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Lecture - 36 Current trends in Surface Modification of Nanomaterials (Part-1)

Hello, today we are going to start our new lecture on some current trends that how we are going to modify our nanocomposites or rather how we are going to modify our sample so that we can use those nanoparticles and we can get some better properties. If you remember in our last some quiet previous lectures, we have already discussed about that how to modify the coatings, how to modify nanofillers but here the main aim of this particular lecture is not to modify the nanocomposites, just to modify the nanofillers first then that modifying nanofillers we are going to use or maybe we are going to coat into the substrate material.

So the topic of this particular lecture depends on the current trends in surface modifications of nanomaterials. So, whatever we are going to discuss in this particular topic that current trends means that recent may be from 2013 from 2014; this technology has been started and that technology we are incorporating to modification of the surface engineering.



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So, first current trends for surface modification of nanomaterials. So, basically there are 3 techniques generally we are adopting actually not there are 3 techniques there are so many techniques, but these all this technique has been classified into 3 board spectrum one is called the doping, another is called the functionalization, another is called the other. Others means some kind of polymerization method or may be some kind of other modification methods.

So, today in this particular lecture only we are going to discuss about the doping. So, here we have seen so many figures that where some where we are using some kind of graphene hybrid nanomaterials, somewhere we are using some carbon nanotubes or may be some carbon dots or may be ghraphene nanoremones and we are trying to modify. So, till today actually we are discussing that how we are going to modify these materials or may be how we are going to modify these materials with some nanocomposites and we are trying to prepare the hybrid nanocomposites, but actually today we are going to do that how that structure; not the chemical structure, but the physical properties of these material can be changed by applying any kind of impurities or may be inserting any kind of impurities or may be the doping materials inside this structure.

So, fist before going to start that what are the going on about the doping; first let us know that what the doping means. So, actually the doping means that we are trying to insert some kinds of dopants or may be the impurities inside some materials or may be some crystal structure of a particular nanoparticals. So, when we are doing generally we are having some limitations, so when we are inserting these impurities less than 1 percent that time only we are calling it as a doping. If the lording percentage will be more than the one percent then it will be categories into some other forms.

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So, here the doping intentionally introduces impurities that are less than 1 percent; already I have said you into an extremely pure intrinsic semiconductor for purpose of modulating its properties. So, here this is one the carbon structure in which we are introducing the nitrogen atom over there and this atom percentage is less than 1 of the whole carbon percentage, so here that is why it is known as the doping.

Then last previous lectures also we are discussed about the coating, so once again just give a glimpse or may be give a just idea that what is coating means. So, a coating must adhere to the one substrate, a coating once applied is exposed to the elements and must withstand abrasion, marring, solvents, water and heat. So, simple I am having the substrate, that substrate will covered by some kind of materials either it can be the virgin materials or may be it kind of some kind of composites materials or that is known as the coating.

And then when we are talking about the composites, so composites is nothing, but it is the mixture of two to 3 elements or may be the two to 3 materials then we are making certain kind of slurry type of mixture or may be that concrete type of mixture or different materials and then either that material directly we can use for some other applications or maybe we that materials we can put into the substrate materials for better physical properties. So, here the composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that when combined produce a material with characteristic different from individual components. So, here you can see that there are several colors like blue yellow grays; that means, the layer by layer they are making certain kind of structure either this materials directly I can use or may be this material I can coat into the substrate material for any other properties.

Now let us know that why we are doping actually what is the main purpose of doing this kind of doping. So, the main aim of this doping to just to increase the electronic properties or may be the semiconductor properties of that particular material. So, that is the main moto of this doping technology, so again we are going into the details; so fist let us know the doping.

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So, as I told already the doping is the process of adding some impurities atoms, replacing the host atoms in the semiconductor. So, generally when will go into the classification of the these doping, we will elaborately discuss that how it is going on; actually either one atom of that particular material can be substituted by that doping materials or may be that doping materials can go into the interstitial site of that particular material, so by this two methods we can do the doping.

These impurity atoms are known as the dopants, so what we are injecting inside the material that is known as the dopants. After addition of these dopants some of the properties of semiconductor can be changed as per the requirements. So, how much

quantity the materials I am inserting, but it should mo less than the 1 percent of whole depends upon the how much semiconductor properties is going to be enhanced. So, here the right hand side we are given the single layer graph instruction. So, in which the top of this that the conduction band and the bellow is the valance band and in between that fermi level is actually stain.

