Surface Engineering of Nanomaterials

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Lecture - 37
Current Trends in Surface Modification of Nanomaterials (Part - 2)

Hi, in this lecture I will introduce you about the current trends in surface modifications of the nanomaterials. This is the part 2. In our last lecture, we have elaborately discussed about the doping, but in this particular lecture, we are trying to discuss about some other methods.

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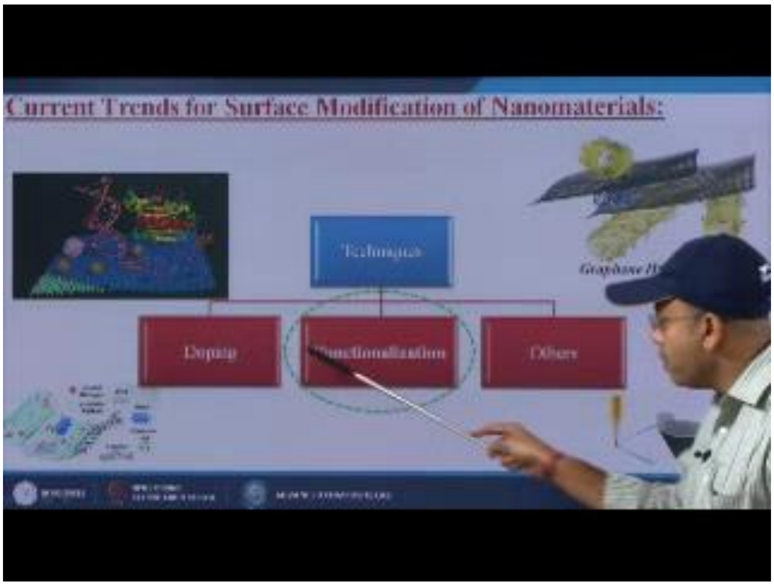

Current Trends for Surface Modification of Nanomaterials:

Technique

Doping

Functionalization

Others

Here if you remember in our last lecture, we have discussed about the doping, but in this particular lecture, we are trying to discuss about the functionalizations. So, functionalization is nothing, but the how we are trying to modify our nanomaterials or maybe that nanoparticles. And next lecture, we are going to discuss some other methods.

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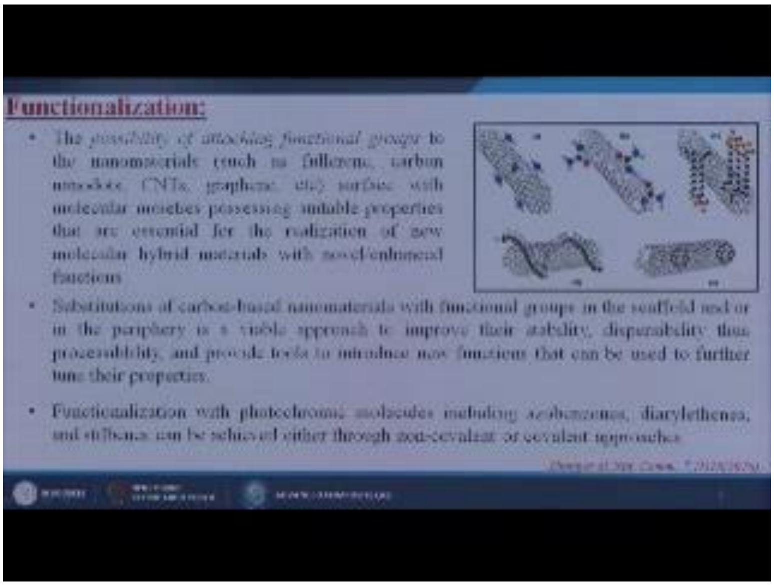

Functionalization:

- The *possibility of attaching functional groups* to the nanomaterials (such as fullerene, carbon nanodots, CNTs, graphene, etc) surface with molecular moieties possessing suitable properties that are essential for the realization of new molecular hybrid materials with novel/enhanced functions
- Substitutions of carbon-based nanomaterials with functional groups in the scaffold and or in the periphery is a viable approach to improve their stability, dispersability thus processability, and provide tools to introduce new functions that can be used to further tune their properties.
- Functionalization with photochromic molecules including azobenzenes, diarylethenes, and stilbenes can be achieved either through non-covalent or covalent approaches

So, first before going to start, first we have to know that what is called the functionalizations. So here the possibility of attaching some functional groups so simple in the doping if you remember, that we are putting or maybe that we are inserting some materials inside our nanoparticles, but in this particular case, for the functionalizations we are not going to insert any materials into our base or maybe that parent materials, just we are attaching some kind of functional groups on surface of that nanomaterials or maybe the surface of the nanoparticles so that we can modify these nanoparticles.

The possibility of attaching the functional groups to the nanomaterials such as fullerene, carbon nanodots, carbon nanotubes, grapheme, surface with molecular moieties, possessing suitable properties that are essential for the realization of new molecular hybrid materials with noble air or maybe the enhanced functions. So, what I am telling that just attaching some kind of functional groups on the side ways of our nanoparticles or maybe the nanofillers, we can enhance some properties.

Here we are trying to show you some examples. So, here this one is the carbon nanotubes. So, we are trying to attach some kind of functionalized group on the surface of these carbon nanotubes either maybe it can wrapped or maybe it can simply stick onto the carbon nanotubes, it can wrap the carbon nanotubes, sometimes it can go inside the carbon nanotubes. So, like this way, we can modify the surface of that particular nanoparticle so that it can show some better properties.

Substitutions of carbon based nanomaterials with functional groups in the scaffold or in the periphery is a viable approach to improve their stability, dispersibility, thus processiblility and provide tools to introduce new functions that can be used to further tune their properties. So, by attaching these functional groups, either we can enhance some existing properties or maybe sometimes we can add some extra properties to that particular material.

Functionalization with photochromic molecules including azobenzenes, diarylethenes and the stilbenes can be achieved either through non-covalent or maybe the covalent approaches. So, when we will come into the details of the functionalizations or maybe how we are going to the functionalizations will see that what are the methods, so actually the 2 methods, one is called the non-covalent and another one is the covalent, by these 2 methods generally we can do the functionalizations of any nanoparticles and these literature has been taken from the nature communications and it has been done or maybe it has been given by the scientist named Zhang. So, he has actually presented this paper; this result in his research paper.

