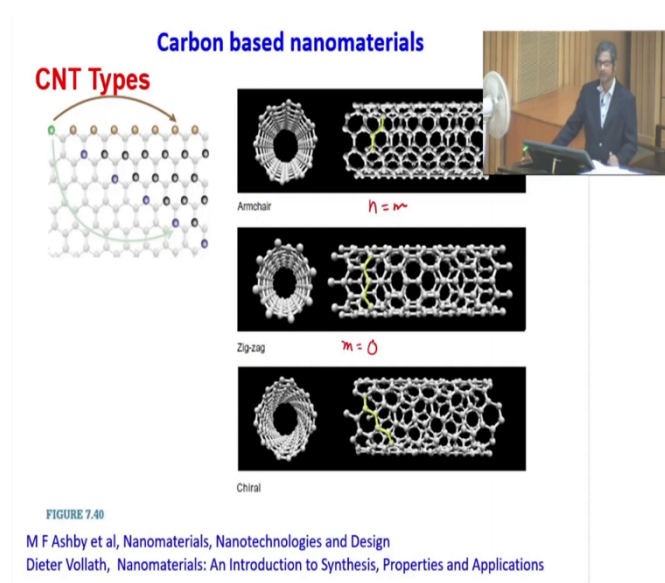
So, this is a typical structure of a graphite layer and we go to this one how this graphite layers are. Things you can see that I can always generate two vectors, one this one other one is this one right. So, now, so, unit vectors a and b and the chiral angle θ unit vector a and b this is a , this is b ok and this is the chiral angle θ you can see here $\theta = 0$ here written ok and so, and this is the.

So, now the how I am going to you know take this vector T and wrap around that will dictate what type of carbon nanotubes produce. So, we can always take C sorry we can always write down $C = n_a a + n_b b$, C is a vector right or $(n_a + n_b)$ is better; they may not have the same values, where a and b is the unit vectors and m and n are the chiral vector numbers, the characteristic orientation of hexagonal in a corresponding graphene sheets ok.

You can clearly see that is where the characteristic and correlation of the graphene thinks ok. So, now in this configuration the value of the chiral vector C is the circumference of the nano tube and the direction relative to the unit vector a is this chiral angle θ . C is at an angle θ with respect to the unit vector a .

The translational vector T is telling us the nano tube length, which is thus perpendicular to the C . So, this parameters describe the way in which the graphene sheets can be rolled up to form this nanotube structure in a regard three types of nanotubes can be produced.

(Refer Slide Time: 20:29)



One is armchair, zigzag and the chiral right. Three types of nanotubes can be produced. So, depending on how you are going to do that zigzag forms when m is equal to 0. What is m ? This is the m . So, that means zigzag forms when b vector has no importance. It is not use only a is used right and so, armchair machine is formed when you know n is equal to m .

So, armchair is forming when $n=m$ and zigzag forms when $m=0$. This always happens and chiral is what when you are doing rotating around this at an angle with that. So, this is how we can generate three different types of nanotubes.

(Refer Slide Time: 21:24)

Carbon based nanomaterials: Synthesis

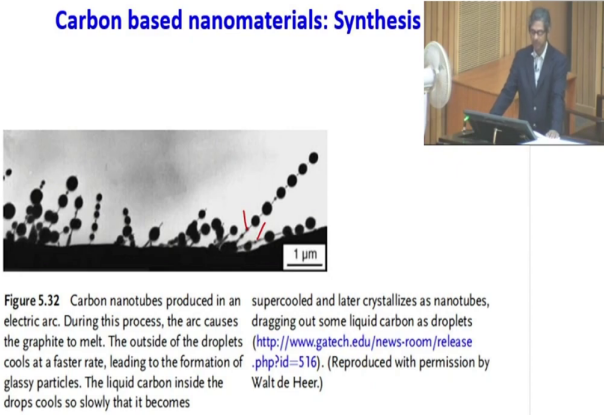


Figure 5.32 Carbon nanotubes produced in an electric arc. During this process, the arc causes the graphite to melt. The outside of the droplets cools at a faster rate, leading to the formation of glassy particles. The liquid carbon inside the drops cools so slowly that it becomes supercooled and later crystallizes as nanotubes, dragging out some liquid carbon as droplets (<http://www.gatech.edu/news-room/release.php?id=516>). (Reproduced with permission by Walt de Heer.)