So when it is going towards the conduction band, generally we are calling it as a end of materials and when it is going to the valance band, then we are p doped material. But generally formidable is stain in between this two then same thing when we are talking about the bi layer graphene also fermi level can also go to the valance side or may be to the conduction side. So, now we have to discuss about some basic conditions that are required for the doping process are given bellow. So, what are the condition because it is not like that like I am bringing some materials or I am taking some materials and buy some chemical means just I am getting the reactions in between these two and one metal or may be one at atom will be inserted into the another one, no of course; it is not like that.

There should be some specific condition; that specific condition should be made by that material so that doping can be done. So, fist one is that that atom which is to be doped in the crystal must be placed at a position same as that of the semiconductor atom. So, when we are talking about the substitution doping, so just one atom from the parent material will be replaced by another atom. So the crystal structure of that particular base of may be the parent material will not be changed, only it will replaced by (Refer Time: 08:30) impurities.

Number two, will be there should be not be any distortion in crystal after insertion of the dopants. So, when I am talking about the parent body, when I am inserting some dopant or impurities into the parent body, the whole crystal structure of a parent body should not be changed, only it can some molecules be inter changed by the impurities materials or may be that impurities material can go to the interstitial site actually which is back end inside the parent materials, but overall the crystal structure of parent material is not going to be changed.

Now, the number third will be the size of dopants should be exactly the same as that of the size of atom of the crystal. Yes of course, because otherwise if the size of crystallized

atom will be changed then automatically the crystal structure will be distorted, may be there is some kind of backend site will be created then the overall parent body crystal structure will be changed, but that is not possible by this doping technology. So, doping technology means the crystallized size of both the parent material and both the doping materials should be same.

And the number 4th and the last is that in a crystal, the percentage of doping should not be more than 1 percent. So, that is the whittle parameter because every material, everything is having some resistibility and capability. So, more than 1 percent that material will not allow inside it. So, always the doping material should be bellow 1 percent on the parent body.

Then we are going to discuss about the types of doping, as I told already there are several types of doping generally by or maybe it is rather some kind of synthesis process by which we are doing on our materials.

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So, fist one is called the according to the position of the dopants in crystal lattice which is nothing, but the interstitial doping. So, fist doping technique is known as the interstitial doping, so from the name itself you can understand whatever the impurities material we are adding into our parent material that is going to the interstitial site because the overall crystal structure is of the particular parent body is not going to be changed. So, where these doping materials will go; actually that doping material will go to the interstitial site of the particular parent body. So, the dopant atom is not incorporated into a crystal lattice, but besides between the crystal atoms on an interstitial site.

For metallic material that have relatively high atomic packing factors, the interstitial positions are relatively small yes of course, because when we are talking about the metallic particles or maybe some kind metal; they are very closely packed. So, getting the interstitials site is very difficult or may be less number of interstitial site is available. So, that time the doping of that particular metallic material is quiet difficult.

Next atomic diameter of an interstitial dopant must be smaller than that of host atoms. Normally the maximum allowable concentration of interstitial dopant is low less than 10 percent. So, here we have given some kind of classical examples, so the examples here the carbon 2 percent concentrations from an interstitials solid solution when added to the iron. So, atomic radius of carbon is 0.071 nanometer which is less than the atomic radius of iron that is 0.124 nanometer. So, here you can see that when we are using this kind of structure, so simple the carbon is going into the interstitial site of the iron structure.

So; that means here the interstitial doping is taking place, here are also some kind of classical examples when we are doing the manganese doping into the zinc oxide still the manganese is going to the interstitial site into the zinc atoms and here also for the aluminum was doped at interstitial site in zinc oxide, simple the aluminum atom is going into the interstitial site of the zinc oxide atoms. So, that is why here just we are trying to show you that how the interstitial doping is taking place inside the material and what are the conditions behind it.

Next we are going to discuss about the substitutional doping, so incorporation of the dopant atom into the host atom which has an atomic inter change and for stable structure you need change atoms, no more than plus minus 15 percent of difference in their ironic radius. So, the radius of those that impurities and the parent body atom should not be variation plus minus 15 percent, so it should be almost same then only the substitution can be possible.

So, the other important parameter for the substitutional doping only this is the prime consideration that the radius that either the atoms more or less.

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Then the second one is called the electro negativity; electro negativity means electro positive one element and more electro negative the other, the greater the is the likelihood that they will form an inter metallic compound instead of a substitutional solid solution, so this is another condition for these kind of doping.