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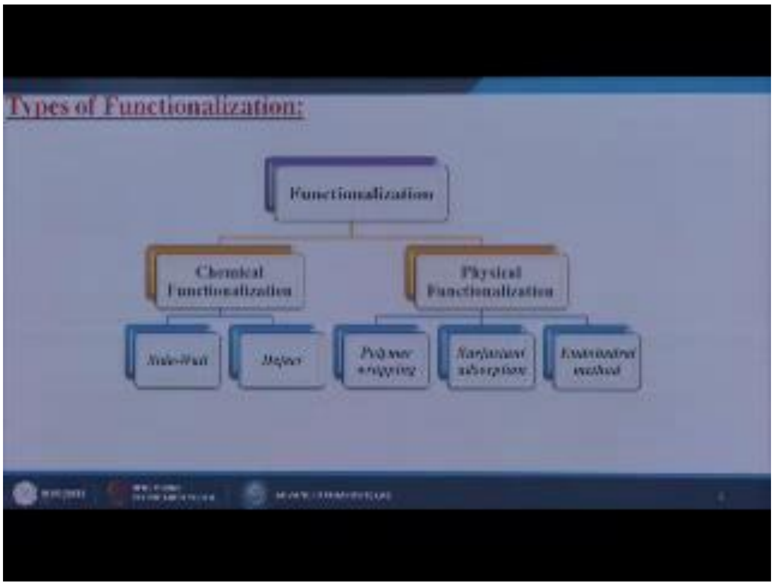

Types of Functionalization:

Functionalization

Chemical Functionalization

Physical Functionalization

Side-Wall

Defect

Polymer wrapping

Surfactant adsorption

Endohedral method

Here we are trying to show you that there are several types of functionalizations and how we can classify those. So, first is called the functionalizations which is divided into 2 types, one is called the chemical functionalizations another one is called the physical functionalizations. The chemical functionalizations is divided into 2, one is called a side wall, another one is called a defect and the physical functionalizations is divided into 3 parts one is called a polymer wrapping, then surfactantent absorptions and endohedral methods. So, here it is divided into 2 classical zones, one is called the chemical functionalizations and the physical functionalizations. So, first it is coming to the chemical functionalizations.

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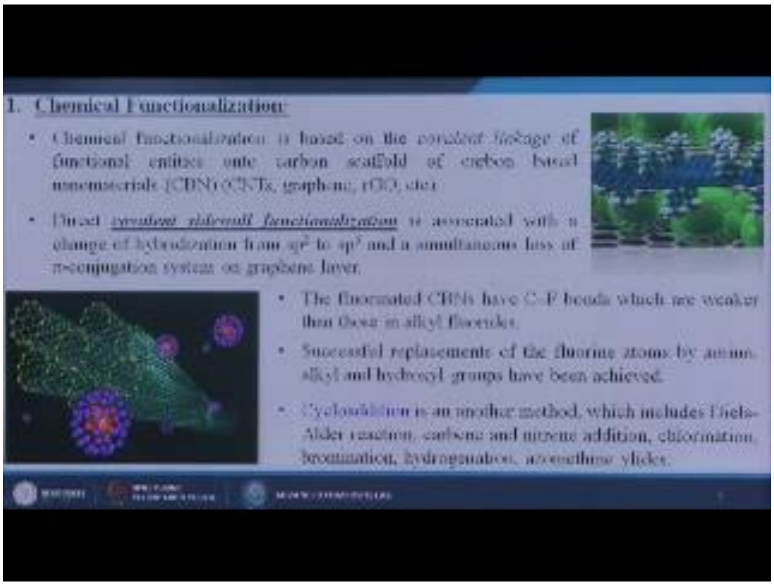

1. Chemical Functionalization

- Chemical functionalization is based on the *covalent linkage* of functional entities onto carbon scaffold of carbon based nanomaterials (CBN) (CNTs, graphene, rGO, etc.)
- Direct ***covalent sidewall functionalization*** is associated with a change of hybridization from sp^2 to sp^3 and a simultaneous loss of π-conjugation system on graphene layer.
- The fluorinated CBNs have C–F bonds which are weaker than those in alkyl fluorides.
- Successful replacements of the fluorine atoms by amino, alkyl and hydroxyl groups have been achieved.
- Cycloaddition is an another method, which includes Diels-Alder reaction, carbene and nitrene addition, chlorination, bromination, hydrogenation, azomethine ylides.

Chemical functionalizations is based on the covalent linkage of functional entities on to the carbon scaffold of carbon based nanomaterials like carbon nanotubes, graphene, reduced graphene oxide, etcetera.

Here the thing is that the chemical functionalization when we are going to do, we should have the covalent linkage in between the functional entities and in between the parent material, then direct covalent sidewall functionalizations is associated with a change of hybridization from sp 2 to sp 3 and this simultaneous loss of pi conjugation system on graphene layer, so simple by the covalent linkage these materials or maybe that these functionalized materials will attach onto the sidewall of the nanoparticles itself.

The fluorinated carbon based nanomaterials have carbon and fluorine bonds which are weaker than those in alkyl fluorides, successful replacements of the fluorine atoms by amino, alkyl and hydroxyl groups have been achieved, cycloaddition is an another method which includes diel, diels alder reaction, carbene and nitrene additions chlorination, bromination, hydrogenation and asomethine ylides. So, these all are the materials by which we can do or maybe these are different techniques by which we can do the modifications or maybe the functionalizations of our nanoparticles.

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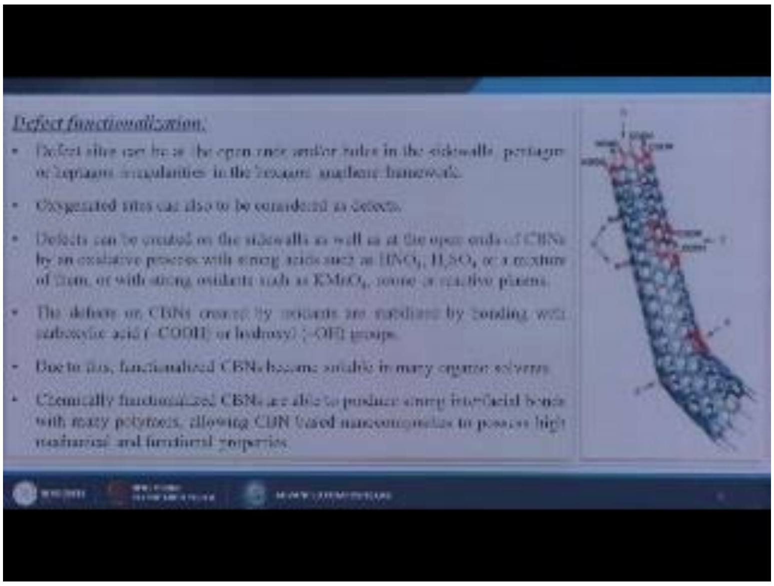