Dieter Vollath, *Nanomaterials: An Introduction to Synthesis, Properties and Applications*

So, that is very important you know how nanotubes are formed very clearly. The chiral occurs when the chiral vector numbers can be assumed any integer values and the chiral angle is intermediate between 0 and 30. So, what is the meaning of this? The chiral vector numbers that is n and m can be any integers. They need not be 0 they need not be equal to each other, but they can be any integers and the angle will be between 30 and 0. Among these three different types of different types of (Refer Time: 22:00) ok.

Among this basically singular nanotubes there are metals though with n minus m equal to k , k is the integer and these ones are actually semiconductors the small band gap and remainders are semiconductor with the band gap that is inversely proportional to change in diameters. So, as you know CNTs can be prepared many ways. Base to prepare CNT is basically arc

discharge method. So, in this method, this is taken for Dieter Vollath's book. In this method arc actually causes the graphite to melt.

So, you can have two graphitic graphite's and then produce arc between them and this arc will cause the graphite to melt. Outside the droplets whatever melt droplets form they cool very fast rate and this can lead to glassy particles. Liquid inside this droplets can cool slowly and it can become super cooled and later on can crystallize as nanotubes dragging out some liquid droplets, liquids carbon as a droplets.

So, carbon nanotubes produced basically by this arc discharge method. You can also produce by as I discussed in the some slide back by you know laser vaporization also. Again, laser is used as a high energy source to melt and when you melt some of the droplets will be under cooled heavily and that is why they can produce nanotubes. You can also produce by some other routes like what? Like this ok.

(Refer Slide Time: 23:30)

Carbon based nanomaterials

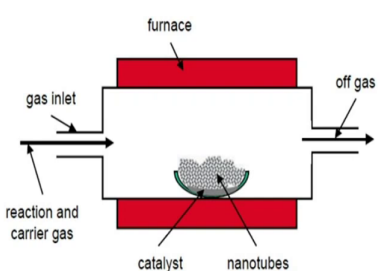


Figure 5.33 Synthesis of carbon nanotubes in a tubular furnace. The essential points in this process are the selection of an appropriate catalyst and a well-suited gaseous precursor.

Dieter Vollath, *Nanomaterials: An Introduction to Synthesis, Properties and Applications*

This is the things which we will discuss a little bit more details and you know this is something which is widely used in the literature or in the experiments. What is that? How this is produced ok? So, synthesis this is basically produced in a tubular furnace. You know the way this is done is as follows correct. If you in electric direct current or in the surface of the electrodes carbon is as we said known to melt.

Sufficiently temperature will drop; liquid carbon becomes super cooled and begins to crystallize. Crystallization nano tube grows through the liquid layer at the cathode that is what is shown in this case. The nanotubes will go. You can see that this droplets they have joined and these are actually tubes ok which has formed because of the under cold liquid droplets. Yield of the nanotube significantly can be improved by metallic catalyst to the carbon electrodes.

However, in order to obtain large amounts of nanotubes more processes that are sophisticated has to be used and most common one is a tubular furnace, which has shown in this picture. And it is heated up to 1300 degree kelvin that is approximately about 1000 degree Celsius at which carbon nanotubes are obtained at the presence of catalyst. Arc discharge leads to very small production of the carbon nanotube that is why this method has come.

For carbon nanotubes, mixture of methane gas and hydrogen is basically allowed to entered into this furnace and which is basically diluted can be diluted by argon. As a catalyst you can use iron, nickel or even alloy of that and this catalyst you know are basically used to start the formation of the nanotubes inside this furnace. So, you have to maintain a critical temperature in the furnace which is about 1300 kelvin and you have to use some metallic catalyst ok that is how this conforms. So, how this is done?

(Refer Slide Time: 25:49)