Next one is called the crystal structure, the crystal structure of metals of both atoms types should be the same and the third one is called the relative valance of participating atoms. Other factors being equal a metal will have more of tendency to dissolve another metal of higher valency than one of the lower valency. This is also another prime factor which I will show you by giving some examples. So, here we have given one example about the nickel substituted into the copper materials, the atomic radius for the copper and nickels are 0.128 and 0.125 nanometer respectively.

Both have the FCC crystal structure, their electro negatives are 1.9 and 1.8, but this is the prime factor, valences are plus 1 for copper and plus 2 for nickel; that means, the valency of this nickel is much higher than copper. So, automatically when we will try to do the substitutional doping, the nickel will go inside the copper; that means, the nickel will be here the dopants and the copper will be the parent body. So, the main criteria of this kind of doping is that whose valency band or maybe the valency will be higher than the another than that will actually inserted inside the body. So, that is the main criteria; that means, the nickel substituted into the copper not the visa versa.

So, here also we have given certain kind of examples that is called the n doped graphene and the means nitrogen doped graphene and the b doped means boron doped graphene.



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So, in n doped graphene actually what is happening; atomic radius of carbon and nitrogen is equal to 70 p m and the 65 p m. Both have the HCP; hexa closely packed crystal structure. Electro negativity is 2.55 for carbon and 3.04 for nitrogen and valances are plus 3 for carbon and the plus 3, plus 5 for nitrogen; it mean nitrogen substituted into graphene because nitrogen is having more valences then the carbon itself.

So, here when we are talking about the pristine grapheme; its crystal structure look like this when we are talking about the born doped graphene simply boron is doing the substitutional doping inside the carbon structure or may be the inside the graphene sheet and that is known as the P type and when we are doing the nitrogen doped grapheme; simply nitrogen is doing the N type because why it is called the b doped graphene means atomic radius of carbon and b is 70 p m and 85 p m; both have same crystal structure electro negativity are 2.55 for C and 2.04 for N, but valences are plus 3e for carbon and plus 3 and plus 2 for boron. So, that in that particular case the doping of boron inside the pristine graphene is very very difficult because more or less the boron valency is less than the carbon, but if it will be equal to that time either carbon can go inside the boron or may be the boron can go inside the carbon itself.

So according to electronic band structure, there are two types of things. When we are talking about the electronic band structure, so we can classify these things into two types one is called a P type semiconductor, another one is called the N type semiconductor then what is the reason behind it.

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So, when P type semiconductor, when it is doped with an element with one less valence electron then the element it replaces a P type semiconductor has more holes than electron, so this is the prime factor that by which we can say whether our doping is P type doping or may be the N type doping in terms of electronic band structure. Then when we are talking about the N type semiconductor, when it is doped with element with one more valence electron than the element it replaces an N type semiconductor has more electrons then hole. So, for N type the electron density will be more then the whole density and for P type, the whole density will be more than the electron density.

Then here are the some classical examples that examples of an N type doping. So, silicon is from group 4 and has 4 valence electron, phosphorous is from group 5 and has 5 valance electron. So, automatically the phosphorous will go inside the silicon because the phosphorous valency is more high then the silicon. So, when silicon is doped with the phosphorous at room temperature there is an extra electron since P has 5 valance electron, the extra electron has very low binding energy and these bond is very easily broken. When the bond is broken the extra electron is free to conduct these extra electron

is free to conduct and P becomes positively charged in this case electron are created without creating additional holes therefore, the semiconductor becomes the N type.

Because the in the N type electron density is more than the hole density and the opposite case is taking place in this particular examples when we are doing the P type doping. So, silicon is from group 4 and has 4 valance electron aluminum is from group 3 and has 3 valence electron. So, when silicon is doped with aluminum at room temperature there is a missing electron that is called a hole a neighboring valance electron can take the place of the hole, when this occurs aluminum becomes negatively charged and the hole moves to the neighbor atom. In this case holes are created without creating additional electrons therefore, the hole density of that the particular material is mode and that is they that semiconductor becomes the P type semiconductor.

Then here is also we are given some examples that an N doped semiconductor and P doped semiconductors, in N doped semiconductors which is also known as the penta valent dopant; there is an electron in the crystal.

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Which is not bound and there for can be moved with relatively little energy into the conduction band, thus the donator energy level is close to the conductor band edge the band gap to overcome is very very small and for P doped semiconductor which is known as the tetra valent dopant, a hole is available which me be already occupied at low energy

by the electron from the valance band, thus the acceptor energy level is close the valance band.