Defect functionalization:

- Defect sites can be at the open ends and/or holes in the sidewalls, pentagon or heptagon irregularities in the hexagon graphene framework.
- Oxygenated sites can also to be considered as defects.
- Defects can be created on the sidewalls as well as at the open ends of CBNs by an oxidative process with strong acids such as HNO_3, H_2SO_4 or a mixture of them, or with strong oxidants such as $KMnO_4$, ozone or reactive plasma.
- The defects on CBNs created by oxidants are stabilized by bonding with carboxylic acid (–COOH) or hydroxyl (–OH) groups.
- Due to this, functionalized CBNs become soluble in many organic solvents.
- Chemically functionalized CBNs are able to produce strong interfacial bonds with many polymers, allowing CBN based nanocomposites to possess high mechanical and functional properties.

Then defect functionalization. So, here from this name itself we can do that when you are using certain kind of nanoparticles on nanofillers some defect sides are present at the side walls of these nanomaterials. So, when we are doing this kind of functionalization, simple these functionalization materials is going or may is attaching with the defect sides of this kind of nanofillers. So, defect sides can be at the open ends and or holes in the sidewalls, pentagon or heptagon irregularities in the hexagon graphene framework. Oxygenated sites can also to be considered as defects. So, here generally when we are talking about this kind of carbon nanotube structure, we can find that there is some kind of defect sides. So, on that particular defect sides, the functional groups is attaching directly.

Defects can be created on the sidewalls as well as of the open end of the carbon based nanomaterials by an oxidative process with strong acids such as sulfuric acid or maybe that nitric acid or a mixture of them or with strong oxidants such as potassium permanganate, ozone or maybe the reactive plasma. So, here sometimes what we are trying to do, if we are trying to modify some kind of nanoparticles or maybe the nanofillers, maybe sometimes we are creating the defects on its surface. So, by applying these kinds of strong acids or maybe some kind of other base materials or maybe the strong regions, that defects can be created on the sidewalls or maybe at the phase or maybe at the end of that particular nanomaterials. So, that simple the functional groups can come and attach at that particular defect sides.

The defects on CBNs created by oxidation oxidants are stabilized by bonding with carboxylic acid group that is COOH or maybe the hydroxyl OH groups, due to these functionalized CBNs become soluble in many organic solvents because we are putting some kind of carboxylic group or maybe some kind of hydroxyl group on this particular nanofiller so that it can soluble into some solvent, chemically functionalized CBNs are able to produce strong inter facial bonds with many polymers allowing CBN based nanocomposites to possess high mechanical and the functional properties. So, by just adding the different functional groups on to the surface of that particular defect of that particular nanofillers, we can modify this kind nanofiller and it can be give some kind of functional and some kind of mechanical properties.

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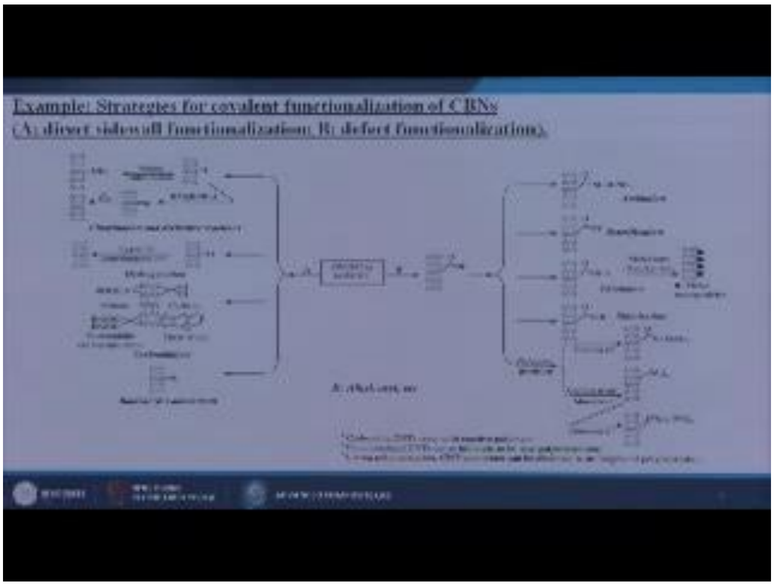

Example: Strategies for covalent functionalization of CBNs

(A: direct sidewall functionalization; B: defect functionalization).

Here is an example that how we are going to do by direct sidewall functionalizations and the defect functionalizations. So, when you are talking about the direct side wall functions, from this particular figure you can understand that whatever the modifications we are trying to do, we are doing on to the sidewall of that particular nanofiller. So, here suppose we have doing the amine substitution over there or maybe some floating substitution over there or maybe some kind of alkyl or maybe aryl group substitution on to the system. So, fluorination and derivatives reaction is going on. So, by which this amine group or maybe the chlorine group can attach at the sidewalls of that particular nano fillers and also we can do by this method by some kind of hydrogenation so that hydrogen bonding or maybe H can be attached to that particular systems, we are doing some kind of cycloadditions. So, some kind of nitrene groups, maybe carbene groups, then diels alder, maybe some kind of nucleophilic cyclopropanations.

These kinds of materials can be easily attached at the sidewall of that particular nanocomposites or maybe the nanofillers not only that some kind of radical also we can attach to that particular systems. So, these all are coming on to the direct sidewall functionalizations. So, when and it is mainly we are doing on to the single wall carbon nanotubes or maybe the multi wall carbon nanotubes, but when we are doing the defects of functional radiations.

So, as I told already in my last slides that defects means either the defect is already presented inside that nanofiller or maybe sometimes we are creating the defects on to that nanofillers to modify or maybe the functionalize the nanofillers. So, in this particular case, we are doing some kind of amidation on to the defect sides, we are attaching some kind of ester groups onto the defect sides, maybe thiolations or maybe some kind of silanization, we are doing on to that defect side itself, not only that sometimes a polymer grafting also we are doing, but this particular topic will discuss in our next lecture.

Here by this way, one is the side wall, another one is the defect we can do the functionalizations of this kind of nanofillers, then here we have try to show some kind of chemical functionalizations of the grapheme, how we can do the chemical functionalizations of this grapheme?