Carbon based nanomaterials


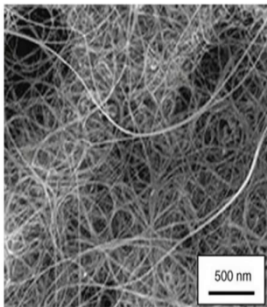
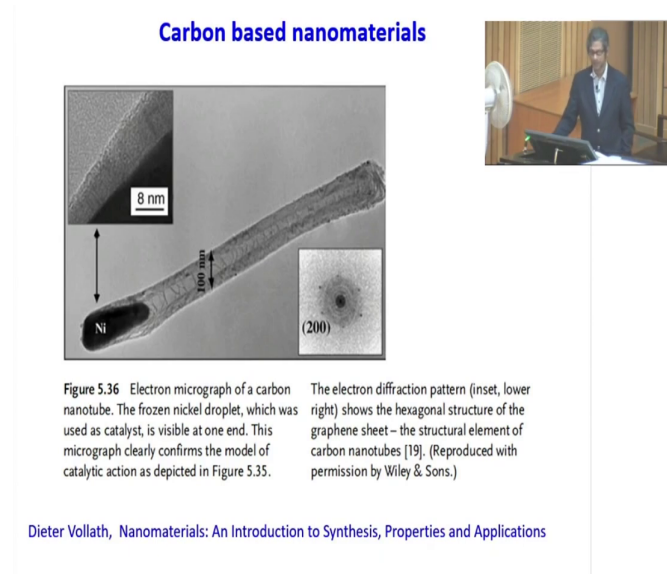


Figure 5.34 Carbon nanotubes made in a tubular furnace as shown in Figure 5.33. Methane was used as the carbon precursor and iron as catalyst. The reaction temperature was approximately 1300K. (Reproduced with permission by Hampel and Leonhardt, IFW Dresden, unpublished results).

Dieter Vollath, [Nanomaterials: An Introduction to Synthesis, Properties and Applications](#)

So, these are the you know nanotubes produced in the tubular furnace you can see. Here methane was used as a carbon precursor. This is taken from the permission with you know Hampel and Leonhardt which are basically available in this book of Dieter Vollath and I acknowledge their contribution. And here iron was used as a catalyst and temperature was used taken 1300 K.

(Refer Slide Time: 26:14)



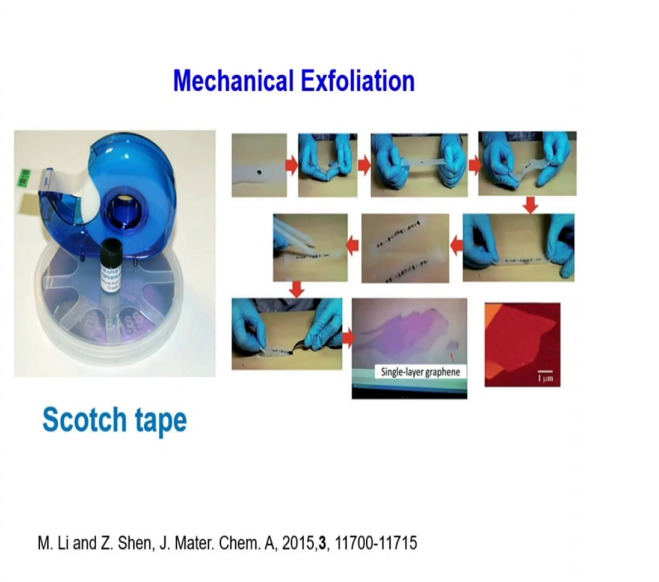
So, let us look at little bit about details of that how this catalyst can help growth of the nanotubes ok. A typical product comprises is basically ball of pool as you have seen in this last picture ok and this is a typical example of carbon nanotubes products inside from the methane.

So, instead of using randomly placed catalyst particle it is possible to prepare in a clear cut patterns of the catalyst particles either by printing or vapor depositions. Therefore, this catalyst basically you know start absorbing carbon and the carbon is it will basically get dissolved inside the metal because most of the metal has you know ability to dissolve carbon.

When more amount of carbon is dissolved in the metallic catalyst then this, they started coming out as carbon nanotubes that is what has been observed in most of the cases. So, this is one such picture. You can see the frozen nickel droplets, which was used as a catalyst and seen at the end of the carbon nanotubes.

The electron diffraction pattern also shows the hexagonal structure of the you know graphene sheet which is very clear. So, these catalyst can you know allow us to produce large quantity of the these kind of nanotubes that is what is the major way means to produce the nanotubes.

(Refer Slide Time: 27:42)

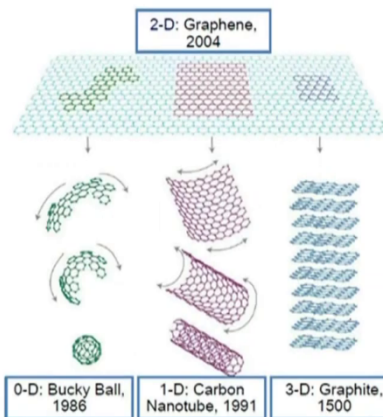


So, let us now discuss a bit about the graphene production routes then we will talk about applications. So, graphene you know is a more you know much recent discovery. It was you know discovered by Novoselov and Geim in UK and then awarded Nobel Prize in 2004. So, the first thing which is widely used is basically known as a Scotch tape technique. This is nothing but mechanical exfoliations.