So, here the same thing we have given in some synthetic illustrations, so this is known as the intrinsic semiconductor were I am having the conduction band and I am having the valance band and in between is known as the band gap. So when we are talking about the doner N type. So, automatically the hole is density is more in that particular case. So, that is why sorry in that particular case the electron density is getting more. So, that is why it became the N type extrinsic N type, but when you are talking about the P type, the hole transportation is more, so hole density is going to be more. So, that is why it is coming into the P type semiconductor, so here all are the some examples rather some of the gathered literature review what we are absorbed and the right hand side we have given that in which year the scientist or people have done this kind of research.

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232	Ilini Material	Depart	Type of Boging	Property Litheorement	Year
	Philos	TT((hallinn))	Sabinninional	Themselectric popernes	2036
1	NO	Cound Maxo-dopod		Electrochemical	2018
1	740	64	Substitutional	Userneal, Structural and . Optical Properties	2010
1	Closean	Zincomme Oxide		Mechanical, Antibucternal	2010
	Rife	11	Subminister	Damstenical	2010
6	WO ₁	No	Amountal.	Electrochemic	2016
	200	Cn.	Substitutional	Optodectomers, magnetic and thermal	2016
(100	P and Cis on-deped	homentical	Documentalytic	2018
	1580.0	54	Substitutional	Optical	2016

So, fist is called the PEBTSE; which is the dopant is known as the thallium, here we have done the substitutional doping; property enhancement thermoelectric properties have been enhanced, it is done in the year of 2016. So, when we are doing by the chitiosan we are using the dopants like zirconium oxide and the property enhancement is mechanical and antibacterial properties, it has been also done in the 2016. When we are using the reduced graphene oxide, we are using the dopant as a boron that is also an substitutional doping as I told already because boron doping is known as a substitutional

doping and it is enhancing the electro chemical properties of that particular material; it has also been done in the year 2016.

When we are using the tungsten oxide then nickel doping is taking place that is known as interstitial doping because nickel is going into the interstitial site into the composite materials. So, which is known as the electro chromic and it has been done in the year 2016.

Same thing when we are doing reduced graphene oxide with phosphorous and co bolt co doped materials. So, it is going on to the interstitial doping, so it is known as it is enhancing the electro catalytic properties of that particular materials, it has also been done in the year 2016. So, from these year we can get the informations that doping is the latest technology which has been invented may be one years back and the peoples are extensively used or may be the modifying the material filler properties or nanoparticle properties so that give a or may be that it can enhance some better physical properties.

1	Host Material	Hopen!	Type of Degrage	Emporty Labourness	200
	MWENDS	N	Nabaltaniaal	Physicochemical	2011
1	Tisin	(G)	Subminannal	Magnetic	201
12	110,	N	International and National altern	Operationalis	2013
187	Graphene	N and S co-sloped	Submitational	Mochanical, Electrochemical	2013
4	100	E mit N ca-depeal	Salasimational	Pletoleminescone	200
8	Graphene	H and N	Subdimmed	Dectorhemas	3011

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Here is also the same thing of a that continuation of the last slide that is multi wall carbon nanotubes, it have been dopant by the nitrogen, it is also one kind of substitutional doping, it is increasing the physiochemical properties; it has been done in the year 2015. Then TIAC2 chromium has been used as a dopant material substitutionl dopant has been done, it is increasing the magnetic properties in the year 2015; it has been done, thent titanium oxide that nitrogen doping has been done, either it might be

interstitial and substitutional site then optoelectronic properties material is getting increased which has been done in the year 2015.

Then graphene that is also a one kind of promising materials as in the field of nanotechnology where we are doing doping of that graphene by nitrogen and sulfur co doped, it is also one kind of substitutional doping mechanical and electro chemical properties is getting enhanced in the year 2015, then we are doing also the modifications of reduced graphene oxide and florin and nitrogen co doped has been taken place, it is also one kind of substitutional doping; the photoluminescence properties of that particular has been enhanced in the year 2013, then here also the another one is that grapheme; it has been done by the boron and nitrogen, substitutional doping have been taken place, the electro chemical properties of that particular material has been enhanced in the year 2011. So, what I am trying to say is that this doping technology is the too latest technology, the people are trying to use or may be that the maximum people is using from last 2 to 3 years.

Then here also I am trying to give certain examples.

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That preparation of boron doped graphene. So, here firstly, the boron oxide or may be the boric acid and the graphene oxide in a mass ratio of 1 is to 2 were mixed and ground then the mixture was annealed at 200 degree centigrade for 4 hours. The oxygen containing groups grafted on the graphene surface are thermally unstable, which are eliminated in the annealing step, the removal of oxygen spices result in some active site that simultaneously react in situ with boric acid result in the boron doping into the grapheme, after that the mixture was refluxed in 3 mole sodium hydroxide solution to remove the residual boric acid, yielding the product of boron doped graphene.