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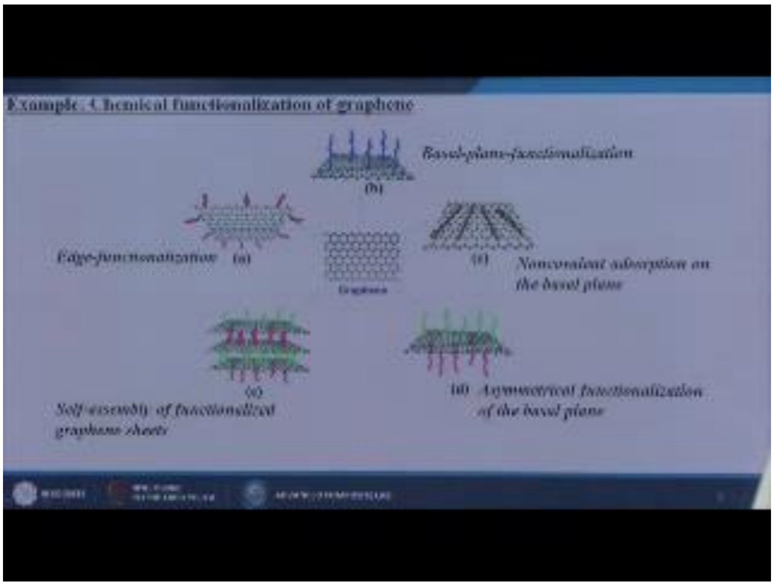

Example : Chemical functionalization of graphene

We can do the H functionalization. So, from this particular figure you can see that graphene is like a sheet. So, it is a 2D material. So, here we can attach some kind of functional groups at the edges of the graphene so that we can do the modifications, we can do some basal plane functional radiations which that functional group attached at the bassal plane of that graphene sheet, sometimes we are attaching some kind of non-covalent absorptions on the basal planem sometimes we can do some asymmetrical functionalizations of the basal plane. So, one side the groups will be different, another side other groups will be attached, sometimes we can do by layer by layer functional modifications also, it is called the self assembly of functionalized graphene sheets. So, by these methods we can do that chemical modifications or maybe the chemical functionalization of graphene.

Next we are going to discuss about the physical functionalization and process. So, from the name itself we can understand that we are doing this functional process by some physical methods.

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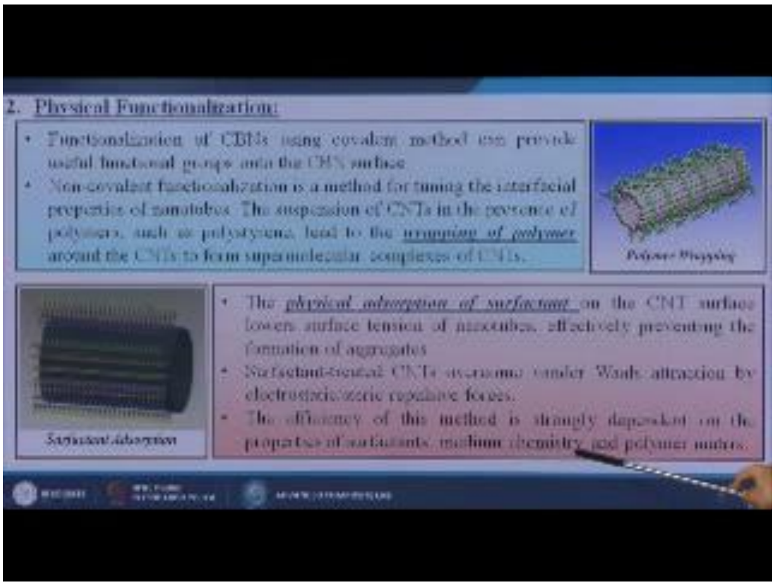

2. Physical Functionalization:

- Functionalization of CBNs using covalent method can provide useful functional groups onto the CBN surface
- Non-covalent functionalization is a method for tuning the interfacial properties of nanotubes. The suspension of CNTs in the presence of polymers, such as polystyrene, lead to the *wrapping of polymer* around the CNTs to form supermolecular complexes of CNTs.

- The *physical adsorption of surfactant* on the CNT surface lowers surface tension of nanotubes, effectively preventing the formation of aggregates
- Surfactant-treated CNTs overcome van der Waals attraction by electrostatic/steric repulsive forces.
- The efficiency of this method is strongly dependent on the properties of surfactants, medium chemistry and polymer matrix.

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Functionalization of carbon based materials or maybe carbon based nanoparticles using covalent method can provide useful functional groups onto the CBN surface, non-covalent functionalization is a method for tuning the interfacial properties of nanotubes, the suspension of CNTs in the presence of polymers such as polystyrene lead to the wrapping of polymer around the CNTs to form the super molecular complexes of CNTs.

Here you can see that we are using certain kind of carbon nanotubes either maybe it is single wall carbon nanotubes or maybe the multi wall carbon nanotubes and the sidewalls is wrapped by some kind of polymer or maybe the polymer chain. So, by wrapping the polymer on to the carbon nanotubes, we can do thus functionalizations or maybe the modifications of the carbon nanotubes material and also the physical absorptions of surfactant that is also another technique on the CNT surface, lower surface tension of the nanotubes effectively preventing the formation of aggregates.

Surfactant treated CNTs overcome Vander walls attractions by electrostatic or maybe the steric repulsive forces the efficiency of this method is strongly dependent on the properties of surfactants medium chemistry and the polymer matrix. So, here whatever the materials we are trying to use, sometimes we are trying to increase its absorption property so that it can absorb certain kind of other functionalized materials towards it. So, by this way we can do the modification or with the functionalization of those particular nanofiller.