So, now, before I discuss about this exfoliation techniques, let me go back to the structure of the graphite. As I said, you know we can always use a blade or a knife to cut off these intermediate bonds and produce this single layer of carbon right. This is a dream for the human for a long time, but it was only realized once you know in the beginning of the century something around 2002 or 2003 this was realized.

(Refer Slide Time: 28:45)

Carbon based nanomaterials



Geim, K., Novoselov, K.S.: The rise of graphene. *Nat. Mater.* **6**(3), 183–191 (2007)

So, how is it possible? You know it is easily possible to create all kinds of structures by using graphene sheet as we have discussed. So, graphene is the basic thing as you can clearly see how by rolling of graphene sheet kind of 0 dimension buckyballs or 1 dimensional nano tubes or even stack of these layers can lead to 3 dimensional graphite ok.

So, buckyballs were discovered in 1986, nanotubes were discovered in 1991 and graphite was discovered long back in 1500 therefore it is nature level material and this is the paper by Geim and Novoselov in nature materials, which is widely respected. So, now, the question is this, how we produce that.

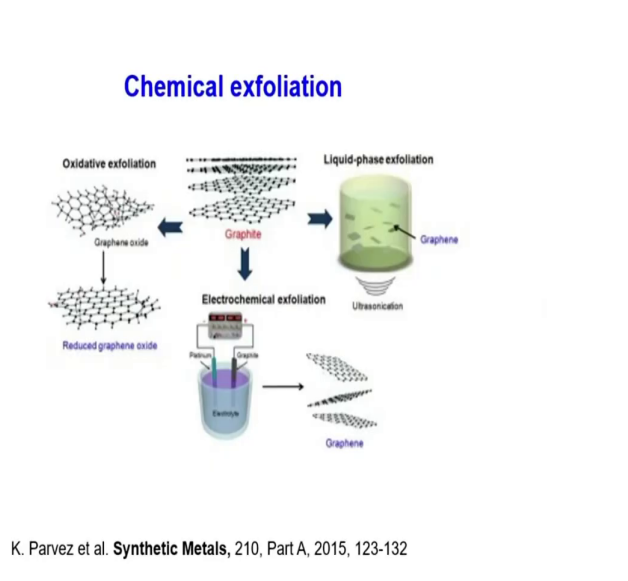
So, this is it you know this picture is taken from the paper by Li and Shen, *Journal of Material Chemistry*. As you can see here the what is done is very simple. You take a double sided tape and then you put this graphite within the tape just basically put the graphite and then close the double sided tape then slowly peel off this step. If you peel off you will basically produce different you know material on the Scotch tape itself.

And then if you look if you use you know use a knife or something to scrub the material which is basically attached to this tape what you will see is there are this layers of graphite presents, but only when you look at very closely that is what is done by Geim and Novoselov you will find they are actually thin layers of grapheme.

Now, how do you confirm that? You can easily confirm by using an optical microscope that is what I always tell to young students that doing experimentations of this order does not require you to use very costly equipments. So, you can take these thin layers which is there on the this Scotch tape and put it on a glass slide. And then you just put it on a optical microscope ok.

And then if you see that these layers are transmitting most of the light then you are 100 percent sure the single layer of graphene because if a single layer of graphene it will not absorb any light. Only when its stacks layers are present like I graphite it becomes opaque to light. So, that is how it is discovered. So, this is known as a mechanical exfoliation, now we can also use technique like chemical exfoliation. What is that?

(Refer Slide Time: 31:16)



Well, most easiest one which you may have heard is the Hummer's or modified Hummer's methods. This particular picture is taken from Pervez et al. So, you have to understand I am using different literature which is available in the internet because these things are not available in a book form or even if it is available the scattered information is available.

So, that is why I have to use such a kind of literature. I acknowledge this literature for use for this kind of lectures. So, what is done here? You can take a graphite and then you can basically put a graphite in a mixture of hydrochloric and nitric acid, it will be boiled in that

acidic momentum. So, if it boils then graphite will exfoliate that means, the layers of graphite will open up, but the same time it will get oxidized.