So, actually what we are doing fist we are trying to make a graphene oxide, but graphene oxide there is so many materials are attached like amen groups or may be some kind of acid groups are attached. So, first we have to (Refer Time: 26:05) that materials so that that groups can be removed from the graphene site and then that area may or may be that (Refer Time: 26:14) will be taken care by the boron atom itself. So, that is why we are doing substitutional graphene boron into the graphene sheet.

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Then advantages of the boron doping over pristine grapheme; boron doped graphene has a lower conductivity hole mobility was estimated to be 550 centimeter square, centimeter square per hold per second at 7.5 percent boron doping with respective pristine graphene probably because of the presence of the defect induced by the doping procedure. Boron graphene nanoribbons have been wildly studied because of their potential to exhibit tunable band gap for the semiconductor industry, which could be used for more versatile application in microelectronic, transport properties of boron doped nanoribbons indicate that the transmittance is strongly depend on the spin state whereas, on pure material in spin degeneration. So, this all are the advantage for which we are making boron doping into the pristine grapheme. Then another example we have given that we doing the nitrogen doping into TI O 2. So, here is the solution based approach to synthesis of NTI 2 nanostructures.

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Generally NaNH 2 has used as a precursors because based on colitis chemistry where the nitrogen concentration and the dopant (Refer Time: 27:36) environment are controlled, to manipulate the dopants environment between interstitials and substitutional while accessing nitrogen concentration ranging from 2 to 17 in atomic percentage.

So, here the doping can be done by both the methods; either may be the substitution or may be the interstitials, but it depends upon the loading of the nitrogen concentration at the time of reactions. So, what are the advantages and improvement in the photocatalytic activities because of its stronger abortion, the highest actual nitrogen doping percentage and the lowest photoluminescence efficiency. The high catalytic efficiency of the former can be attributed to the small crystallite linty, high crystallity and intense light abortion in the visible light reigns.

So, these all are the added advantage or may be that added property which we are getting by doing this kind of doping into the titanium dioxide. Then here also we are given another example that preparation of the co doped zinc oxide and properties enhanced with the doping.

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So co doped zinc oxide nanoparticles where synthesized using co precipitation method in which the co (Refer Time: 28:49) acetate dehydrate was used as the precursors actually which is giving you the cobalt atom at the particular point. So, here through these EUV spectra we are trying to prove that if we are trying to increase the cobalt percentage, how it is affecting into the doping then here we are showing some kind of photoluminescence spectra. So, if we are increasing the percentage of zinc oxide then how it is affecting into the photoluminescence spectra and same thing is we are getting in a magnetic characterization also.

So, when you are talking about the optical the UV emission peek of co doped zinc oxide samples exhibited large blue shift from 410 to 390 nanometer, photoluminescence the UV near band emission wavelength was found to be red shifted for co doped of zinc oxide compared to pure zinc oxide from pure zinc oxide from 361 to 340 magnetic pure zinc oxide exhibits diamagnetic behavior where co doped doping in zinc oxide make the samples ferromagnetic at room temperature and magnetization values are increased with the increase of co concentrations.

So, simple by doing cobalt doped into the zinc oxide we are enhancing its optical properties, we are enhancing its photoluminescence properties not only that we are enhancing its magnetic properties. So, by doing a simple single doping by the chemical root, we are trying to enhance this kind of properties of that particular material. Now we

are come up to our last slide which is nothing, but that it will give a glimpse of that total lecture what we are going to discussed or may be what we have discussed in our previous slides.

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We have studied various new trends for surface modification of nonmaterials yes of course, mainly we have discussed about the doping technology, how we are doing the doping. Dopants chemically adhere to the nonmaterial due to which result in huge improvement electronic properties which help for development of ultra small and fast electronic devise, synthesis of various doped nanometers have been reported with the shows enhanced properties with the doped nanomaterials, properties of boron doped graphene n doped titanium oxide, cobalt zinc oxide have been shown to absorb effect of doping of different dopants in some demanding nonomaterials.

So actually in this particular lecture, we are trying to establish the doping technology and then by giving so many examples we are trying to establish that how the doping is actually changing the material properties, by which method we can do the doping, what are the classifications or may be the division of that particular doping technology and then how we can make the sample, how we can prepare the samples for showing the different properties and not only that how the doping is improving our material characteristics.

Thank you.