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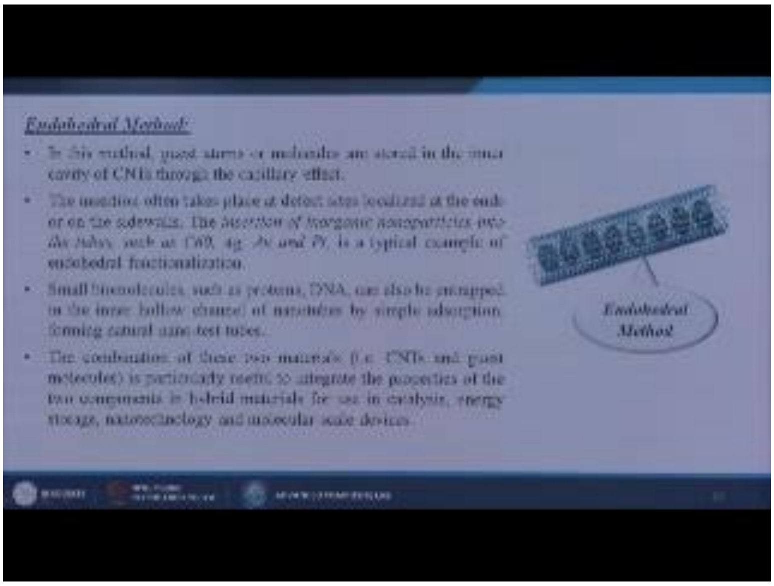

Endohedral Method:

- In this method, guest atoms or molecules are stored in the inner cavity of CNTs through the capillary effect.
- The insertion often takes place at defect sites localized at the ends or on the sidewalls. The *insertion of inorganic nanoparticles into the tubes, such as C60, Ag, Au and Pt,* is a typical example of endohedral functionalization.
- Small biomolecules, such as proteins, DNA, can also be entrapped in the inner hollow channel of nanotubes by simple adsorption, forming natural nano-test tubes.
- The combination of these two materials (i.e. CNTs and guest molecules) is particularly useful to integrate the properties of the two components in hybrid materials for use in catalysis, energy storage, nanotechnology and molecular scale devices.

Then there is also another method or maybe another classical approach by which we can do the functionalization of our nanoparticles that is called the Endohedral method. So, in this method guest atoms or molecules are stored in the inner cavity of the CNT s through the capillary effect. So, you know that what is the CNT, the CNT is nothing but it is a hollow tube. So, it is both the ends are open and it is like a pipe. So, if there is having a one layer of that particular material, we are calling it as a single wall nanotube, when they are is having the multiple layer, we are calling it as a multi walled carbon nanotubes, when we are having only 2 layer, we are calling it as a double layer carbon nanotubes.

It is a very good promising material from the carbon family. So, the insert is totally the hollow one. So, what we are trying to do? We are trying to incorporate certain materials inside this hollow tube. So, that by doing this one, we can do the modifications because till now we are talking that we are adding some materials on the top of the surface itself, not only that we are trying to attach some functionalized group on the defect sides of the materials. But in this particular case, what we are telling that we are inserting some materials inside the holes or maybe inside the pipes, what are those materials? The insertion often takes place at defect sites localized at the ends or on the sidewalls. The insertion of inorganic nanoparticles into the tubes such as C60 which is nothing but known as the fullerene, then some kind of silver particle, then gold particle and the platinum is a typical example of endohedral functionalization. So, simple we are inserting certain kind of fullering materials, some kind of silver particles or maybe the gold particle or maybe the platinum particles inside the carbon nanotubes.

Small biomolecules such as proteins DNA because that is a very very promising area for the biomedical application, when you are trying to do or maybe we are trying to make certain kind of proteins or maybe some kind of enzymes or maybe some kind of DNAs or may be the RNAs, simply we are inserting into the nanofillers and whole thing we are putting inside our body. So can also be entrapped in the inner hollow channel of nanotubes by simple adsorption process forming natural nano test tubes, it can be done in our laboratory. It is the simple methods by doing also we can do the modification of this kind of nanofillers.

The combination of these 2 materials that is carbon nanotubes and the guest molecules means what we are inserting into it, either maybe fullering or maybe silver particle, gold particle, platinum particle or maybe some kind of bioactive materials like proteins or maybe some kind of serums or maybe some kind of RNA or maybe the DNA is particularly useful to integrate the properties of the 2 components in hybrid materials for the use in catalysis, maybe we can use that materials for the catalytic applications, some energy storage applications, maybe some super capacitor or maybe some energy storage devices applications, then nanotechnology and the molecular scale devices or maybe some biomedical equipments.

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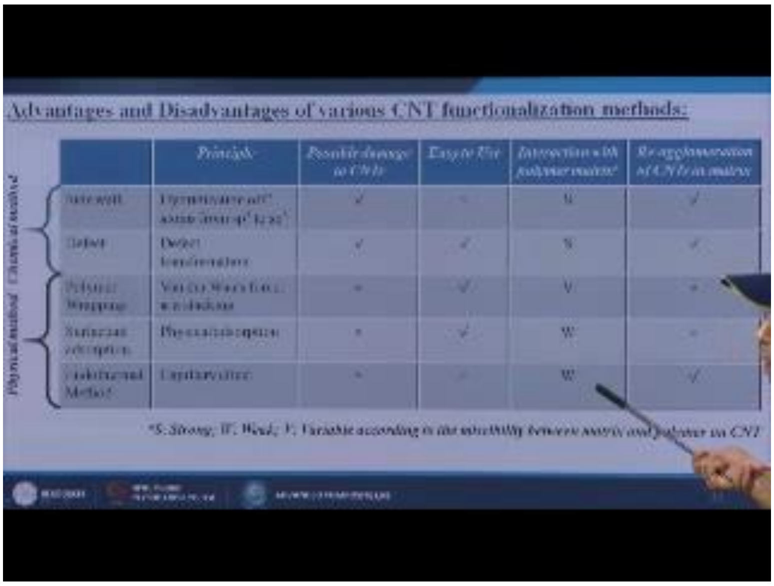

Advantages and Disadvantages of various CNT functionalization methods:

		Principle	*Possible damage to CNTs*	*Easy to Use*	*Interaction with polymer matrix**	*Re-agglomeration of CNTs in matrix*
Chemical method	Sidewall	Hybridization of C atoms from sp^2 to sp^3	✓	×	S	✓
	Defect	Defect transformation	✓	✓	S	✓
Physical method	Polymer Wrapping	Van der Waals force, π-π stacking	×	✓	V	×
	Surfactant adsorption	Physical adsorption	×	✓	W	×
	Endohedral Method	Capillary effect	×	×	W	✓

**S: Strong; W: Weak; V: Variable according to the miscibility between matrix and polymer on CNT*

Next we are trying to show you that what are the advantages and disadvantages of various carbon nanotubes functionalization methods. So, when we are talking about the chemical methods, it is divided into 2 - one is called a side wall and another one is called the defect. So, when you are talking about the sidewall the principle is that hybridization of carbon atoms from sp 2 to sp 3, possible damage to CNTs, yes of course, it is possible, easy to use, no, it is not easy to use, interactions with polymer matrix is yes, means; that means, it is very very strong and re-agglomeration of CNTs in matrix always it is possible because we are using very tiny particles of that nanofiller. So, when you are trying to mix those filler inside our polymer, due to its large surface area and high aspect ratio always they try to agglomerate.