So, once it get oxidized you have to you will get graphitic oxides or what is known as a (GO) popularly. Then you can use some reducing agents to reduce graphitic oxide or what is called (RGO) that is basically not exactly graphene, but maybe several layers of graphite are present. You can also do this is the simple one which is used what is known as oxidative exfoliations which is easy to do in lab and experiments.

Second one what you can do is you can do an electrochemical exfoliations, where you can use electrochemical cell. You can use a platinum and graphitic electrodes and a electrolyte and then you can apply huge current to it. Therefore, what will happen is because of application of current and you know here from the graphite the things will be removed atom by atom or layer by layer and get deposit on the platinum electrode ok. It is used as a cathode and graphite is used as anode.

So, graphitic material will get removed from that and then deposit on the layers of the platinum. So, then if you scratch on the platinum what you can get is a graphene layer ok or what you can do is you can use liquid phase exfoliations. What is that? This has also been discovered sometime back, you can use a grinder mixture what is we used in the kitchen; kitchen blenders or kitchen grinder mixtures can be used.

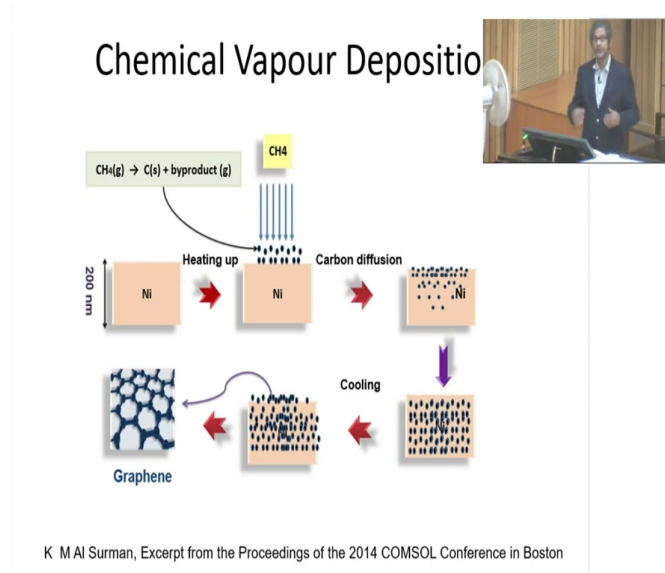
In kitchen blender kitchen grinder mixture we can have liquids certain kind of liquids and you can prove this graphite in that. These liquids are used to reduce the surface energy the interfacial bonds energies between the layers of the graphite. Then you can use shear flow.

So, once you have a liquid and if you use you know in a jar of mixing mixer jar or basically then you have to I mean blades will move at a very high speed and because of that a turbulent flow is created and this flow then can allow this layer to be removed one by one. I can produce graphene.

In fact, this is the technique in which you can produce large quantity graphene and this is now widely used to prepare large quantity graphene. In fact, it is available in the market also you can buy that. Therefore, this is how the chemical exfoliation techniques works. So, compared

to physical exfoliation technique chemical exfoliation technique is more versatile and it can lead to large scale production of the graphene also which is very important for any applications.

(Refer Slide Time: 34:37)

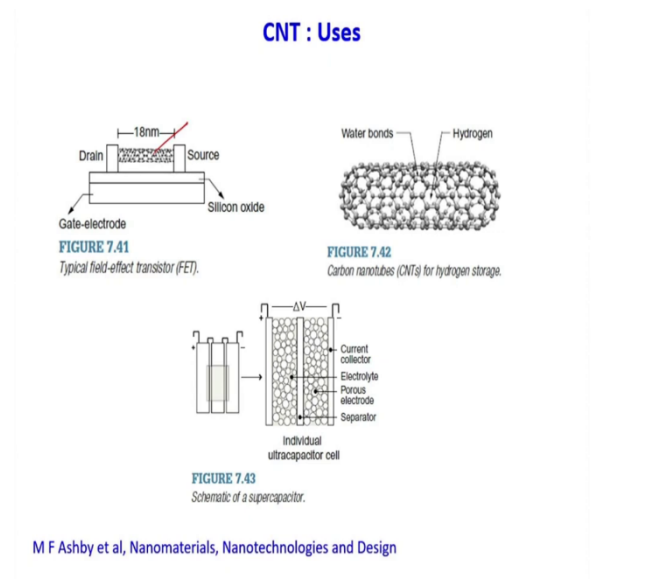


Now, the last technique which is I will talk about the deposition is the chemical vapour deposition or it is known as CVD. CVD is you know it is basically a thin film deposition technique. So, here also we can use catalyst like nickel. So, what is done is basically take a nickel plate, heat it up to certain temperatures and then you know you can use mixture of basically you can use methane gas.

And once the methane gas is dissociated at high temperature and it will produce carbon and byproduct is as a gas which is mostly basically moisture. And this carbon then can deposit its dissolve inside the nickel and then once nickel will be super saturated again nanotubes only form on the surface of the nickel.

So, sorry graphene will form on the surface of the nickel. This is taken from K. M Al Surman is basically there is a conference in 2014 in COMSOL and this particular picture was depicted there. So that means we can produce graphene by physical exfoliation, chemical exfoliation or by physical vapour chemical vapour depositions.

(Refer Slide Time: 35:44)



So, now, we will talk about in the next 5-6 minutes or so, we will talk about how we can use CNTs and graphene. So, this is for the CNTs. CNTs can be used for typical field effect transistors or you can use for hydrogen gas storage or you can use you must have heard about that you can use a super capacitors ok. So, let us talk a little bit about it.

Field effect transistor is basically type of transistor used for weak signal amplifications and you know they are currently made from silicon. Silicon is widely used material that is why this is it. However, these devices are still a few 100 nanometer in size. The use of CNT is with size less than 1 nanometers in diameter would allow you know more of these switches to be part of this chip. So, in FET the current flows to the CNT, ok.

You are putting you can see this is CNT layers kept here, current flows to the CNT with the semiconductor pattern properties along the path called channel ok. You can see there is a channel like that. One side of the channel is a gold electrode called source other side there is a drain ok right. So, with a small voltage to apply to the silicon substrate which can act as a gate in FET, the conductivity of CNT can change by more than million times.

So, it can then allow us to amplify the signal which is very common. Another application of CNT is the in the fuel cells or batteries ok both in case of storage of purposes. So, in case of fuel cell CNTs can have can be used as a storage of hydrogen, particularly for the automotive

applications ok. And you know this is it can basically take about 6.5 weight percent of the hydrogen ratio of hydrogen to hydrogen storage hydrogen to storage material is about 6.5 percentage that is 0.065 which is not bad, but not very good also.

So, hydrogen level can be achieved higher energy can be achieved by gaseous and liquid hydrogen which is hardened can store in the cages of this graphitic network ok. You can also use you know this CNTs for other purposes like as you said super capacitors ok. So, what is that? The super capacitors are basically what? This is because CNTs exhibit its high porosity, large specific area, high electrical conductivity and chemical stability as compared to other materials.

In the conventional capacitor, energy is typically stored by transfer of electrons from one metal electrode to another metal electrode separated by electronically insulated material. The capacitance will depends the separation distance between these and the dielectric constants between of these electrodes. In case of super capacitor there is instead of electrical double layer.

Say, you can see that there is an electrical double layer created between these two things and each layer contains highly porous electrodes supported by an electrode. In addition, applied potential on the positive electrodes attracts a negative ion, so, the in the electrolyte wherein potential on the negative electrode attracts the positive ions. The dielectric material between these two electrodes, prevent the charges from crossing between the two electrodes.

If the electrodes are made of CNTs, effective charge separation is about few nanometers compared to separations of the order of micrometers in ordinary capacitors. Therefore, hence they are called super capacitors. You can also use this you know for other purposes like flat panel display or you can use in fact, CNTs as emitters.

(Refer Slide Time: 39:34)

CNT : Uses

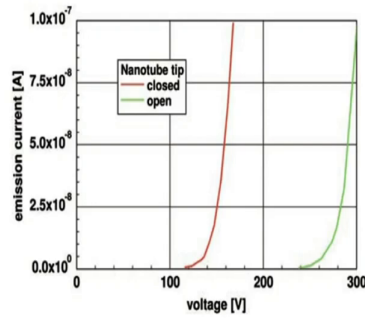


Figure 5.22 Electron field emission characteristics of carbon nanotubes. Here, the electron emission of closed and open nanotubes is compared [10].

CNTs can use as you know for high value of emitters like in case of electro-microscopes, where you need large electrons can come up. So, you can see if depending on the closed or open loop you can have different amounts of currents. Emission currents produce 10 to the power minus 3 to 10 to the power minus 7. Sorry, 10 to the power minus 10 to the power 8 amperes can be produced depending on that. Electron emission is closed now open nanotubes is open nanotubes are compared.