That is the main drawback of using this kind of nanoparticles into some matrix or maybe some into some alloys or maybe into some blends, then when you are talking about that defect, generally the principle is the defect transformations possible damage to the CNTs is of course possible, easy to use, it is very easy to use, interaction with the polymers is very strong re-agglomeration of CNTs in matrix is possible.

Then when we are talking about the physical method, when you are talking about the polymer wrapping on to that particular nanoparticles, the principle is due to the Van der Waal’s force or maybe the pi pi stacking then possible damage of the CNTs not possible because just we are wrapping one material on top of that then easy to use, of course, it is possible, we means variable according to the miscibility between matrix and polymer on the CNT because that is the addition in between the polymer and the carbon nanotubes and then re-agglomeration of CNTs in matrix that is also not possible.

Then when you are talking about the surfactant absorptions, generally this is based on the physical absorption process possible to possible damage to the CNTs is not possible, easy to use; it is easy, it is very very weak interactions with the polymer matrix, then re-agglomeration is not possible.

When you are talking about the endohedral method, it is generally based on the capillary effect because whatever the material we are trying to insert, due to the capillary effect it is going inside that tube or maybe that inside that material. So, possible damage of the CNTs is not possible, then easy to use, it is not also easy to use, interaction with the polymer matrix is very very weak because whatever the functional group we are putting that is going inside the nanotube not the surface and re-agglomeration of CNTs is matrix is very very good.

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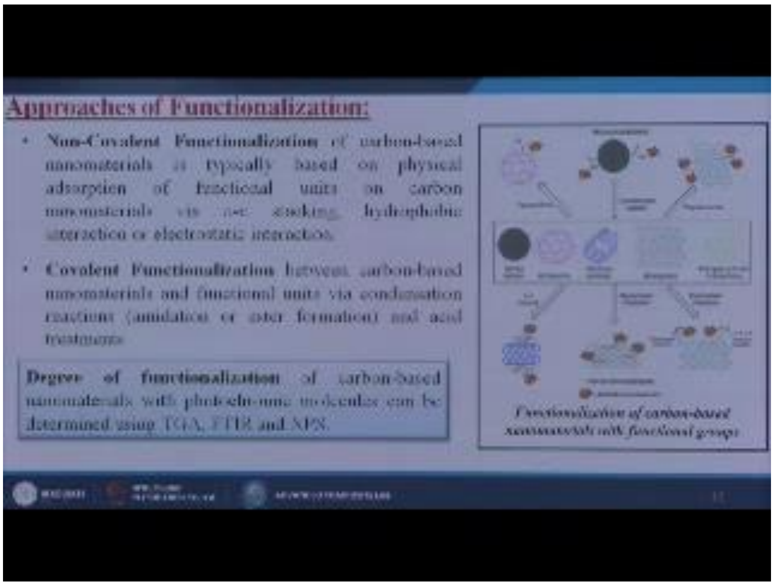

Approaches of Functionalization:

- **Non-Covalent Functionalization** of carbon-based nanomaterials is typically based on physical adsorption of functional units on carbon nanomaterials via π-π stacking, hydrophobic interaction or electrostatic interaction.
- **Covalent Functionalization** between carbon-based nanomaterials and functional units via condensation reactions (amidation or ester formation) and acid treatments.

Degree of functionalization of carbon-based nanomaterials with photochromic molecules can be determined using TGA, FTIR and XPS.

Functionalization of carbon-based nanomaterials with functional groups

Here what is the approach is that by which we can do this kind of functionalizations. So, first one is called the non-covalent functionalizations and second one is called the covalent functionalizations. Then here for the non-covalent functionalizations of carbon based nanomaterials is typically based on the physical absorption of functional units of carbon materials like the pi pi interactions or maybe the pi pi bonding in between the functionalized groups and your nanofillers or maybe the nanoparticles or sometimes it is called the pi pi stacking, hydrophobic interactions or maybe some kind of electrostatic interactions.

But when you are talking about the covalent functionalization, covalent functionalization between carbon-based nanomaterials and functional units via condensation reactions like amidations or maybe the ester formations or may the esterifications and the acid treatments. So, here by 2 methods, one is called the covalent method another one is called a non-covalent method we can do the functionalizations of these kind of nanoparticles.

Here these all of the materials which we are going to do the functionalization, one is called a carbon nano dot then it is a 0D fuller in 1D carbon nanotubes, 2D graphene sheet and polycyclic aromatic hydrocarbons. Then by cycloadditions, we can do the modifications, it is known as the covalent modifications and then condensation reactions also we can attach some kind of groups and mainly amine groups onto the surface, then we can do some kind of polymerizations onto the graphene sheets or maybe that graphene flicks and not only that below one is called that non-covalent modifications where we are doing some kind of pi pi stacking or maybe the pi pi interactions in between the functional groups and in between the your carbon nanotubes, then we are doing some kind of hydrophobic interactions over there and also we can do some kind of electrostatic interactions on to the graphene surface.

So, some kinds due to some kind of hydrogen bonding some kind of electrostatic bonding we can do these kind of non-covalent modifications and here this is known as the photochromic molecules which is attaching to the surface. So, here the whole picture is about the functionalization of carbon based nanomaterials with the functional groups by which just simply we are trying to show that how we are doing the covalent functionalizations and how we are doing the non-covalent functionalizations.