(Refer Slide Time: 40:10)

CNT : Uses

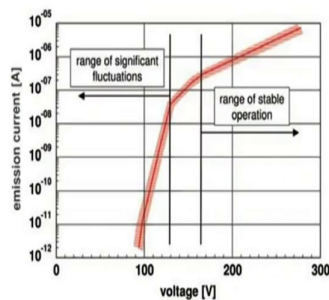
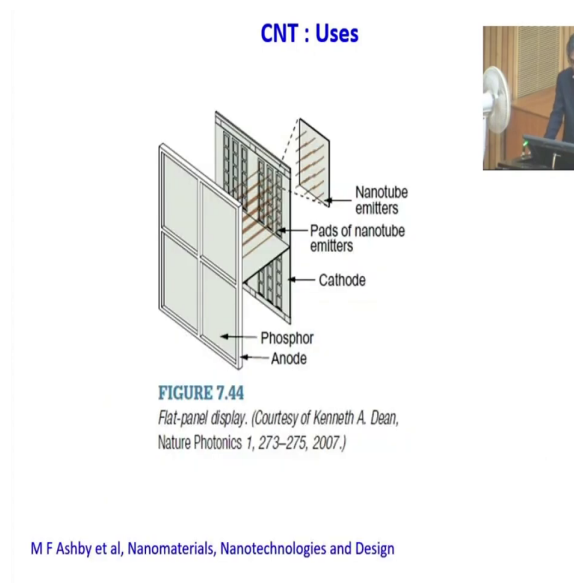


Figure 5.23 Field emission current of carbon nanotubes determined on bundles of carbon nanotubes embedded in a matrix of electrically nonconducting polymer [11]. Within the range of lower voltages, significant fluctuations of more than 50% are observed.

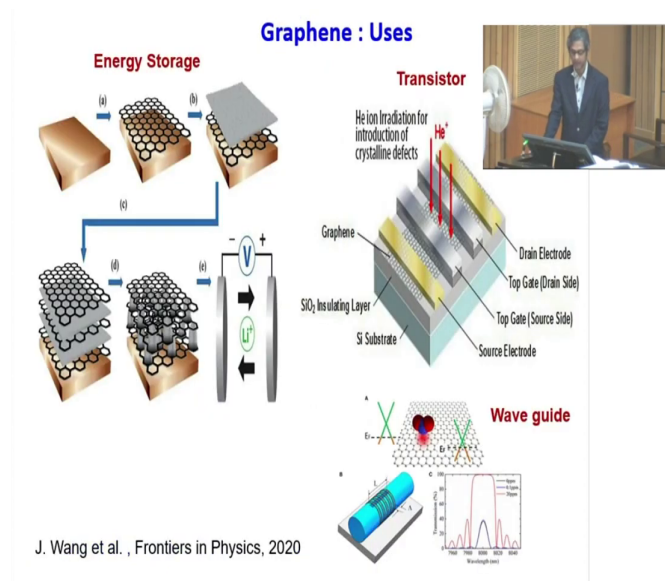
Well field emission current of carbon nanotubes depends on the bundle of nanotubes embedded in a matrix of electrically non-conductive polymers. So, you can see the range of fluctuations are present for certain values of voltage and high value of voltage, this become very stable that is what is the another use of CNTs.

(Refer Slide Time: 40:34)



CNT is also can be used for flat panel display ok. We all know the flat panel TVs or flat panel display now. So, we can use CNTs as on the elements of the flat panel display which is now widely utilized.

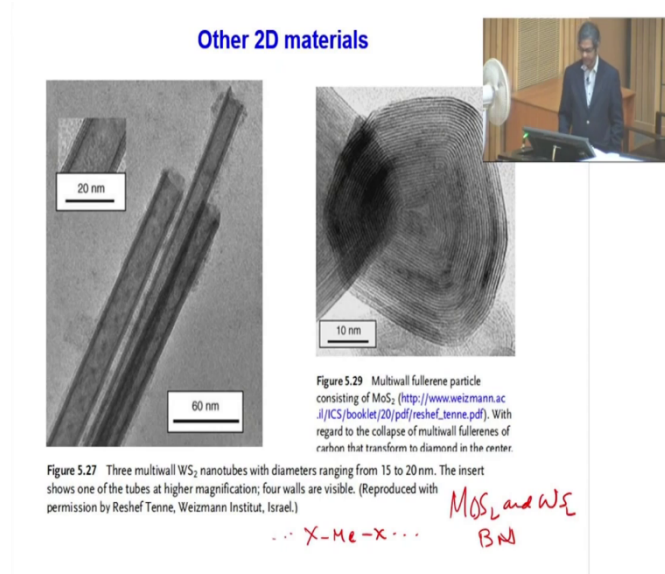
(Refer Slide Time: 40:48)



So, whatever graphenes, graphene can use again for many various applications including energy storage, transistor or even wave-guides ok. And you know this is all taken from the book from the paper by J. Wang et al in Frontier Physics very recently and energy storage is obviously, they can be used for various chemistry like super capacitors also they can be used.