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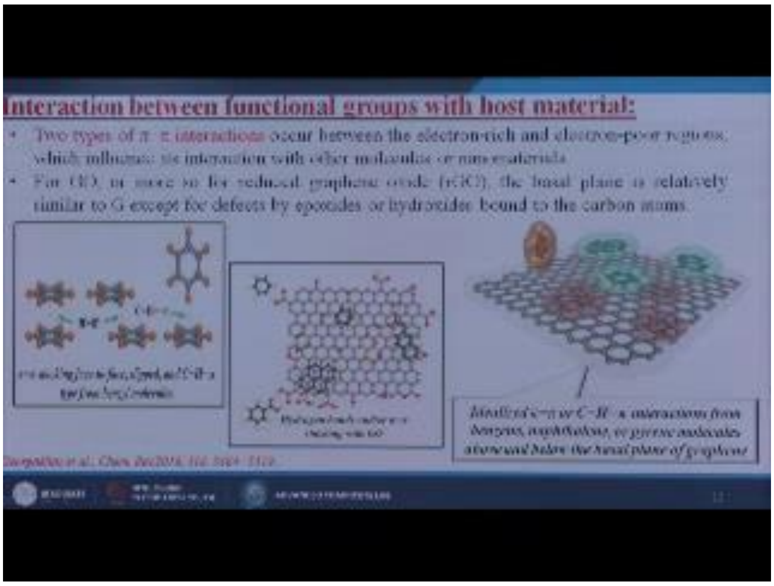

Interaction between functional groups with host material:

- Two types of π–π interactions occur between the electron-rich and electron-poor regions, which influence its interaction with other molecules or nanomaterials.
- For GO, or more so for reduced graphene oxide (rGO), the basal plane is relatively similar to G except for defects by epoxides or hydroxides bound to the carbon atoms.

Idealized π–π or C–H···π interactions from benzene, naphthalene, or pyrene molecules above and below the basal plane of graphene

Georgakilas et al., Chem Rev 2016, 116, 5464–5519

Now in this particular slide, we are going to show you that how the interaction is going between the functional groups with the host materials. So, as I told already so generally there are 2 things one is called the covalent bonding another one is called a non-covalent bonding. So, 2 types of pi pi interactions occur between the electron reach and electron poor regions which influence is interactions with other molecules or nanomaterials. So, as I told in my last slides that this is the main vital factor by which the functionalized group attaching to the nanomaterials that is called the pi pi interactions or maybe the pi pi stacking or maybe the pi pi bonding.

For graphene oxide or more, so for reduced graphene oxide, the basal plane is relatively similar to graphing graphene except for defects by epoxides or hydroxides bound to the carbon atoms. So, here in this particular case you can see that when this functionalization is taking place, same till the pi pi bonding is taking place, but in this particular case when you are doing the modifications, it is having the carbon atom, then it is having the hydrogen atom, then first carbon is attaching with the hydrogen then through hydrogen it is having the pi pi interactions in between the nanofillers and the functionalized group.

Here also the hydrogen bonds and or that pi pi stacking with the graphene oxide sheets is taking place, in some places the hydrogen bonding is taking place some cases the pi pi bonding is taking place, here this is also the another good examples that idealized pi pi or maybe that carbon hydrogen pi interactions from benzene, naphthalene or maybe the pi in molecules above and below the basal planes of the graphene. So, as I told already some groups are attached on top of the sheets some groups are attached the bottom of the sheets itself. So, sometimes it is going to get the pi pi interactions, sometimes it is going to get carbon hydrogen pi interactions.

This is also some kind of literature review studies and this has been done by the Georgakilas and he has been presented this paper in some chemical review journal in the year of 2016.

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Some examples of functionalized group with enhanced properties:

S. No.	Host Material	Group	Attachment	Property Enhancement	Year
1.	Graphene	Benzoyl Peroxide	Covalent	Electronic and Optical	2016
2.	C-H	Alicyclic Amines	Covalent	Pharmacokinetic	2016
3.	Graphene	Di-bromo-carbene	Covalent	Optical & Electronic Properties	2016
4.	rGO	RuO_2	Covalent	Electrochemical	2015
5.	Transition Metal Dichalcogenides	[illegible] and Methyl Moieties	Covalent	Photoluminescence	2015
6.	Graphene	O, N and Fluorine	Covalent	Thermal & Electrical Properties	2015
7.	Wood based Cellulose Fibers	$BaTiO_3$	Covalent	Piezoelectric and mechanics	2014
8.	CNT	Carboxyl & Hydroxyl	Covalent	Electrical and Mechanical	2014

Here are the some examples of the functionalized groups with enhanced properties, what are those? First is that we are using the host material as a graphene then what type of functional group we are trying to attach, that is benzoyl peroxide and attachment is covalent type means covalent bonding is taking place, then property enhancement generally electronic and optical properties is going to be enhanced and it has been done in the year 2016. When you are talking about the carbon hydrogen, some kind of may host materials we are attaching that alicyclic amines, it is also be doing by the covalent bonding, it is having some pharmacokinetic property enhancement is taking place, it has been also done in the year 2016.

When you are talking about the graphene, we are using some kind of di bromo carbene and attachment is covalent, generally optical and electronic properties is enhancing, it has been done in the year 2016. We have done some modification of reduced graphene oxide by the ruthenium oxide group because ruthenium oxide is the functional groups which is attaching to the reduced graphene oxide by the covalent bonding which is nothing, but the enhancing the electrochemical properties of that particular material, it has been done in the year of 2015.

Then we have done the modification of transition metal dichalcogenides grapheme, maybe some wood based cellulose fibers or maybe some carbon nanotubes, carbon nanotubes, we have done the modification by carboxyl group and hydroxyl group, it is also one kind of covalent bonding. So, for the electrical and mechanical properties enhancement we have done these kinds of modifications. So, it has been done in the year 2014.

Here also we have done also some modifications carbon nanotubes with the pour firing derivatives, maybe it can be attached by the covalent functionalization or maybe the non-covalent functionalizations, it can increase the optical and electrical properties of that particular material, it is little bit older, it has been done in the year of 2013. Then we have done some kind of modification of the silicon carbide surface, we have done the functional groups whatever we have used is that organ of sealants. So, it is also a mixture of some amino propyldiethoxymethylsilane and the octadecyltrimethoxysilane, it is a mixture and then attachment is covalent types, then property enhancement is generally electrical and chemical properties, it has been announced in the year 2013.

We have done the modification of fullerene by the imidazolines, it is also a covalent type; it is having some unique synthesis process in the year 2013 it has been done. Again we have done the modification of graphene by aryldiazonium covalent bonding solubility, electron mobility and sensor activity. So, that is also some added advantage that we are using these materials for the sensor applications and not only that it has been done in the year of 2011. Then we have used some modifications of the graphene nanoribbon, where we have used the fore nitro phenyl groups, it is also the covalent edge bonding has been taken place, it has been enhanced the electrical properties of that particular material and it has been done in the year of 2010.