And they can use as a transistor ok in a transistor basically as layer between two electrodes because they have high electrical conductivity. They can also be used as wave-guides because their unique function optical properties because of the localization of the you know optical waves it can be used for wave-guides.

(Refer Slide Time: 41:36)



So, with this let me also talk about some other 2D materials. As you know there are many other 2D materials, which have come recently and they are very famous in fact, as famous as what, graphene or carbon nanotubes ok. So, let us talk a little bit about those also then we can wind up this lecture.

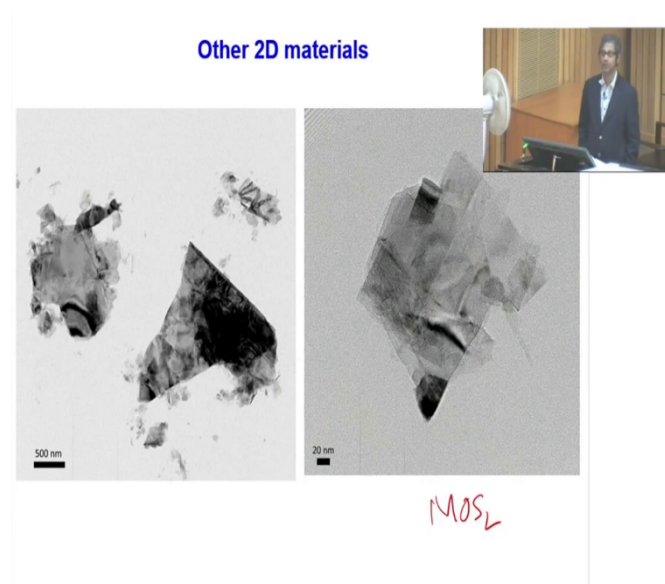
As you know, long back Tenne et al has reported that this is from the UK from the US sorry the all compounds which are crystallized in layer structure can be used to form nanotubes or fullerene like structures. And first nanotube consisting of without any carbon material is MoS_2 and WS_2 , which have typically known as a MoS_2 and WS_2 , but structures are lesser observed with selenides of molybdenum and tungsten also.

You know the important thing is that each layer structure is like this X-Me-X, where X is the sulfur or selenate and M is the M is the metal and this is repeated. So, within each triple package of layers, there is a covalent bonding within there is a covalent bonding then outside this triple package, there is this Van der Waals bonds.

Hence, packets can be shifted against each other and this is the reason why MoS_2 and WS_2 are like graphite and the technical basis technically they are used as a lubricants. Similarly, recently we have also seen boron nitride ok BN boron nitride, for boron nitrides, they have no free electrons.

So, therefore, they are insulators. Therefore, you can produce 2D insulators also ok. So, you can see here multiwall fullerene particles of MoS₂ also can reproduce here many layers of this MoS₂ has been come together self assembled and produced.

(Refer Slide Time: 43:52)



You can also have MoS₂ layers. This is taken from our own work MoS₂ 2D. You can see they are transparent to electrons, very thin they are produced by sonochemical techniques. So, in a nutshell what I discussed today is that about CNTs and graphenes and some other 2D materials their processing routes and some of the applications. I thought this is important for nanomaterials. So, we should know about it.

(Refer Slide Time: 44:24)

Polymer Nanocomposites

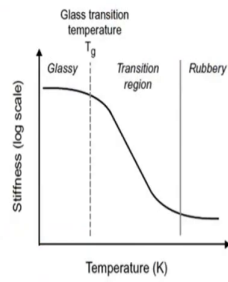


FIGURE 7.45
Various polymer states as a function of temperature.



FIGURE 7.46
Electrical percolation in polymer nanocomposites.

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

The next lecture so in lecture number 29, we are going to talk about polymer nanocomponents. So, that is the lecture number 29 and that should wind up our course.

Thank you.