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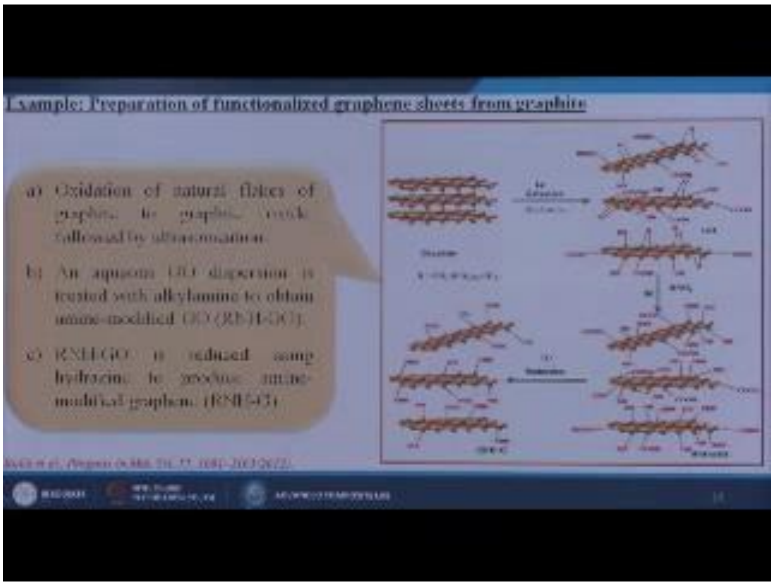

Example: Preparation of functionalized graphene sheets from graphite

a) Oxidation of natural flakes of graphite to graphite oxide followed by ultrasonication.

b) An aqueous GO dispersion is treated with alkylamine to obtain amine-modified GO (RNH-GO).

c) RNH-GO is reduced using hydrazine to produce amine-modified graphene (RNH-G).

Here we are trying to show you some examples that how we are functionalizing the graphene sheet from the graphite. So, here first what we are doing? We are doing the oxidations of the natural flecks of graphite to graphite oxide followed by the ultrasonications. Here I am having the graphite sheet graphite is the simple method whatever we are using in our pencils or maybe some other materials, it is very very easily available from the environment itself. So, we have to collect those graphites then we have to do the oxidation process of that graphites and the vigorous sonications can be taken place by which some acid group or maybe some hydroxyl group will be attached on that graphite sheet and it will become the graphene oxide.

Then after graphene oxide we are doing the amine modifications over there. So, some amide group is attached to that person to that particular graphene oxide. So, actually the graphene oxide is having that there are so many functional groups are attached with the graphite sheet. So, when after that we have to do the reduction process that reduction also can be done by different methods, one is called NABH 4 modifications or maybe sometimes we can do it by the hydrothermal threatening. So, by the hydrothermal treatment also we can reduce that graphene oxide to the reduced graphene oxides.

Here by these methods, simply we can delete some functional groups. So, that the single layer graphene or maybe some few layer graphene can be observed for particular things. So, an aqueous graphene oxide dispersion is treated with alkylamine to obtain the amine modified graphene oxide, then amine modified graphene oxide is reduced using hydrogen hydrate to produce the amine modified graphene. So, like this way we can attach some functional groups to that material and then like this way we can reduce it to the reduced graphene oxide from the graphene oxides and also it has been taken from the progress in material science which has been published in the year of 2012 by the Kuila Et Al.

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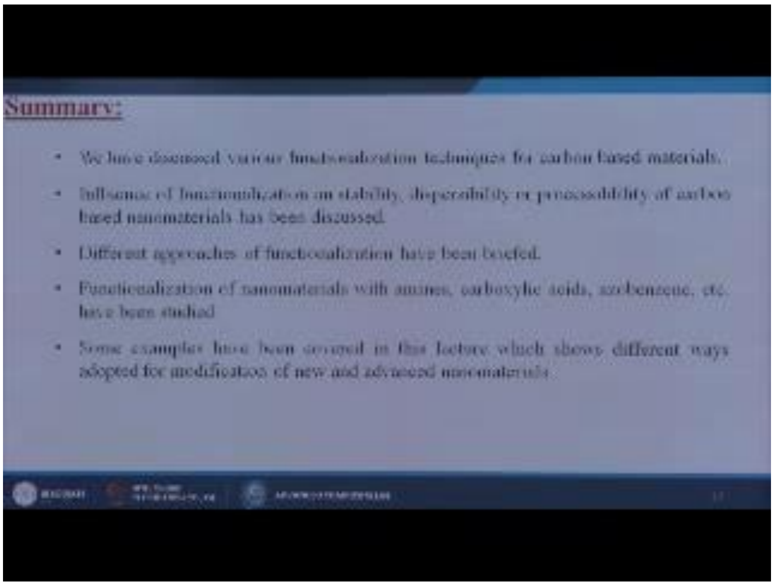

Summary:

- We have discussed various functionalization techniques for carbon based materials.
- Influence of functionalization on stability, dispersibility or processability of carbon based nanomaterials has been discussed.
- Different approaches of functionalization have been briefed.
- Functionalization of nanomaterials with amines, carboxylic acids, azobenzene, etc have been studied
- Some examples have been covered in this lecture which shows different ways adopted for modification of new and advanced nanomaterials.

Here we come to the summary of our particular lecture. So, we have discussed various functionalization techniques for carbon based materials, influence of functionalization on stability, dispersibility or processability of carbon based nanomaterials has been discussed. Different approaches of functionalization have been done in this particular case, in this particular case also functionilization of nanomaterials with amines, carboxylic acids, azobenzene, etcetera have been studied some examples have been covered in this lecture which shows different ways adopted for modification of new and advanced nanomaterials. But those examples are very very few.

So, actually we have done, last lecture we have done about the doping in this particular lecture actually we are trying to give you a glimpse of the functionalizations. So, if you remember, we just for your knowledge we are a once again I am telling you that functionalization is taking place by the 2 methods, one is called by side wall and other one is called the defect sides. So, functional groups you can attach on to the side wall of your nanomaterials or maybe you can create certain kind of defects onto your nanomaterials. So, that functional groups can directly go to the defects or maybe some defects are already present on to nanomaterials, you can attach that functional groups to that particular defect sides.

Now again we have discussed that how the bonding is taking place, some cases we have shown that generally the covalent bonding or maybe by the non-covalent bonding, we have shown you the pi pi interactions or maybe the pi pi stacking or maybe the pi pi bonding in between your functionalized groups, we have shown you the hydrogen bonding over there or maybe some kind of low molecular bonding also we have shown over there. Then based of these bonding is how we are trying to modify our nanofillers we have given some kind of source of examples over there, then also the last one is called thank you.